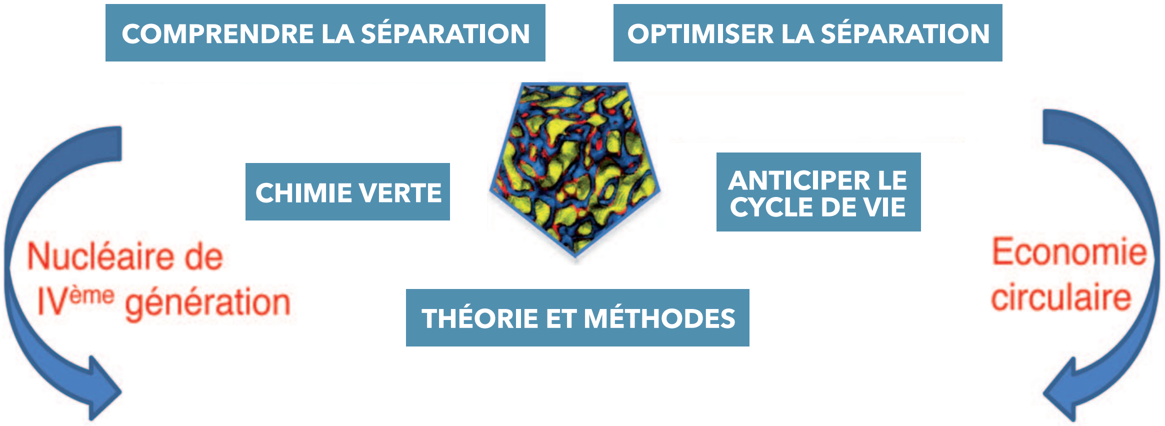
INSTITUT DE CHIMIE SÉPARATIVE DE MARCOULE

CHIMIE ET PHYSICO-CHIMIE DU RECYCLAGE

CYCLE DU COMBUSTIBLE NUCLÉAIRE

MÉTAUX STRATÉGIQUES ET AU-DELÀ



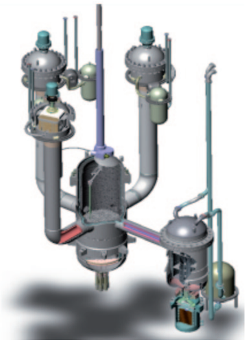
COMPRENDRE LA SÉPARATION

OPTIMISER LA SÉPARATION

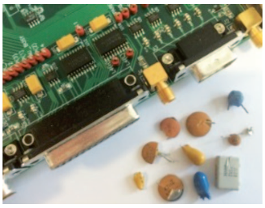
CHIMIE VERTE

ANTICIPER LE CYCLE DE VIE

THÉORIE ET MÉTHODES



Progresser dans une chimie
et une physico-chimie
au service des **procédés**
et des **matériaux** du
nucléaire du futur…
Appliquer nos compétences
à la chimie du recyclage en
général.

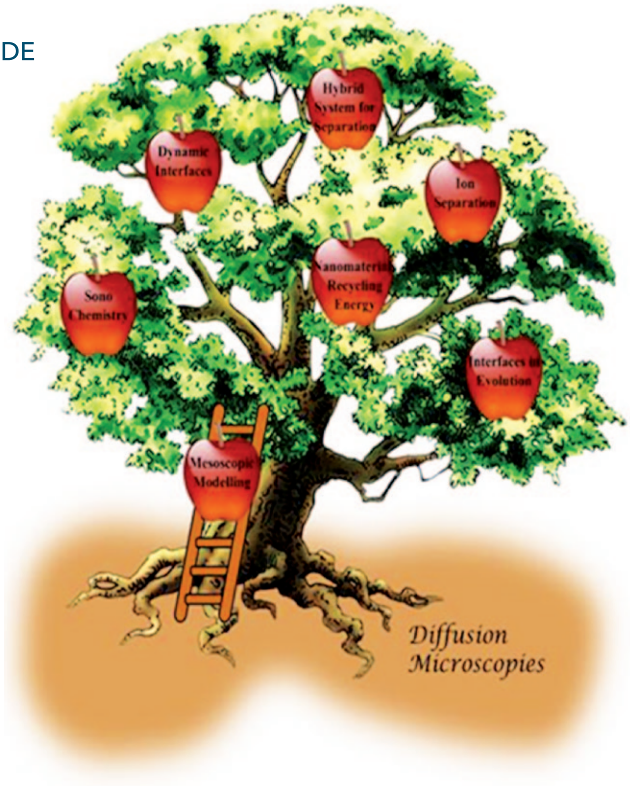


INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCOULE

SCIENTIFIC REPORT 2015 - 2018

ICSM staff as in April 2018

INSTITUT DE CHIMIE SÉPARATIVE DE MARCOULE



La production d'énergie à partir de combustibles fossiles dont l'impact négatif sur le climat et l'environnement est aujourd'hui inacceptable, accompagné de nouvelles exigences en matière de sécurité des installations et de gestion de leurs déchets, mais également la nécessité d'un recyclage considéré jusqu'à présent comme exceptionnel, mais qui doit devenir la règle universelle et économiquement acceptable, confrontent les scientifiques à une demande sociétale forte pour des solutions maîtrisées en matière de technologies pour les énergies décarbonées, inscrite dans les lois du 13 juillet 2005 et du 18 août 2015. Le « nucléaire durable » du futur, fermant le cycle reposera sur des avancées dites « en rupture » via une chimie séparative mettant en jeu des fluides complexes mis en oeuvre dans des dispositifs optimisés.

Au-delà du domaine nucléaire, dans un monde fini en ressources naturelles, fermer les cycles relève d'une démarche de tri sélectif maitrisé, qu'il s'agisse de séparation ionique, moléculaire ou colloïdale. Recycler les matières dites « stratégiques » comme les terres rares, les platinoïdes ou certains métalloïdes comme le germanium ou l'antimoine est un premier défi d'importance pour cette chimie séparative qui relève des nanosciences.

Dans le but de développer une recherche fondamentale au service des « utopies nécessaires » de la chimie pour l'énergie, l'unité mixte CEA/CNRS/UM/ENSCM crée en 2007 est constituée de huit équipes travaillant en synergie :

- *Systèmes hybrides pour la séparation (Daniel MEYER)*
- *Chimie des ions aux interfaces actives (Olivier DIAT)*
- *Tri ionique par des systèmes moléculaires auto-assemblés (Stéphane PELLET-ROSTAING)*
- *Sonochimie dans des fluides complexes (Sergueï NIKITENKO)*
- *Nanomatériaux pour l'énergie et le recyclage (Xavier DESCHANELS)*
- *Interfaces des matériaux en évolution (Nicolas DACHEUX)*

Ces groupes s'appuient sur deux équipes transverses de méthodologies de l'observation dans l'espace réel (microscopies), l'espace réciproque (diffusion rayons X, neutrons et lumière) et la modélisation statistique en conditions réelles représentatives de l'utilisation en température, humidité, durée :

- *Etude de la matière en mode environnementale (Renaud PODOR)*
- *Modélisation et chimie théorique (Jean-François DUFRECHE).*

Avant d'entreprendre des études forcément longues et détaillées ou d'en proposer un financement, il est bon d'identifier à quel besoin se raccorde prioritairement une étude (thèse, projet post-doctoral, projet d'excellence). Ceci est d'autant plus nécessaire qu'une grande fraction des travaux de l'ICSM est co-signée de deux équipe ou plus, et présentée oralement devant des communautés de disciplines très différentes. Le lecteur trouvera systématiquement pour l'éclairer un code de couleur lui permettant d'identifier quel est le moteur de chaque étude (et non son contenu, bien sûr) :

COMPRENDRE LA SÉPARATION :

Il s'agit de caractériser du point de vue microstructural et thermodynamique les systèmes moléculaires organisés fonctionnels qui contrôlent le tri ionique par transfert aux interfaces. Le but est d'aller vers la prédictibilité des transferts d'espèces entre phases « en contact » aussi bien dans le cas liquide-liquide que dans le cas liquide-solide. Ceci nécessite un mélange de disciplines allant de la physique statistique à la chimie analytique en passant par les nanosciences qui s'identifient en « iénaïque ».

OPTIMISER LA SÉPARATION :

Concevoir une séparation fondée sur la connaissance des mélanges de fluides complexes prévoit la synthèse, la formulation et la mise en œuvre rationnelle des systèmes extractants sélectionnés dans des dispositifs de recyclage spécifiques. Les systèmes chimiques de transfert d'espèces sont modélisés à l'échelle de la liaison chimique avec le premier voisin ainsi qu'aux échelles supramoléculaires et mésoscopiques afin de permettre une utilisation optimisée et intensifiée. Le but ici est de diminuer le nombre de plans d'expériences grâce a des modèles prédictifs qui peuvent être couplés à terme aux grand logiciels de bilan de masse qui aident à dimensionner pré-pilotes, pilotes ou installations de production, aussi bien dans le domaine nucléaire que non-nucléaire.

CHIMIE VERTE :

Il s'agit d'intégrer dans la chimie pour l'énergie les douze principes de la chimie verte ainsi que les principes du « green engineering » dans la chimie du recyclage. Ceci s'applique des technologies l'énergie durable car renouvelable. Une action emblématique[1] concerne les aimants permanents qui sont couteux en terme d'énergie et d'effluents. Leur cycle de vie en milieu marin est calculé pour une vingtaine d'années, et un recyclage économe en énergie est un besoin stratégique. Ajouté à l'étude de procédés de séparations en rupture, un effort particulier est porté sur la sonochimie, science des réactions chimiques induites par les ultrasons dans des régimes de cavitation, l'une des chimies furtives car très avare de production d'effluents.

ANTICIPER LES CYCLES DE VIE :

Il s'agit d'observer et de comprendre la durabilité des matériaux d'usage, la dégradation et la corrosion de surface d'origine chimique ou radiative qui dépendent aussi, au-delà de la simple composition des matériaux, de leur voie de synthèse. Ceci permettra d'adapter les matériaux et les fluides d'usage aux dispositifs de recyclage associés. Ceci s'applique aussi dans le domaine du nucléaire aux combustibles et aux matrices de stockage, mais aussi hors nucléaire, aux matériaux d'usage dans les installations nécessaires aux économies d'énergie : en effet le recyclage des matières premières (construction, routes, déchets électroniques, biomasse « perdue ») est une voie d'accès très efficace vers une réduction de la consommation d'énergie.

THÉORIE ET MÉTHODES D'OBSERVATION :

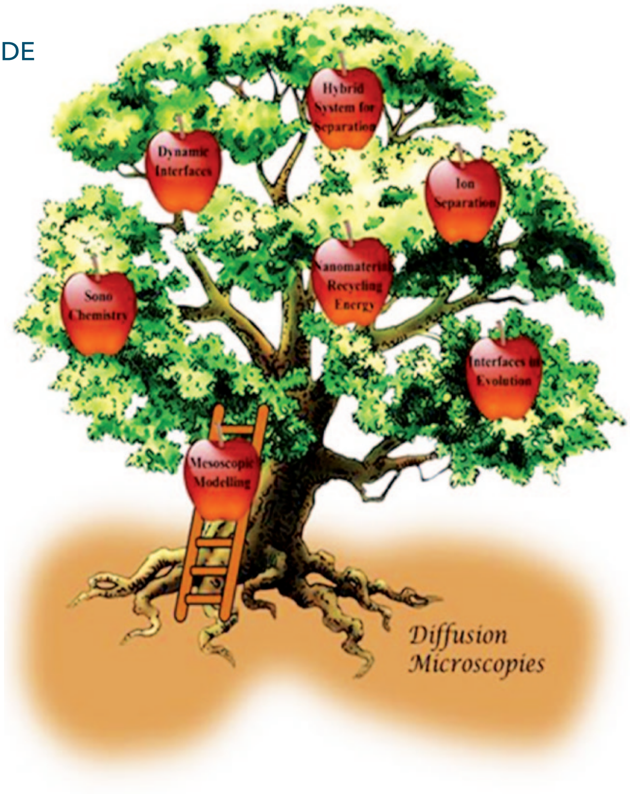
La quasi-totalité des méthodes de séparation ioniques ou moléculaires dépendent de systèmes auto-assemblés : il faut les observer en microscopie environnementale mais aussi par diffusion X-neutrons et lumière dans l'espace réciproque. La théorie physico-chimique statistique a pour but de modéliser les processus de séparation, notamment en assurant le couplage entre l'échelle supramoléculaire et l'échelle mésoscopique. Sans physico-chimie statistique, aucune méthode de séparation d'espèces moléculaires ne peut être maitrisée, car pour tous systèmes connus et utilisés, les énergies de transfert entre phases sont de l'ordre de l'agitation moléculaire (kT/Molécule ou encore kJ/Mole)

L'Institut de Chimie séparative de Marcoule, créé sans murs en 2007, est dirigé par Stéphane Pellet-Rostaing depuis 2013. Situé à 110 km au NE de Montpellier et à 25 km au Nord d'Avignon, l'ICSM fait partie du **Pôle de Chimie Balard** et du LABEX « **Chemisyst** » (2012 – 2022) sur la chimie des systèmes moléculaires et interfaciaux. Ayant démarré effectivement ses activités de recherche en janvier 2010, l'Institut est dimensionné pour accueillir en 2019 cinquante chercheurs permanents, autant de non-permanents thésards et post-doctorants, ainsi qu'une équipe de trois techniciens et ingénieurs exploitants.
Les propositions de stages au niveau master, post-doc et thèses sont accessibles sur le site **www.icsm.fr**.

---

[1] Soutenu a l'ICSM par le projet ERC Advanced REE-_CYCLE (07/2013 à 07/18), ainsi que de son extension POC XXX

**INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCOULE**



The production of energy from fossil fuels whose negative impact on the climate and the environment is today unacceptable, accompanied by new requirements for the safety of the facilities and the management of their waste, but also the need for a recycling considered until now as exceptional, but which must become the universal and economically acceptable rule, confront the scientists with a strong societal demand for controlled solutions in technologies for the carbon-free energies, inscribed in the laws of July 13th 2005 and August 18, 2015. The «sustainable nuclear power» of the future, closing the cycle will rely on so-called «breakthrough» advances via a separation chemistry involving complex fluids implemented in optimized devices.
Beyond the nuclear field, in a world finite in natural resources, closing cycles is part of a controlled extraction/purification process, whether ionic, molecular or colloidal separation. Recycling of so-called «strategic» materials such as rare earths, PGMs or some metalloids such as germanium or antimony is a first challenge in this separation chemistry that belongs to the nanosciences.

Closing cycles of fuels and materials used in energy production does not rest only on progresses on synthetic chemistry of molecules or materials, but also on separation with its two linked side-processes: dissolution and reformation of materials. As long as primary resources are involved, ionic, molecular or colloidal separation are the three processes to be understood and modeled predictively in order to allow growth of the recycling industry, as the core of the circular economy.

In order to develop a fundamental research for the «necessary utopia» of chemistry for energy, the joint unit CEA/CNRS/UM/ENSCM created in 2007 consists of eight teams working in synergy:

> - *Hybrid Systems for separation (Daniel MEYER)*
> - *Ions at active interfaces (Olivier DIAT)*
> - *Ion separation by self-assembled molecular systems (Stéphane PELLET-ROSTAING)*
> - *Sonochemistry in complex fluids (Sergueï NIKITENKO)*
> - *Nanomaterials for energy and recycling processes (Xavier DESCHANELS)*
> - *Evolution of surfaces of materials (Pr. Nicolas DACHEUX)*
>
> *This six teams that are highly specialized are firmly associated to two transverse teams focused on methodologies of microscopic observation in real space, and reciprocal space as well as statistical physics modelling to represent real conditions of use such as temperature, humidity:*
>
> - *Material study by environmental methods (Renaud PODOR)*
> - *Modeling and theoretical chemistry (Pr. Jean-François DUFRECHE).*

Before undertaking necessarily lengthy and detailed studies or proposing funding, it is important to identify the need for a study (PhD, post-doctoral project…). This is the more necessary as a large part of ICSM's work is co-signed by two or more groups, and is presented orally to communities of very different disciplines. The reader will always find a color code to help him to identify what is the driving force of each study:

UNDERSTANDING SEPARATION PROCESSES:

The aim is here to characterize microstructures combined t a statistical thermodynamics approach of the functional organized molecular systems that perform ionic separation. The main target is to develop predictive modeling of ions, molecules and colloids. Processes under mechanistic study include liquid-solid precipitation, liquid-liquid spontaneous as well as triggered separation via controlled phase transfer.

OPTIMIZING SEPARATION PROCESSES:

The aim is here to synthetize, formulate and implement a knowledge-based recycling technology. Once an efficient separation has a predictable behaviour, the systems chemistry as well as chemical engineering at supra-molecular, colloidal and macroscopic scale must be optimized in order to design an efficient system with economic feasibility. Here, it is needed to imagine and implement recycling strategies, with a peculiar attention to actinides and lanthanides.

GREEN CHEMISTRY:

Chemistry for energy, including chemistry of separation processes, must consider and implement the twelve principles of green chemistry as well as those of "green extraction engineering". Mainstream concerns chemical treatment of all types of "wastes" including the degraded thermal energy present in all devices producing electricity to recover "value". Special attention is devoted to sonochemistry, the science of mastering chemical reactions induced by ultra-sound.

ANTICIPATING LIFE-CYCLE:

Observation at meso-scale of surface degradation and electro-chemical corrosion evidences that life-time extension depends not only on raw elemental composition, but also from the synthesis path used for producing the materials used. The knowledge of surface degradation mechanisms under chemical, electrochemical and radiative stress is needed to adapt materials and circulating fluids used in recycling plants, but also to nuclear fuels and storage materials.

METHODS IN MODELING AND OBSERVATIONS AT MESO-SCALE:

Nearly all efficient methods of ionic or molecular separation rely on self-assembled chemical "systems". Their size is in the nanometer range. Those need to be observed in "real" situation, i.e. in environmental electron microscopy, or by scattering of X-rays, light and neutrons. Combining real-space and reciprocal space analysis allows to couple structural analysis to statistical physical chemistry, with a special focus on modeling separation processes with a special attention to the coupling of the supramolecular scale to the mesoscopic scale.

The Institute for Separation Chemistry of Marcoule has been created as a virtual laboratory in 2007 and is managed by Stéphane Pellet-Rostaing since 2013. Located 110 km NE of Montpellier and 25 km north of Avignon, ICSM is part of the **"Pôle de Chimie Balard"** and one of the partners of the Excellence laboratory **"Chemisyst"** 2012-2022, devoted to the Long Range chemical interactions (LRI) at work in "systems chemistry". Having effectively began its research in January 2010, ICSM facilities are planned for hosting in 2019 about fifty permanent and as many non-permanent scientists (up to now more than forty Nationalities), plus staff devoted to administration safety and infrastructure.

Open national and international PhD and post-doc positions are available on web-site: **www.icsm.fr.**

**INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCOULE**

FOREWORD

The joint research unit "Marcoule Institute for Separation Chemistry" was created jointly by CEA, CNRS, University of Montpellier and Ecole Nationale Supérieure de Chimie de Montpellier in March 2007.
The building has been inaugurated in June 2009 and the laboratories have obtained authorisation to start experiments including a few grams of depleted uranium and natural thorium in January 2010.

In December 2018, ICSM brings together around hundred people, including 45 permanent staff and 51 non-permanent scientists (35 doctoral students, 15 postdoctoral fellows/ATER/CDD, 1 senior CDD). In addition, more than 20 master students join the eight teams for a few months every year. Thus, the number of non-permanent staff has in fact reached 55% of the total staff, which corresponds to the level of operation of the Institute. ICSM aims to develop a fundamental research whose main objective is to «open the choices» for the development of separation chemistry processes, integrating the issues of the nuclear energy and the challenges of the circular economy as real opportunities for innovation, unique recognition in France, and international visibility.

A yearly practical summer school in separation chemistry is held yearly for a full week since the first edition 2006 in Montpellier. Since 2012, the Practical summer school is organized in common with the associated teams within the Excellence laboratory "CheMISyst". The common theme of the 48 teams federated in the Chemisyst (2012-2022) is chemistry using the so-called Long Range Interactions, i.e. molecular interactions beyond binding to the nearest neighbour[1]. Since 2014, the summer school is organized jointly with the International Research and Training Group IRTG 1524"Small Structures Near Interfaces".

Resources in Uranium are scarce, if only the 235 isotope is used and wastes related to nuclear energy production are potentially dangerous. The use of fast neutrons effectively enhances existing resources in national independence, but will be based on new separation processes, that can be modelled using predictive theory. Understanding and optimizing separation in the nuclear fuel cycle of the future remains an important aim of the ICSM. Enlarging this central goal to the needs for chemistry of recycling, for instance strategic metals, is crucial for developing alternative energy technologies: all the materials developed in the domain of batteries that are the unavoidable companion of intermittent "green" energies
must be recycled with an acceptable amount of energy and effluents. Renewable energy technologies, if implemented, open an immense field for better recycling technologies for all materials involved, since all these materials have life cycles of the order of 30 years, close to the time planned for their implementation.

The report gives here an overview of the work published and submitted since January 2015. The eight active research teams still work in the direction of the scientific open questions as defined and published by the French academy. Separation chemistry, a branch of physical chemistry, is a key part of « green chemistry », and strongly linked to nanosciences, colloids and interface since all separations are sourced in phase transfer: liquid-liquid, liquid-solid or even liquid-interface in the case of foam flotation.
Separation chemistry is the basis of recycling technology, while recycling is the basis of circular economy and circular economy is the only sustainable strategy in a world of limited resources. All scientists, engineers, technician and students have the common goal to gain the knowledge needed to improve methods in this field.

Stéphane Pellet-Rostaing

Thomas Zemb

---

[1] Special issues devoted to interactions beyond first neighbor appeared in "Current Opinion in Colloids and Interfaces" as special issues in 2015 and 2016

ICSM – PERMANENTS 2015 - 2018

Direction ICSM

STATUT	NOM	PARTENAIRE
Directeur	PELLET-ROSTAING S.	CNRS
Directeur adj.	ZEMB Th.	CEA/DRF
Adj. Directeur	ALPE-CONCHY D.	CEA/DEN
Assistante	MARTIN H.	CEA/DEN
Gestionnaire	MENASRIA A.	UM
Secrétaire/Gestion	RUSSELLO V.	ENSCM
Gestionnaire	VIDAL A.	CNRS
Exploitation	CARMINATI F.	CEA/DEN
Exploitation	VARON R.	CEA/DEN
ISI	DIAS M.	CEA/DEN

- *45 permanents au 01/12/2018 dont*
- *14 CEA/DEN & 8 CEA/DRF*
- *13 CNRS, 7 UM & 4 ENSCM*

Equipe 1 - LHYS

STATUT	NOM	PARTENAIRE
Chef d'équipe	MEYER D.	CEA/DEN
CR	BOURGEOIS D.	CNRS
Chercheur	CARBONI M.	CEA/DRF
MDC	MAYNADIE J.	UM

Equipe 2 – L2IA

STATUT	NOM	PARTENAIRE
Chef d'équipe	DIAT O.	CEA/DRF
Chercheur	BAUDUIN P.	CEA/DRF
MDC	GIRARD L.	ENSCM
IR	JONCHERE A.	CNRS

Equipe 3 - LTSM

STATUT	NOM	PARTENAIRE
Chef d'équipe	PELLET-ROSTAING S.	CNRS
MDC	ARRACHART G.	UM
Technicienne	BAUS-LAGARDE B.	CEA/DEN
Chercheur	DOURDAIN S.	CEA/DRF
IE	GIUSTI F.	CNRS

Equipe 4 - LSFC

STATUT	NOM	PARTENAIRE
Chef d'équipe	NIKITENKO S.	CNRS
CR	CHAVE T.	CNRS
Chercheur	PFLIEGER R.	CEA/DEN
Chercheur	VIROT M.	CEA/DEN

Equipe 5 - LNER

STATUT	NOM	PARTENAIRE
Chef d'équipe	DESCHANELS X.	CEA/DEN
Chercheur	CAUSSE J.	CEA/DEN
Chercheur	REBISCOUL D.	CEA/DEN
IE	REY C.	UM
MDC	TOQUER G.	ENSCM

Equipe 6 - LIME

STATUT	NOM	PARTENAIRE
Chef d'équipe	DACHEUX N.	UM
MDC	CLAPAREDE L.	UM
CR	CLAVIER N.	CNRS
CR	MESBAH A.	CNRS
Chercheur	SZENKNECT S.	CEA/DEN

Equipe 7 – L2ME

STATUT	NOM	PARTENAIRE
Chef d'équipe	PODOR R.	CNRS
Ingénieur	BRAU H-P	CEA/DEN
MDC	CAMBEDOUZOU J.	ENSCM
Technicien	CORSO B.	CEA/DRF
IE	LAUTRU J.	CNRS
IE	LE GOFF X.	CNRS
IE	MAYNADIE S.	CNRS
Ingénieur	ODORICO M.	CEA/DRF

Equipe 8 - LMCT

STATUT	NOM	PARTENAIRE
Chef d'équipe	DUFRECHE J-F	UM
Chercheur	DUVAIL M.	CEA/DRF
Chercheur	SIBOULET B.	CEA/DEN

INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCOULE

ICSM – NON PERMANENTS 2015 - 2018

EQUIPE DIR

CDD ITA
ROUSSIGNE Elisabeth 02/07/2018-31/12/2019

EQUIPE 1 LHYS

APPRENTI
SIMOES Alizée 01/09/2014-31/08/2017
BOUSSMEN Moustapha 28/09/2015-27/09/2016
LAGAE-CAPELLE Eléonore 01/10/2018-30/09/2021

CDD ITA
PEREZ Emilie 09/12/2013-08/06/2015
LASZCZYK Marjorie 13/04/2015-31/05/2017
TRAVERS Dorian 01/09/2016-31/12/2016
MASTRETTA Régis 01/12/2016-31/05/2018
TOUNKARA Halima 25/10/2017-24/10/2018
MASTRETTA Régis 15/04/2015-14/10/2016 (intérim)

DOCTORANT
SINI Karima 01/10/2015-13/08/2016
BRAIBANT Bertrand 27/10/2014-26/10/2017
NAVARRO AMADOR Ricardo 03/11/2014-02/11/2017
GENESIO Guillaume 01/10/2015-30/09/2018
LACANAU Valentin 01/10/2016-30/09/2019
CHEVALIER Aline 16/10/2017-15/10/2020
DURAIN Julie 16/10/2017-14/10/2020
RE Elisa 04/10/2017-05/10/2020
MOUSSAOUI Sayed-Ali 02/10/2018-01/10/2021
LORIGNON Fabrice 31/10/2018-30/10/2021

POST-DOCTRANT ou CHERCHEUR
WANG Jingxian 17/10/2017-16/04/2019

EQUIPE 3 LTSM

CDD ITA
LARRIBAU Arthur 01/08/2016-31/12/2016

POST-DOCTORANT ou CHERCHEUR
CHAPRON Simon 01/09/2015-09/12/2016
SARAVIA Alvaro 26/09/2016-31/12/2016
MARY Fanny 15/09/2015-14/03/2016
LEJEUNE Manuel 28/07/2017-27/07/2018
MOSSAND Guillaume 30/07/2017-
HAQUIN Victor 02/10/2017-01/04/2019
LOPEZ Cesar Augusto 01/05/2018-30/04/2019

DOCTORANT
ARRAMBIDE CRUZ Carlos 01/10/2014-30/09/2017
REY Julien 04/11/2013-03/11/2016
WEHBIE Moheddine 01/06/2013-31/05/2016
LOPIAN Tobias 01/12/2014-30/11/2017
SUKHBAATAR Tamir 07/11/2014-06/11/2017
PLEINES Maximilian 02/11/2015-01/112018
ARTESE Alexandre 02/11/2016-01/11/2019
WINKLER Robert 02/11/2016-01/11/2019
FELINES Nicolas 16/10/2017-15/10/2020
LU Zijun 07/11/2017-06/11/2020
BEN-GHOZI BOUVRANDE Justine 23/10/2018-22/10/2021
OYE AUKE Ruth 01/10/2018-30/09/2021
XING Chen 08/10/2018-07/10/2022

EQUIPE 2 L2IA

CDD ITA
FADEL Ophélie 12/11/2014-11/11/2015
SMOLYAKOV Georges 05/07/2016-04/01/2018

CDD Chercheur
GOMES RODRIGUES Donatien 18/04/2016-17/04/2017

DOCTORANT
MERHI Tania 01/10/2017-30/09/2020
WANG Jing 16/10/2017-15/10/2020
HOHENSCHUTZ Max 03/01/2018-02/01/2021

POST-DOCTORANT ou CHERCHEUR
PHAM Thanh Tung 20/02/2015-19/03/2017
MICHEAU Cyril 08/02/2016-07/02/2017
MALINENKO Alla 04/01/2016-31/03/2017

EQUIPE 4 LSFC

DOCTORANT
DALODIERE Elodie 22/10/2014-21/10/2017
OUERHANI Temim 01/11/2013-31/10/2016
NOUAILLE Florence 01/02/2014-31/01/2017
SIERRA SALAZAR Andres 01/10/2014-30/09/2017
JI RAN 01/10/2015-30/09/2018
PARIZOT Lauréanne 01/01/2015-31/12/2018
BONATO Laura 16/10/2017-15/10/2020

CEA
CNRS
UM ENSCM
Partis
Autres

EQUIPE 5 LNER

DOCTORANT
LOU Yu 11/10/2013-10/10/2016
SHEHAYEB Sanaa 15/01/2015-11/11/2017
MANSAS Clémentine 03/11/2014-02/11/2017
SANANES ISRAEL Susan 01/10/2015-30/09/2018
BAUM Markus 02/11/2015-14/12/2018
MONNIER Julien 14/10/2016-13/10/2019
LU Zijie 01/10/2017-30/09/2021
RUSSO Baptiste 09/10/2017-08/10/2020
BOUBON Rémi 01/10/2017-30/09/2020
LIN Jun 15/10/2018-14/10/2021

POST-DOCTORANT ou CHERCHEUR
ARENA Hélène – 21/11/2016-20/01/2019

EQUIPE 6 LIME

APPRENTI
VILBERT Pierre 27/09/2016-30/09/2017

POST-DOCTORANT ou CHERCHEUR
ALBY Délhia 19/03/2018-18/03/2019
RAFIUDDIN Mohamed Ruwaid 18/06/2018-17/06/2019

DOCTORANT
CORDARA Théo 04/11/2014-03/11/2017
GAUSSE Clémence 04/11/2013-03/11/2016
HACENE CHERKASKY Yannis 09/02/2015-08/02/2018
ESTEVENON Paul 10/2015-10/2018
QIN DanWen 01/09/2016-31/08/2019
DALGER Thomas 14/10/2016-13/10/2019
MANAUD Jérémie 02/10/2017-01/10/2020
BERTOLOTTO Solène 10/2017-10/2020
MASSONNET Malvina 15/10/2018-14/10/2021
KACZMAREK Thibault 15/10/2018-14/10/2021

CDD ITA
SARAVIA Alvaro 03/01/2017-29/10/2018

CEA
CNRS
UM ENSCM
Partis
Autres

EQUIPE 7 L2ME

POST-DOCTORANT ou CHERCHEUR
BEN KACEM Ilyes 08/01/2018-07/07/2019

DOCTORANT
GOUZE Benoit 15/01/2013-15/01/2016
NKOU BOUALA Galy 04/11/2013-01/10/2016
COGNET Marine 01/10/2016-30/09/2019
TRILLAUD Victor 14/10/2016-13/10/2019
DELOBEL Florimond 01/12/2015-30/11/2018

CDD ITA
FOURNIER Sébastien 04/11/2015-03/11/2016
CHEVREUX Pierrick 28/08/2017-21/12/2018

EQUIPE 8 LMCT

DOCTORANT
HOCINE-METAHRI Sarah 01/10/2014-30/09/2017
BLEY Michael 02/11/2015-01/11/2018
COSTE Amaury 01/10/2016-30/09/2019
SPADINA Mario 01/02/2016-31/01/2019
COQUIL Mathilde 10/2017-10/2020
MARIN Vatin 15/10/2018-14/10/2021
HILAIRE Lolita 15/10/2018-14/10/2021

POST-DOCTORANT ou CHERCHEUR
KARMAKAR Anwesa 20/01/2015-19/01/2016
GOURDIN Simon 20/09/2016-19/09/2017

ICSM ERC

CDD ITA
LEPROU-TACONET Aline 01/09/2014-31/03/2016

CONSEILLER SCIENTIFIQUE
MÖHWALD Helmut 01/02/2014-31/01/2018

APPRENTI
SAGI Orlane 19/09/2016-18/09/2017

CDD ITA
KELLER Barbara 02/05/2018-31/10/2018

DOCTORANT
PENISSON Christophe 01/10/2015-30/09/2018

POST-DOCTORANT ou CHERCHEUR
SYLL Ousmane 06/02/2014-30/06/2015

ORIGINE GÉOGRAPHIQUE DU PERSONNEL DE L'ICSM

① MEXIQUE
② GUATEMALA
③ COLOMBIE
④ PÉROU
⑤ ARGENTINE
⑥ ANGLETERRE
⑦ IRLANDE
⑧ ESPAGNE

⑨ ALLEMAGNE
⑩ BELGIQUE
⑪ ITALIE
⑫ CROATIE
⑬ RÉPUBLIQUE TCHÈQUE
⑭ POLOGNE
⑮ ROUMANIE
⑯ UKRAINE

⑰ TUNISIE
⑱ MAROC
⑲ ALGÉRIE
⑳ GUINÉE
㉑ MALI
㉒ CONGO
㉓ LIBAN
㉔ RUSSIE

㉕ MONGOLIE
㉖ CHINE
㉗ INDE
㉘ VIETNAM
㉙ AUSTRALIE

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

ICSM
Main Equipments

Permanent team

Renaud Podor (CNRS)
Béatrice Baus-Lagarde (CEA)
Henri-Pierre Brau (CEA)
Bruno Corso (CEA)
Alban Jonchère (CNRS)
Joseph Lautru (CNRS)
Xavier Le Goff (CNRS)
Sandra Maynadié (CNRS)
Michaël Odorico (CEA)
Cyrielle Rey (UM)

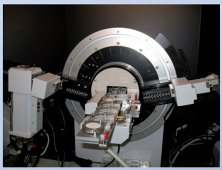
The equipments are shared in the Pole Balard Analysis and Characterization Platform

Analyses of solids and surfaces


Environmental Scanning Electron Microscopy


Transmission Electron Microscopy


Atomic Force Microscopy


X-Ray Diffractometer

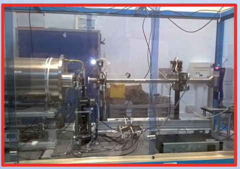
Thermal Analyses (ATG / TMA)



Surface Analyses

Analyses of liquid or solids

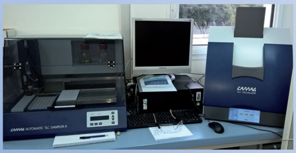
Vibrational Spectroscopies


SAXS


NMR



Alpha Spectrometer

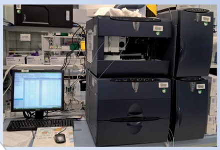

Thin Layer Chromatography Sampler

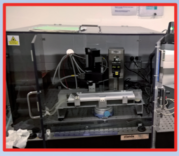
XRF Spectrometer


Analyses of liquids


ICP-AES


DLS Zetasizer

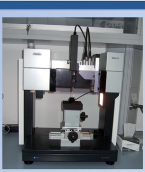

Ion Chromatography


Langmuir Trough

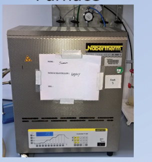

DLS / SLS

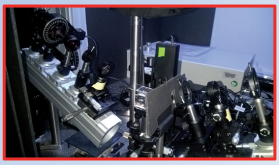
Other equipments


Glove Box


Liquid / Liquid Interfaces


Solvent Drying System

Furnace



SHG

Sonoluminescence Reactor

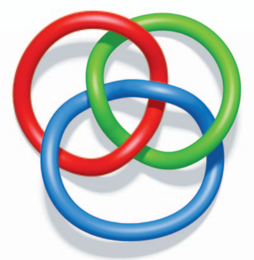

ORGANISATION OF THE QUADRIENNAL REPORT 2015-2018 OF ICSM

Each of the eight active research groups gathers researchers and engineers from different skills, who publish in various domains in the corresponding journals, and who participate at different international meetings.

A large fraction of crucial results are obtained and published in common between teams within ICSM, associating theoretical and practical expertises and via regional, national and international collaborations.

Through three main clusters, focused objectives of the research actions undertaken guide the choice of financially supported priorities within the large autonomy of creative chemists working at ICSM.

Clusters:



INNOVATION IN EXTRACTION AND RECYCLING

OPTIMIZING OF MATERIALS LIFE-CYCLE FOR ENERGY

METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

Focused objectives:

Understand chemical mechanisms underlying processes of chemical **separation** and develop predictive models

Optimize known methods for **separation**, in order to imagine, propose and test optimized or innovative separation methods.

Anticipate the **life-cycle** of materials used in the context of nuclear and alternative energy productions

Develop **"Green Chemistry"** in all its facets, including sonochemistry.

Develop **Theories** and **Methods** for characterisation and modelling.

Whatever the clusters, small coloured lateral marks appearing on each page of report identify the objectives related to each scientific theme. The research objectives spread from science directly related to nuclear energy and to non-nuclear recycling and material chemistry, with a large part of research with "dual" interest.
At the end of this report covering 2015-2018, references directly relevant to research are done. Research in the nuclear domain, non-nuclear domain as well as the "dual interest" research are identified by red, black and blue colours. By "dual" research, research in separation chemistry that is of interest as well for nuclear than for non-nuclear separation chemistry is meant.

NUCLÉAIRE - DUAL - NON NUCLÉAIRE

Collaborations actives en cours (depuis 2015) avec des partenaires nationaux et européens.

EN FRANCE

- ① STRASBOURG
- ② LILLE
- ③ RENNES
- ④ NANCY
- ⑤ LYON
- ⑥ GRENOBLE
- ⑦ BORDEAUX
- ⑧ LIMOGES
- ⑨ LA ROCHELLE
- ⑩ MONTPELLIER
- ⑪ CAVAILLON
- ⑫ ALÈS
- ⑬ SACLAY

EN EUROPE (HORS FRANCE) :

- ① BERLIN
- ② REGENSBURG
- ③ JULICH
- ④ BARCELONE
- ⑤ CARDIFF
- ⑥ LJUBJANA
- ⑦ HUELVA
- ⑧ AMSTERDAM
- ⑨ MESSINE
- ⑩ DELPHES
- ⑪ LONDRES
- ⑫ MILAN
- ⑬ AALBORG

LES MISSIONS SCIENTIFIQUES CONTRACTUELLES DE L'ICSM (2015-2020)

Dans le but de développer la recherche fondamentale au service d'un nucléaire durable et économe de matières, le CEA, le CNRS et les deux établissements publics d'enseignement associés à ce projet, l'Université de Montpellier et l'Ecole Nationale Supérieure de Chimie de Montpellier, se groupent pour créer l'Institut de Chimie Séparative de Marcoule, autour de huit équipes ayant pour mission de rechercher des solutions sur des verrous identifiés dans les procédés actuels autour du cycle du combustible nucléaire et de progresser dans la connaissance fondamentale associée. A terme, le but est l'émergence de technologies en rupture dans le domaine de la chimie séparative applicables à l'ensemble du cycle du nucléaire de 4ème génération et extensibles pour le mix énergétique au-delà des procédés directement liés à l'électronucléaire seulement. Ainsi, les études de l'ICSM concernent également les énergies renouvelables économes de ressources et sans impact sur l'effet de serre et, d'une façon générale, la chimie pour le développement durable par une approche influencée par les progrès cognitifs très importants durant ces vingt dernières années dans le domaine des nanosciences. Les acquis scientifiques escomptés dans le domaine de l'énergie renouvelable déboucheront sur de nouvelles technologies utilisables pour l'extraction ou le recyclage des métaux stratégiques. Aux procédés de recyclage sont associés des matériaux d'usage, dont l'évolution des surfaces et donc le cycle de vie doit être prédictible sous stress chimique, thermique ou radioactif.

THÉMATIQUE 1

SYSTÈMES HYBRIDES POUR LA CHIMIE SÉPARATIVE (LHYS)

Cette thématique propose l'étude des propriétés de systèmes moléculaires et supramoléculaires auto-assemblés, à base de métaux (d et f) avec pour objectif principal d'appréhender au mieux les mécanismes sous-jacents à la séparation d'éléments d'intérêt. Il s'agit de déterminer le rôle des interactions entre un centre métallique et ses environnements proches et lointains dans un processus d'organisation de la matière afin de comprendre un comportement de séparation de métaux, et mettre à profit cette organisation pour contrôler les propriétés de structure et de réactivité des matériaux moléculaires obtenus.

Les systèmes d'étude expérimentale considérés sont notamment des solutions organiques composées de divers précurseurs moléculaires, permettant la solubilisation d'un métal sous forme d'un complexe moléculaire. Par leur structure moléculaire, ces systèmes doivent permettre la modulation des interactions entre un métal et son environnement à différentes distances et échelles d'énergies. Les interactions principales d'intérêt sont les interactions métal-molécule (chimie moléculaire) et molécule-molécule (chimie supramoléculaire). Dans le cadre de la chimie séparative, l'assemblage spécifique entre un métal et des systèmes moléculaires polyfonctionnels permet la formation d'un polymère hybride solide de type polymère de coordination, à partir d'éléments en solution. Ces systèmes permettent alors la séparation des métaux par auto-assemblage spécifique lié au champ cristallin du métal et non uniquement lié à des grandeurs de la physique classique (électrostatique, polarisation et dipôle). Cette approche ouvre la voie d'un tri des métaux par «précipitation» piloté par la géométrie de coordination et ouvre un nouveau champ d'investigation des propriétés physiques et chimiques de ces objets, plus particulièrement dans le domaine des nouvelles technologies de l'Energie décarbonées.

D'une manière générale, cette recherche a pour objectif de dépasser l'étude de la seule liaison de coordination dans un complexe métallique où l'ion est en interaction au niveau des nuages électroniques avec un «site complexant» identifié, modélisable au niveau quantique, et doit s'étendre aux interactions au-delà du premier voisin, modélisable au niveau mésoscopique, pour former soit des phases complexes spécifiques à un métal dans un solvant, soit des assemblages spécifiques type polymère de coordination.

THÉMATIQUE 2

CHIMIE DES IONS AUX INTERFACES ACTIVES (L2IA)

La chimie aux interfaces - ou chimie colloïdale des fluides complexes - est en pleine mutation. Une opportunité est donc ouverte par les progrès de cette chimie, en particulier dans le cas de l'extraction liquide/liquide. L'effort de recherche est à focaliser sur la caractérisation de la distribution à l'échelle nanométrique des ions et colloïdes près des interfaces macroscopiques, aussi bien sur les aspects statiques que dynamiques, avec un effort important sur l'aspect cinétique de transfert entre deux milieux fluides non miscibles. Déclinée dans le cas des actinides et des lanthanides, cette problématique est d'importance pour le tri ionique associé au cycle du combustible mais aussi pour de nombreux cas de dépollution et recyclage. On passerait, pour l'adsorption des ions en solution, de la démarche purement expérimentale à l'établissement de modèles prédictifs, aussi bien sur des fluides complexes ultra-divisés froids (non radioactifs) que des systèmes méso et microporeux chauds qui pourront être étudiés expérimentalement dans Atalante. Dans les domaines non-nucléaires liés aux énergies alternatives, les progrès dans cette direction cognitive sont porteurs de progrès en décontamination et en éco-extraction notamment.

THÉMATIQUE 3

TRI IONIQUE PAR LES SYSTÈMES MOLÉCULAIRES AUTO-ASSEMBLÉS (LTSM)

Dans les procédés associés au recyclage – nucléaire ou non -, lorsqu'un ion en solution est en équilibre à travers une interface avec une dispersion de complexants en conditions d'usage, la phase aqueuse ainsi que la phase non-aqueuse sont des solutions loin de l'idéalité. Ce sont des systèmes moléculaires organisés : micelles, microémulsion, colloïdes, cristaux liquides, que l'on peut considérer par la thermodynamique statistique comme des « nanophases » réactives. Ces nanophases dispersées présentent des effets coopératifs très puissants et sélectifs, qui sont la base des procédés de tri ionique efficaces et maîtrisés. Mais, via des « effets tunnel » dus aux espèces adsorbées aux interfaces, ces nanophases sont aussi à l'origine du peu d'efficacité en termes de flux massiques des méthodes de tri ionique. La compréhension des mécanismes physico-chimiques qui gouvernent le tri ionique doit ainsi permettre le design et la synthèse de systèmes chélatants optimisés, mis en œuvre dans les procédés d'extraction/séparation considérés biphasiques (liquide/liquide, solide/liquide) ou monophasiques (membranaire, flottation, précipitation). L'activité globale de l'équipe LTSM est ainsi dédiée à la problématique de la séparation d'ions par transfert entre phases liquides, dont l'une au moins est un fluide complexe auto-assemblé. A travers la conception, la synthèse et l'optimisation de structures moléculaires chélatantes, cette équipe s'intéresse à la compréhension et à la maîtrise des phénomènes qui influencent le tri ionique par des équilibres spécifiques d'ions entre deux fluides séparés par une interface, conditionnés par des systèmes moléculaires organisés. La sélectivité comme la cinétique d'extraction, qui résulte de la combinaison d'interactions locales avec les plus proches voisins et d'interactions « longue distance » telles que les forces de dispersion (effets de type Hofmeister alias chaotrope/cosmotrope, forces d'hydratation) sont alors abordées.

Au-delà du domaine purement nucléaire, ces effets sélectifs sont étudiés et mis en œuvre dans différents procédés liés au recyclage de matières associées à la production d'énergie et, plus généralement, dans les optiques de développement durable, par exemple en décontamination ou pour le recyclage sélectif des métaux stratégiques au-delà des applications liées à l'électronucléaire, c'est-à-dire comprenant aussi les énergies alternatives.

THÉMATIQUE 4

SONOCHIMIE DANS DES FLUIDES COMPLEXES (LSFC)

La cavitation acoustique observée dans les liquides soumis à des ultrasons de puissance conduit à des conditions extrêmes au sein des bulles, au moment de leur implosion, qui sont à l'origine de la réactivité chimique inhabituelle (sonochimie) ainsi que de l'émission de lumière, connue sous le nom de sonoluminescence. La mesure du spectre de sonoluminescence permet de sonder l'intérieur des bulles, d'obtenir des informations sur les températures atteintes et sur la présence d'espèces excitées.

En effet, chaque bulle de cavitation peut être considérée comme un microréacteur chimique à plasma qui ne nécessite pas l'addition de réactifs spécifiques et ne génère pas de déchets supplémentaires, respectant ainsi les principes de l'industrie nucléaire du futur et de la chimie «verte». Une des potentialités de la sonochimie réside en la synthèse de matériaux monodispersés composés de sous-unités de taille nanométrique. En effet, en fonction des conditions opératoires, des nanoparticules avec des propriétés contrôlées (catalytiques, magnétiques, etc.) peuvent être synthétisées, ceci grâce aux espèces réactives formées in situ ainsi qu'aux effets thermiques locaux très importants autour des bulles de cavitation. La combinaison des ultrasons et des catalyseurs nanostructurés permet d'améliorer significativement l'efficacité des réactions catalytiques grâce à une dispersion efficace de la phase active et l'activation de surface de catalyseur.

A proximité de surfaces solides macroscopiques, les bulles de cavitation sont susceptibles d'imploser asymétriquement et de donner ainsi naissance à des micro-jets de liquide venant frapper violemment les surfaces solides. Combinés aux ondes de chocs résultant de l'implosion sphérique de bulles plus éloignées de surface, ceux-ci peuvent mener à des phénomènes tels que l'érosion de surface, la fracturation de grains, l'augmentation du transfert de masse, ou encore la diminution des couches de diffusion. De par sa simplicité d'utilisation et d'insertion potentielle dans une étape de procédé industriel, l'apport des ultrasons est aujourd'hui considéré aussi dans le domaine du nucléaire. Entre autres, le phénomène de cavitation acoustique pourrait contribuer à faciliter la dissolution du combustible nucléaire du futur ou améliorer la décontamination de déchets industriels.

THÉMATIQUE 5

NANOMATÉRIAUX POUR L'ENERGIE ET LE RECYCLAGE (LNER)

Cette thématique porte sur la recherche relative aux nanomatériaux utilisés dans le domaine de l'énergie (matériaux d'usage) et intervenant dans les procédés de recyclage. Les thématiques de recherche couvrent les méthodes innovantes de synthèse de matériaux structurés à différentes échelles, leur fonctionnalisation, leur caractérisation et l'étude des phénomènes mis en jeu lors des différentes étapes d'élaboration, complétées par l'étude de leurs propriétés d'intérêt et de leur comportement.

L'ensemble des études menées au sein de cette équipe est relatif à des composites de nature (porosités, phases hybrides, oxydes, carbures..), de taille (nano, méso et/ou micro) et de structure (ordonnée ou amorphe) contrôlées et présentant une ou plusieurs fonctionnalités (chimie séparative, propriétés optiques renforcées, incorporation d'éléments actinides…). Par ce type de structure hiérarchique, les propriétés physiques (fissuration, tenue à l'irradiation, propriétés optiques) mais aussi chimiques (extraction, lixiviation) de ces matériaux présentent des performances hautement non linéaires par rapport à celles des matériaux massifs, rendant ainsi possible le modelage de ces propriétés en fonction des applications souhaitées. Dans tous les cas, pour concevoir ces matériaux, les avancées de la chimie « douce » (sol-gel, colloïdale, émulsion, hydrothermale,…) sont mises en œuvre afin d'obtenir des réactivités lentes et contrôlées permettant alors une caractérisation précise et parfois « in situ » des différentes étapes réactionnelles et donc une meilleure maîtrise du matériau final. Cette démarche multi-échelle s'applique aussi vers les matériaux auto-cicatrisants ou auto-réparants utilisés dans le domaine de transformation ou de stockage de l'énergie.

THÉMATIQUE 6

INTERFACES DE MATÉRIAUX EN EVOLUTION (LIME)

La conception de nouveaux procédés et de nouveaux matériaux pouvant être mis en œuvre à des températures et des pressions significativement plus élevées devrait permettre de réaliser les avancées technologiques nécessaires au développement des réacteurs nucléaires du futur. Ces mêmes matériaux devront alors présenter des propriétés permettant de résister à plusieurs types d'agressions : thermique, chimique, radiative, …

Les thématiques développées au sein du laboratoire ont donc pour principal objectif de décrire et de comprendre les phénomènes siégeant aux interfaces de matériaux d'intérêt pour le nucléaire : interfaces solide/solide au cours d'étapes de frittage (densification) et interfaces solide/liquide lors d'opérations de dissolution ou d'étapes de lixiviation ou d'altération sous contraintes. Il s'agit alors d'appréhender la synthèse puis la densification d'un matériau en regard des propriétés d'usage requises pour une application donnée.

Les expérimentations relatives aux interfaces solide/solide s'inscrivent principalement dans l'étude du frittage à travers les différents mécanismes intervenant lors de la densification d'un matériau (consolidation de l'objet, grossissement de grains, réduction de la porosité). Dans ce cadre, le couplage d'expérimentations in situ et ex situ permet non seulement d'analyser les différentes étapes de la densification et d'obtenir des données le plus souvent uniquement accessibles par modélisation mais également d'aboutir à l'obtention de cartes de frittage (« carte d'identité microstructurale » d'un matériau représentant la taille de grains vs. taux de densification) dans un délai très court. Il en découle alors une optimisation des conditions expérimentales en fonction de la microstructure désirée.

Concernant l'évolution des interfaces solide/liquide, il s'agit de permettre à terme l'optimisation des propriétés de certains matériaux utilisés (ou à utiliser), notamment pour l'aval ou l'amont du cycle électronucléaire. Pour cela, la démarche développée consiste à coupler une approche cinétique à travers l'établissement de l'expression multiparamétrique de la vitesse de dissolution avec une approche thermodynamique visant à déterminer des données associées aux phénomènes de saturation siégeant aux interfaces. Dans ce cadre, le volet cinétique inclut la mise en évidence des paramètres affectant l'interface en évolution aussi bien en solution (pH, Eh, complexants, T, …) que ceux associés au solide (structure et défauts structuraux, microstructure). Les expériences menées en conditions proches de la saturation visent, quant à elles, à identifier les phases néoformées potentielles issues de la dégradation des matériaux en cours de dissolution puis d'acquérir les données thermodynamiques associées à leur solubilité. Il s'agit principalement d'évaluer leur impact sur les relâchements élémentaires en solution.

Cette démarche transversale initialement mise au point sur des matériaux présentant un intérêt pour l'amont ou l'aval du cycle du combustible électronucléaire (phases minérales uranifères d'intérêt, combustibles, matrices de confinement spécifique, …) a pour vocation à être étendue à d'autres champs d'activité notamment à ceux relevant de la chimie séparative hors nucléaire.

THÉMATIQUE 7

ETUDES DE LA MATIÈRE EN MODE ENVIRONNEMENTAL (L2ME)

Dans ce nouveau Laboratoire d'Etudes de la Matière en Mode Environnemental (L2ME), la fusion des compétences et savoir-faire correspond à la volonté de coupler les informations microscopiques et macroscopiques obtenues par l'ensemble des techniques expérimentales disponibles au sein du L2ME, à partir d'un socle de compétences de microscopie électronique à balayage en mode environnemental. Il s'agira de décrire encore plus précisément le comportement de l'échantillon en maîtrisant, lors de l'enregistrement des mesures, les paramètres physiques auxquels est soumis l'échantillon (température, taux d'humidité, nature des gaz, pression…).

Le contrôle des paramètres de l'environnement d'un échantillon ouvre le champ de l'expérimentation in situ et l'accès à la détermination de grandeurs physiques originales. Les avancées récentes en microscopies à rayons X et électroniques permettent de voir directement des agrégats supra-moléculaires en solution avec une résolution inégalée à ce jour. L'apport de ces modes d'imageries à la compréhension fine de certaines propriétés des matériaux (auto-cicatrisation, frittage, dissolution) ou à l'observation de la morphologie d'objets résultant de l'auto-association de molécules est essentiel.

Une analyse chimique couplée à une imagerie pour l'étude des surfaces en évolution permet un suivi des mécanismes de réarrangement de surface, allant de la description des mécanismes de dissolution des matériaux jusqu'à de réelles expériences de recuit des matériaux in situ.

La caractérisation multi-échelle de la matière, du nanomètre au micron, repose sur une maîtrise des mesures dans l'espace réciproque dans une large dynamique d'intensité et de vecteur de diffusion. Ici, diffusion aux petits angles et diffraction utilisant des rayons X durs nécessaires pour l'étude d'éléments de Z élevés doivent être utilisées conjointement pour la caractérisation multi-échelle statistique des matériaux permettant de contourner les effets dus au choix d'images représentatives. A ce niveau, des grandeurs physico-chimiques allant jusqu'aux potentiels d'interaction, aux interfaces fractales et aux courbures peuvent être déterminées directement, en contrôlant conjointement température et activité du solvant.

Les matériaux divisés, leurs surfaces, les fluides, leurs mélanges et les associations faibles de molécules ayant des propriétés de transport ionique particulières ne peuvent être modélisés avec succès qu'après une caractérisation statistique de haute sensibilité même en cas de faible contraste, elle-même couplée avec une description microscopique précise des objets.

Au-delà de la collaboration étroite avec les équipes spécialisées, la pratique et l'interprétation physique et chimique des spectres de diffusion-diffraction et des images de microscopie sont une discipline scientifique à part entière, conduisant à des recherches propres dans les nanosciences et des collaborations scientifiques directes avec des équipes externes à l'ICSM. L'équipe permet aussi d'apporter un soutien à l'utilisation de grands instruments (sources de rayons X et de neutrons) pour les recherches menées dans les autres équipes.

THÉMATIQUE 8

MODÉLISATION MÉSOSCOPIQUE ET CHIMIE THÉORIQUE (LMCT)

La modélisation à l'échelle mésoscopique est nécessaire à toute modélisation prédictive : elle s'impose non seulement pour l'étude des états d'équilibre que pour la prédiction des propriétés de transport dans le cadre des systèmes chimiques étudiés à l'ICSM. En association avec les équipes en charge de la chimie quantique au sein du Pôle Balard et de la dynamique moléculaire dans les départements de R&D de Marcoule, ce laboratoire de chercheurs théoriciens constitue une équipe transverse travaillant en étroite collaboration avec les autres équipes de l'ICSM.

L'approche de ce groupe est multi-échelles : la matière est décrite par des modèles à des niveaux de descriptions variés, du plus microscopique (description atomique) jusqu'au niveau macroscopique (modèles des sciences de l'ingénieur). Un intérêt tout particulier se manifeste pour le traitement des interactions à l'échelle intermédiaire (échelle mésoscopique ou à solvant continu) car celle-ci constitue l'échelle principale des phénomènes étudiés à l'ICSM. Le lien entre les échelles de description est explicitement réalisé par cette équipe : les paramètres des modèles les plus macroscopiques ne sont pas obligatoirement ajustés car ils peuvent être obtenus à partir des descriptions aux échelles plus petites. Le but final est de proposer une description de la matière pratique suffisamment simple pour faire le lien avec l'échelle pondérale modélisée dans les départements de R&D de Marcoule, en tenant compte des effets microscopiques complexes là où ceux-ci ont un rôle. Une telle approche nécessite de développer des méthodes de chimie théorique et de thermodynamique statistique nouvelles adaptées.

Cette stratégie est particulièrement approfondie pour l'extraction liquide/liquide, pour les phases aqueuses et organiques en contact. Les espèces à extraire sont essentiellement des électrolytes, soit forme d'ions dissociés hydratés, mais aussi de paires d'ions et d'ions complexes, au-delà des lanthanides et actinides motivés essentiellement par les applications dans le cycle du combustible nucléaire du futur, mais incluant les espèces d'intérêt pour les énergies alternatives.

Convention signée le 18-12-2014 par Bernard Bigot (CEA),
Alain Fuchs (CNRS), Pascal Dumy (ENSCM)
et Michel Robert (Université de Montpellier II)

MESOSCOPIC MODELLING AND THEORETICAL CHEMISTRY*

L'équipe est constituée au 1er Septembre 2018 de :

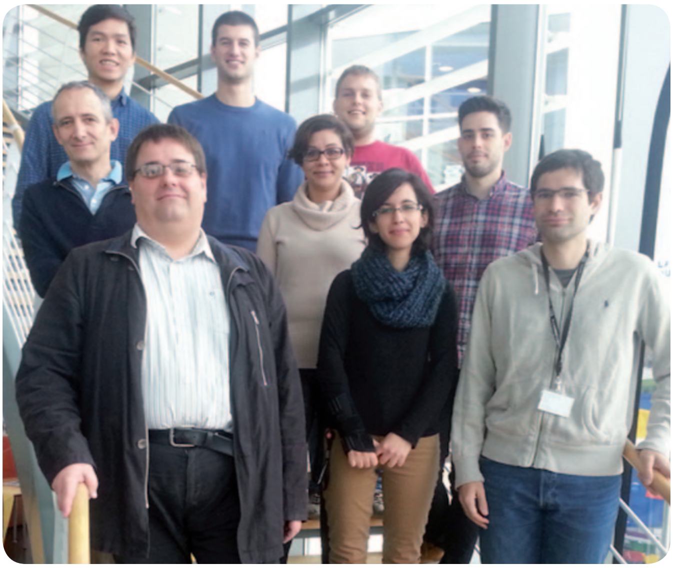
- 1 Professeur Université Montpellier, responsable d'équipe – Prof. Jean-François Dufrêche,
- 1 Chercheure CEA/DRF – Dr. Magali Duvail
- 1 Chercheur-Ingénieur CEA/DEN - Dr. Bertrand Siboulet

Post-doctorants :

- Thanh Tung Pham (CEA/DEN), de 2015 à 2017 : Modélisation expériences de SHG (génération de seconde harmonique), en collaboration avec le L2IA
- Simon Gourdin (DRF, ERC REE-Cycle), de octobre 2016 à septembre 2017 : Extraction des terres rares par des modèles de microémulsions
- Anwesa Karmakar (DRF, ERC REE-Cycle), de janvier 2015 à mars 2016 : Extraction des terres rares
- Yushu Chen (CEA/DEN), d'octobre 2013 à octobre 2015 : Modélisation des phases organiques pour la séparation, en collaboration avec Ph. Guilbaud (DMRC).

Doctorants :

- Marin Vatin (CEA DEN), depuis octobre 2018 : modélisation de l'extraction liquide/liquide, en collaboration avec Ph. Guilbaud (DMRC).
- Lolita Hilaire (CEA/DEN-DMRC), depuis octobre 2018 : modélisation des phénomènes de coalescence, localisée à l'ICSM et au DMRC (S. Charton).
- Mathilde Coquil (CEA/DEN-DMRC), depuis octobre 2017 : Identification des contributions à l'origine de la sélectivité en extraction liquide/liquide, localisée à 50% à l'ICSM et à 50% au DMRC (M.-C. Charbonnel et N. Boubals).
- Amaury Coste (UM, ANR DYNAMISTE), depuis octobre 2016 : Etude des solutions concentrées d'alumino-silicates.
- Mario Špadina (CEA/DRF et ERC REE-Cycle) depuis mars 2016 : Modélisation par DFT classique de l'agrégation en phase organique pour la séparation, en collaboration avec K. Bohinc (Univ. Ljubljana).
- Anne-Françoise de Guerny (Labex CalSimLab), depuis octobre 2016 : Thèse sur le calcul mathématique des interactions faibles, en collaboration avec Y. Maday (LJLL, UMPC) et J.-Ph. Piquemal (LCT, UPMC), localisée à l'UPMC-Paris 6.
- Michael Bley (CEA/DEN), 2015 – 2018 : Modélisation moléculaire de l'activité en solution pour l'extraction liquide-liquide, en collaboration avec Ph. Guilbaud (DMRC), soutenance le 21 novembre 2018.
- Sarah Hocine (MESR, UM), 2014 – 2017 : Simulation moléculaire d'oxydes pour la séparation, soutenance le 28 septembre 2017.
- Thanh Nghi Nguyen (CEA/DEN), 2012 – 2015 : Modélisation moléculaire de l'extraction liquide-liquide, en collaboration avec Ph. Guilbaud (DMRC), soutenance le 4 décembre 2015.
- Arnaud Villard, (MESR, UM), 2012 – 2015 : Etude de la séparation par les nonatitanates poreux, soutenance le 27 octobre 2015.

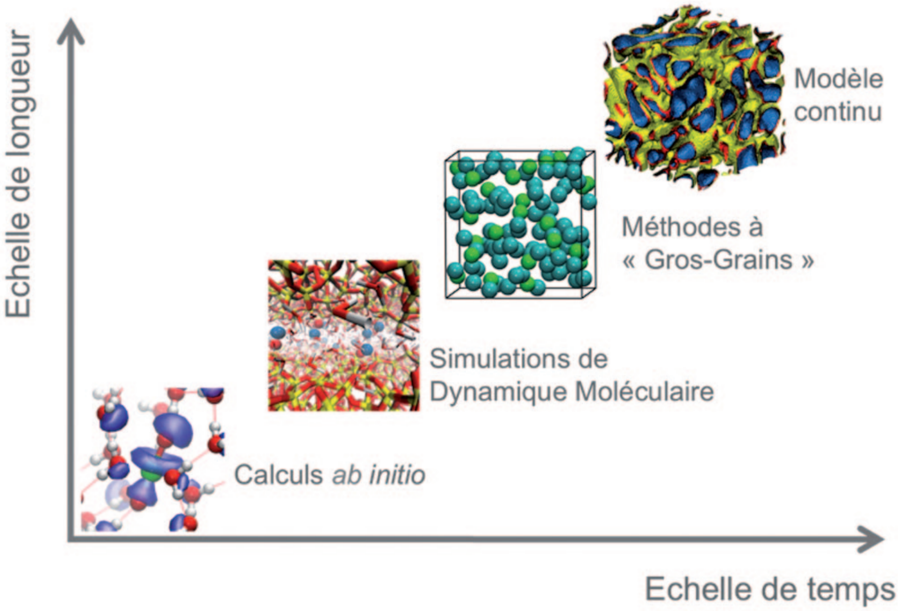


---

*Thématique 8 de la page 24

Les objectifs de l'équipe de modélisation consistent à étudier les systèmes complexes, en particulier ceux mis en jeu dans la chimie séparative, par une approche multi-échelle avec un intérêt tout particulier pour les modélisations aux échelles intermédiaires (mésoscopiques ou nanoéchelles).

Les moyens mis en œuvre par l'équipe sont représentés sur les figures qui suivent. La description la plus fondamentale est celle de la mécanique quantique (calculs ab initio) capable de représenter l'acte élémentaire. Elle est en particulier étudiée pour déterminer la complexation moléculaire et elle peut aider également à améliorer les modèles classiques. Ceux-ci peuvent être étudiés par la dynamique moléculaire pour caractériser la structure des milieux, leurs propriétés d'équilibre et le transport, mais seulement sur des échelles assez faibles (quelques nanomètres et nanosecondes tout au plus). Les études des milieux complexes reposent donc sur des descriptions à des échelles intermédiaires (modèles à « gros grain », théories à solvant continu, dynamique brownienne, équations intégrales, fonctionnelles de la densité (classique), couplage de modes, théorie des interfaces, etc.) qui sont implémentées pour décrire la physico-chimie des processus et faire le lien avec le génie chimique. L'originalité de cette équipe de modélisation vient en particulier du fait que le passage d'échelle est presque systématiquement étudié. Les échelles les plus microscopiques permettent ainsi d'améliorer les modélisations macroscopiques, non seulement en leur fournissant des paramètres, mais aussi en améliorant directement leurs équations fondamentales.

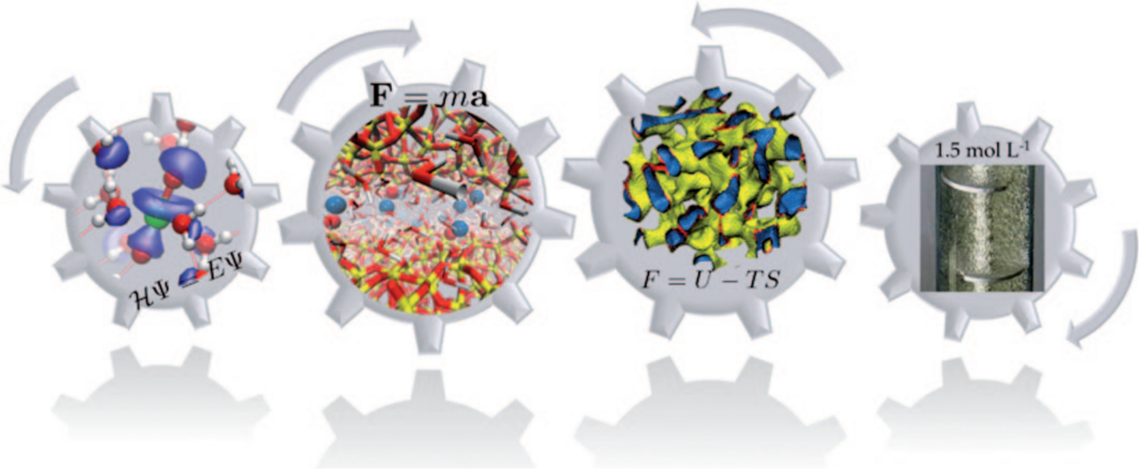


Un tel programme est réalisé dans différents contextes de la chimie séparative et permet de résoudre plusieurs problèmes ouverts :

- Modélisation de l'extraction liquide-liquide. Une approche à gros grains permet de déterminer les propriétés thermodynamiques dans les différentes phases (aqueuse et organique). Cette méthode est peu à peu développée pour des systèmes de plus en plus complexes.
- Etude des milieux poreux, en particulier ceux utilisés pour la séparation (oxydes, verres poreux, etc.). Le but est ici d'obtenir le maximum d'informations des expériences et de préciser les mécanismes physico-chimiques sous-jacents. Des études sont aussi menées sur les argiles de stockage.

Au niveau fondamental, nous étudions particulièrement la théorie des électrolytes pour les propriétés d'équilibre et de transport. Certaines applications sans lien direct avec la séparation ont été menées. Ainsi, en nanotechnologies, le rôle du bruit ionique a été étudié en relation avec des expériences utilisant des transistors à un électron. Les modèles de microémulsions sont aussi mis en œuvre pour l'étude des diagrammes de phase ternaires de ces milieux.

Toutes ces études sont réalisées en collaboration avec les expérimentateurs et, en particulier, ceux de l'ICSM. Les méthodes aux échelles intermédiaires peuvent ainsi être validées par comparaison aux expériences et aux modélisations moléculaires. L'idée à terme est de proposer une vision globale des processus où chaque mécanisme est intégré dans l'échelle de description la plus adaptée et où les liens entre les différents éléments de l'engrenage sont explicités. Les fondements de la thermodynamique statistique nous font comprendre qu'une telle tâche est au moins a priori faisable pour les processus d'équilibre, mais elle est plus délicate pour les phénomènes dynamiques, en raison de la nécessité de découpler les différentes échelles de temps, ce qui n'est pas toujours possible.



Le groupe de modélisation a ainsi à la fois des activités en lien direct avec les expérimentateurs de l'ICSM (présentées dans ce livret dans les pages du laboratoire expérimental correspondant), et aussi une activité méthodologique propre dont la suite présente une sélection.

The main goal of the modeling team consists in studying complex systems, and especially the ones involved in separation chemistry, from a multi-scale approach with a special interest for the models at the intermediate scale (mesoscopic models or nanoscale).

The methodology is presented in the figure. The most fundamental description is the one of quantum mechanics (ab initio calculations). It is able to represent elementary events. It is particularly performed in order to study complexation and it can also improve classical models. The latter can be studied from molecular dynamics in order to characterize the material structure, the equilibrium and transport properties, but only at relatively short scales (typically a few nanometers and a few nanosecond – not more). Thus the description of complex systems is possible only thanks to intermediate scale methods (coarse-graining, continuous solvent models, Brownian dynamics, integral equations, classical density functional theories, mode-coupling, interface theory, etc.) implemented in order (i) to describe the physical-chemistry of the processes and (ii) to link the result with chemical engineering. The originality of the team comes from the fact that the scale transition is almost systematically studied. The most microscopic scales allow the improvement of the macroscopic models, not only by providing the value of the physical parameters, but also by solely improving the macroscopic fundamental equations.

Such a program is applied in different domains and especially to separation chemistry issues:

- Modeling of liquid-liquid extraction. A coarse-graining method allows the calculation of the thermodynamic quantities in the various phases (aqueous and organic solvent phases). This method is developed for more and more complex systems.
- Porous Media, especially the one involved in separation (oxides, porous glasses; etc.). Here the goal consists in getting the maximum information from experiments and in characterizing the relevant underlying mechanisms. We also study clays for the storage of wastes.

At the more fundamental level, we especially study electrolyte theory for transport and equilibrium properties. Some applications with no direct connection with separation chemistry have been made. For example in nanotechnologies, the role of ionic noise has been studied with connection to experiments involving one-electron transistors. Microemulsions models are also studied in order to model ternary phase diagrams.

These works have been performed in collaboration with the experimentalists and, in particular, the one of ICSM. The methods at the intermediate scales can be validated from the comparison to the experiments and to molecular modeling results. The final idea would be to propose a global view of processes where every mechanism is integrated in the most adapted level of description, the link between the various models being explicated. Fundamentals of statistical thermodynamics help us to understand that such a project is at least a priori possible for the equilibrium processes, but it is much more difficult for dynamical properties, because of the need to uncouple the various time scale, which is not always possible.

Thus the modeling group has activities in direct connection with ICSM experimentalists (presented in this book in the sections of the corresponding experimental laboratories), but also methodological activities, a part of them being presented in the following pages.

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

Mesoscopic Modelling and Theoretical Chemistry

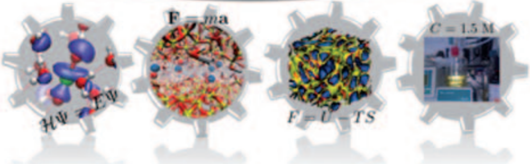
Laboratoire de Modélisation Mésoscopique et Chimie Théorique

(LMCT)

Permanent team

Jean-François DUFRECHE (UM)
Magali DUVAIL (CEA)
Bertrand SIBOULET (CEA)

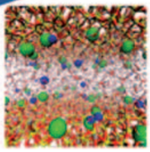
From atoms and molecules ...



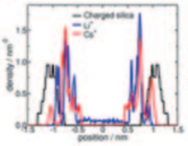
... to the macroscopic world.

Liquid – Solid Interface

Porous glass
Geological media

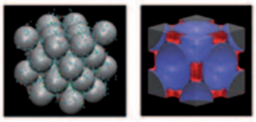


Aqueous solution confined between two walls of a porous glass.



Li⁺ (blue) and Cs⁺ (green) distribution between two walls of silica obtained from molecular dynamics simulations.

Atomistic simulations, together with **mesoscopic** methods (Density Functional Theory, Lattice-Boltzmann, homogenization, ...) performed in a **multiscale appraoch**.

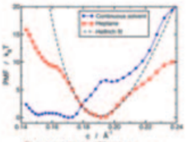


Mesoscopic modelling of ion transport through charged porous media by Brownian Dynamics (left) and Lattice-Boltzmann (right) simulations.

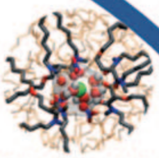
Liquid – Liquid Interface

Solvation effects
Microemulsion

Solvation effects estimated thanks to **Molecular Dynamics** simulations.



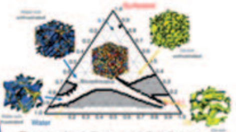
Free energy profile as a function of the curvature of the micelle in implicit (blue) and explicit (red) solvent.



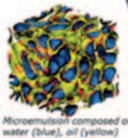
Molecular dynamics simulations of a reverse micelle.

Molecular and **mesoscopic modelling** of **organic solutions** involved in **ion separation** methods.

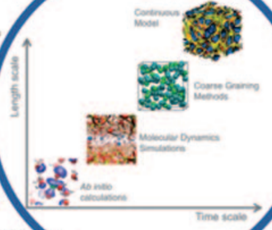
Microemulsion thermodynamical properties determined *via* **mesoscopic modelling.**

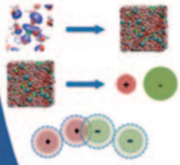


Ternary phase diagram predicted using our model for a rigid microemulsion.



Microemulsion composed of water (blue), oil (yellow) and surfactant (red).

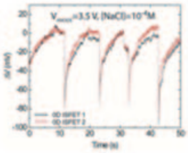


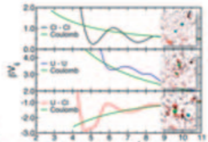


A **multiscale coarse graining procedure** developed to derive such models from **atomistic descriptions** to the models of **chemical engineering** (BiMSA, *etc.*).

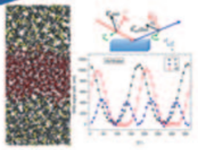
Electrolysis of NaCl electrolyte solutions at the surface of a ***ISFET nanocaptor****.*

Every period represents one bubble emission.



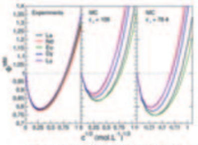


McMillan-Mayer potential profile of $Cl^- - Cl^-$, $UO_2^{2+} - UO_2^{2+}$, and $UO_2^{2+} - Cl^-$ in water calculated using "umbrella-sampling" molecular dynamics simulations.

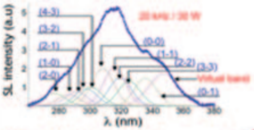


Molecular modelling of ***Second Harmonic Generation experiments****. The non linear response of the interface, which depends on the hyperpolarisability of the molecules can be modelled in order to describe the structure of the interfacial domain.*

An important contribution devoted to the **interpretation of experimental devices**.



Osmotic coefficients obtained from coarse-grained atomistic simulations for the series of lanthanoid chloride solutions as a function of the square root of the concentration.



Deconvolued ***sonoluminiscence*** *spectrum of OD ($A^2\Sigma^+ - X^2\Pi$) system in D_2O/Xe mixture at low ultrasound frequency (20 kHz).*

Ions in Solution

Coarse-graining method

Unravelling the experimental devices

IONS AT ACTIVE INTERFACES*

L'équipe est constituée au 1^er^ Septembre 2018 de :

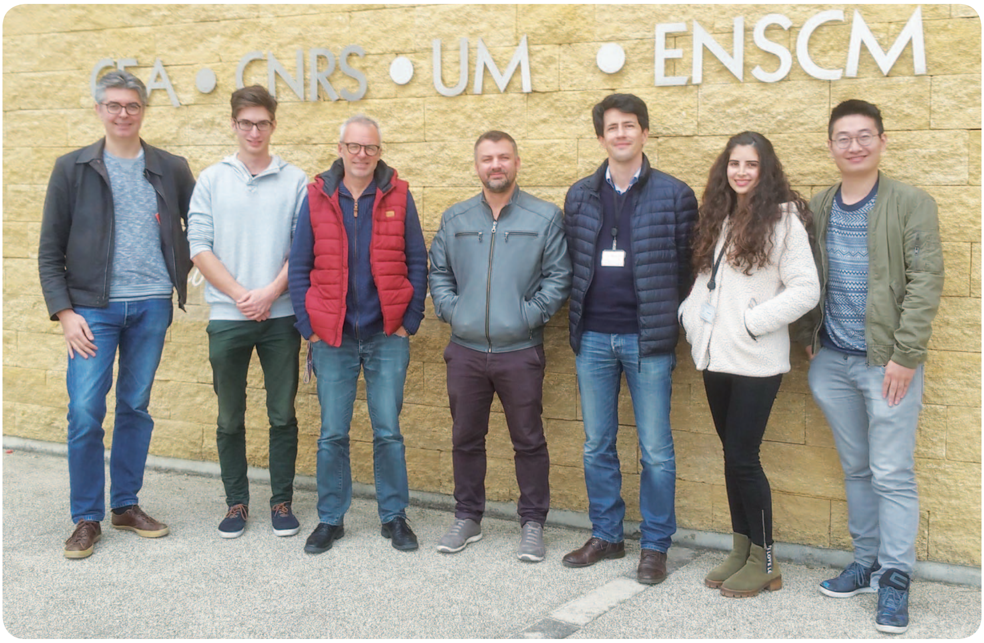
- 1 chercheur CEA/DRF resp. d'équipe (Dr. O. Diat),
- 1 chercheur CEA/DRF (Dr. P. Bauduin),
- 1 enseignant-chercheur ENSCM (Dr. L. Girard),
- 1 ingénieur d'étude CNRS (A. Jonchère)

Post-doctorants 2015-18 :

- Cyril Micheau (DEN, 2015-2016) : Flottation du césium d'effluents aqueux via des argiles.
- Alla Malinenko (ANR CATASURF, 2016-2017) : Réponse électro-acoustique de colloïdes hybrides de POM.
- Thang Pham (ANR ILLA, 2015-2016) : Modélisation du signal SHG pour des études d'interface liquide/liquide.
- Ophélie Fadel (labcom Vect'OLEO, 2015-16) : Extraction de principes actifs de plantes.
- Donatien Gomez-Rodrigues (labcom Vect'OLEO, 2015-16): Extraction en phase triglycérides : simulation de l'aggrégation en phase huile.
- Georgy Smolyakov (contrat ADIONICS en collaboration avec LTSM et le LHYS, 2016-17) : Extraction liquide/liquide pour désalination de l'eau.
- Bappaditya Naskar (DEN-ANR CATASURF, 2013-2014) : Interaction entre nano-ions et interfaces.

Thésards 2015-18 :

- Thomas Büchecker (Université de Regensburg, 2015/2018) : Réflectivité du rayonnement sur interfaces liquide/liquide.
- Tania Merhi (MNRT ENSCM, 2017-20) : Physico-chimie des bis-dicarbollides : Application en biochimie.
- Jing Wang (phare CEA, 2017-20) : Extraction par solvant : étude d'une interface liquide/liquide contenant des ligands en associant des mesures d'optique non linéaire et de la simulation par dynamique moléculaire
- Max Hohenschutz (Region/Extrahtive, 2017-20) : Mines et mousses



---

*Thématique 2 de la page 21

Parmi tous les phénomènes physiques et chimiques liés à la fabrication du combustible nucléaire et des déchets de dissolution, à la problématique de l'extraction et la séparation des ions dans de nombreux procédés de recyclage de métaux et de leurs stockages dans différents types de matrices, le vieillissement de ces matériaux sous différents stress chimiques ou radiatifs qui sont examinés dans les laboratoires de l'ICSM, le groupe des «ions aux interfaces actives (L2IA)» prend plus particulièrement en charge une recherche fondamentale concernant la distribution d'espèces telles que des ions, des molécules ou des agrégats à proximité d'interfaces fluides d'échange et les conséquences de cette répartition sur la réactivité de ces interfaces. Le génie chimique lié à cette activité de séparation des ions en solution et développé entre autres au CEA doit utiliser au maximum le potentiel des matières colloïdales pour assurer une sélectivité ionique et une séparation dans un processus continu après la dissolution du combustible nucléaire ou d'un lavage de décontamination. Ces méthodes requièrent une connaissance approfondie de l'adsorption des ions à partir d'une solution aqueuse vers une interface liquide-liquide ou encore liquide-air. Plus que les interactions électrostatiques décrites dans une théorie DLVO, la polarisabilité, les forces de dispersion, le réseau des liaisons hydrogène, la complexation ionique, les interactions entre les ions et leurs environnement doivent être considérés; c'est pourquoi des systèmes modèles ainsi que des géométries d'analyse sont à imaginer pour permettre de mettre l'accent sur la physique et chimie de la spécificité de chaque effet. Actuellement nous pouvons rassembler nos études fondamentales sous 3 axes prioritaires schématisés sur la figure suivante.

Dans ce rapport, parmi les nombreux sujets en cours qui nous impliquent mais impliquent aussi des collaborations extérieurs, nous avons sélectionné des exemples sur lesquels nous sommes porteurs ou plutôt les acteurs principaux : un premier exemple concerne donc l'étude d'interface liquide/liquide en utilisant plusieurs techniques d'investigation, surface tension, optique non linéaire, réflectivité du rayonnement afin de pouvoir appréhender l'organisation des ions et molécules extractantes autour de l'interface pendant un processus de transfert d'espèces. C'est actuellement un travail de thèse. Cette étude s'inscrit dans un projet plus large sur l'extraction par solvant en se focalisant de plus en plus sur l'aspect dynamique et sur lequel s'intéressent d'autres équipes de l'ICSM et des départements de la DEN au sein de Marcoule (DEN/DMRC) et avec qui nous collaborons faisant le lien entre expérience et simulation par dynamique moléculaire. Un deuxième exemple choisi concerne la flottation ionique avec une visite sous un angle différent de la flottation par mousse en utilisant des détergents bi-fonctionnels (extraction sans solvant). Les travaux de recherche se poursuivent dans le cadre d'une ANR intitulée Foamex et d'une thèse région. Le troisième exemple correspond à notre 3eme axe d'étude, les nano-ions et leurs propriétés potentielles de super-chaotropie avec un certain nombre d'ouvertures scientifiques en catalyse chimique, en chimie séparative et chimie supramoléculaire ou en biologie. Enfin il y a un « à part ça », avec une étude sur la solubilisation de molécules polaires et anti-oxydantes pour des activités type santé – un programme Labcom s'est terminé en 2017 mais une collaboration avec l'université de Regensburg se poursuit. Nous menons également des études autours de systèmes ternaires méso-structurées sans tensioactifs qualifiés de microémulsion ultra-flexibles avec un intérêt de solubilisation d'espèces peu solubles en phases pures aqueuses ou organiques mais pour lesquels il y a un intérêt à être séparé d'autres espèces plus solubles, le tout sans utilisation d'agents amphiphiles. Enfin d'autres activités sont menées en exploitant le couplage de ces études ainsi que de nouveaux développements instrumentaux (exemple avec reflectivité de neutron et fluorescence gamma, mis en place d'une machine de force par interférométrie).

In the context of chemistry at interfaces, our goal is to answer to some issues related to charged solutes in solution that can adsorb at liquid / liquid and liquid / air interfaces and can be extracted and separated taking into account of their speciation in solution. We are focusing our studies on issues encountered in nuclear fuel treatment at la Hague plant but also in mining processes of ionic separation or in water remediation from mineral contaminates. Stated in the case of actinides and lanthanides, but also for heavy metals and other ionic aggregates this issue is important to any issue of recycling and transfer of active species. We must move from purely experimental approach to the establishment of predictive models. The L2IA laboratory operates mainly in the axis «Understand the separation?» and "Methods and Theory" and we follow three main axis of research: I) Investigation of transfer phenomena at Liquid/liquid interface involved in a solvent extraction process, II) ion foam flotation and III) Ion specific effect of nano-ions or investigation of the super-chaotropic effect.

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

L2IA : laboratory of ions at active interfaces

Permanent team

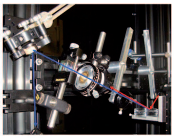
Olivier DIAT (CEA)
Pierre BAUDUIN (CEA)
Luc GIRARD (ENSCM)
Alban JONCHERE (IE-CNRS)

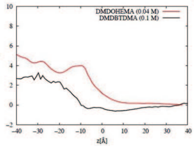
Adsorption/desorption mechanisms of ions and other charged supramolecular aggregates and/or their transfer through liquid or soft interfaces

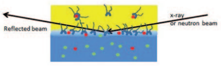
Liquid-liquid interface

Techniques, models, Correlation, bulk/interface

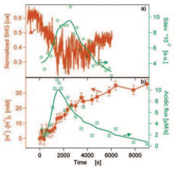
Liquid interfaces probed by **linear and non linear optics, by light x-ray and neutron** scattering and reflectivity

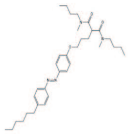


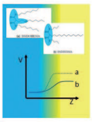




Interfacial potential of transferred ions from reflectivity measurements (TGI)





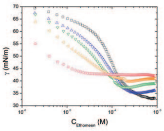


ions transfer, separation concentration

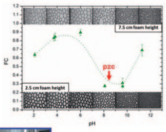
Studies on solvent extraction

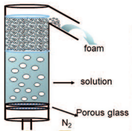
Re-explore solvent-free separation processes

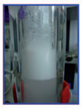
Extraction/transfer in bio-systems

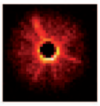


Experiments / model



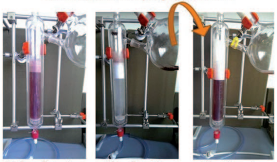






Charged species separation and concentration in a foam.
Physical chemistry approach

Decontamination / recycling by pH stimulus



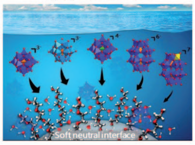
Before flotation After flotation After flotation

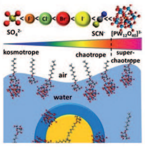
Liquid /air interface

Ion and particle flotation

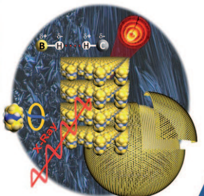
Responsive foam, recycling

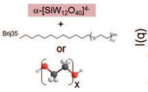
polyoxometalates

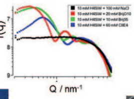




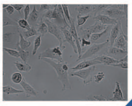
dicarbollides

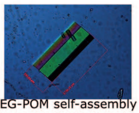




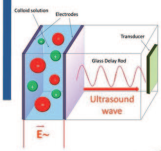


I2-COSAN in Hela cells





PEG-POM self-assembly



Electro-acoustic technique

Nano-ions at interfaces

Interactions with soft surfaces

Applications to biological systems

LABORATOIRE DU TRI IONIQUE PAR LES SYSTEMES MOLECULAIRES AUTO-ASSEMBLÉS*

L'équipe est constituée au 1er Septembre 2018 de :
1 DR CNRS responsable d'équipe (Stéphane Pellet-Rostaing),
1 MDC UM - HDR (Guilhem Arrachart)
1 Ingénieur CEA/DRF - HDR (Sandrine Dourdain)
1 Technicienne CEA (Béatrice Baus-Lagarde)
1 Ingénieur de recherche CNRS (Fabrice Giusti)

Post-doctorants :

- Simon Chapron (ERA-MIN, 2015-2017) : Ligands pour la récupération de terres rares de mines secondaires
- Fanny Mary (ANR SILEXE, 2015-2016) : TSIL pour le recyclage du palladium
- Carlos Ruiz (Andalucia Talent Hub, 2015-2016) : extraction des terres rares de phosphogypse
- Raphaël Turgis (ANR SILEXE, 2014-2016) : TSIL pour le recyclage de métaux stratégiques
- Georgiy Smolyakov (ADIONICS, coll. L2IA/LHYS, 2016-2018) : Mécanismes d'extraction par la formulation Flionex
- Manuel Lejeune (POC SYNEXTRACT, coll. LNER, 2017-2018) : Chromatographie Synergique pour la purification de terres rares
- Guillaume Mossand (CNRS, 2017-2018) : Extraction de l'uranium de l'eau de l'eau de mer par des résines chélatantes
- Victor Haquin (AREVA 2017-2019) : Compréhension de l'extraction de l'uranium et de ses impuretés en milieu sulfurique
- Cesar Augusto Lopez (UM LABEX 2018-2020) : Mécanismes d'extraction en milieux liquides ioniques

Doctorants :

- Julien Rey (DEN/ERC, 2013-2016) : Etude des mécanismes d'extraction synergiques en séparation liquide-liquide
- Moheddine Wehbie (Cèdre Franco-Libanais, 2013-2016) : Système chélatant organisés pour l'extraction sélective de métaux stratégiques
- Tamir Sukhbataar (CTCI AREVA, 2014-2017) : Approche multi-échelle pour la compréhension de mécanismes d'extraction de l'uranium en milieux liquides ioniques
- Tobias Lopian (ERC, 2014-2017) : Caractérisation d'une microémulsion pauvre en eau et adaptive à l'extraction de métaux.
- Carlos Arrambide (Contrat Doctoral UM2, 2014-2017) : Méthodologies de synthèse de résines formo-phenoliques chelatantes : vers une extraction solide-liquide optimisée des métaux stratégiques
- David Bengio (CEA/DEN, 2015-2018) : Comportement électrochimique des terres rares en milieu liquide ionique (co-direction thèse)
- Alexandre Artese (CEA/DEN thèse phare, 2016-2019) : Caractérisation de ligands bifonctionnels N,P pour la co-extraction U/Pu en milieu nitrique.
- Robert Winkler (CEA/DRF, 2016-2019) : Approche « tout en un » pour la mise en oeuvre de matériaux hybrides à hautes capacités extractantes
- Nicolas Felines (CEA/DEN thèse phare, 2017-2020) Monoamides énantiopurs pour l'extraction de l'uranium
- Zijun Lu (CEA/DEN 2017-2020) : Solution of amphiphilic ion pairs in equilibrium with an aqueous phase: mechanistic study of extraction
- Justine BenGhozi-Bouvrande (CEA/DEN 2018-2021) : Les liquides poreux : un nouveau concept pour l'extraction liquide liquide
- Ruth.Oye-Auke (Contrat Doctoral UM, 2018-2021) : Méthodologies de synthèse et étude de résines biosourcées thermodurcissables pour la récupération de métaux d'intérêt
- Chen Xing (China Scholarship Council (CSC), 2018-2022) : Concentration and selective recovery of uranium using nanofiltration processes
- Sahar Belfqueh (Région-BRGM, 208-2021) : Recyclage et valorisation des terres rares contenues dans des solutions faiblement acides
- Fatima Bekkar (PNE, accueil 18 mois, 2018-2019) : Synthèse contrôlée de résine chélatantes pour le recyclage
- Asmaë El Mangaar (CEA/DEN 2018-21) : Comparaison des efficacités de la séparation et de la co-précipitation de terres rares par solvants classiques et par co-solvants

---

**Thématique 3 de la page 21*

L'équipe « Tri Ionique par des Systèmes Moléculaires Auto-assemblés » (LTSM) est aujourd'hui constituée de 5 permanents, Guilhem Arrachart, Maître de Conférence UM (09/2009), Sandrine Dourdain (07/2010), Ingénieur CEA/DRF, Béatrice Baus-Lagarde, Technicienne CEA/DEN, et Fabrice Giusti, Ingénieur de recherche CNRS, récemment recruté par mutation (07/2018) et Stéphane Pellet-Rostaing, Directeur de Recherche CNRS (01/2009).

Cette équipe a initié concrètement des travaux de recherche dans le domaine de la synthèse de ligands et de matériaux spécifiques pour la séparation d'ions, mis en œuvre dans des procédés d'extraction classiques (liquide/liquide, solide/liquide) ou non conventionnels (membranes, solvants non usuels, pertraction) avec une orientation dans la compréhension des mécanismes qui gouvernent la séparation.

Comprendre et optimiser les procédés de tri ionique est à l'origine de l'axe de recherche majeur du groupe LTSM visant la conception et la synthèse d'extractants spécifiques originaux ainsi que l'étude des mécanismes associés qui gouvernent l'affinité et la sélectivité, notamment par des phénomènes coopératifs supramoléculaires. La possibilité d'exalter la complexation par auto-association des complexants sous forme de micelles, fibrilles ou cristaux liquides, doit être explorée, pouvant conduire à des procédés en rupture de tri ionique qui seront ensuite à développer en partenariat avec les équipes actuelles en ingénierie chimique de R/D de Marcoule.
Au-delà du domaine purement nucléaire, ces effets sélectifs sont étudiés et mis en œuvre dans différents procédés liés au recyclage de matières associées à la production d'énergie et plus généralement, dans les optiques de développement durable, par exemple en décontamination ou pour le recyclage sélectif des métaux stratégiques.

Du point de vue des disciplines abordées, et comme résumé précédemment, le LTSM se situe clairement dans l'approche nanosciences et développe en outre une recherche à caractère fondamental en adéquation avec les orientations initiales de l'Alliance ANCRE et de la SNRI (aujourd'hui Stratégie Europe 2020) dans le cadre des énergies renouvelables et de l'économie circulaire. Cela couvre aussi bien l'ensemble du cycle du combustible nucléaire (amont et aval du cycle) actuel et futur que celui des métaux d'intérêt (métaux stratégiques et chimio-toxiques), allant de l'extraction des métaux des minerais (uranium, lanthanides, etc) au retraitement du combustible nucléaire usé (élimination des éléments radiotoxiques) ou au recyclage des déchets de la mine urbaine (DEEE). La chimie du LTSM doit s'approprier l'évolution des nanosciences : systèmes moléculaires organisés, nanomatériaux et compréhension des forces en jeu à l'échelle nanométrique.

L'implication du LTSM dans les programmes de recherche du CEA à travers leur segmentation (Energie Nucléaire, technologies pour l'Industrie et la communauté scientifique, Socle de la recherche fondamentale), le programme interdisciplinaire du CNRS NEEDS, des collaborations industrielles directes (Morphosis, ADIONICS) ou par l'ANR (CD2I), par l'Europe (ERA-MIN)) ainsi que par des financement de maturation de projets (SATT Ax-LR), mais aussi des programme européens (ERC REE-Cycle, H2020 REFRAM) et internationaux comme les programmes Franco-Libanais Cèdre ou Franco-Indien CEFIPRA, les programmes de co-financement par la région, ainsi que la coordination de l'axe « recyclage et décontamination » du LABEX Chemisyst et celle du GDR SENA (Franco-Russe) sont à l'origine des projets de recherche commun avec CEA/DEN, CEA/DSM, le BRGM, l'Université de Montpellier (ICGM, IEM), l'Université de Savoie (LCME), l'Université de Lorraine (IJL), l'Université de Lyon (IRCE), l'Université Libanaise (Beyrouth), l'IPCE (Moscou), Argonne (USA), le CNEA (Argentine), le CSIR-NML, ou encore les industriels TND, AREVA, Morphosis, Chemec Oy, Tata.

En marge des activités de recherche, le LTSM réalise des contrats de prestation (synthèse à façon, analyses ICP, RMN…) pour le CEA/DEN, le laboratoire PROMES et d'autres industriels (VEOLIA, Cis-Bio).

The group «Ion Separation by Self-assembled Molecular Systems» (LTSM) is today made up of 4 permanent staff, Guilhem Arrachart, Lecturer UM (09/2009), Sandrine Dourdain (07/2010), Engineer CEA/DRF, Beatrice Baus-Lagarde, Technician CEA/DEN, who recently joined the team (04/2015) following the departure of Véronique Dubois, also Technician CEA/DEN, Fabrice Giusti, Research Engineer CNRS who recently joined the team (07/2018) and Stéphane Pellet-Rostaing, CNRS Research Director (01/2009). This group has initiated practical research in the field of ligands and specific materials for ion separation used in conventional extraction processes (liquid/liquid, liquid/solid) or unconventional (membranes, "green" solvents, pertraction) with a focus on the understanding of mechanisms that govern the separation. Understand and optimize the ion extraction/separation processes is at the origin of the main challenge of LTSM that must help to the design and synthesis of specific extractants and the study of associated mechanisms governing the affinity and selectivity, especially through cooperative supramolecular phenomena. The ability to exalt the self-association by coordination as micelles, fibrils or LCD, must be explored, which could lead to processes out of ion separation which will then develop in partnership with existing engineering R§D departments of Marcoule centre. Beyond the purely nuclear domain, the selective effects are studied and implemented in different processes related to recycling of materials associated with energy production and more generally in the perspective of sustainable development, such as decontamination or selective recycling of strategic metals.

The LTSM is clearly located in the nanoscience approach and also develops a fundamental research related to the initial orientations of the Alliance ANCRE and SNRI (today 'Europe 2020 Strategy') in the context of renewable energy and circular economy. This covers the current and future nuclear fuel cycle (upstream and downstream) as well as the metals of interest (strategic metals and chemo-toxic), from the extraction from ores (uranium, lanthanides, etc.) to the spent nuclear fuel reprocessing (removal of radio-toxic elements) or the recycling of WEEE.

The involvement of LTSM in the CEA research programs through their segmentation (Nuclear Energy Technology for Industry and the scientific community base of basic research), the interdisciplinary program of CNRS NEEDS, industrial collaborations (direct (ADIONICS), through ANR (CD2I), by Europe (ERA-MIN)), European program (ERC REE-Round, H2020 REFRAM), the Franco-Lebanese "Cèdre" program, as well as the coordination of the axis « recycling and decontamination « of the LABEX Chemisyst and that of the GDR SENA (Franco-Russian) are at the origin of the joint research projects with CEA/DEN, CEA/DRF, Montpellier University (ICGM, IEM), Savoie University (LCME), Lorraine University (IJL), Lyon University (ESRD), Lebanese University (Beirut), EICP (Moscow), Argonne (USA), CNEA (Argentina), TND, ORANO, Morphosis, Chemec Oy. Alongside the research, LTSM performs service contracts (synthesis, analysis and characterization, expertises ...) to the CEA/DEN and other industrial (VEOLIA, ONET-Technology, St Gobain, Cis-Bio).

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

LTSM : Ion Separation by Self-Assembled Molecular Systems

Permanent team

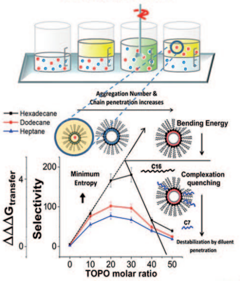
Stéphane PELLET-ROSTAING (CNRS)
Sandrine DOURDAIN (CEA)
Beatrice BAUS-LAGARDE (CEA)
Guilhem ARRACHART (UM)

Design, synthesis and studies of specific ligands and materials for ion extraction and separation.
Focus on the understanding of the molecular and supramolecular mechanisms governing affinity and selectivity.

Understand mechanisms

Solvent extraction
Synergistic effects

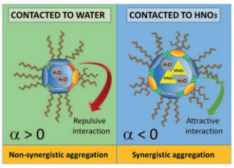
Extraction mechanisms



Supramolecular aggregation

Effect of self-assembly of extractant molecules on extraction (SAXS, SANS measurement...)

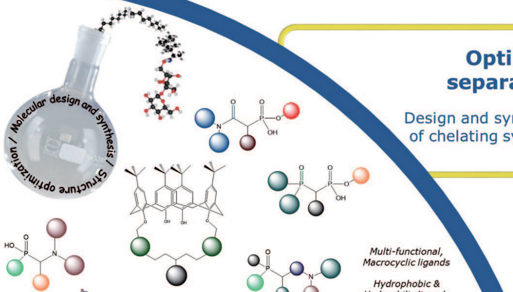
Synergistic effects



Thermodynamic investigation of synergy in solvent extraction

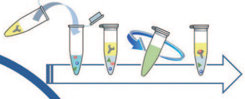
Optimize separation

Design and synthesis of chelating systems



Multi-functional, Macrocyclic ligands

Hydrophobic & Hydrophilic ligands



Liquid/Liquid extraction

- Nuclear fuel processing and reprocessing
- Extraction and recycling of strategic metals
- Decontamination of aqueous effluents

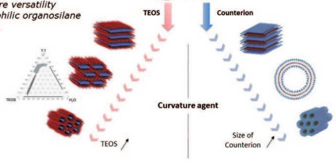
Understand and Optimize

Ion Extraction/Separation in Conventional and Unconventional Processes

Hybrid materials:

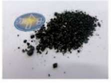
- Methodologies for hybrid materials synthesis (SiO_2, TiO_2, ZrO_2... based materials)
- Extraction and decontamination processes

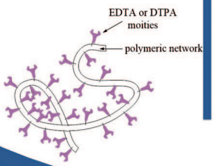
Nanostructure versatility thanks to amphiphilic organosilane



Chelating organic resins :

- Synthesis of chelating ion exchange resins
- Extraction and decontamination processes



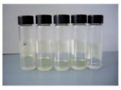


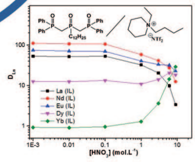
Extracting materials

Hybrid materials
Organic resins

Ionic liquids :

RTIL's & TSIL's as alternative systems for solvent extraction





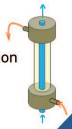
Extraction and recycling of strategic metal

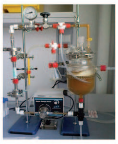
Selective extraction of REEs from leaching solution of mines or Waste Electrical and Electronic Equipment (WEEE).

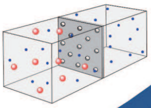
Unconventional extraction processes :

Nano-filtration
Assisted by complexation

Pertraction







Alternative processes

Green processes

HYBRID SYSTEMS FOR SEPARATION*

L'équipe est constituée au 1er Septembre 2018 de :
Permanent Staff:

- Head of the team CEA/DEN (2007-) Dr. Daniel Meyer
- Researcher CNRS (2009-) Dr. Damien Bourgeois : Liquid-liquid separation, toxicology
- Professor Assistant UM (2009-) Dr Jérôme Maynadié : Molecular and coordination chemistry
- Researcher CEA/DSM (2014-) Dr Michaël Carboni : Molecular materials, MOF

Post-doctoral:

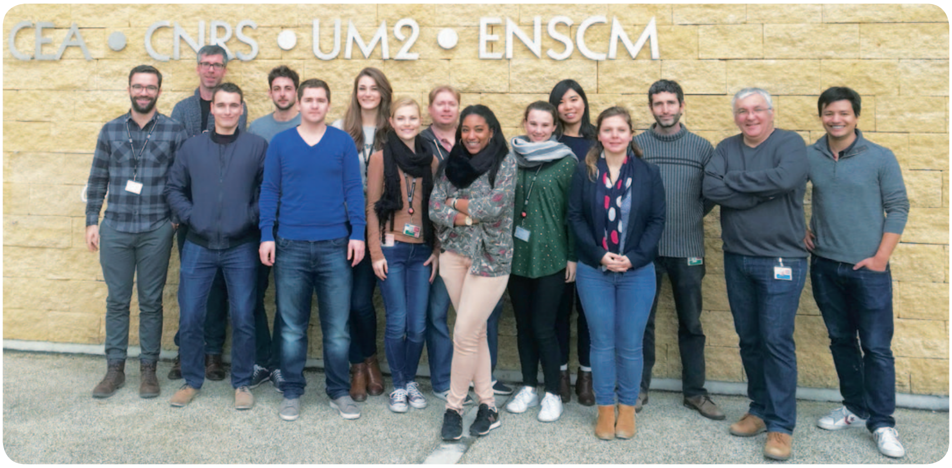
- Jingxian Wang (2017-)

PhD:

SayedAli Moussaoui (2018-), Fabrice Lorignon (2018-), Aline Chevalier (2017-), Elisa Re (2017-), Julie Durain (2017-), Marine Cognet (2016-2019), Guillaume Genesio (2014-2018) , Ricardo Navarro (2013-2017), Bertrand Braibant (2014-2017), Violaine Goudy (2012-2015), Kevin Ruffray (2012-2015)

Technicians:

Marjorie Laszczyk (2015-2017), Regis Mastretta (2015-2016), Emilie Perez (2014-2016), Alexia Agot (2014-2015), Halima Tounkara (2017-2018)



The team

Main frame of the team research is transition metals, lanthanides and actinides coordination chemistry. The team has focused his research on the development of complex molecular systems and hybrid solid materials such as coordination polymers and metal-organic frameworks (MOFs) in the field of separation chemistry, advanced materials, nuclear toxicology and energy storage.

If the studies are usually done at a fundamental level, several other projects, in collaboration with industrials, are focused on applied research.

Main thematic can be classified as:

- Molecular supramolecular chemistry

From molecular systems to hybrid materials through polymerization process (condensation, redox coupling…) for the control of shapes and properties (nanoparticles, nano-hybrid…),

Molecular systems (based on Ru-catalyst) for the energy storage (photo-reduction of CO_2)

- Materials

Hybrid materials as precursors for hard materials such as ceramics,

Hybrid materials for environmental purposes (Energy storage, metal extraction, depollution),

Bone mimetic materials for uranium and/or metal toxicology studies.

- Hydrometallurgical separation

Weak interactions and molecular topology in liquid-liquid separation, development of fluorinated systems, multi-phase separation,

Selective precipitation by metal-assembling to form hybrid materials (coordination polymers, MOFs…) as high value final products,

Recycling of metals (liquid-liquid, solid-liquid…).

---

*Thématique 1 de la page 20

Molecular compounds

CO_2 photo-reduction

Ru-Co bimetallic species have been studied for the CO_2 photo-reduction to compare their reactivity with related hybrid material. The main objective of these studies is the transposition of molecular homogeneous reactivity into a heterogeneous material. TON's of several hundreds were observed for a first series of compounds.

Nano-structuration of actinide material

To continue our work on actinide nanoparticles and nanocrystals by molecular approaches (collaboration with JRC ITU), a new way to multiscale nanocomposite materials has been considered by coupling molecular reactivity and supramolecular metal-assembling.

Materials

Coordination polymers and MOFs

The LHYS is interested in the development of hybrid materials (coordination polymers, MOFs…) as precursors of hard materials such as carbides and oxides and as materials for energy (photophysic, electrochemistry, catalysis…).

The main goal of the precursor development is to control the structure, composition, microstructure and shape of the converted material.

For the energy, the LHYS works on the development of photo-physical charge separation hybrid devices for the CO_2 reduction or the water splitting. These devices are developed as bulk materials or as thin films on transparent conducting oxides.

Coupling energy issues with precursor's synthesis from waste was realized by the team in the frame of electrochemical energy storage. Ni, Co and Mn were purified from a Li-ion waste stream as MOF, directly used as an electrode material in a button cell leading to a higher current density (700 mAh/g) than the original battery (280 mAh/g).

Biomimetic materials: synthetic bones

To understand the behavior of uranium in bone tissues at the microscopic level (chemical, biochemical and cell), the LHYS has developed synthetic bone materials (collaboration CEA/DRF, KIT-INE, INSERM, Université de Nice). This approach allows to build-up bone mimetic material containing a controlled amount of uranium, avoiding animal experimentations.

Metal separation by hydrometallurgy

Main frame of these studies is the understanding of the fundamental interactions driving metal separation in solid-liquid and liquid-liquid processes. To progress in this field, the LHYS has developed three approaches:

d transition metals and f-elements (lanthanides) comparison

In the nuclear spent fuel recycling, understanding the behavior of the main fission products in a liquid-liquid process is challenging and important. In recently developed CEA processes, Pd, Mo, Zr and lanthanides show unwanted behavior during actinide (III) and lanthanide separation. Recent studies have shown a specific metal and diluent extraction behavior regarding the importance of the interactions driving the separation.

Fluorinated molecular systems

These systems have been developed to model and understand the importance of the low energy interactions (Van der Waals) in a liquid-liquid separation system with amphiphilic type extracting molecules and their correlation with the complexation properties.

Precipitation by metallic self-assembling

These studies are focused on the use of specific organic linkers for the synthesis of hybrid materials containing specific metallic species from a complex mixture of metals. From a fundamental point of view, in this process the driving forces are not only electrostatic and polarization, but mainly due the coordination behavior of the metals and the ligands and the stability of the final structural building. From an applied point of view, as described for battery recycling, this approach can lead to high value products such as new precursor for battery electrode materials.

Applied research

Thermal management of engine exhaust by silicon carbide (2014-2017)

This project deals with the control of the thermal behavior of a car engine exhaust catalyst using silicon carbide.

CO_2 from metallurgy conversion (2014-2018)

This project handles with the opportunity to reuse the carbon dioxide produced by metallurgy industry. It deals essentially with the carbonation of magnesium silicate into magnesium carbonate for an economic valorization after purification.

Li-ion battery recycling (2013-2015)

This project was a direct collaboration with VEOLIA/SARPI. Main objective was to recover and value the metallic species in a Li-ion battery recycling stream.

Electric waste recycling (2015-2016)

This project is a spin-off application of the fundamental research results obtained for the palladium and lanthanides behavior in the frame of nuclear spent fuel recycling studies.

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

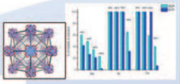
Hybrid System for the Separation

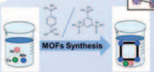
Laboratoire des Systèmes Hybrides pour la Séparation (LHyS)

Permanent team

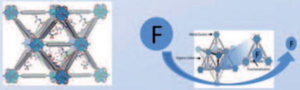
Daniel MEYER (CEA)
Damien BOURGEOIS (CNRS)
Michaël CARBONI (CEA)
Jerôme MAYNADIE (UM)

Extraction Separation



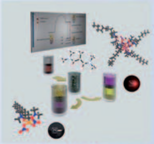


Selective precipitation of porous material



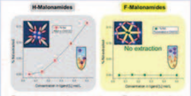
Extraction of metals or organic molecules by MOFs

Metal solvent extraction and separation



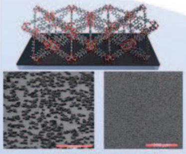
Coordination Aggregation

3-Phases systems



Fluorinated systems

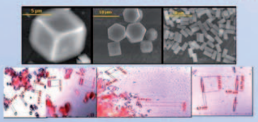
Materials Tailoring



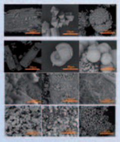
UiO-67@RuDCBPY

MOF grafted on substrates (ITO or FTO)

Micrometric scale morphology of hybrid materials

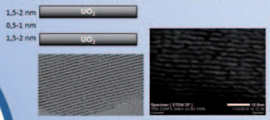


Coordination polymers

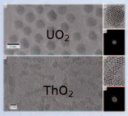


MOF

Nanometric scale organisation of actinide materials

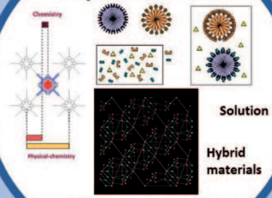


Nano-rhods UO_2



Nano crystals

Molecular Supramolecular



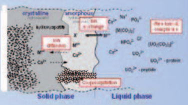
Solution

Hybrid materials

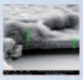
Self-assembly

Nuclear Toxicology

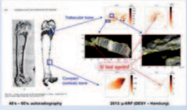
Uranium – bone toxicology, multi disciplinary approach



Uranium – bone exchanges

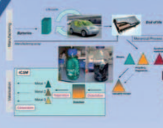


Biomimetic uranium containing apatites

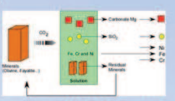


Uranium – bone Localisation and speciation

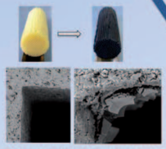
Applied Research



Li-ion Car batteries recycling

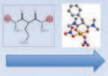


Conversion of CO_2 from steel industry to valuable products



Thermal exhaust management of combustion engines

WEEE (electronic board) Pd recycling



Pd high value material

Physical Properties

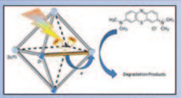
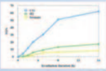
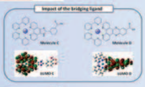
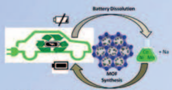


Photo-chemical organic pollutant destruction by hybrid materials

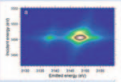


Photochemical CO_2 and H_2O reduction





Electrochemical energy storage using MOF materials through metal recycling



ThO_2 nanoparticle d-f orbital hybridisation high covalency

SONOCHEMISTRY IN COMPLEX FLUIDS*

L'équipe est constituée au 1er Septembre 2018 de :
Sergueï Nikitenko (CNRS)
Rachel Pflieger (CEA/DEN)
Tony Chave (CNRS)
Matthieu Virot (CEA/DEN)

Doctorants :

- Xavier Beaudoux : Dissolution sonochimique d'oxydes de lanthanides et de PuO2 assistée par ultrasons (thèse soutenue en 2015, codirection CEA/DEN/DRCP-ICSM)
- Témim Ouerhani : Effet de l'azote et de l'ammoniaque sur les spectres de sonoluminescence et l'activité sonochimique (thèse soutenue en 2016, UM-ICSM)
- Elodie Dalodière : Synthèse et caractérisation de colloïdes de Pu (thèse soutenue en 2017, codirection ICSM-CEA/DEN/DRCP)
- Andrés Felipe Sierra Salazar : Waterborne catalytic materials with original design (thèse soutenue en 2017, Erasmus Mundus – ICG/IEM/ICSM - University of Messina – University of Delft)
- Florence Nouaille : Développement d'un procédé innovant de conversion d'oxyde d'uranium en peroxyde d'uranium (thèse soutenue en 2017, BDI CNRS-AREVA, codirection ICSM- Université de Lille)
- Ran Ji : Study of acoustic cavitation near metal surfaces contaminated by uranium (2015-2018, CEA/DEN/EDDEM-ICSM)
- Lauréanne Parizot : Etude de la cavitation par impact et par ultrasons pour la dégradation des composés organiques (2016-2019, Investissements d'Avenir ANDRA, CADET, codirection ICSM - IJLRA)
- Laura Bonato : Réactivité d'oxydes d'actinides nanostructurés en vue de leur dissolution sous l'effet de la cavitation acoustique (2017-2020, CEA/DEN-ICSM)
- Sara El Hakim : Réactions sonocatalytiques et photocatalytiques en présence de nanocatalyseurs innovants pour l'énergie et l'environnement (2018-2021, UM-ICSM)

L'objectif principal du laboratoire de sonochimie dans les fluides complexes (LSFC) consiste à mener des études fondamentales sur les mécanismes des réactions sonochimiques (réactions chimiques induites par la propagation d'ondes ultrasonores entre 16 kHz et 1 MHz dans un milieu fluide) en solutions homogènes et dans des systèmes hétérogènes solide-liquide.

Les effets observés en sonochimie ne résultent pas d'une interaction directe entre les ondes ultrasonores et les ions ou molécules mais sont étroitement liés au phénomène de cavitation acoustique : la nucléation, croissance et implosion rapide de micro-bulles de gaz ou de vapeur de solvant dans les liquides soumis à un champ ultrasonore.

Le temps d'implosion est de l'ordre de la microseconde et le phénomène résultant induit des conditions locales de température et de pression extrêmes, estimées à plusieurs milliers de degrés et plusieurs centaines d'atmosphères, couplées à des vitesses de refroidissement de l'ordre de 10^{10} K.$^{s-1}$. De récentes études démontrent la formation d'un plasma hors-équilibre dans les bulles au moment de l'implosion.

Cette concentration locale d'énergie constitue l'origine des phénomènes d'émission de lumière par les bulles de cavitation – la sonoluminescence, mais également de l'activité chimique en solution et de l'évolution des systèmes en phase hétérogène. En résumé, chaque bulle de cavitation peut être considérée comme un microréacteur chimique à plasma qui ne nécessite pas d'ajout de réactifs spécifiques et ne génère pas de déchets supplémentaires, respectant ainsi les principes de la chimie « verte ».

Les thématiques du LSFC :

- *Spectroscopie de sonoluminescence*
- *Réactivité sonochimique à l'interface solide-liquide*
- *Synthèse sonochimique de nanomatériaux et sonocatalyse*
- *Sonochimie des actinides*

---

*Thématique 4 de la page 21

The main objective of the laboratory of sonochemistry in complex fluids (LSFC) is to carry out a fundamental research on the sonochemical reactions (chemical reactions induced by power ultrasound at 16 kHz – 1 MHz frequency range) in homogeneous solutions and heterogeneous solid-liquid systems. The effects observed in sonochemistry are not based on direct interaction between the ultrasonic waves and ions or molecules but rather on the phenomenon of acoustic cavitation: the nucleation, growth, and quick implosion of microbubbles of gas or vapor produced in liquids subjected to an ultrasonic field. Transient implosion of cavitation bubbles induces extreme local conditions of temperature and pressure, estimated at thousands of degrees and several hundred atmospheres, coupled with extremely high cooling rate of the order of 10^{10} K·s $^{-1}$.

Our recent studies revealed the formation of a nonequilibrium plasma inside imploding bubbles. This local concentration of energy is the origin of the light emission known as sonoluminescence, but also the origin of chemical activity in solutions as well as of the evolution of heterogeneous systems. In summary, each cavitation bubble can be considered as a plasma-chemical microreactor that does not require the addition of specific reagents and generates no additional waste, thus respecting the principles of green chemistry.

The specific topics of LSFC:

• Multibubble sonoluminescence
• Sonochemical reactivity at solid-liquid interfaces
• Sonochemical synthesis of nanomaterials and sonocatalysis
• Sonochemistry of actinides

Projets (collaborations)

- 2016-2019, Investissements d'Avenir ANDRA, CADET « Cavitation Assistée pour la DEconTamination des eaux » (Institut Jean le Rond d'Alembert)
- Sonoluminescence dans les fluides complexes (LCME, Chambéry ; Université de Melbourne, Australie ; DPI Göttingen, Allemagne)
- Dissolution sonochimique des oxydes d'actinides (CEA/DEN)
- 2015-2017, Sonochimie de l'uranium (Comurhex/AREVA; Université de Lille)
- Sonochimie du plutonium (CEA/DEN)
- Colloïdes de plutonium(IV) (CEA/DEN ; JRC Karlsruhe Allemagne ; ESRF Grenoble ; 2015-2016 projet TALISMAN, 2018-2019 projet Bottom Up SONISCOP)
- 2015-2017, Synthèse sonochimique de nanomatériaux et applications en catalyse (Erasmus Mundus, ICG ; IEM ; Université de Messine ; Université de Delft ; Université du Cap)
- 2018-2019, Synthèse sonochimique de nanoparticules pour les applications biomédicales (TORSCAL)
- 2018-2019, Dispersion ultrasonore de fibres naturelles (APM FORENSIA)

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

Sonochemistry in Complex Fluids

Laboratoire de Sonochimie dans les Fluides Complexes

Permanent team

Sergueï NIKITENKO (CNRS)

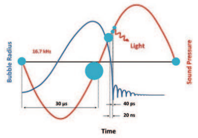
Tony CHAVE (CNRS)
Rachel PFLIEGER (CEA)
Matthieu VIROT (CEA)

The propagation of **ultrasound waves** (16 kHz – 1 MHz) in **liquid media** may lead to the **acoustic cavitation** phenomenon which is the **nucleation**, **growth** and rapid **implosive collapse** of **gas** and **vapour**-filled **microbubbles**

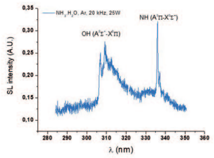
Each **acoustic bubble** can be considered as a **plasma chemical reactor** providing **highly energetic processes** at almost **room temperature**

Sonoluminescence

Origin of Sonochemistry: *Acoustic Cavitation*



Sonoluminescence (SL) is the **emission** of **light** from the **UV** to the **near IR** during the **collapse** of acoustic **bubbles**

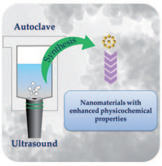


A **non-equilibrium plasma** is formed, whose characteristics can be **studied** by **emission spectroscopy** of **excited species**

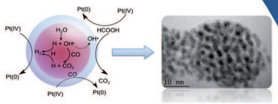
Nanoparticles and Sonocatalysis

AOP processes and Catalysis

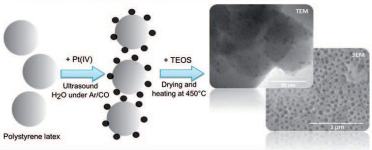
Sono-hydrothermal synthesis of **nanomaterials**



Sonochemical synthesis of **NPs** in **dilute** aqueous **solutions**



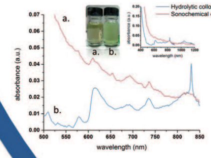
Porous silica **matrix decorated** with **Pt NPs**



Main Research Fields

An colloids and related behavior
Refractory AnO$_2$ dissolution
An ions redox control and stabilization

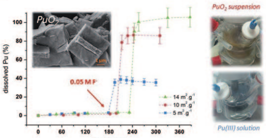
Sonochemical preparation of **stable salt-free Pu intrinsic colloids**



Glove box in **Atalante** facility
(DRCP collaboration)

Sonication at high or low frequency under different gaseous atmosphere. On-line UV-Vis-NIR spectroscopy measurements.

Reductive dissolution of **PuO$_2$** in **mild conditions**

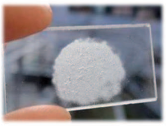


20 kHz dissolution in the presence of Ti particles (Ar, 17 W.cm^{-2}, 0.5 M HNO$_3$ / 0.1 M NH / 1 M HCOOH)

Actinide Sonochemistry

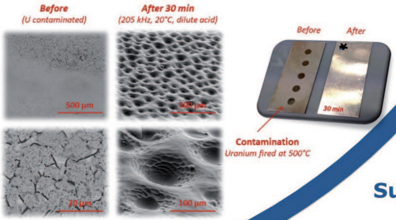
Asymmetric Collapse of Bubbles at the Interface

Erosion and Fragmentation
Thickening of diffusion layers
Acceleration of the mass transfer



Silica glass sonicated in pure H$_2$O
180 min, Ar, 20 kHz, 49 W.cm^{-2}

Decontamination of metallic **surfaces** in **dilute solutions**



Extended Surface-Bubble Interaction

NANOMATERIALS FOR ENERGY AND RECYCLING PROCESSES*

L'équipe est constituée au 1er Septembre 2018 de :

- 1 chercheur CEA/DEN responsable d'équipe (Dr. X. Deschanels (HDR)),
- 2 chercheurs CEA/DEN (Dr. D. Rebiscoul (HDR) et Dr. J. Causse)
- 1 enseignant-chercheur ENSCM (Dr. G. Toquer)
- 1 IE de l'UM2 (C. Rey)

Post-doctorants :

- Hélène Arena (ANR CARAPASS, 2016-2018), Développement d'absorbeurs solaires sélectifs de type nanocomposites SiC-TiC pour centrales solaires à concentration (CSP)
- Manuel Lejeune (POC SYNEXTRACT, coll. LNER, 2017-2018) : Chromatographie Synergique pour la purification de terres rares

Doctorants :

- Jun Lin (CEA/DRF, 2018-2021) : Comportement des silices mésoporeuses sous irradiation par des ions de haute énergie
- Rémi Boubon (CEA/DEN PIA ANDRA, 2017-2020) : Etude de l'évolution de l'interface entre les géopolymères et l'alliage Mg-Zr
- Baptiste Russo (Région/CEA-DEN, 2017-2020) : MatéRIaux nanocompoSites pOreux élaborés à partir de balle de riz de Camargue uTilisés comme sOrbants (RISOTO)
- Zijie Lu (CSC Chine, 2017-2021) : Study of colloidal sol-gel transition for the elaboration of actinides oxides materials with controlled and organized mesoporosity
- Julien Monnier (CEA/DEN, 2016 – 2019) : Synthèse d'oxydes d'actinides par combustion des nitrates
- Martin Leblanc (CEA/DEN, 2016 – 2019) : Synthèse d'oxydes d'actinides dédiés à la fabrication de Mox (GEN IV) par dénitration thermique avancée en présence d'additifs organiques (affectation principale CEA/DEN/DMRC)
- Markus Baum (CEA/DEN, 2015 – 2018) : Etude de la chimie de l'eau en présence d'ions dans les silices nanoporeuses
- Susan Sananes Israel (UM, 2015 - 2018) : Evolution sous contraintes de silices nanoporeuses gréffées par voie CO_2 supercritique
- Sanaa Shehayeb (UM/Université Liban, 2015 – 2017) : Récepteur solaire photo-thermique obtenu par électrophorèse de nanoparticules à propriétés optiques sélectives
- Clémentine Mansas (CEA/DEN, 2014 – 2017) : Extraction sur phases solides à partir de matériaux cœur-couronne : un cœur extractant sélectif, une couronne comme précurseur de matrice de confinement
- Yu Lou (CEA/DEN, 2013 – 2016) : Comportement des silices mésoporeuses sous irradiation ionique

Collaborateurs temporaires :

- Patricio Alastuey (Doctorant, Universidad Nacional de Tucumán, Sept – Dec. 2018) : Synthesis of nanostructures transparent ox-ides: study of the effect of doping on their electrical, optoelectronic and photovoltaic properties
- Alicia Sommer Marquez (Associated Professor,
Yachay Tech University, Juin – Aout 2018) : Encapsulation of photosynthetic plant cells within hierarchical silica monolith enriched with chlorophyll-a by high internal phase emulsion (HIPE) for CO_2 adsorption

---

*Thématique 5 de la page 22

Le laboratoire LNER développe plusieurs compétences scientifiques, techniques et d'enseignement pour répondre aux défis posés par la recherche sur les énergies dé-carbonées. Le fil conducteur de l'ensemble des thématiques de recherche du LNER est le développement de matériaux structurés à différentes échelles du point de vue de la compréhension des phénomènes mis en jeu lors des différentes étapes d'élaboration, complété par l'étude des propriétés d'intérêt de ces matériaux. Ainsi, le couple « maîtrise et compréhension de l'élaboration d'un matériau mésostructuré – propriétés physico-chimiques » définit l'ensemble des recherches développées au LNER, à la fois dans un objectif cognitif mais également dans un objectif applicatif, en lien avec les diverses collaborations industrielles (et/ou CEA) existantes ou à venir.

L'ensemble des études menées au sein de cette équipe concerne les composites présentant plusieurs structures, de nature (porosités, phase hybrides, oxydes, carbures..), de taille (nano, méso et/ou micro), et de forme (ordonnée ou amorphe) contrôlées et présentant une ou plusieurs fonctionnalités (chimie séparative, propriétés optiques renforcées, incorporation d'éléments actinides…). Par ce type de structure hiérarchique, les propriétés physiques (fissuration, tenue à l'irradiation, propriétés optiques), mais aussi chimiques (extraction, altération) de ces matériaux présentent des performances hautement non linéaires par rapport à celles des matériaux massifs, rendant ainsi possible le modelage de ces propriétés en fonction des applications souhaitées. Dans tous les cas, la conception de ces matériaux met en œuvre les avancées de la chimie « douce » (sol-gel, colloïdale, émulsion, hydrothermale,…) afin d'obtenir des réactivités lentes et contrôlées permettant alors une caractérisation précise et parfois « in situ » des différentes étapes réactionnelles et donc une meilleure maîtrise du matériau final.

Les thématiques principales développées au LNER dans la période 2015-2018 sont résumées dans les pages suivantes et peuvent s'inscrire dans les 5 grands thèmes suivants :

- *Le développement de différentes voies d'élaboration de matériaux nanostructurés : du précurseur (colloïde, solution, émulsion…) au matériau (poudre, couche mince ou massif).*
- *Physico-chimie des suspensions colloïdales : propriétés de la suspension et mécanismes mis en jeu lors de la mise en forme (électrophorèse, coating, transition sol-gel).*
- *Propriétés extractives des matériaux fonctionnalisés à l'échelle nanoscopique (l'extractant « hybride - solide »).*
- *Etude de l'impact d'un stress physique (irradiation, compaction) ou chimique (milieu très acide ou très basique) sur la structure hiérarchique d'un matériau.*
- *Chimie des ions en milieu confiné*

This team (LNER) presents strong scientific, technical as well as teaching skills to meet challenges arising from research on nanomaterials for low-carbon energy. The common thread of all the LNER research topics is the development of structured materials at different scales, with the aim of understanding the phenomena involved in the different stages of synthesis, supplemented by studying the properties of interest of these materials. Therefore, both part, i.e. "control and understanding of mesostructured nanomaterials synthesis" as well as "physico-chemical properties" sets up the outline of all the research activities taking place in the LNER. This is done for both cognitive goals as well as for applications goals through industrial collaborations (and/or CEA).

The whole research studies led in this laboratory concerns nanocomposites of various kind (porosity, hybrid phases, oxides, carbides…), various sizes (nano-, meso- and/or micro-), various structure (ordered or amorphous), all controlled, with different functions (separative chemistry, optical properties, actinide incorporation). These hierarchical structures allows enhancement not only of the physical properties (cracking, resistance to radiation, optical properties) but also chemical properties (extraction, leaching) of these nanomaterials with regard to bulk materials. In all cases, the synthetic routes use soft chemistry (sol-gel, colloidal precursor, emulsion templates or hydrothermal conditions) in order to work with more controlled slow reaction kinetics allowing fine characterisation, in-situ in some cases, of all different reaction steps. This generally led to a better control of the final shaping of the nanomaterials.

The LNER research topics for the period 2015-2018 are summarised in the following pages and can be divided in 5 main themes:

- Nanostructured materials synthetic routes: From precursor (colloid, solution, emulsion…) to the final material (powder, thin film, bulk).
- Colloidal suspension physic-chemistry: Properties and mechanisms involved in the material shaping (electrophoresis, coating, sol-gel transition)
- Extraction properties of functionalised nanomaterials: From macroscopic (efficiency, influence of macroporosity) to nanoscopic scale (mesopore functionalisation)
- Influence of physical stress (compaction, radiation) or chemical (acid, base) on the hierarchical structure of nanomaterials
- Ion chemistry in confined media

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

Nanomaterials for Energy and Recycling

Laboratoire des Nanomatériaux pour l'Energie et le Recyclage (LNER)

Permanent team

Xavier DESCHANELS (CEA)
Diane REBISCOUL (CEA)
Cyrielle REY (UM)
Guillaume TOQUER (ENSCM)
Jérémy CAUSSE (CEA)

Main Objectives

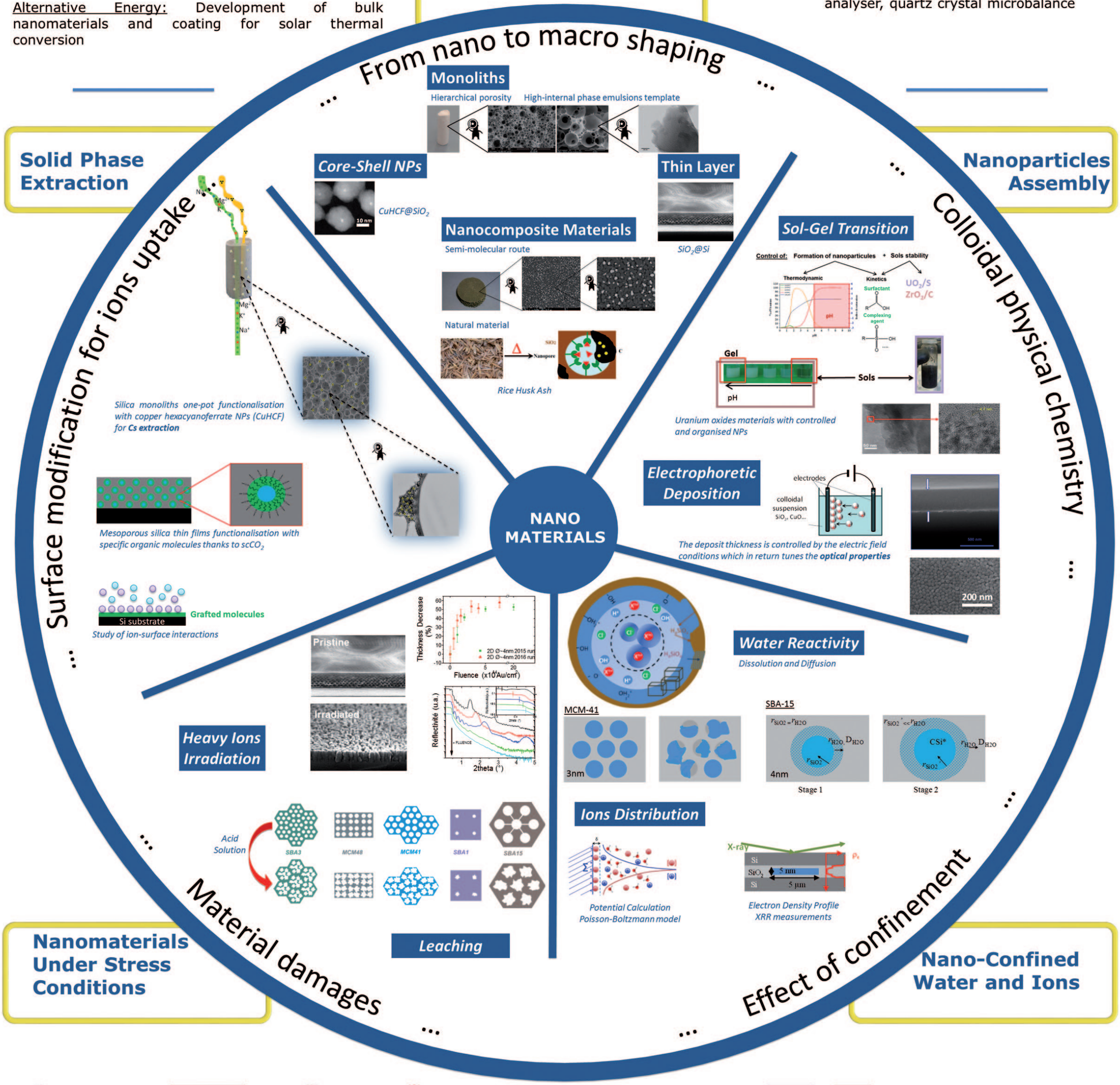
Nuclear Energy: Development of new synthetic routes to design nanostructured materials either for decontamination purposes or for nuclear fuels

Alternative Energy: Development of bulk nanomaterials and coating for solar thermal conversion

Nanostructuration

Instrumentation

gas adsorption/desorption, ionic chromatography, TDA/TGA, elemental analyser, quartz crystal microbalance



From nano to macro shaping …

Monoliths

Hierarchical porosity

High-internal phase emulsions template

Core-Shell NPs

CuHCF@SiO$_2$

Thin Layer

SiO$_2$@Si

Nanocomposite Materials

Semi-molecular route

Natural material

Rice Husk Ash

Solid Phase Extraction

Surface modification for ions uptake …

*Silica monoliths one-pot functionalisation with copper hexacyanoferrate NPs (CuHCF) for **Cs extraction***

Mesoporous silica thin films functionalisation with specific organic molecules thanks to scCO$_2$

Grafted molecules

Study of ion-surface interactions

Nanoparticles Assembly

Colloidal physical chemistry …

Sol-Gel Transition

Control of: Formation of nanoparticules + Sols stability

Uranium oxides materials with controlled and organised NPs

Electrophoretic Deposition

*The deposit thickness is controlled by the electric field conditions which in return tunes the **optical properties***

NANO MATERIALS

Water Reactivity

Dissolution and Diffusion

Ions Distribution

Potential Calculation
Poisson-Boltzmann model

Electron Density Profile
XRR measurements

Nano-Confined Water and Ions

Effect of confinement …

Heavy Ions Irradiation

Leaching

Material damages …

Nanomaterials Under Stress Conditions

EVOLVING INTERFACES IN MATERIALS*

L'équipe est constituée au 1er Septembre 2018 de :
- 1 Professeur des Universités, responsable d'équipe (Pr. N. Dacheux)
- 2 Chercheurs CNRS (Dr. N. Clavier ; Dr. A. Mesbah)
- 1 Chercheur CEA (Dr. S. Szenknect)
- 1 Maître de conférences (Dr. L. Claparède)

Post-doctorants :
A. Saravia (LIME/LHyS), D. Alby, M.R. Rafiuddin, I. Ben Kacem (L2ME/LIME)

Doctorants :
- F. Tocino, C. Gausse, T. Cordara, T. Dalger, V. Trillaud (LIME/L2ME), D. Qin, J. Manaud (LIME/LHyS), S. Bertolotto, Y. Cherkaski (DMRC/DTN), Paul Estévenon (DMRC/ICSM), Lénaïc Desfougères (DMRC/EMSE/ICSM)

Le laboratoire d'étude des Interfaces de Matériaux en Evolution (LIME) a pour objectif de décrire et de comprendre les phénomènes siégeant aux interfaces solide/solide et solide/liquide de matériaux d'intérêt pour le nucléaire du futur, aussi bien au cours d'étapes de frittage (densification), que de dissolution (de lixiviation ou d'altération) sous contraintes.

Les expérimentations relatives aux interfaces solide/solide s'inscrivent dans l'étude du frittage à travers les divers mécanismes intervenant lors de la densification d'un matériau (consolidation de l'objet, grossissement de grains, réduction de la porosité). Dans ce cadre, le couplage d'expérimentations in situ et ex situ permet non seulement d'analyser les différentes étapes de la densification et d'obtenir des données accessibles uniquement par modélisation mais également d'aboutir à l'obtention de cartes de frittage (taille de grains vs. taux de densification) dans un délai très court. Il en résulte une optimisation des conditions expérimentales en fonction de la microstructure désirée. Concernant l'évolution des interfaces solide/liquide, il s'agit de permettre à terme, l'optimisation des propriétés de certains matériaux utilisés (ou à utiliser) aussi bien pour l'aval que pour l'amont du cycle électronucléaire. Cette démarche consiste, en particulier, à appréhender et à comprendre les liens étroits reliant d'une part, la composition et/ou la morphologie d'un solide et d'autre part, sa propension à se dissoudre ou à s'altérer.

Dans ce but, la première étape de l'étude consiste à développer ou à optimiser les conditions de synthèse de combustibles modèles de type oxyde ($Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_2$, $Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$, …) en privilégiant l'usage de précurseurs cristallisés de manière à améliorer la réactivité et la « frittabilité » des oxydes préparés à haute température. En outre, l'utilisation de méthodes de synthèse par voie humide, généralement favorables à l'amélioration de la répartition cationique au sein du solide, a permis d'étendre le domaine d'existence de

---

*Thématique 6 de la page 22

telles solutions solides. Dans ce cadre, en parallèle de la préparation de complexes moléculaires d'actinides, un effort particulier a porté sur la précipitation directe d'oxydes hydratés de morphologie contrôlée (Thèse de Jérémie Manaud, 2017-2020). Ces travaux ont notamment permis de préparer des microsphères de UO_2 présentant une architecture multi-échelle ou sous la forme de cristallites nanométriques présentant une forte surface spécifique. Les étapes de conversion des précurseurs en matériaux oxydes ont par la suite été examinées à travers le couplage de nombreuses techniques (thermiques, diffractions, microscopiques, spectroscopiques). Il en a découlé l'identification des intermédiaires réactionnels successivement formés lors de la conversion ainsi que des transformations chimiques et morphologiques de l'échantillon.

Sur la base de ces résultats, le frittage des oxydes mixtes $Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_2$, $Ce_{1x}Nd_xO_{2x/2}$ et $Th_{1x}Y_xO_{2x/2}$ a été étudié de manière à identifier les paramètres d'intérêt de la poudre initiale (surface spécifique, homogénéité, influence de la présence de carbone résiduel, …). L'histoire d'un solide, soit le lien entre le précurseur utilisé, sa conversion en oxyde, et la microstructure finale du compact densifié a ainsi pu être établie (Thèses de Julien Martinez, ICSM-DEC-AREVA, 2011-2014), par exemple au moyen de cartes de frittage permettant in fine de contrôler la microstructure des matériaux céramiques considérés (thèse de Yanis Cherkaski, ICSM-DTN, 2015-2018).
Par ailleurs, des expériences mettant en œuvre l'observation in situ des phénomènes de densification ont été menées par microscopie électronique à balayage environnementale à haute température (HT-MEBE). Des données inédites relatives à la cinétique de croissance granulaire ou à la mobilité des joints de grains lors du stade final de la densification ont ainsi été acquises. En outre, les travaux menés dans le cadre des thèses de Galy Ingrid Nkou Bouala (ICSM-DEC, 2013-2016) puis de Victor Trillaud (ICSM, 2016-2019) sur des composés modèles de morphologie sphérique contrôlée (CeO_2, ThO_2 et UO_2) ont conduit à l'acquisition de données expérimentales cinétiques et thermodynamiques originales relatives à la première étape du frittage (élaboration des ponts) qui ont été confrontées aux résultats issus des modèles numériques.

Concernant l'étude des interfaces solide/liquide, des expériences de dissolution ont été entreprises en conditions de faible ou de fort renouvellement de la solution lixiviante. Pour les solutions solides $Th_{1-x}U_xO_2$, une étude multiparamétrique a démontré le rôle majeur joué par la composition chimique sur la durabilité chimique des matériaux et sur les mécanismes gouvernant la dissolution des matériaux (Thèse de Florent Tocino, 2012-2015). La confrontation des paramètres décrivant la cinétique à l'échelle macroscopique (ordres partiels par rapport à l'activité en proton, énergie d'activation apparente) avec l'évolution de l'interface solide/solution suivie par MEBE *operando* (surface réactive, composition) a confirmé la modification du mécanisme de dissolution prépondérant (rédox *vs.* réactions de surface) en fonction de la teneur en uranium (IV) et de l'acidité du milieu de dissolution. Pour de nombreuses conditions expérimentales, le contrôle de la dissolution par des réactions de surface a souligné les liens étroits existant entre la microstructure du matériau (entre autre à travers l'homogénéité et la réactivité de surface, …) et sa résistance à l'altération ou à la corrosion aqueuse. Il est apparu que la présence d'éléments lanthanide au sein de la structure fluorine ($Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$) affecte significativement la durabilité chimique des solides en raison de la fragilisation du réseau cristallin consécutive à la formation des lacunes en oxygène. De manière analogue, la présence d'éléments platinoïdes au sein de UO_2 a été étudiée dans le cadre de la Thèse de Théo Cordara (ICSM – DMRC/AREVA, 2014-2017). Ces études ont souligné l'existence de phénomènes catalytiques significatifs, liés à la présence de ces éléments au sein du solide ou en solution. Plus récemment, l'étude de la contribution d'espèces azotées potentiellement catalytiques (dont HNO_2) a été initiée (Thèse de Thomas Dalger, ICSM/DMRC, 2016-2019). Parallèlement, des expérimentations ont été réalisées sur des échantillons monocristallins de UO_2 (Thèse de Solène Bertolotto, DMRC/ICSM, 2017-2020) afin de s'affranchir de toute contribution microstructurale.

Un second axe de recherches, en lien avec l'amont du cycle, a été initié dès 2009 en partenariat avec le DMRC (CEA Marcoule). Des expérimentations relatives à la phase métatorbernite $Cu(UO_2)_2(PO_4)_2$, 8 H_2O ont été réalisées en partenariat avec AREVA tandis que celles portant sur les silicates de thorium et d'uranium (IV) font l'objet d'une collaboration internationale (Prof. A. Navrotsky, UC-Davis, Prof. R.C. Ewing, Université de Stanford et X. Guo, Washington State University). Ces études ont d'abord porté sur le système thorium – uranium – silicate, à travers la préparation puis la purification de solutions solides d'uranothorite $Th_{1-x}U_xSiO_4$ puis de la coffinite $USiO_4$ en conditions hydrothermales. Les données thermodynamiques relatives à la solubilité de ces phases ($K_S°$, $\Delta_R H°$, $\Delta_R G°$, $\Delta_R S°$) ont été acquises aussi bien lors des tests de dissolution que par microcalorimétrie. Elles ont permis d'apporter des indications quant à la possible «coffinitisation » de UO_2 au contact d'une solution aqueuse silicatée. Plus récemment, l'étude des silicates d'actinides (Th, Np, Pu) a été réalisée dans le cadre de la thèse de Paul Estévenon (DRCP/ICSM, 2015-2018) tandis que la réaction de coffinisation de UO_2 est actuellement étudiée au sein d'un projet collaboratif quadripartite Amphos/SKB/Univ. Standford/ICSM.

Enfin, un troisième axe de recherches a porté sur l'étude de phases phosphatées, dont la rhabdophane, la monazite et le xenotime (en tant que matrices de confinement spécifique de certains radionucléides). Ces travaux, ont été initiés au cours de la thèse de Clémence Gausse (2013-2016). Ils ont d'abord consisté à préparer des échantillons pulvérulents de rhabdophane et de monazite, puis à les soumettre à des tests de lixiviation en conditions de sous- et de sursaturation. Ils ont abouti à la détermination de données thermodynamiques (K_S°, $\Delta_R H^\circ$, $\Delta_R G^\circ$, $\Delta_R S^\circ$) d'intérêt pour la chimie des phosphates d'éléments lanthanides mais également d'éléments actinides. Une suite logique à ce travail a consisté à incorporer des éléments actinide tétravalents par substitution couplée $2\ Ln^{III} \Leftrightarrow An^{IV} + M^{II}$ (solutions solides monazite/cheralite) ou $Ln^{III} + PO_4 \Leftrightarrow An^{IV} + SiO_4$ (solutions solides monazite/huttonite). Ce travail est poursuivi dans le cadre de la thèse de David Qin (bourse du China Scholarship Council, 2016-2020). Une étude similaire sur le système xénotime/thorite est également développé dans le cadre de l'ANR X-MAS.

The 'Evolving Interfaces in Materials' group (LIME) aims to describe and understand the various phenomena occurring at the solid/solid and solid/liquid interfaces, and of interest for the (current and future) nuclear fuel cycle concepts. They are mainly related to the sintering (densification) of ceramic materials as well as to their alteration (leaching or dissolution) under various chemical and/or physical stresses.

The experiments dedicated to the solid/solid interfaces are mainly devoted to the study of sintering through the different mechanisms driving the densification of a material (i.e. mechanical consolidation, grain growth and decrease of the global porosity). In this framework, coupling of in situ and ex situ techniques allowed us not only to analyze the different steps of the densification but also to yield original data usually only accessible through modeling. Sintering maps (which represent the variation of grain size vs. densification rate) were also obtained rapidly. It resulted in an optimization of the experimental conditions applied for sintering, that was associated to an improved monitoring of the final microstructure.

In the case of the solid/liquid interface, the final goal is also to optimize several properties of some materials in use (or to be used) both in the front- or back-end of the nuclear fuel cycle. Particularly, the approach developed consists in the understanding of the links existing between the chemical composition and/or the morphology of a solid, and its ability to dissolve.

In this aim, the first step of our studies generally dealt with the preparation of mixed oxides considered as model compounds for nuclear fuels ($Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_2$, $Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$, …). The initial precipitation of crystallized precursors was favored for the synthesis, in order to improve the reactivity and the sintering capability of the prepared powders. Also, such wet chemistry routes generally led to improve the homogeneity of the cationic distribution, which subsequently extended the range of formation of the oxide-based solid solutions. In parallel to the synthesis of actinides-bearing molecular complexes, a particular attention was paid to the direct precipitation of hydrated oxides with a controlled morphology. These studies particularly led to the preparation of UO_2 microspheres with a hierarchical architecture, and of various compositions of $(An^{IV},Ln)O_2$ nanocrystals (An = Th, U) exhibiting a very high specific surface area. The thermic conversion leading to the final oxide form was also examined through various techniques (diffraction, spectroscopy, microscopy, …), which allowed us to identify the reaction intermediates as well as to point out the chemical and morphological transformations of the samples.

On this basis, the sintering of $Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_2$, $Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Y_xO_{2-x/2}$ was studied in order to point out the powder-related parameters (specific surface area, homogeneity, amount of residual carbon, …) that can impact significantly the densification process. The thermal history of a solid, which includes the precursor chosen for the preparation, its conversion and the final microstructure of the sintered pellet, was then described (PhD of Julien Martinez, ICSM/DEC/AREVA, 2011-2014). The establishment of sintering maps, which can be used to control in fine the microstructure of ceramics, was undertaken for several materials of interest such as $Th_{1-x}Y_xO_{2-x/2}$ solid solutions (PhD of Yanis Cherkaski, ICSM/DTN, 2015-2018). Also, several experiments using the *in situ* observations of densification phenomena were undertaken through high temperature environmental scanning electron microscopy (HT-ESEM). Original data linked to the kinetics of grain growth or grain boundaries mobility were then determined for bulk CeO_2 and ThO_2 samples. Besides, the studies undertaken in the framework of the PhD works of Galy Ingrid Nkou Bouala (ICSM/DEC, 2013-2016) and Victor Trillaud (ICSM/DMRC, 2016-2019) concerning spherical oxide model compounds (CeO_2, ThO_2 and UO_2) led to the first experimental data concerning the kinetics and thermodynamics of the first step of sintering (elaboration of necks between the grains). Moreover, these results were compared to the data coming from the numerical simulations developed at CEA.

The study of the solid/liquid interface was undertaken by the means of dissolution tests conducted either with high or low renewal of the leaching solution. For $Th_{1-x}U_xO_2$ solid solutions, the multiparametric study has demonstrated the prevailing role played by the uranium(IV) mole loading over the chemical durability of the samples and the mechanisms driving the dissolution process (Florent Tocino PhD, 2012-2015). The comparison of the parameters describing the dissolution kinetics at a macroscopic scale (partial order related to the proton activity, apparent activation energy) with the evolution of the solid/liquid interface, monitored by operando ESEM observations (evaluation of both evolving reactive surface and chemical composition during dissolution) also confirmed a modification of the predominant dissolution mechanism (redox vs. surface reactions) with the uranium (IV) incorporation rate and the leachate acidity. For numerous operating conditions, the control of the dissolution through surface reactions, particularly involving the adsorption of protons on reactive surface sites, underlined the tight links existing between the material's microstructure (homogeneity, surface reactivity, …) and its resistance to aqueous corrosion. The presence of lanthanide elements within the fluorite-type structure ($Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$) also deeply affected the chemical durability of the solids, mainly through the weakening of the crystal network due to the formation of oxygen vacancies. In a similar way, the presence of PGM elements within UO_2 was investigated (Théo Cordara PhD, ICSM-DMRC/AREVA, 2014-2017). Such experiments revealed the huge role of catalytic phenomena linked to the presence of PGM elements in the solid and in solution. More recently, the particular contribution of nitrogen based species (incl. HNO_2) was initiated (Thomas Dalger PhD, ICSM-DMRC/AREVA, 2016-2019). Simultaneously, several experiments were performed on UO_2 single crystals in order to erase the contribution of microstructural parameters (Solène Bertolotto PhD, DMRC-ICSM, 2017-2020).

A second research topic, linked to the front-end of the nuclear fuel cycle, started in 2009 in collaboration with DMRC (CEA Marcoule). Studies concerning the metatorbernite phase ($Cu(UO_2)_2(PO_4)_2 \cdot 8\ H_2O$) are currently pursued in partnership with AREVA, while experiments dedicated to thorium and uranium (IV) silicates are undertaken in the framework of an international collaboration (Prof. A. Navrotsky, UC-Davis, Prof. R.C. Ewing, Stanford University and X. Guo, Washington State University). These studies initially concerned the Th-U-SiO_4 system, with the preparation of $Th_{1-x}U_xSiO_4$ uranothorites and $USiO_4$ coffinite samples under hydrothermal conditions. Purification of the most U-enriched compounds was also undertaken in order to get the rid of $Th_{1-x}U_xO_2$ and SiO_2 by-products. For the uranium silicate system, the mechanisms leading to the formation of coffinite were elucidated, while the synthesis yield and the purification process were optimized. Moreover, thermodynamic data of these silicate phases (K_S°, $\Delta_R H^\circ$, $\Delta_R G^\circ$, $\Delta_R S^\circ$) were collected, both from dissolution tests and calorimetry measurements. These data already shed some light about the possible "coffinitization" of UO_2 when contacted with aqueous solution containing silicates (Amphos/SKB/Univ. Standford/ICSM collaboration). More recently, the study of actinides silicates (Np, Pu, Am) was performed in the framework of the PhD work of Paul Estévenon (DMRC/ICSM, 2015-2018).

Finally, a last research topic was devoted to the study of phosphate-based waste forms for the specific conditioning of radionuclides, including rhabdophane, monazite and xenotime. This work was initiated in the framework of the PhD work of Clémence Gausse (2013-2016). Experiments first aimed to prepare rhabdophane and monazite powdered samples, then to use them for leaching tests in under- and over-saturation conditions. This led to the determination of thermodynamic data (K_S°, $\Delta_R H^\circ$, $\Delta_R G^\circ$, $\Delta_R S^\circ$) of interest for the chemistry of lanthanides and actinides phosphates. The natural follow-up of this work then consists in the incorporation of tetravalent actinides through different coupled substitution, i.e. $2\ Ln^{III} \Leftrightarrow An^{IV} + M^{II}$ (monazite/cheralite solid solutions) or $Ln^{III} + PO_4 \Leftrightarrow An^{IV} + SiO_4$ (monazite/huttonite solid solutions). Preparation of these samples is now studied in the frame of the PhD work of David Qin (China Scholarship Council grant, 2016-2020). The same study is now also developed on the xenotime/thorite system within the ANR X-MAS project.

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

Evolving Interfaces in Materials

Laboratoire des Interfaces de Matériaux en Evolution
(LIME)

Permanent team

Nicolas DACHEUX (UM)
Nicolas CLAVIER (CNRS)
Stéphanie SZENKNECT (CEA)
Adel MESBAH (CNRS)
Laurent CLAPAREDE (UM)

Main objectives

Foresee and control the physico-chemical parameters driving the dissolution and the long-term behaviour of the studied materials (fuels, radwaste matrices, minerals…)

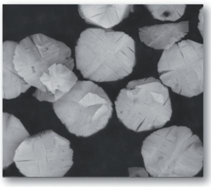
Understand the physico-chemical phenomena at the solid/ solid and solid/ liquid interfaces.

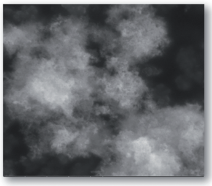
Evidence and understand the links between the microstructure of solid (through sintering) and its chemical durability (dissolution, leaching, corrosion).

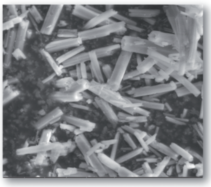
Control of the microstructure

From the precursor to the target material

Thorium, **uranium** and **lanthanides** based **oxides**, **phosphates**, **silicates** …



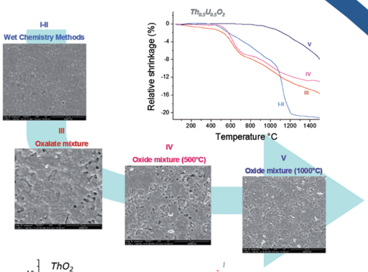


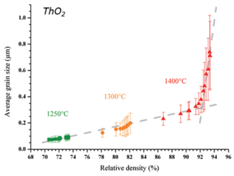


Sintering

From the powder to the dense pellet

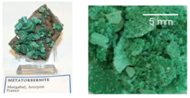
Influence of the **chemical homogeneity** on the **sintering: thermodynamics** and **kinetics**



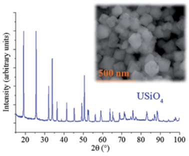


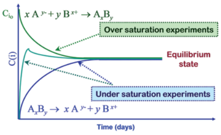
Construction of **sintering maps** through the **original coupling** of **ESEM** and **dilatometry experiments**

Natural analogues *vs* **synthetic samples**

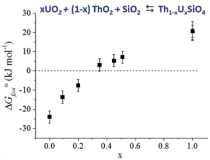


Optimisation of the preparation of **pure synthetic phases**





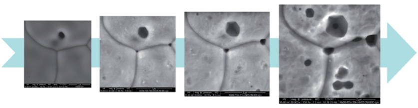
Determination of **solubility constants** and associated **thermodynamic data**



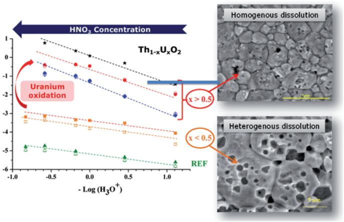
Solubility & thermodynamics

Thorium and uranium based minerals

***Operando* observation** of the evolving **solid/ liquid interfaces** by **ESEM**



Measurements of **the macroscopic dissolution rates**
Comparison with the **microscopic approach**



Prioritization of physico-chemical parameters impacting the **dissolution kinetics**

Dissolution kinetics

Multi-parametric studies
Evolving interface

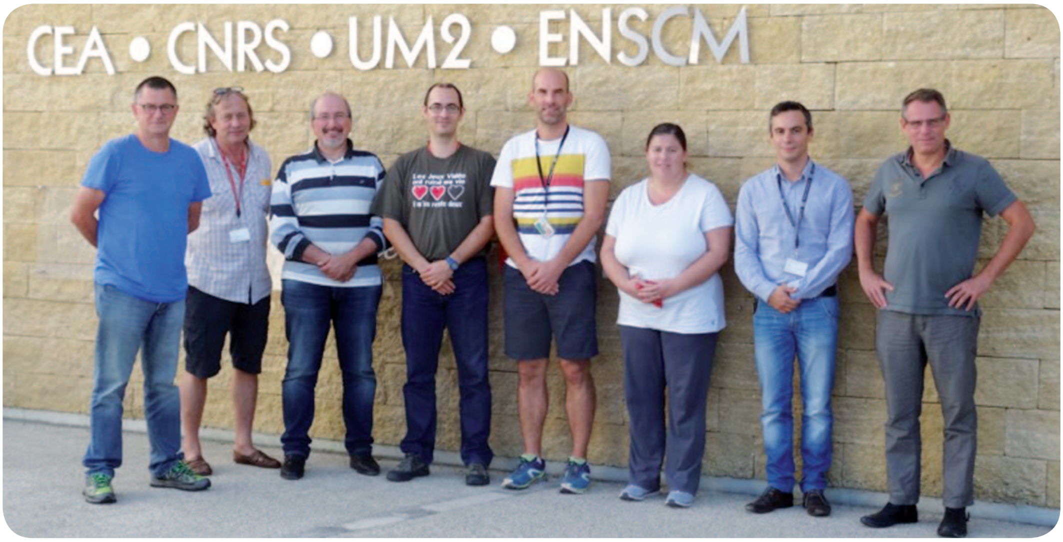
ETUDES DE LA MATIÈRE EN MODE ENVIRONNEMENTAL*

L'équipe est constituée au 1er Septembre 2018 de :
- 1 ingénieur de recherches CNRS responsable d'équipe (Dr Renaud Podor),
- 3 ingénieurs d'études CNRS (Sandra Maynadié, Joseph Lautru, Dr Xavier Le Goff),
- 2 ingénieurs CEA (Henri-Pierre Brau, Michael Odorico),
- 1 technicien CEA (Bruno Corso)

Post-doctorants 2015-18 :
- Ilyes Ben Kacem (UM – Labex, 2018-2019) : Characterization of evolving solid/liquid interfaces during dissolution by 3D analysis at the microscopic scale by SEM.

Thésards 2015-18 :
- Galy Ingrid Nkou Bouala (CEA CFR, 2013-2016) : Premier stade du frittage des dioxydes de lanthanides et d'actinides : une étude in situ par MEBE à haute température.
- Hélène Aréna (CEA CTCI Areva, 2012-2016) : Effets compétitifs et cumulatifs des éléments chimiques sur la vitesse résiduelle d'altération de verres nucléaires.
- Victor Trillaud (CEA CFR, 2016-2019) : Premier stade du frittage du dioxyde d'uranium : une étude in situ par MEBE et MET à haute température.
- Florimond Delobel (ISL, 2015-2018) : Elaboration de carbure de silicium par Spark Plasma Sintering pour des applications en protection balistique.

Non permanents :
- Johan Salacroup (Salarié SATT AxLR, 2016-2018) Développement d'une cellule d'observation in situ de matériaux en cours de dissolution par microscopie électronique à balayage environnementale.
- Sébastien Fournier (CNRS, 2015-2016) Ingénieur d'études CNRS Caractérisation des Matériaux
- Pierrick Chevreux (CNRS, 2017-2018) Ingénieur de recherches CNRS Caractérisation des Matériaux



---

*Thématique 7 de la page 23

Le Laboratoire d'Etudes de la Matière en Mode Environnemental (L2ME) résulte de la fusion, préconisée par l'AERES, des deux laboratoires de Diffraction-Diffusion (LDD) et de Microscopies en Mode Environnemental (LM2E), effective depuis le 1er janvier 2014. Cette fusion des compétences et savoir-faire correspond à une volonté affichée de coupler les informations microscopiques et macroscopiques obtenues par l'ensemble des techniques expérimentales disponibles au sein du L2ME. Il s'agit de décrire encore plus précisément le comportement de l'échantillon en maitrisant, lors de l'enregistrement des mesures, les paramètres physiques auxquels est soumis l'échantillon (température, taux d'humidité, nature des gaz, pression…).

Le contrôle des paramètres d'environnement échantillon, dans le domaine de la microscopie, permet l'observation directe d'objets usuellement reconnus comme non observables par les techniques d'imageries conventionnelles, et ouvre le champ de l'expérimentation *in situ* et l'accès à la détermination de grandeurs physiques originales. En particulier, les avancées récentes en microscopies à rayons X et électroniques permettent d'accéder à l'observation directe des agrégats supramoléculaires en solution avec des résolutions, spatiale et temporelle, inégalées à ce jour, sans nécessité de mettre en œuvre des techniques de préparation d'échantillons lourdes et génératrices d'artéfacts.

Le couplage de dispositifs dédiés (humidité contrôlée ou haute température) avec des microscopes électroniques de conception récente permet la compréhension fine de certaines propriétés des matériaux (auto-cicatrisation, frittage, démouillage, dissolution, réactivité chimique…). L'expérimentation *in situ*, l'imagerie haute résolution, couplée à l'analyse chimique locale du matériau, permet un suivi direct des mécanismes de réarrangement de surface, allant de la description des mécanismes de dissolution des matériaux jusqu'à de réelles expériences de recuit des matériaux *in situ*.

En parallèle, une approche multi-échelle de caractérisation de la matière, du nanomètre au micron, est développée. Elle repose sur une maitrise des mesures dans l'espace réciproque dans une large dynamique d'intensité et de vecteur de diffusion. Ici, diffusion aux petits angles et diffraction utilisant des rayons X durs sont utilisées conjointement pour la caractérisation multi-échelle statistique des matériaux, permettant de contourner les effets dus au choix d'images représentatives. A ce niveau, des grandeurs physico-chimiques allant jusqu'aux potentiels d'interaction, aux interfaces fractales et aux courbures peuvent être déterminées directement, en contrôlant conjointement température et activité du solvant.

Cette approche expérimentale est complétée par une capacité de développement instrumental « à façon » d'outils adaptés qui se base principalement sur les savoir-faire des membres de l'équipe. Il s'agit là de répondre à des besoins de recherche spécifiques exprimés par les chercheurs de l'ICSM. Les développements technologiques peuvent porter non seulement sur de l'instrumentation légère (porte-échantillons, etc), mi-lourde (cellules dédiées) ou lourde (reconstruction d'un appareil).

Les compétences de l'équipe dans la pratique instrumentale et l'interprétation des spectres de diffusion-diffraction et des images de microscopie permettent des développements méthodologiques originaux. Ces savoir-faire et développements sont partagés avec les équipes de recherches, internes ou externes à l'institut et ils conduisent à l'acquisition de résultats scientifiques inédits.

Un premier ensemble de résultats porte sur la caractérisation de matériaux par microscopie électronique à balayage environnementale, et plus particulièrement sur l'étude de leur réponse à des contraintes spécifiques lors d'expériences menées *in situ* (effet de l'humidité relative ou de la température). L'un des résultats marquants obtenus en mode humidité contrôlée est la mise en place d'outils et de méthodes d'analyses originales d'observation et d'analyse des processus de dissolution des matériaux, basées sur la reconstruction 3D des surfaces à partir d'images MEBE mais également par microscopie à force atomique (AFM). Ces outils ouvrent la voie à la caractérisation précise de mécanismes locaux de dissolution. Les études menées à haute température ont permis d'accéder à des observations et des informations relatives aux différents stades du frittage des céramiques totalement inédites à ce jour. D'autres propriétés telles que le démouillage de couches minces de métaux sur différents types de substrats et pour différentes applications (Piles à combustible ; coll. Imperial College London / Surfaces texturées ; Saint Gobain Recherche – UMR 125), l'oxydation d'alliages haute température (applications aéronautiques ; coll. IJL – UMR 7198), l'oxydation de carbure d'uranium ou encore le vieillissement des matériaux pour piles à combustibles (Coll. Imperial College London) ont également été étudiées avec succès dans le cadre de collaboration avec des laboratoires d'autres universités.

Un second ensemble de résultats porte sur le développement d'outils spécifiques de caractérisation des matériaux. Les projets Celdi (soutenu par la SATT AxLR) et FurnaSEM (projet Readynov soutenu par la Région Occitanie) sont actuellement menés pour développer respectivement une cellule d'étude directe de la dissolution / corrosion des matériaux dans la chambre d'un MEB et une série de fours (haute et très haute température) miniatures pour MEB. En parallèle, un projet de reconstruction d'un microscope électronique à transmission (MET) est mené en interne à l'ICSM. Ces actions fortement appliquées sont (ou seront) valorisées dans les années à venir aux travers de collaborations avec des acteurs économiques locaux (société NewTEC, etc) voire au travers de la création d'une startup.

LABORATORY FOR THE STUDY OF MATTER IN ENVIRONMENTAL CONDITIONS

The research group «Study of the Matter in Environmental Conditions » results from the fusion between the LDD (Diffusion and Diffraction group) and the LM2E (Microscopy under Environmental Conditions) group which took place in January 2014. This fusion was driven by the idea to combine the information obtained at the microscopic and at the macroscopic scale using the know-how and competences available in both laboratories. The main goal is to describe precisely the behavior of a sample submitted to reactive conditions by controlling relative humidity, temperature, nature of the gases, gas pressure while recording images or performing measurements.

The control of the sample environmental conditions, in the field of electron microscopy, allows observing directly objects that are generally not observable by the conventional imaging techniques. This paves the way to in situ experiments and this can yield to the measurement of physical parameters and activation energies. As an example, recent advances in the field of soft X-ray microscopy and electron microscopies allow the direct observation of supramolecular aggregates in solution with a very high resolution, without any specific sample preparation and with unexpected spatial and time resolutions.

Coupling specific stages or cells (controlled relative humidity or high temperature) with modern electron microscopes allows the precise characterization of physico-chemical properties such as self-healing, sintering, dissolution, chemical reactivity through in situ experiments …

In parallel, a multi-scale approach for matter characterization ranging from the nanometer to the micrometer scale is being developed. It relies on the mastering of measurements in the reciprocal space in a wide dynamics of intensities and scattering vectors. Here, small-angle scattering and diffraction using hard X-rays are jointly used for the statistical multiscale characterization of the materials, allowing us to bypass the problem linked to the selection of representative images. Therefore, physico-chemical data including interaction potentials, fractal interfaces and curvatures can be directly determined by simultaneously controlling temperature and solvent activity.

This approach is completed with the instrumental development of specific tools, based on the know-how of the lab team with the aim to answer specific research objectives. These developments can cover small tools (sample holders, etc), stages with dedicated applications or the complete refurbishing of apparatus.

The skills of the team in terms of instrumentation and interpretation of XRD and SAXS spectra, as well as in the recording of electron microscopy images and image processing, allow developing original technical methodologies. The know-how of the L2ME team is shared with other research teams, yielding to the obtaining of original scientific data and results.

A first set of results relates to the characterization of materials by environmental scanning electron microscopy, and more particularly to the study of their response when they are submitted to specific constrains during in situ experiments (relative humidity, temperature…) One of the main results obtained during the observation of materials under controlled relative humidity conditions is the development of new strategies for the study of dissolution processes, based on image processing as well as 3D surface reconstruction. These tools pave the way to the precise determination of very local dissolution processes1. In parallel, original experimental data – and knowledge - relative to the first stage of sintering have been recorded during experiments performed with the ESEM combined with a high temperature stage. Several other properties such as the dewetting of thin metal films (with application as functional materials or anodes for SOFC – Respective collaboration with Saint Gobain Recherche – UMR 1252 and Imperial College London), the oxidation of alloys (aeronautic applications – Coll. with IJL – UMR 7198), the oxidation of UC or the aging of materials for SOFC cathodes3 (Coll. with Imperial College London) have been successfully studied in the framework of national and international academic collaborations.

A second set of result deals with the development of specific tools for the characterization of materials. The CelDi (funded by SATT AxLR) project is dedicated to the development of a stage that can be implemented in a SEM to observe directly the dissolution and/or corrosion processes. The FurnaSEM project (funded by Occitanie Region) is devoted to the development of a new series of high temperature furnaces that can be implemented in SEMs. In parallel, a project aiming to the refurbishing of a TEM and fully funded by ICSM has been successfully conducted. These actions will be further exploited through collaborative development with local industrial partnership (NewTEC company, etc) or through the creation of a company.

INSTITUT DE CHIMIE SEPARATIVE DE MARCOULE

Study of Matter in Environmental Conditions

Laboratoire des études de la Matière en Mode Environnemental

(L2ME)

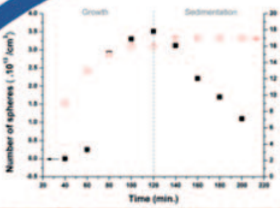
Permanent team

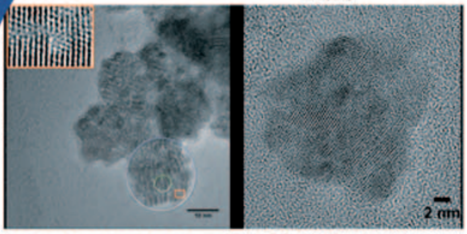
Renaud Podor (CNRS)
Henri-Pierre Brau (CEA)
Julien Cambedouzou (ENSCM)
Bruno Corso (CEA)
Joseph Lautru (CNRS)
Xavier Le Goff (CNRS)
Sandra Maynadié (CNRS)
Michaël Odorico (CEA)

To develop *in situ* experimentation and associated analytical methods

Instrumentation / capabilities: TEM Jeol 200CX, Environmental scanning electron microscope FEI Quantax 200 ESEM-FEG, Scanning electron microscope TESCAN Vega3, Bruker 400 MHz NMR spectrometer, SEM/TEM Specimen preparation Lab, AFM Bruker Multimode 8, Small angle X-ray Scattering, Brucker D8 ADVANCE diffractometer.

Highly hydrated compounds

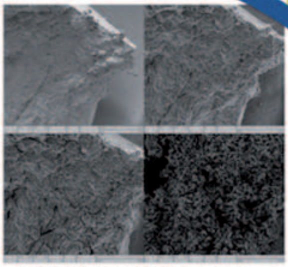




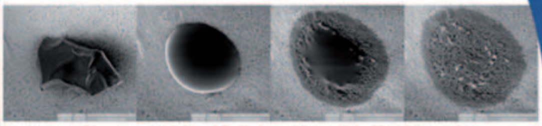
Growth of UO_2 microspheres

From G.I. Nkou Bouala et al., CrystEngComm 16, 2944-2954 (2014)

High temperature study



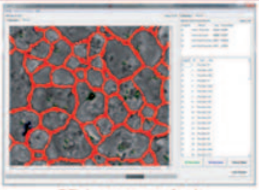
UC Oxidation (Collaboration with Imperial College London)



Glass reactivity (Collaboration with IJL, Nancy)

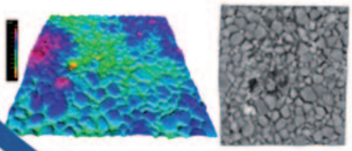
New analysis methods

In situ dissolution stage (Collaboration with SATT AxLR and NewTec)



2D image analysis (Collaboration with STIC/GPSI)

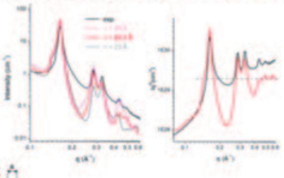
3D surface reconstruction



SAXS analyses on granular porous materials

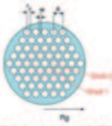
Silica dissolution

Comparison of experimental and calculated SAXS patterns



Specific surface area determination

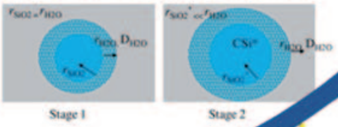
(S_{meso} ~ 800 m²/g)



Geometical model used to calculate SAXS patterns

From J. Cambedouzou & O. Diat, J. Appl. Cryst. 45, 662-673 (2014)

2 stages of SBA-15 evolution vs time



INNOVATION IN EXTRACTION AND RECYCLING

INNOVATIONS POUR L'EXTRACTION ET LE RECYCLAGE

INNOVATION IN EXTRACTION AND RECYCLING

Via the knowledge of the supramolecular, weak and long-range interactions, for a technological break-through in eco-friendly separation chemistry.

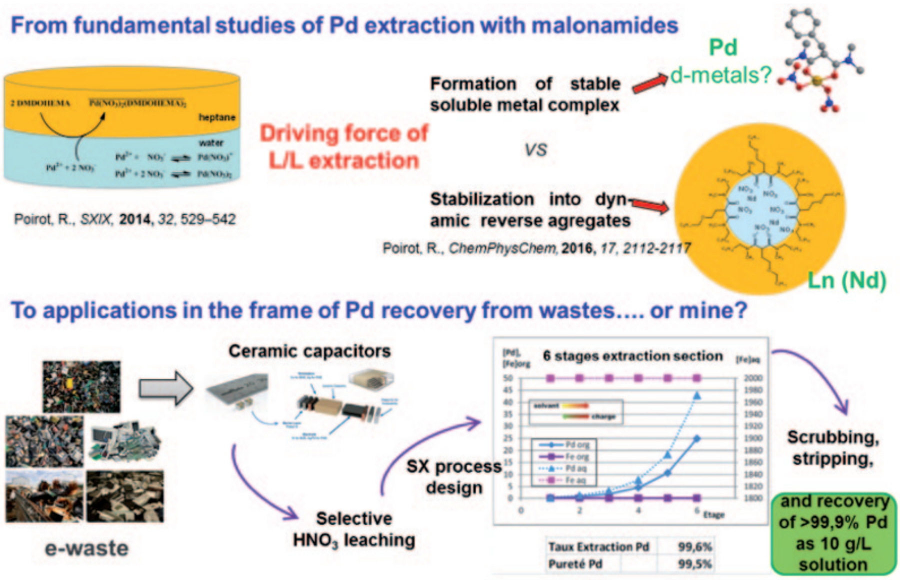
INNOVATION POUR L'EXTRACTION ET LE RECYCLAGE

Via la connaissance des interactions supramoléculaires, faibles et à longue distance, pour une rupture technologique sur des procédés écoresponsables en chimie séparative.

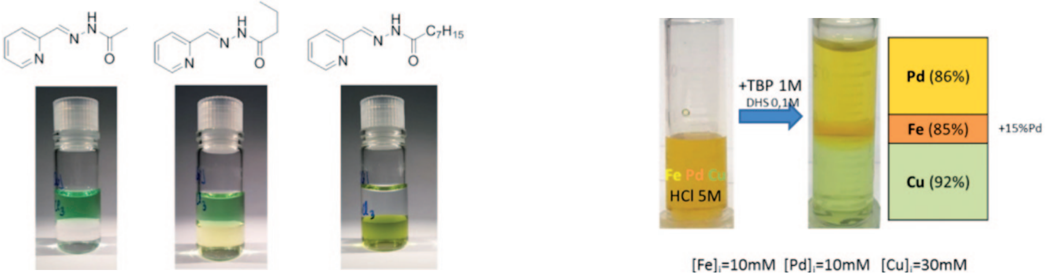
SYSTEM CHEMISTRY, STRONG-WEAK INTERACTION CORRELATION, 3 PHASES SYSTEMS, LIQUID LIQUID SEPARATION

R. Poirot, B. Braibant, M.C. Dul, S Dourdain, X. Le Goff, D. Bourgeois, D. Meyer

Better understanding of how a metal ion usually not soluble in an organic phase can be maintained into it by using an extractant is one of the main challenges in the liquid-liquid separation field. One part of this challenge is to elucidate the role of the interactions which can take place at the molecular level, especially the relations between first order interactions (such as chemical bonding or electrostatic interactions) and low energy second order interaction (H bonding, polarisation, dipole…).
The research done in this field is focused on the formulation of separation solvents and the related molecular topology[1], the development of fluorinated molecules[2], combinatorial dynamic approaches and the setup of triphasic systems[3]. *(Figure 1)*



A *Noble Metal separation: Fundamental to applied research*



B *Future: Combinatorial dynamics (H2O/CHCl3)*

C *Future: triphasic systems*

Figure1: Compilation of L/L separation research

---

[1] R. Poirot, X. Le Goff, O. Diat, D. Bourgeois, D. Meyer « **Metal Recognition Driven by Weak Interactions: a Case Study in Solvent Extraction.**», ChemPhysChem , 2016 17,2112–2117.

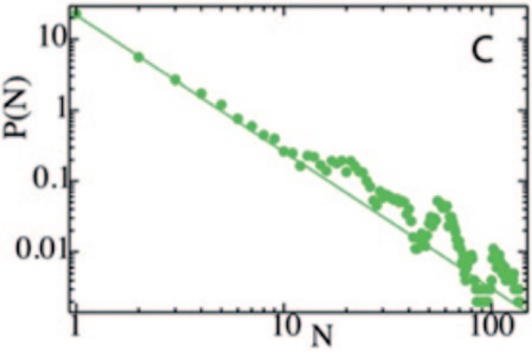
[2] B. Braibant, X. Le Goff, D. Bourgeois, D. Meyer - «**Impact of the Long-Range Electronic Effect of a Fluorous Ponytail on Metal Coordination during Solvent Extraction**» - Chem Phys Chem , 2017 18, 24, 3583

[3] B. Braibant, D. Bourgeois, D. Meyer - «**Three-liquid-phase extraction in metal recovery from complex mixtures**» Separation and Purification Technology 2018 195, 367

PRE-OUZO STRUCTURE IN TERNARY SYSTEMS OR ULTRAFLEXIBLE MICROEMULSION WITHOUT CONVENTIONAL SURFACTANT

Th. Zemb, O. Diat, T. Lopian (ICSM)- D. Touraud, S. Schöttl, J.Markus, D. Horinek, W. Kunz (Université de Regenburg)
S. Prevost (ILL-Grenoble), I. Grillo (ILL-Grenoble), S. Marcelja (ANU_Canberra)

Beginning over 40 years ago, a curious type of microemulsions—as transparent dispersion of two immiscible liquids separated by an interfacial film—at thermodynamic equilibrium has been described as "pre-Ouzo," "detergent-less," or surfactant-free microemulsions. The experiments in ternary systems containing one hydrotropic co-solvent were ambiguous, and therefore, there was no need to come up with a general theory. Evidence of the existence of well-defined sizes in the aggregates formed obtained by specific deuteration in neutron scattering established the need for the extension of self-assembly theories based on Derjaguin-Landau-Verwey-Overbeck theory (DLVO), bending, or phase transfer energy. We introduced a general free energy expression for weak self-assembly, where solvation effects and entropy compete without the influence of film bending that explains all experimental results for this class of microemulsions. Molecular dynamics showed how these structures can emerge form overall well-known critical fluctuations in ternary fluids. Analysis of MD snapshots shows aggregate size distribution function in number of oily molecules (see figure left); UFME forming "pre-ouzo" aggregates show not only the common power-law dependence near a critical point, but also a preferred size with a maximum at around 50 to 100 "solute" molecules aggregated together, a typical size for classical micelles. The structural investigation of a benchmark ternary solution of solvents (n-octanol/ethanol as the hydrotrope /water) via neutron and X-ray scattering techniques[1] confirms the structure of ultra-flexible microemulsion (UFME) as a dynamic formation of droplets associated to a critical point and stabilized by a thin excess adsorption of the hydrotrope at the interface between water-rich and oil-rich domains. On the octanol-rich side, the nanostructure is better described as a dynamic random 3D network of chain-like associations of OH groups, as tested by a "bump" in the medium angle scattering region, close to the one present in pure octanol and simulated as well by MD[2]. Importantly, this study hints at an explanation for the stability of Ouzo droplets: we propose that any Ouzo spontaneous emulsion (see fig. right) is in fact in dynamic equilibrium with pre-Ouzo, as a parallel to kinetically long-term stable nanoemulsions that are in equilibrium with classical microemulsions that we have to show in scattering results coming soon.



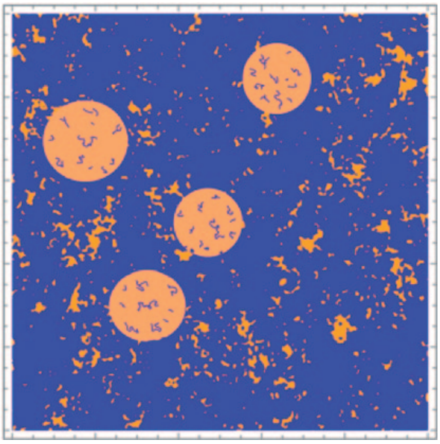


*Fig. **left:** Emergence of surfactant-free micelles from ternary solutions - Typical histogram shown per number on log scale of the size distribution of aggregates of octanol containing between 1 and 100 molecules as obtained from molecular dynamics. **right:** In the metastable Ouzo region, illustration of the solvent-rich spontaneous structured emulsion droplets in dynamics coexistence with the structured water-rich reservoir. The micrometer-sized droplets are not drawn at scale; the pre-Ouzo structures are of the order of 2-5 n m.*

---

[1] Prevost, S.; Lopian, T.; Pleines, M.; Diat, O.; Zemb, T. **Small-Angle Scattering and Morphologies of Ultra-Flexible Microemulsions.** J. Appl. Crystallogr. 2016, 49 (6), 2063–2072.

[2] Schöttl S., Lopian T., Prévost S., Touraud D., Grillo I. , Diat O., Zemb T., Horinek D. - **Combined MD/SAS analysis of organization on a nanometer-scale in ternary solvent solutions containing a hydrotrope** – 2018 submitted

FOAM FLOTATION FOR ION EXTRACTION AND CONCENTRATION

P. Bauduin, L. Girard, A. Jonchère, O. Diat

The process called ion flotation allows to concentrate ions or other charged entities from an aqueous solution within a foam that can be produced at the top of the solution. Foam is created by introducing gas bubbles in the solution that contains surfactant molecules at very low concentration (close to CMC).To maintain a high foam stability in order to limit the solution transport within the foam thanks to an efficient drainage, some specific foaming agents have to be used. Multifunctional surfactants such as AKYPOs or ETHOMEENs, both being pH-sensitive and containing ethylene oxide groups are good candidates because they can interact with multi-charged ions without precipitation. We have shown in previous studies that monovalent cations are much more depleted from the foam films than divalents or even trivalents and thus are difficult to concentrate using this type of foam flotation[1,2].

In the scope of nuclear incident on the Fukushima power plant in Japan soils remediation contaminated by radioactive cesium became a mission of great importance. Prussian blue and its analogues (PBA) represent a class of materials which is well established for the selective sorption of the heavy and radioactive metals such as cesium and thallium. We have shown that cesium cations can be removed from solution via first their sorption in PBA nanoparticles that can be synthesized in situ the solution and then through the flotation of the nanoparticles *(Fig. left)*. Size and surface properties of the nanoparticles along with the surfactant chemistry are main parameters determining the efficiency of decontamination process in this procedure. Cesium can be efficiently removed from aqueous solution, down to the ppb level[3].

Our researches along this flotation axis continues within an ANR FOAMEX in collaboration with ESPCI, BRGM and a local start-up EXTRACTHIVE (see the summary at the end of the document).

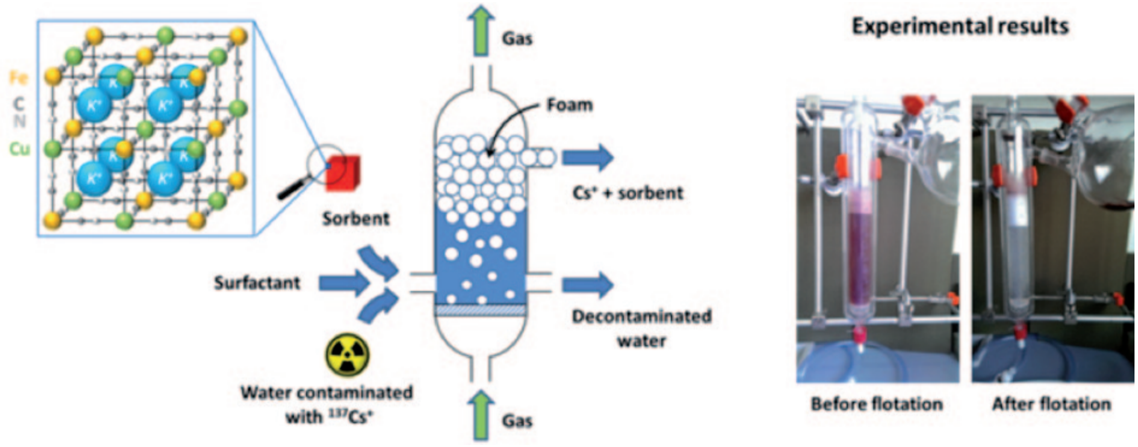


Fig. ***Left:*** *Schematic representation of foam flotation using a solid sorbent synthesized in-situ (Prussian blue analog nanotiles – PBA-NP).* ***Right:*** *Pictures obtained before and after flotation process showing qualitatively the concentration of PBA-NPs charged with Cs cations.*

[1] Micheau C., Schneider A., Girard L., Bauduin P. - **Evaluation of ion separation coefficients by foam flotation using carboxylate surfactant** - Colloids and Surfaces A: Physicochemical and Engineering Aspects (2015) 470 52 – 59.
[2] Micheau C., Diat O., Bauduin P. - **Ion Foam Flotation of Neodymium: From Speciation to Extraction** - J. Mol. Liquids (2018) 253 217-27.
[3] Dedovets D., Bauduin P., Diat O. - **Procédé de séparation sélectif d'un cation métallique à partir d'un milieu aqueux** - French patent application, Jan 2015, n° EN 15 56604.

RECYCLING OF NOBLE METALS FROM SPENT CATALYSTS BY SELECTIVE DISSOLUTION

M. Virot, T. Chave, X. Beaudoux, G. Leturcq (CEA-Marcoule, France), G. Durand (Avignon University, France), J. Ravaux, N. Clavier, N. Dacheux, D. Horlait, S. I. Nikitenko

Cerium-based oxides combined with platinum group metals (PGM, ex: Pt, Pd, Rh) are responsible for performances of automotive catalytic converters that may contain up to 15 g of PGM depending on the considered vehicle. Recycling such materials, known to be highly refractive towards dissolution, appears nowadays as an economically viable alternative but remains nevertheless poorly studied. Reductive dissolution of ceria is considered in LSFC group to provide eco-friendly and efficient methods for their recycling. Such investigation may be of interest for a large audience beyond the scope of automotive catalyst recycling including nuclear industry. Particularly, ceria exhibits redox properties and crystallographic similarities with PuO_2 thus justifying its consideration.

Ceria dissolution has been studied in mild conditions through catalytic reduction processes involving Pt nanoparticles (NPs) previously deposited at the oxide surface by sonication (Ar, 18 $W.cm^{-2}$, 20 kHz)[1]. Further dissolution was studied as a function of different parameters such as stirring, sonication, dissolution media, and temperature. The quantitative dissolution of CeO_2 can be observed in dilute HNO_3-HCOOH-$[N_2H_5][NO_3]$, $[HNO_3]$-$[N_2H_5][NO_3]$ or H_2SO_4-HCOOH mixtures at 40°C ***(Figure 1)***. Such procedure allows to recover Pt by filtration and was also studied with cerium-lanthanide mixed oxides[1]. The incorporation of trivalent (Gd, Nd) or tetravalent lanthanides (Tb) into the ceria matrix results in higher dissolution rates and yields attributed to a weakening of CeO_2 fluorite structure for Gd and Nd; and a higher redox potential for Tb. More generally, catalytic dissolution of CeO_2/Pt based-materials offers a simple and non-expensive route to separate and recycle Pt[1].

The facile, rapid, and complete reductive dissolution of CeO_2 and ceria-based oxides (Pt/CeO_2, $(Ce_{0.75}Zr_{0.25})O_2$, and $(Ce_{0.8}Tb_{0.2})O_2$) at room temperature under stirring was recently reported in a mixture composed of ascorbic acid and a dilute mineral acid ***(Figure 1.c)***[2].

Dissolution kinetics were compared as a function of the nature and concentration of reactants, firing temperature and reactive surface area of the considered oxides. Whatever the considered sample, the complete and congruent (for mixed oxides) oxide dissolution can be observed in 0.5 M ascorbic acid in the presence of dilute nitric or sulfuric acid. For Pt/CeO_2 samples, dissolution goes with Pt aggregation that can be easily recovered from the solution after processing [2].

This eco-friendly method appears very promising for catalyst recycling.

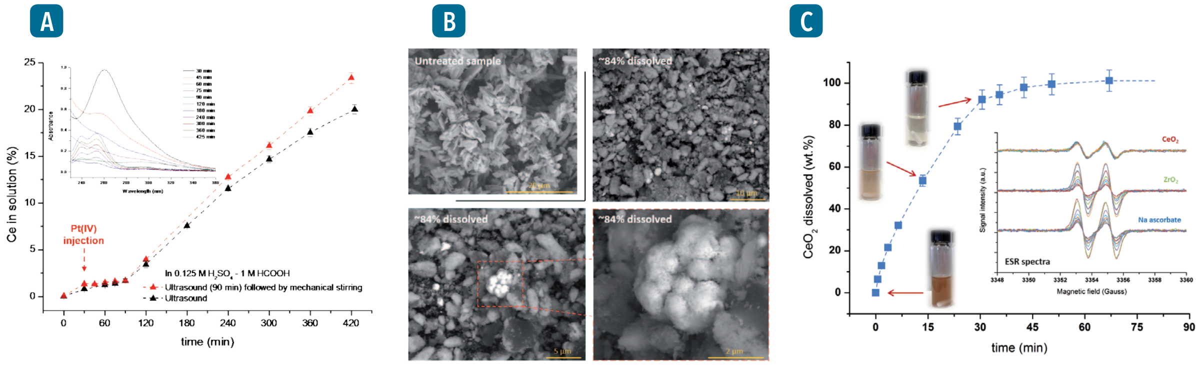


Figure 1: **A** *Kinetics of CeO2/Pt catalytic dissolution (40°C, Ar, 54 m^2g^{-1}) under ultrasound or mechanical stirring (after reduction of Pt(IV) at 18 Wcm^{-2}) in H_2SO_4 - HCOOH mixture.* **B** *SEM images of CeO_2 powder after catalytic dissolution at 40°C (Pt appears bright);* **C** *Dissolution curve of CeO_2 (250 m^2g^{-1}) suspensded in 0.5 M ascorbic acid / 0.75 M HNO_3. Inset shows ESR spectra evidencing the consumption of ascorbyl radicals by CeO_2.*

[1] X. Beaudoux, M. Virot, T. Chave, G. Leturcq, N. Clavier, N. Dacheux, S. I. Nikitenko, **Catalytic dissolution of ceria-lanthanide mixed oxides provides environmentally friendly partitioning of lanthanides and platinum**, Hydrometallurgy 151 (2015) 107-115.
[2] X. Beaudoux, M. Virot, T. Chave, G. Durand, G. Leturcq, S. I. Nikitenko, **Vitamin C boosts ceria-based catalyst recycling**, Green Chem. 18 (2016) 3656-3668.

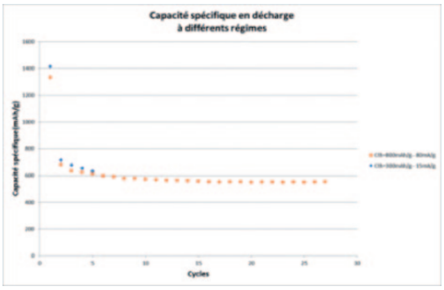
DEVELOPMENT OF A RECYCLING PROCESS FOR LITHIUM ION BATTERY BY CONVERSION OF WASTE AS VALUABLE METAL ORGANIC FRAMEWORKS

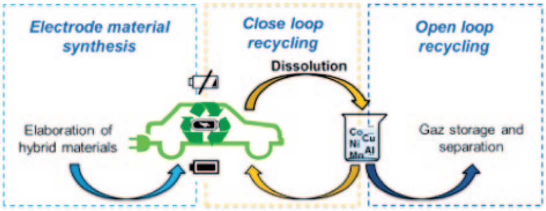
Marine Cognet, Michaël Carboni, Daniel Meyer - T. Gutel, D. Peralta (CEA-Grenoble, France)

Energy storage is one of the biggest challenges for next decades. As the available supplies of fossil energy are decreasing there is a real necessity to find alternatives with the development of clean and renewable energies. The management of renewable energy production requires efficient electrochemical energy storage devices to use it at anytime and anywhere. In recent years, Li-ion batteries (LiBs) have been developed and successfully commercialized for portable devices as smart phones, laptops or cars. However, there are some limitations (capacities, toxicity…) for a larger use of LiBs and new technologies are needed. Moreover, current recycling processes are not well enough developed or economically interesting and only 50% of actual LIBs in weight are recycled due to the law (Directive EU 2006/66/CE) hinders a sustainable development.

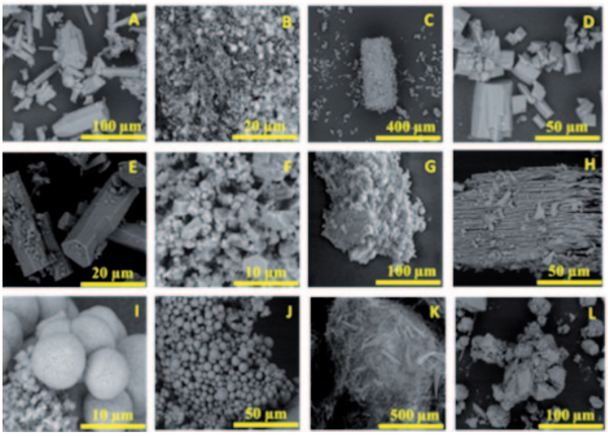
LiBs are usually composed of graphite for the negative electrode and metal oxides for the positive one. As oxides, a mixture of cobalt, nickel, manganese has been largely used in the development of the LiB (NMC batteries). Our team has recently proposed a new recycling process by selective precipitations of these toxic metals as valuable materials (Metal organic Frameworks (MOFs)[1]. Indeed, MOFs consist in inorganic nodes (clusters) bind together by organic linkers and they have gained a lot of popularity mostly due to their high surfaces and tuneable structures. MOFs have been used in many applications as gas storage, heterogeneous catalysis, extraction or metals separation. Recently, MOFs have also been used as electrode materials and have revealed to be very promising for this field[2].

In collaboration with the CEA Grenoble (LITEN), the MOFs obtained from simulant battery waste solution have been tested as electrode in a coin cell. They have revealed capacities as high as 460 mAh/g (2 times higher than the actual technology) with a good cyclability (the capacity is maintained after charge/discharge 50 cycles). From this proof of concept, our effort are now to use real LiBs waste and first results show the possibility to obtain MOF materials with high quality.





Battery circular economy



Ni, Co Mn and mixed Ni-Co-Mn MOFs

[1] (a) E. Perez, R. Navarro Amador, M. Carboni, D. Meyer. **«In-Situ Precipitation of Metal-Organic Frameworks from a simulant battery waste solution»** Mat. Lett., 2016, 167, 188. (b) E. Perez, M.L. Andre, R. Navarro Amador, F. Hyvrard, J. Borrini, M. Carboni, D. Meyer. **«Recovery of metals from simulant spent lithium-ion battery as organophosphonate coordination polymers in aqueous media»** Journal of Hazardous Materials, 2016, 317, 617.
[2] M. Cognet, T. Gutel, D. Peralta, J. Maynadie, M. Carboni, D. Meyer **"Iron(II)-Benzene Phosphonate Coordination Polymers as an Efficient Active Material for Negative Electrode of Lithium-Ion Batteries"** Journal of the electrochemical society, 2017, 164, 12, A2552-A2554

METALLIC SURFACE MANIPULATION BY CAVITATION

R. Ji, M. Virot, R. Pflieger, R. Podor, X. Le Goff, S. I. Nikitenko

Surface treatment under high-power ultrasound is widely used for degreasing, biological decontamination, scaling, and more simply for cleaning. Chemical effects arising from acoustic cavitation in combination with non-conventional activation of surfaces may help dispersing contaminants bound to surfaces in solutions. In comparison to conventional procedures, the microscopic size of acoustic bubbles generated during sonication allows the decontamination of surfaces with irregular shapes and complex geometries. Holes, cracks, folds, and machining areas may be treated without addition of concentrated chemicals avoiding restrictive, laborious and often dangerous handling of materials. In nuclear industry, ultrasound-assisted decontamination of surfaces can be of particular interest for dismantling and decommissioning ending life nuclear facilities. The reductions of effluent volumes and time processing coupled to a decrease in the activity level of the generated wastes is an important challenge with financial and environmental potential benefits.

Sonochemical decontamination of metallic surfaces has been investigated in the sonochemistry group for several years. A sonochemical set-up has been developed to treat solid surfaces as a function of various parameters including the nature of the solution, ultrasonic frequency, gaseous atmosphere, emitter/sample distance, etc. Various metallic surfaces are studied in the lab using lanthanide (as surrogates) and actinide oxides as pollutants. Decontamination of surfaces can be carried out in dilute solutions at near ambient temperature and pressure. *Fig. 1* shows a metallic surface contaminated with a uranyl solution and treated at high-frequency ultrasound (205 kHz) in dilute acid solution. The surface was rolled (like a snail) to simulate a complex geometry. Alpha spectrometry experiments confirmed the complete decontamination of the sample which occur through the ultrasonically-controlled dissolution of the surface[1].
After treatment, microscopy pictures *(SEM on Fig. 1)* allowed the observation of an original pitted surface evidencing the complete removal of the contamination[2].

Such results are very promising towards dismantling and decommissioning of technological wastes. It is important to emphasize that technological opportunities related to industrial ultrasound propagation are nowadays huge (high volumes with batch or continuous processing, coupling of ultrasonic frequencies or techniques, indirect sonication, etc.). Such application for surface treatment at the large scale can therefore be considered as a viable alternative.

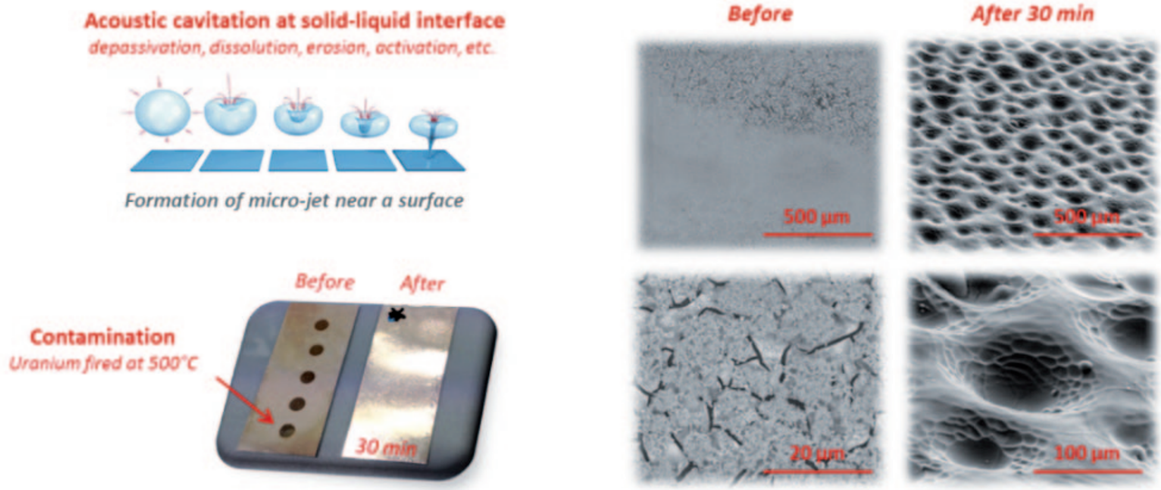


Fig. 1: Anticlockwise direction shows a scheme representative of the formation of a micro-jet near a solid surface; a picture of a U-contaminated metallic surface previously rolled to simulate a complex surface before and after 30 min sonication (205 kHz); and SEM pictures of a contaminated metallic surface before treatment (the surface is almost completely covered by contamination) and after 30 min sonication.

[1] Ji R. **Study of acoustic cavitation near metal surfaces contaminated by uranium**, Thesis 2018 ICSM, University of Montpellier.
[2] Ji R., Virot M., Pflieger R., Podor R., Le Goff X., Nikitenko S. I. **Controlled "golf ball shape" structuring of Mg surface under acoustic cavitation**, Ultrasonics Sonochemistry, 40 (2018) 30-36.

NANO-IONS SPECIFIC EFFECT : SUPERCHAOTROPY

P. Bauduin, L. Girard, A. Jonchère, O. Diat

Ionic species, such as polyoxometalates (POMs) or (metal-) boron clusters are at the frontier between ions and (charged-) colloids due to their nm size. We have shown that the large size and low charge density of POMs, compared to classical ions, are responsible for a peculiar behavior called "super-chaotropy". This property refers to the strong propensity of nano-ions to adsorb at neutral polar interfaces, via non-specific interactions[1]. The super-chaotropy scales with the charge density and, to a lesser extent, with the polarizability. It has strong effects on phase transitions in soft matter and can, for example, give an explanation on the origin of the famous "POM-etherate" phase formation. A simple way for evaluating and classifying nano-ions, such as POMs, according to their super-chaotropy was proposed via the cloud point (temperature) variation[2]. The super-chaotropic behavior of nano-ions opens opportunities in separation science, catalysis, and for the design of nanostructured hybrid materials.

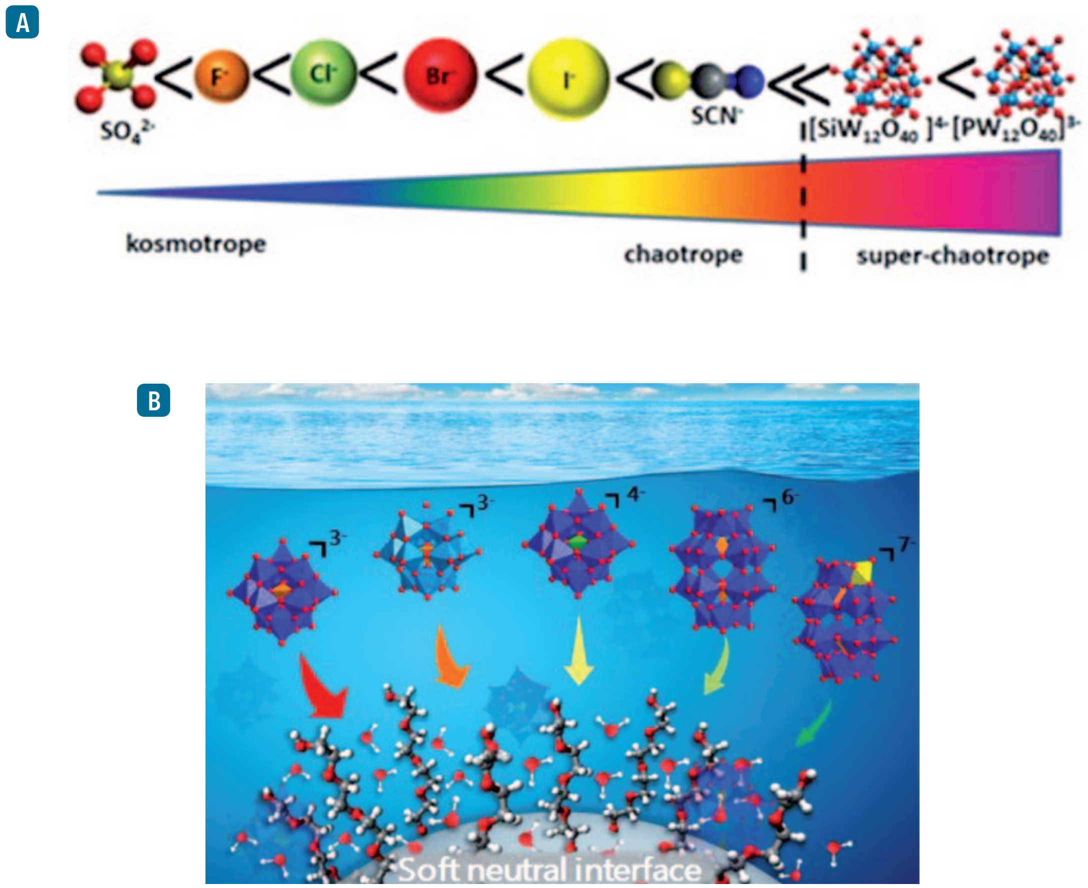


Fig. **A** *Beyond the Hofmeister series on the "chaotropes" side with Kegging POM as an example.* **B** *Schematic representation of various POM anions in interaction with non-ionic micelles, the strength of the interaction depends on the POM's charge density decrease from right to left.*

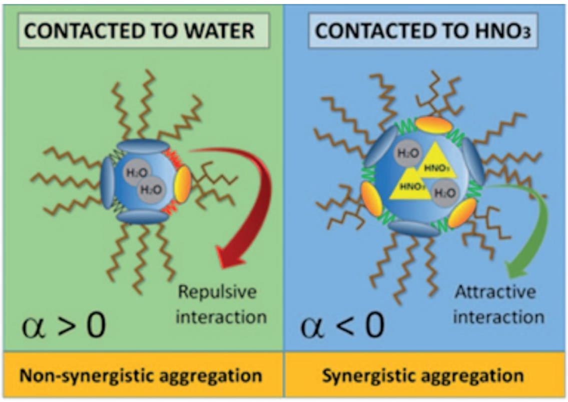
[1] Naskar B., Diat O., Nardello-Rataj V., Bauduin P. - **Nanometer-Size Polyoxometalate Anions Adsorb Strongly on Neutral Soft Surfaces** - J. Phys. Chem C (2015) 119(36) 20985-92

[2] Buchecker T., Schmid P., Renaudineau S., Diat O., Proust A., Pfitzner A. Bauduin P.- **Ranking of Keggin- and Dawson-type polyoxometalates in the Hofmeister series according to their ability to adsorb on polar neutral surfaces** - Chem. Comm. (2018) 54 pp1833-36

THERMODYNAMIC ORIGIN OF SYNERGY?

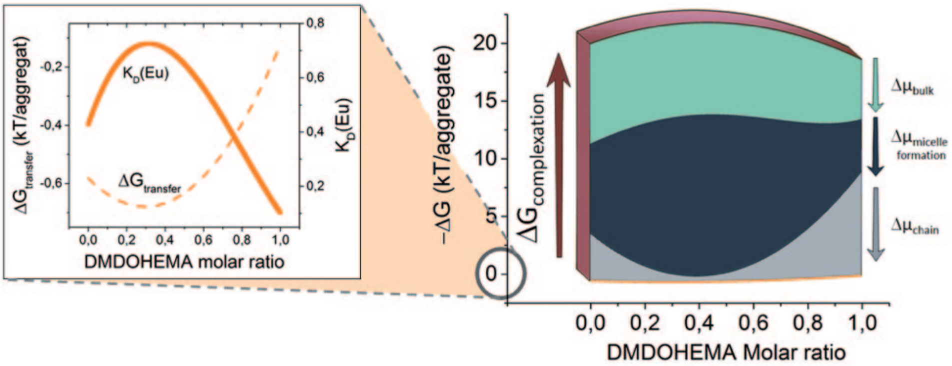
J. Rey, S. Dourdain, J-F. Dufrêche, M. Bley, S. Pellet-Rostaing, T. Zemb
L. Berthon, J.M. Muller (CEA-Marcoule)

Revisiting aggregation of water-poor mixed reverse micelles, we proposed to identify the thermodynamic origins of synergy in solvent extraction by considering aggregation of extractants. We independently investigated the effect of water, acid and extracted cations on aggregation and extraction. Thermodynamic equations were proposed to describe synergistic aggregation in the peculiar case of synergistic solvent extraction using a greater critical aggregation concentration (CAC) than that of usual surfactants, as well as specific interactions between extractants due to the presence of water, acid and cations. Distribution of two extractant molecules in monomers and reverse micelles was assessed, leading to an estimation of the in-plane interaction parameter between extractants in the aggregates.



Based on this model, we studied the N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide (DMDOHEMA) and di(2-ethylexyl) phosphoric acid (HDEHP) mixture and show that adding nitric acid enhances synergistic aggregation at the equimolar ratio of the two extractants and that this configuration can be related to a favored enthalpy of mixing.

We further decomposed the free energy of transfer in the case of synergistic solvent extraction. This model implies a balance between the transfer free energy of an ion from an aqueous phase to an organic phase as a combination of four distinct terms related to long range interactions and complexation free energy[1]. We showed how complexation is strongly counter-balanced by the energy cost to pack electrolytes and water into the hydrophilic core of reverse aggregates, by the cost in entropy for the formation of reverse aggregates, and by the interfacial curvature energy. Finally, we could point out that extraction can mainly be attributed to a minimal cost in curvature energy when complexation energy is maximized[2].



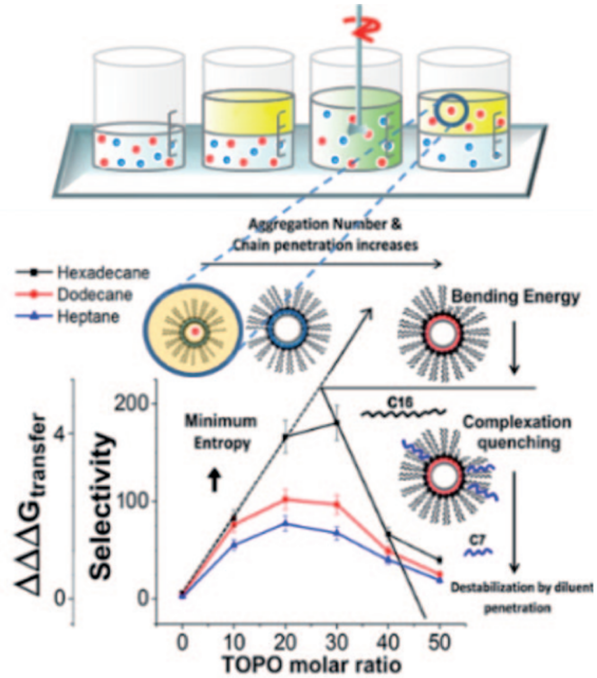
[1] J. Rey, S. Dourdain, J-F. Dufrêche, L. Berthon, J. M. Muller, S. Pellet-Rostaing and T. Zemb - **Thermodynamic Description of Synergy in Solvent Extraction:I-Enthalpy of Mixing at the Origin of Synergistic Aggregation** - Langmuir (2016) 32 49 13095-13105

[2] J. Rey, M. Bley, J-F. Dufrêche, S. Dourdain, L. Berthon, S. Pellet-Rostaing and T. Zemb - **Thermodynamic Description of Synergy in Solvent Extraction: II –Themodynamic balance of motors implied in synergistic extraction**- Langmuir (2017) 33, 46, 13168-13179.

DILUENT EFFECT ON SYNERGISTIC EXTRACTION: A COMBINATION OF CONFIGURATIONAL ENTROPY, FILM BENDING AND PERTURBATION OF COMPLEXATION

J. Rey, O.Pecheur, S. Dourdain, S. Pellet-Rostaing, T. Zemb
L. Berthon (CEA-Marcoule), J. Jestin (LLB, CEA-Saclay)

Playing with conventional alkanes we investigated the physical origin of the "diluent effect" on synergistic extraction. As diluents are traditionally expected to modify aggregation without perturbing chelation mechanisms, this study aimed at evaluating the importance of aggregation in the synergistic extraction mechanisms, our driving question being:
"How do diluents affect the relative values of extraction free energy and aggregate formation free energy?"
This question remains marginal: one often considers the extractions as the result of well-defined competing complexes, where the balance reactions used do consider ligand activity in the diluent, but one does not consider the activities of diluent. Different diluent with different chain lengths, from heptane to hexadecane, were tested on the solvent extraction system containing extractants, Di-(2-ethylhexyl)phosphoric acid (HDEHP) and tri-octyl phosphine oxide (TOPO) in various ratios. The combination of these two molecules is known to allow a synergistic extraction of uranium in a ratio 4:1. The results obtained for 3 diluents are sketched in the following figure.



We showed that these synergistic properties are related to a favored aggregation, and combined SAXS and SANS measurements pointed out the solvent lipophily influence on this system: complete fit of the data evidenced the presence of core shell reverse-micelle like aggregates, into which the penetration of diluent having shorter chain length was found to induce lower extraction efficiency. In presence of conventional alkanes, configurational entropy and curvature free energy of the aggregates were therefore shown to monitor the synergy as well as the diluent effect on extraction.
Looking at aggregation effects on solvent extraction, we showed that the intensity of the unexplained synergy peak is strongly dependent on the "penetrating" or "non penetrating" nature of the alkanes used as diluent. This experimental determination allowed us to attribute the synergy to a combination of entropic effects favoring extraction and extractant film bending energy, opposed to perturbation of the first coordination sphere by penetration[1].

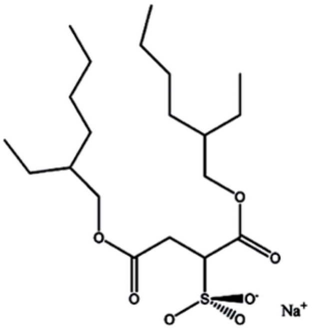
---

[1] J. Rey, S. Dourdain, L. Berthon, J. Jestin, S. Pellet-Rostaing, T. Zemb - **Synergy in extraction system chemistry: combining configurational entropy, film bending and perturbation of complexation** - Langmuir (2015) 31 7006.

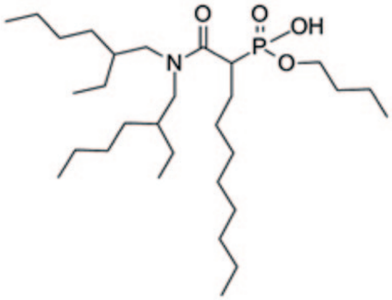
EXPLOITING THE AGGREGATION? FORMULATION OF A NEW SYNERGISTIC EXTRACTANT/ SURFACTANT MIXTURE FOR RARE EARTH EXTRACTION

J. Rey, S. Atak, S. Dourdain, G. Arrachart, S. Pellet-rostaing
L. Berthon (CEA-Marcoule)

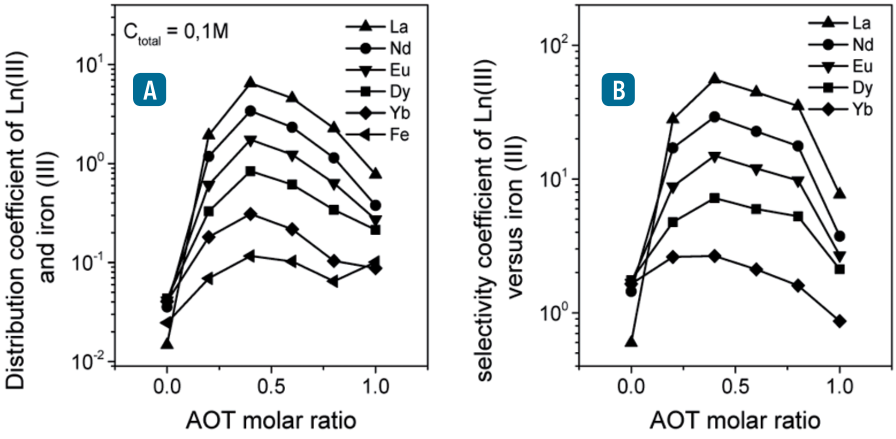
As part of the ERC project REEcycle, we proposed the formulation of a new synergistic extractant system for the extraction rare earth elements from aqueous phosphoric acid solution containing large quantities of impurites currently found in urban mines and secondary deposits. This new synergistic system is original in its concept as it contains in the association of the bifunctional extractant amido-phosphonate, known for its high efficiency for the recovery of uranium from phosphate rocks, with the AOT surfactant molecule known to form reverse micelles in aliphatic diluents[1].



AOT Bis(2-ethylhexyl) sulfosuccinate sodium



DEHCNPB
butyl-N,N-di(2-ethylhexyl)carbomoyl-nonylphosphonate



The mixture was found to extract synergistically rare earth elements with high distribution coefficients (D), and is high Separation Factor (S.F.) toward iron (III) from acid phosphoric solution[2].

A complete thermodynamic study of its extraction properties was also investigated showing this system has the ability to extract REEs from a wide range of phosphoric acid concentration which is often the case in industrial processes [1].

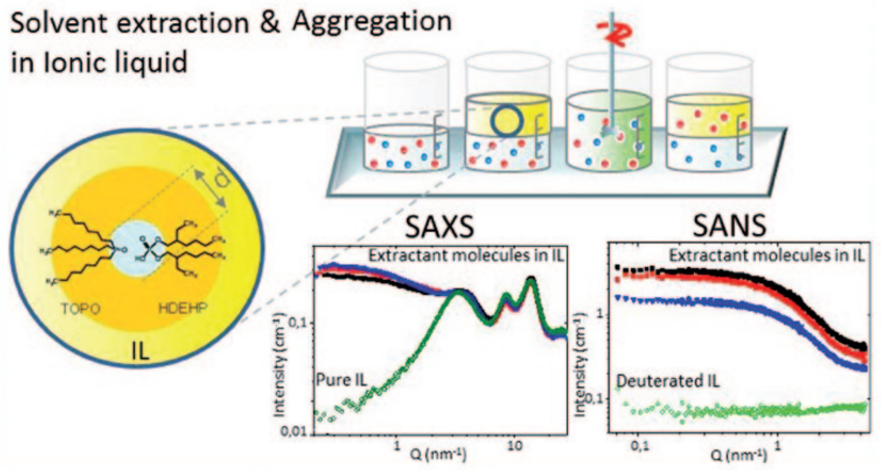
[1] J. Rey, S. Atak, S. Dourdain, G. Arrachart, L. Berthon, S. Pellet-Rostaing - **Synergistic Extraction of Rare Earth Elements from phosphoric medium using mixture of surfactant AOT and DEHCNPB** - Solvent Extraction and Ion Exchange (2017) 35, 5,321-331.

[2] J. Rey, G. Arrachart, S. Dourdain, S. Atak, S. Pellet-Rostaing - **Procédé liquide-liquide d'extraction de terres rares par association d'un extractant bifonctionnel et d'un tensioactif** - FR 3055906 A1 (15/09/2016)

IONIC LIQUID AS DILUENT IN SOLVENT EXTRACTION: FIRST EVIDENCE OF SUPRAMOLECULAR AGGREGATION OF A COUPLE OF EXTRACTANT MOLECULES

T. Sukhbaatar, S. Dourdain, R. Turgis, J. Rey, G. Arrachart, S. Pellet-Rostaing

A recent challenge in solvent extraction is to replace conventional organic solvents (often toxic and volatile), with ionic liquids (IL). Depending on the extraction systems tested, these new solvents can lead to better efficiency than the conventional ones. Although some assumptions based on ion exchanges have been proposed in the literature, the involved mechanisms are still poorly understood. So far, no study was conducted to evaluate the IL effect on the aggregation properties of the extractant molecules, even though ILs are known to modify the curvature radii of surfactant microemulsions.



Investigating the HDEHP/TOPO system in Omim[Ntf2] ionic liquid as diluent, very different extraction properties were observed as a synergistic peak shifted to 50% of TOPO ratio. Aggregates signals similar to the ones observed in conventional diluents were evidenced from SAXS measurements *(Figure2)*. However the strong structural peaks of the IL prevent a proper fit analysis. Therefore the synthesis of fully deuterated IL was proposed, allowing the measurement of SANS spectra with no structural peak.

The IL's deuteration enables full characterization of the aggregates.

The trend observed with increasing TOPO percentages is similar to the one obtained in deuterated dodecane. Considering a core-shell model as in the common organic diluents, the increase of scattered intensity observed in IL could be interpreted in terms of aggregation number (Nag) and of penetration of the diluent in the apolar shell[1].

These behaviors will be deeper investigated in further study supported by the LABEX chemisyst. On different systems, the effect of ionic liquids as diluent will be related to an estimation of the important thermodynamic driving force of extraction, such as configurational entropy and binding energy of aggregates.

---

[1] T. Sukhbaatar, S. Dourdain, R. Turgis, J. Rey, G. Arrachart, S. Pellet-Rostaing - **Ionic liquid as diluent in solvent extraction: First evidence of supramolecular aggregation of a couple of extractant molecules** - Chem. Commun. (2015) 51 15960.

IONIC LIQUIDS BASED EXTRACTION: PERFORMANCES AND MECHANISTIC INVESTIGATIONS OF CRITICAL METALS EXTRACTION

R. Turgis, C. Micheau, B. Baus Lagarde, G. Arrachart, S. Pellet-Rostaing
M. Draye (U. Chambéry), S. Legeai (IJL), Terra Nova Développement (TND)

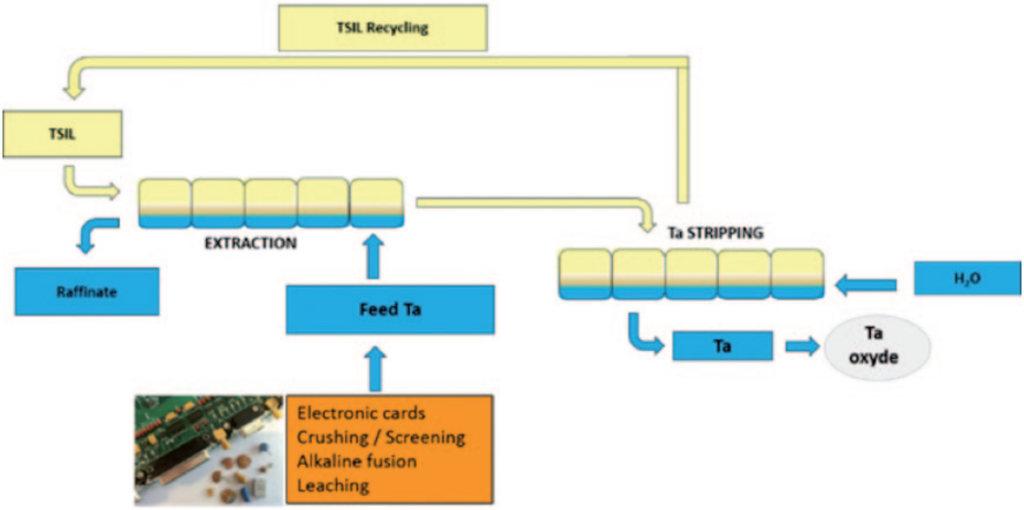
Due to the growing environmental awareness and the development of green chemistry, intense research studies have been devoted to the development of alternative processes limiting the use of volatiles. Ionic liquids (ILs) exhibit several properties that make them attractive for the replacement of common organic diluents, among them a wide liquid range, good thermal stability, the ability to solubilize a wide range of solutes, a very low vapor pressure, and non-flammability.

Therefore, as part of EMILI project (Labex Project CheMISyst: ANR-10-LABX-05-01) and SILEXE project (ANR – 13 – CDII – 0010), we investigate Room Temperature Ionic Liquids (RTILs) as unusual media for strategic metal recycling, especially rare earths elements, tantalum, gold and palladium, through the use of a selective extraction (or back-extraction)/electrodeposition process starting from specific ligands using ILs as diluent and Task Specific Ionic Liquids (TSILs) as extractants.

The extraction of rare earth elements (REEs) from nitric acid solution with a powerful triphosphine trioxide (TPO) ligand was studied using ILs as diluent in comparison to a classical solvent (benzyl ether). TPO seems to be 10 to 100 times more efficient when it is dissolved in IL media whatever the concentration of nitric acid involved. Mechanistic investigations have been performed thanks to the determination of the stoichiometry of the complex(es) involved in the extraction (slope analysis method, NMR experiments …). We demonstrate that solvation of the ligands and/or the complexes is thus very different in these two systems and could be the reason why ligands are more efficient in ionic liquids[1].

In this context, we also develop a novel family of TSILs bearing various ketone or phosphonate groups and cations. The extraction behavior of Ta with these TSILs was investigated in comparison to commonly used extractant such as MIBK or TBP. The results for the TSILs show that high D values can be achieved for the selective separation of Ta. Furthermore, the recovery process for Ta after extraction was performed with water and recyclability was successfully established[2].

Such system can be used for the recovery of Ta from leaching solution of Waste Electrical and Electronic Equipment (WEEE). A flowsheet has been proposed which is now implemented in a pilot scale.



---

[1] R. Turgis, G. Arrachart, V. Dubois, D. Virieux, S. Michel, S. Legeai, M. Lejeune, M. Draye, S. Dourdain, S. Pellet-Rostaing - **Performances and mechanistic investigations of a triphosphine trioxide/ionic liquid system for rare earth extraction** - Dalton Transactions (2016) 45(3), 1259-1268

[2] R. Turgis, G. Arrachart, S. Pellet-Rostaing, M. Draye, S. Legeai, D. Virieux, C. Thomas - **Processes for extracting and recovering tantalum from acid aqueous phase by an ionic liquid** -WO 2017025547 A1 / FR 3040060 A1 (2017)
R. Turgis, G. Arrachart, S. Michel, S. Legeai, M. Lejeune, M. Draye, S. Pellet-Rostaing - **Ketone functionalized task specific ionic liquids for selective tantalum extraction** - Separation and Purification Technology (2018) 196, 174-182

DESIGN AND SYNTHESIS OF BIFUNCTIONAL MOLECULES FOR THE EXTRACTION OF STRATEGIC METALS

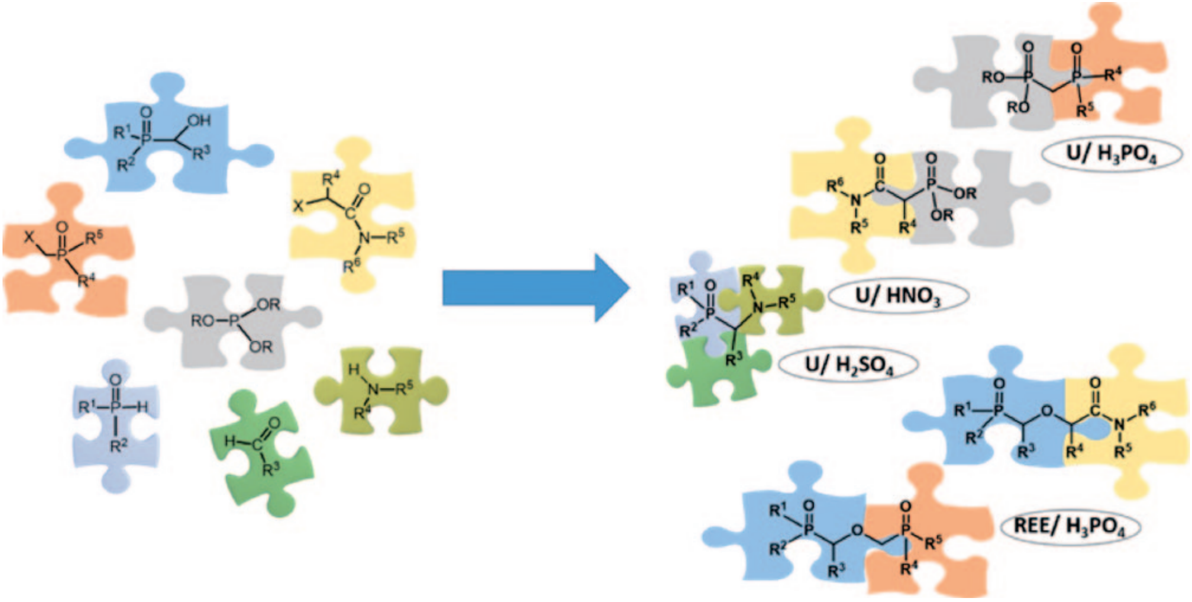
R. Turgis, A. Leydier, F. Mary, G. Arrachart, S. Pellet-Rostaing, G. Bernier, M. Miguirditchian (CEA-Marcoule)

Despite the fact that methods for extraction of strategic metals (such as uranium, rare earth elements) from an acidic medium (nitric, sulfuric or a phosphoric) are relatively robust processes, more efficient system in terms of extraction efficiency or selectivity with respect to competitors ions remains relevant.

Based on the design of new extracting agent able to extract uranium from a nitric, sulfuric or phosphoric medium, we designed, synthesized and evaluated new bifunctional extractants carrying an amine, amide group and a phosphoric acid group or a phosphine oxide group…. Such ligands possess and mimic the properties of the components of the AMEX, DAPEX or URPHOS process in one entity[1].

These new bifunctional ligands were found to extract selectively hexavalent uranium U^{VI} with high distribution coefficient (D) and selectivity towards competitors in acid solution.. Investigations have been carried out in order to emphasize the properties of the ligand: acid extraction, ligand, acid and uranium concentration dependency. From the acquisition of the results, the design of a flowsheet has been implemented for phosphoric acid recovery that is in industrial development by ORANO.

From a similar approach, we synthesized a series of bifunctional molecules with a central oxygen structurally related to glycolamides compounds for the extraction and separation of rare earth elements (REEs). We focused focus our investigation on the effects of structural modification on the extraction efficiencies. The combination of an amide, a P=O donor site, and a central oxygen in such glycolamide ligand showed interesting extraction properties for heavy rare earth elements from phosphoric acid solutions[2].



---

[1] A. Leydier, G. Arrachart, R. Turgis, G. Bernier, C. Marie, M. Miguirditchian, S. Pellet-Rostaing. **«Recovery of uranium (VI) from concentrated phosphoric acid using bifunctional reagents»** Hydrometallurgy 2017, 171, 262-266
A. Leydier, R. Turgis, G. Arrachart, V. Dubois, S. Pellet-Rostaing - **Compounds with phosphine oxide and amine functions as ligands for uranium(VI) extraction from aqueous solutions of sulfuric acid** - WO2016156591 A1 / FR 3034417 A1 (2016),
G. Arrachart, S. Chapron, A. Leydier, S. Pellet-Rostaing, R. Turgis - **Utilisation de composés bifonctionnels, à fonctions acide phosphonique/phosphonate et amine, pour extraire l'uranium(VI) de solutions aqueuses d'acide nitrique** - FR. 17 59993 (23/10/2017).

[2] M. Miguirditchian, G. Bernier, V. Pacary, C. Balaguer, C. Sorel, R. Berlemont, M. Bertrand, B. Camès, A. Leydier, R. Turgis, G. Arrachart, S. Pellet-Rostaing, H. Mokhtari - **Development of a new solvent extraction process for the selective recovery of uranium from phosphoric acid** - Solvent Extraction and Ion Exchange (2016) 34(3), 274
F. Mary, G. Arrachart, S. Pellet-Rostaing, A. Leydier, V. Dubois - **Use of novel compounds for selectively extracting rare earths from aqueous solutions including phosphoric acid and associated extraction method** - WO 2016177695 A1 / FR 3035880 A1(2016)

LANTHANIDES (III) SEPARATION BY DIGLYCOLAMIDES CAVITAND

M. Whebie, B.Baus Lagarde, G. Arrachart, S. Pellet-Rostaing
I. Karamé (Liban)

The positive effect of preorganization of ligands on a platform on the extraction efficiency has been established in the literature.

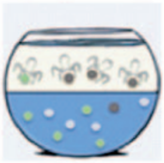
Among different macrocycles, cavitands analogues of C-methylcalix(4)methyl-resorcinarene provides an excellent preorganized platform for the coordination of host systems due to its conformational rigidity, which is assured by the methylene bridging between the hydroxyl groups of two neighboring phenyl rings.

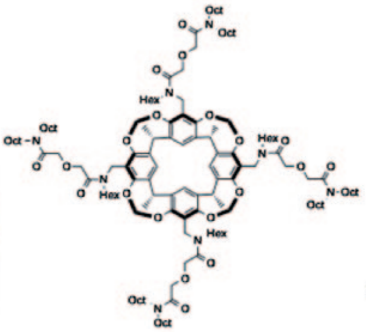
In the present study, the functionalization of resorcinarene with four diglycolamide groups have been performed thanks to peptide coupling or click chemistry making the platform useful for the extraction of rare earth elements (REEs)[1].

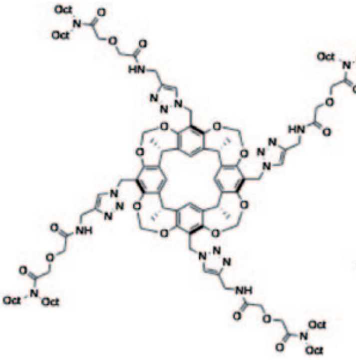
With both DGA-cavitand, the extraction of heavy rare earth element (HREE) is favored at high HNO3 concentration, indicating the possibility to a selective extraction of HREE.

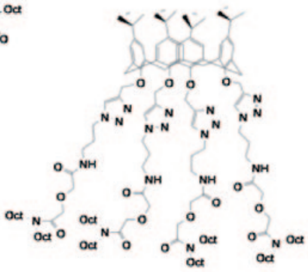
The stoichiometry of the extraction was established by the slope analysis method and an extraction mechanism was proposed from the estimation of thermodynamic parameters. It appears that the presence of triazole ring (Tz) did not have an effect on the extraction performances but play a significant role on the structure of the ligands leading to different possibility for the stoichiometry of the complexes. From the extraction behavior of the tetra-DGA-resorcinarene ligands, we present the possibility for the extraction and separation and stripping of dysprosium (and/or neodymium) from used permanent magnets.

Also we show that ionic liquid-based extraction system using diglycolamide functionalized macrocyclic platforms resorcin[4]arene cavitand or t-butylcalix[4]arene provided selectivity for the heavier and middle lanthanides while for the conventional diglycolamide ligand such as TODGA in IL systems no specific selectivity has been observed [2].









---

[1] M. Wehbie, G. Arrachart, I. Karamé, L. Ghannam, S. Pellet-Rostaing - **Triazole Diglycolamide Cavitand for Lanthanide Extraction** - Separation and Purification Technology (2016) 167, 17-24
M. Wehbie, G. Arrachart, I. Karamé, L. Ghannam, S. Pellet-Rostaing - **Diglycolamide-Functionalized Resorcinarene for Rare Earths Extraction** - New Journal of Chemistry (2016) 40, 9344-9351.
M. Wehbie, G. Arrachart, C. Arrambide Cruz, I. Karamé, L. Ghannam, S. Pellet-Rostaing - **Organization of diglycolamides on resorcinarene cavitand and its effect on the selective extraction and separation of HREEs** - Separation and Purification Technology (2017) 187, 311-318

[2] M. Wehbie, G. Arrachart, I. Karamé, L. Ghannam, S. Pellet-Rostaing - **Ionic liquid-based extraction system using diglycolamide functionalized macrocyclic platforms for the extraction and recovery of lanthanides** - Dalton Transactions (2017) 46, 16505-16515

POLYMERIC RESINS FOR THE RECOVERY OF METALS OF INTEREST

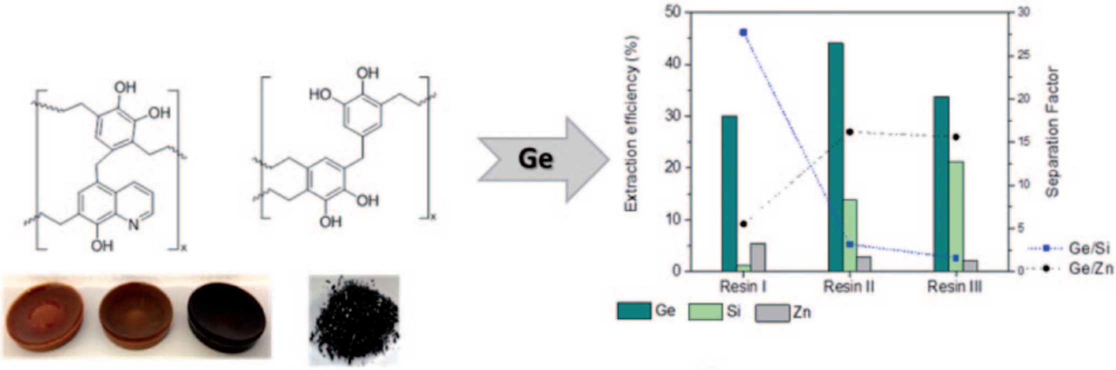
C. Arrambide Cruz, G. Arrachart, S. Pellet-Rostaing

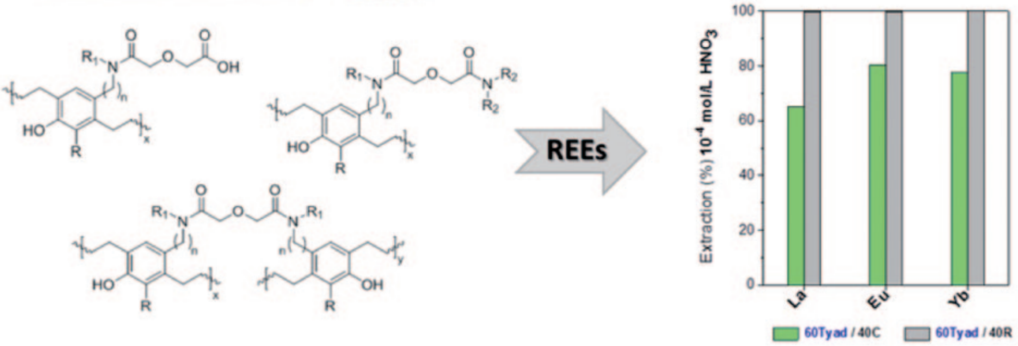
Extraction of specific targeted species (rare earth, heavy metals, transition metals, radionuclides) from industrial (mining deposit and urban mining) and nuclear effluents is an important issue in the recycling and / or decontamination processes. A large number of organic and inorganic solids, chelating or ion-exchanging materials, have been developed for selective ionic separation by solid / liquid process.

The aims of this project are the syntheses of chelating original systems and then the preparation of specific formo-phenolic based ion exchange resins. A study on the understanding of the synthesis of these resins as well as their performance in the extraction of valuable elements was realized in order to highlight the potential of these resins for the recovery and valorisation of strategic elements such as germanium, rare earth elements[1].

From the formo-phenolic resins incorporated with catechol and 8-hydroxyquinoline, we have been able to show that the selective recovery of germanium from silicon or zinc was possible, depending on the proportion of each phenolic precursors in the polymeric matrix[2].

The synthesis of the phenolic precursors by integrating ligands such as diglycolamic acid and diglycolamides allowed the use of resin for the recovery of rare earths elements.





---

[1] C. Arrambide Cruz, PhD 2017 - **Méthodologies de synthèse de résines formo-phenoliques chelatantes : vers une extraction solide-liquide optimisée des métaux stratégiques**.

[2] C. Arrambide Cruz, S. Marie, G. Arrachart, S. Pellet-Rostaing - **Selective extraction and separation of germanium by catechol based resins** - Separation and Purification Technology (2018) 193, 214-219.

DEVELOPMENT OF A METHODOLOGY FOR THE SYNTHESIS OF HYBRID SILICA WITH HIGH EXTRACTANT CAPACITY

R. Winkler, R. Besnard, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing

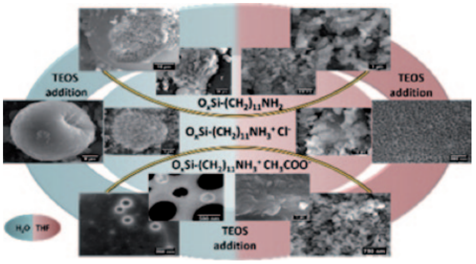
In the context of solid-phase extractants, the organically functionalized silica should have a high density of functional groups with a satisfying homogeneity and accessibility. These requirements are usually difficult to obtain with conventional approaches.

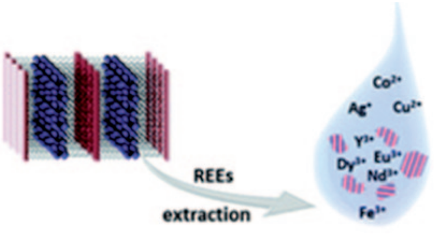
The present work aims to establish a critical examination of the self-assembly of amphiphilic organosilane in different condition in order to study the phenomena that influence the self-associative properties of amphiphilic molecules in the controlled preparation of mesoporous materials and nanoparticles with specific chelating properties. Based on their amphiphilic properties, such organosilica precursors could be hydrolyzed to spontaneously give structured materials without requiring further addition of external surfactant. The structural features of the nanostructured organic/inorganic hybrids has been studied as a function of catalytic and thermal effects[1].

We showed that the structural and morphological versatility offered by this so-called "all-in-one" approach, result in combinatory effects of the addition of TEOS, the role of curvature agent played by a counter-ion and with the change of solvent during the sol-gel process[2].

Various silica-based materials bearing amine groups with a densely functionalized surface have been prepared from condensable amphiphile molecules. The availability of such functional groups was established in particular with the immobilization of the platinoid salt. These platinoid salt complexes in the stable sandwich-layered structure can be changed into metallic nanoparticles after reduction treatment[3].

Also, various glycolamic acid groups have been introduced at the interface between two bilayers on the hybrid material obtained after condensation of silylated amines. The resulting materials exhibit a large number of amic acid groups which exhibit adsorption properties for rare earth elements[4].





[1] R. Besnard, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing - **Structural study of hybrid silica bilayers from "bola-amphiphile" organosilane precursors: catalytic and thermal effects** - RSC Advances (2015), 5(71), 57521-57531.

[2] R. Besnard, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing - **Tuning the nanostructure of highly functionalized silica using amphiphilic organosilanes: Curvature agent effects** - Langmuir (2016), 32 (18), 4624–4634.

R. Besnard, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing - **Tuning the Morphology of Functionalized Silica using Amphiphilic Organosilanes** - Journal of Sol-Gel Science and Technology (2017) 81(2) 452–467.

[3] R. Besnard, J. Cambedouzou, G. Arrachart, X. F. Legoff, S. Pellet-Rostaing - **Organosilica-metallic sandwiches materials as precursors for palladium and platinum nanoparticle synthesis** - RSC Advances (2015) 5(95), 77619–77628

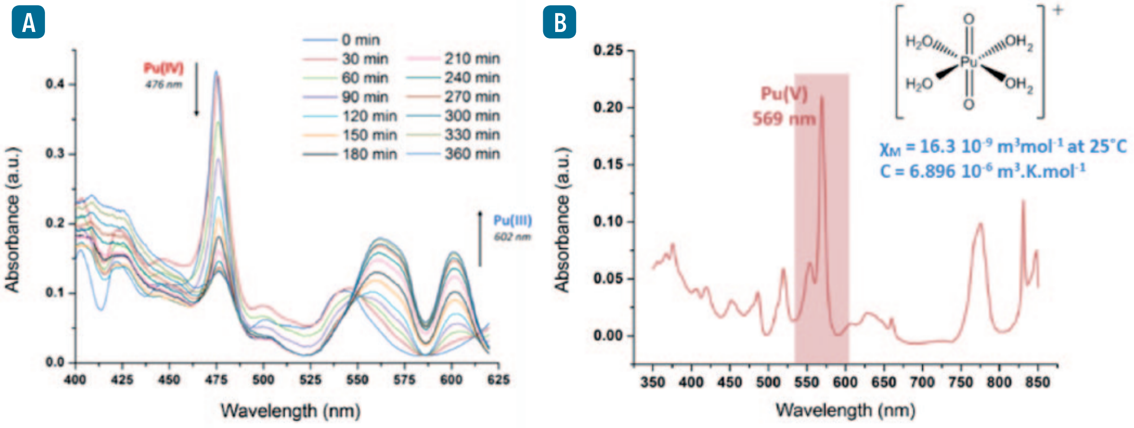
[4] R. Besnard, R. Winkler, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing - **Ion extraction applications of bilayer-structured hybrid silicas**- Materials Chemistry Frontiers (2018) 2, 1031-1039

SONOCHEMISTRY OF ACTINIDES IN HOMOGENEOUS SOLUTIONS

M. Virot, E. Dalodière, T. Dumas (CEA/DEN/DMRC), C. Berthon (CEA/DEN/DMRC), D. Guillaumont (CEA/DEN/DMRC), P. Moisy (CEA/DEN), S. I. Nikitenko

Sonochemistry has attracted considerable attention due to the mild and efficient reaction conditions it enables. The observed effects are generally attributed to acoustic cavitation which is the nucleation, growth, and rapid implosive collapse of gas and vapor-filled micro-bubbles. This phenomenon enables the generation of in-situ redox species with controlled kinetics and therefore suggests the possible application of ultrasound in actinide chemistry. [1] The adjustment of the An oxidation state during recycling processes is important for their recovery and separation necessarily performed with very high yields.

In collaboration with DMRC department (Atalante facility, Marcoule), the behaviors of Pu(III), Pu(IV) and Pu(VI) have been investigated in various aqueous solutions under low and high frequency ultrasound. In 1 M HNO_3, ultrasound has no effect toward Pu(IV), while Pu(III) can be rapidly oxidized to Pu(IV) due to the autocatalytic formation of HNO_2 induced by HNO_3 sonolysis. [2] When an anti-nitrous reagent is added (e.g., NH_2SO_3H), Pu(IV) can be sonochemically reduced to Pu(III). The reduction follows a first order reaction law and leads to a steady state where Pu(IV) and Pu(III) coexist in solution *(Fig 1.a.)*. This observation is attributed to the sonochemical generation of H_2O_2 which formation is highly dependent upon ultrasound conditions (f, P_{ac}, gas…). [1] Pu(V) has recently gained much attention due to its potential contribution to the environmental migration of An. However, the preparation of concentrated and pure Pu(V) solutions is quite difficult and often hindered by its great instability towards disproportionation, thus limiting the accessibility to physical and chemical property data. The rapid and facile ultrasound preparation of stable Pu(V) solutions free from the admixtures of the other Pu oxidation states has been recently demonstrated *(Fig 1.b.)*. [3] The mechanism deals with the sonochemical reduction of Pu(VI) in weakly acidic perchloric solutions with the in-situ generated H_2O_2 which kinetics can be dramatically enhanced under high frequency and Ar/O_2 atmosphere. The solutions were found to be stable for more than one month which allowed accurate structural and magnetic property characterizations by XAFS, NMR and DFT calculations.



[1] Dalodière E., Virot M., Moisy P., Nikitenko S. I. **Effect of ultrasonic frequency on H2O2 sonochemical formation rate in aqueous nitric acid solutions in the presence of oxygen**, Ultrasonics Sonochemistry, 29 (2016) 198-202.
[2] Virot M., Venault L., Moisy P., Nikitenko S. I. **Sonochemical redox reactions of Pu(III) and Pu(IV) in aqueous solutions**, Dalton Transactions, 44 (2015) 2567-2572.
[3] Dalodière E., Virot M., Dumas T., Guillaumont D., Illy M.-C., Berthon C., Guerin L., Rossberg A., Venault L., Moisy P., Nikitenko S. I. **Structural and magnetic susceptibility characterization of Pu(V) aqua ion using sonochemistry as a facile synthesis method**, Inorganic Chemistry Frontiers, 5 (2018) 100-111.

SONOCATALYTIC OXIDATION OF ORGANIC COMPOUNDS

T. Chave, L. Parizot, N. M. Navarro, S. I. Nikitenko
M.E Galvez and P. Da Costa (UPMC)
P. Pochon (CEA/DRCP), N. Perkas and A. Gedanken (Bar-Ilan University, Israel)

Water remediation and treatment of industrial wastewaters containing organic compounds such as carboxylic acids, dyes or complexing agents are today's topics and worldwide concerns. Several techniques appear promising for the treatment of such kind of aqueous effluents like advanced oxidation process (AOP) or wet air oxidation for more concentrated aqueous effluents. Sonochemistry is a promising approach that can be considered for water treatment since OH• radicals can be generated during water sonolysis. However, despite the extreme local conditions observed during acoustic cavitation phenomenon, and the generation of oxidizing and non-selective species, using ultrasonic irradiation alone is efficient only at low concentration in organic pollutants.

Former studies carried out within our laboratory were focused on the degradation of oxalic acid using platinum based catalyst at 20 kHz and 360 kHz ultrasonic frequency. Experiments were conducted at 40°C within tightly closed glass reactor allowing the gas atmosphere to be controlled and oxalic acid (0.05M) degradation rate comparison between argon, Ar/O_2 mixture (20 vol% O_2) and pure O_2 conditions was achieved in presence of 2 $g.L^{-1}$ of 3 wt% Pt/TiO_2 catalyst. Obtained results show that the coupling of ultrasound with Pt/TiO_2 catalyst and oxygen accelerates drastically the oxidation of oxalic acid in aqueous solutions compared to silent conditions. The present study clearly points out that the catalytic activity enhancement of Pt/TiO_2 in presence of Ar/O_2 is principally due to two phenomena: (i) better dispersion of the catalyst under ultrasound compared to mechanical stirring even under high frequency ultrasound and (ii) in situ formation of chemically reactive species such as OH• radicals and hydrogen peroxide. [1]

Even if using ultrasonic irradiation with Pt based catalyst gives interesting result, and clearly points out a synergetic effect, the use of scare and expensive materials like platinum should be avoided. This is within this framework a new approach was developed based on the employment of noble free catalyst such as Co_3O_4/TiO_2 for the degradation of EDTA. [2] The EDTA degradation assays were carried out under high ultrasonic frequency at 345 kHz under Ar/O_2 (20%) gas atmosphere at various temperatures (from 20 to 50°C). In all experiments 200 mL of 5 mM EDTA solution were ultrasonically irradiated in presence of 1 g/L of 1 to 6 wt% Co_3O_4/TiO_2 catalysts. The results clearly indicate that the Co_3O_4/TiO_2 catalyst is very stable under these conditions and shows a higher EDTA degradation rate compared to Pt/TiO_2 catalyst. The reaction mechanism is depicted in Fig. 1 and implies the oxidation of EDTA with Co^{3+} catalyst site and reoxidation of Co^{2+} with in situ formed radicals. Finally, more 1 mmol of EDTA can be totally defunctionnalized within 8 hours of ultrasonic treatment with a mineralization percentage close to 20% at 40°C with Co_3O_4/TiO_2 catalyst whereas no significant EDTA degradation is observed at the same conditions in the presence of H_2O_2 without ultrasound.

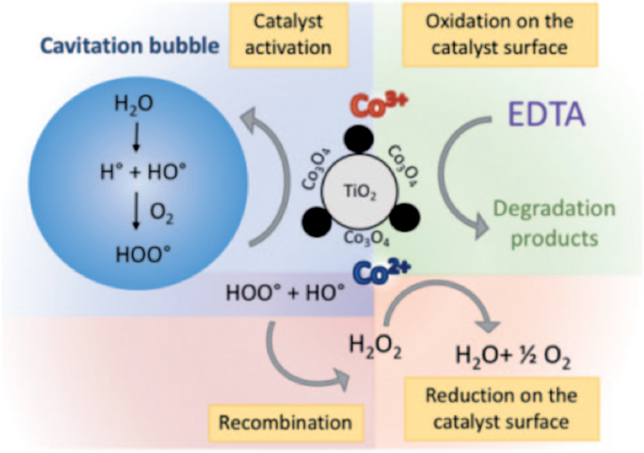


Fig. 1: Mechanism of EDTA sonocatalytic degradation on Co_3O_4/TiO_2 catalyst.

[1] Chave T., Navarro N. M., Pochon P., Perkas N., Gedanken A., Nikitenko S. I. **Sonocatalytic degradation of oxalic acid in the presence of oxygen and Pt/TiO_2**, Catalysis Today, 29 (2015) 512-516.
[2] Parizot L., Chave T., Galvez M-E., Dutilleul H., Da Costa P., Nikitenko S. I. - **Sonocatalytic oxidation of EDTA in aqueous solutions over noble metal-free Co_3O_4/TiO_2 catalyst** - Applied Catalysis B: Environmental (2018) in press.

SOLUBILIZATION OF POLAR ANTI-OXYDANT IN A VEGETABLE OIL

O. Fadel, D. Gomes-Rodriguez, A. Jonchere, P. Bauduin, L. Girard, O. Diat
and OLEOS/Hallstar partner

The extraction of active principles contained in plant substrates and their concentrations in natural oils are the basis of the technological concept developed by OLEOS, offering a new generation of cosmetic active ingredients. These ingredients include for example antioxidants and are relatively fragile compounds outside their native environment. However, their formulation in Oléoactifs® results in a remarkable stability of these active principles for several months at room temperature. The principle is based on the theory of «polar paradox of antioxidants» There is a large interest to add in a vegetable oil polar antioxidants that can organize and act in synergy with the non-polar antioxidants. This concept also enhances biological synergism in vivo in particular for the skin, between the properties of fatty acids and micronutrients oil and those of different bioactive extracts. But to date, this technology is limited by two major obstacles: 1 / the concentration of polar compounds using lipo-extractable oil is limited. 2 / the supra-molecular organizations of the various extracted compounds within the oil are not known and therefore the results of the oil- extraction remain empirical and difficult to be controlled at the industrial level. However, the oleo-extraction or the conception of structured vegetable oils is today a promising industrial challenge for green eco-ingredients, with no chemical or synthetic process and more bio-available and easily formulated than hydro-alcoholic based extracts. The expertise of the ICSM and those of OLEOS on lipids and oil-extraction is really complementary to overcome these issues. Through the Labcom VECT'OLEO we had developed ternary systems [vegetable oil + natural complexant (PG3DS) + bioactive compound] offering increased performance in terms of concentration and stability through better control of the mesoscopic organization of oily systems[1,2].

Beyond the innovative products and processes that VECT'OLEO had directly provided to OLEOS for its competitive development, the joint laboratory had contributed to the necessary understanding to optimize routes, methods of extraction by nonpolar oily solvents and methods of analysis as well.

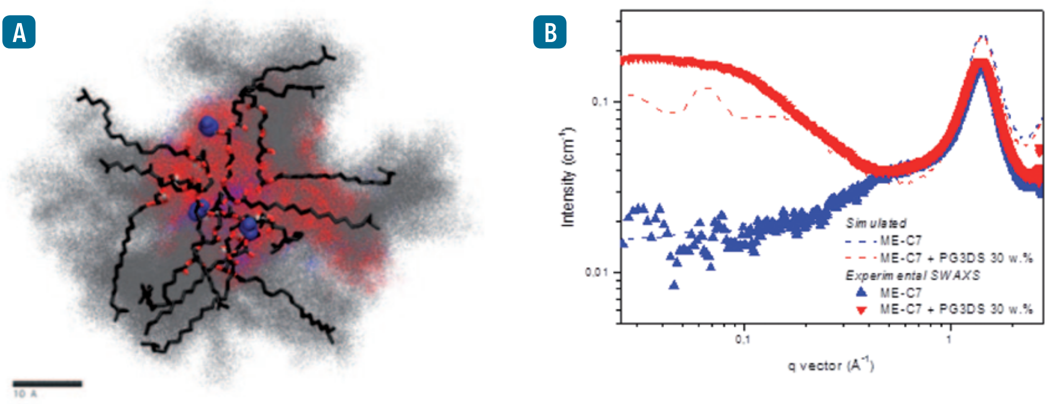


fig. **A** *Snapshot of an observed aggregate of PG3DS in methylheptanoate (ME-C7) with an aggregation number of 8 (trajectories superposition of carbon atoms (light grey), oxygen atoms from PG3DS (red) and oxygen of water (in blue), obtained by molecular dynamics simulations.* **B** *Superposition of SWAXS intensities (data points) and simulated structure factors S(q) from MD simulations (continuous curves) – extracted from ref. 2.*

---

[1] Fadel O., Girard L., Gomes Rodrigues D., Bauduin P., Le Goff X., Rossignol-Castera A., L'Hermitte A., Diat O. - **Micellisation in vegetable oils: A structural characterisation** - Colloids and Surfaces B: Biointerfaces (2017) 154, 279–286

[2] Gomes Rodrigues D., Fadel O., Girard L., Bauduin P., Le Goff X., Rossignol-Castera A., L'Hermitte A., Diat O. - **Self-assembly of a bio-based extractant in methyl esters: combination of small angle X-ray scattering experiments and molecular dynamics simulations** - Green Chemistry (2017) 19, 4680-4689

LIFE-CYCLE OPTIMIZATION OF MATERIALS FOR ENERGY

OPTIMISATION DU CYCLE DE VIE DES MATÉRIAUX POUR L'ÉNERGIE

LIFE-CYCLE OPTIMIZATION OF MATERIALS FOR ENERGY

Via the understanding of the chemical and physico-chemical mechanisms linked to the evolution of liquid-solid and solid-solid interfaces in materials for energy production (nuclear and alternative).

OPTIMISATION DU CYCLE DE VIE DES MATERIAUX POUR L'ENERGIE

Via la compréhension des mécanismes chimiques et physico-chimiques en lien avec l'évolution des interfaces liquide-solide et solide-solide des matériaux pour la production d'énergie (nucléaire et alternative).

SYNTHETIC MATERIALS FOR THERMODYNAMICS OF U AND Th-BEARING PHASES

Szenknect Stéphanie, Mesbah Adel, Clavier Nicolas, Dacheux Nicolas
Guo Xiaofeng, Shelyug Anna, Navrotsky Alexandra (UC. Davis)

Each step of the nuclear fuel cycle involves chemical processes governed by thermodynamics. The "front end" of the nuclear fuel cycle includes mining of uranium or thorium ores, their processing and purification, and finally the fuel fabrication.

The "back end" corresponds to the direct disposal or reprocessing of "spent fuel" and to the conditioning/disposal of nuclear wastes in an appropriate repository. Understanding the behavior of actinides in these processes relies on thermodynamic calculations, which requires well constrained thermodynamic data. However, thermodynamic data are lacking for numerous U or Th-bearing phases. In order to determine consistent sets of thermodynamic data, ICSM in collaboration with UC Davis developed a methodology based on the preparation of single phase compounds then on the association of solubility measurements with oxide melt solution calorimetry to ac thermodynamic data. This methodology was applied with success to coffinite[1,2,3], $USiO_4$, uranothorite solid-solutions *(Fig. 1)*[4], $Th_{1-x}U_xSiO_4$, and more recently to rhabdophanes[5,6], $LnPO_4 \cdot nH_2O$ and Thorium Phosphate Hydrogenphosphate Hydrate[7], $Th_2(PO_4)_2(HPO_4) \cdot H_2O$.

To derive a consistent set of thermodynamic data, the Gibbs free energy at 298 K from solubility experiments was combined with the enthalpy of formation measured by oxide melt solution calorimetry to obtain the entropy of formation at 298 K without relying on the temperature dependence of solubility data. However, some contributions to the entropy can not be determined by calorimetric measurements solely. These contributions could be related to structural disorder (especially linked to the presence of structural water molecules), site-mixing, vacancies, as well as disorder in the orientation of hydrogen bonds associated with interstitial H_2O. The calorimetric data will be also combined with solubility data to evaluate the thermodynamic stability of the phases of interest, especially for fine-grained, poorly crystalline or hydrated phases, which are widespread in nuclear hydrometallurgical processes and long-term behavior of nuclear waste matrices.

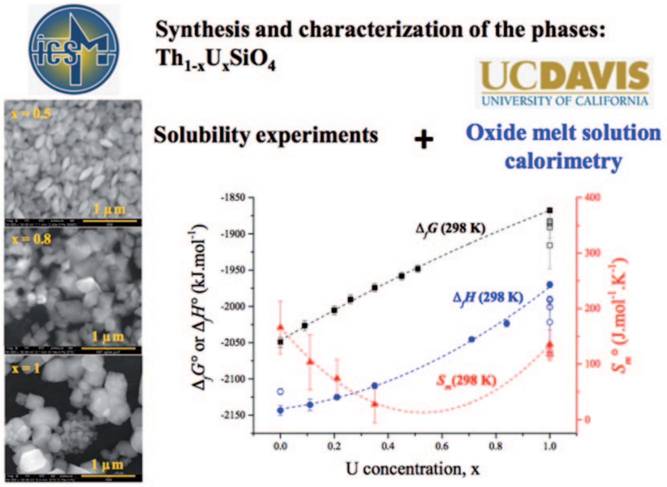


Fig. 1: Determination of thermodynamic properties of uranothorite solid-solutions combining wet chemistry route of synthesis, solubility experiments and calorimetry.

---

[1] S. Szenknect, A. Mesbah, T. Cordara, N. Clavier, H.-P. Brau, X. Le Goff, C. Poinssot, R.C. Ewing, N. Dacheux. – **First experimental determination of the solubility constant of coffinite** – Geochimica Cosmochimica Acta (2016) 181, 36-53.

[2] X. Guo, S. Szenknect, A. Mesbah, S. Labs, N. Clavier, C. Poinssot, S.V. Ushakov, H. Curtius, D. Bosbach, R.C. Ewing, P.C. Burns, N. Dacheux, A. Navrotsky. – **Thermodynamics of formation of coffinite, $USiO_4$** – Proceedings of the National Academy of Sciences of the USA (2015) 112, 6551-6555.

[3] Szenknect S., Dacheux N., Ewing R. C., Navrotsky A. – **Reply to comment by Konings and Plyasunov on "First experimental determination of the solubility constant of coffinite"** – Geochimica et Cosmochimica Acta (2017) 212 (Supplement C), 374-376.

[4] X. Guo, S. Szenknect, A. Mesbah, N. Clavier, C. Poinssot, D. Wu, H. Xu, N. Dacheux, R. Ewing, A. Navrotsky – **Energetics of Uranothorite ($Th_{1-x}U_xSiO_4$) Solid Solution** – Chemistry of Materials (2016) 28, 7117-7124.

[5] Gausse, C., Szenknect, S., Qin, D.W., Mesbah, A., Clavier, N., Neumeier, S., et al. – **Determination of the solubility of rhabdophanes $LnPO_4 \cdot 0.667\ H_2O$ (Ln = La to Dy)** – European Journal of Inorganic Chemistry (2016) 28, 4615-4630.

[6] Shelyug A., Mesbah A., Szenknect S., Clavier N., Dacheux N., Navrotsky A. – **Thermodynamics and stability of rhabdophanes, hydrated rare earth phosphates $REPO_4 \cdot n\ H_2O$** – submitted to Frontiers in Chemistry (2018).

[7] Qin D., Gausse C., Szenknect S., Mesbah A., Clavier N., Dacheux N. – **Solubility product of the thorium phosphate hydrogen-phosphate hydrate ($Th_2(PO_4)_2(HPO_4) \cdot H_2O$, TPHPH)** – The Journal of Chemical Thermodynamics (2017) 114, 151-164.

IMMOBILIZATION OF URANIUM IN CONTAMINATED GROUNDWATERS THROUGH META-TORBERNITE PRECIPITATION

Szenknect Stéphanie, Mesbah Adel, Clavier Nicolas, Lautru Joseph, Podor Renaud, Dacheux Nicolas
Descostes Michael (Orano-BG Mines)

Uranium ore mining, processing and manufacturing can contribute to groundwater contamination. Uranium is transported in groundwater mainly as dissolved U(VI) species, which can threaten ecosystems in the vicinity of contaminated sites. High costs associated with pump-and-treat remediation strategies and toughening of regulatory requirements regarding sewage discharge have prompted research into more effective methods. In this frame, ICSM and Orano have developed a new method to immobilize U(VI) in a non labile uranyl phosphate phase, meta-torbernite $(H_3O)_{0.4}Cu_{0.8}(UO_2)_2(PO_4)_2 \cdot 7.6H_2O$. The low solubility and the high stability of this phase under a wide range of environmental conditions was demonstrated through the determination of its thermodynamic properties and geochemical simulations[1]. The ubiquity of meta-torbernite in oxidized secondary U ore deposits, contaminated sediments or mine tailings strengthen this conclusion.

On the other hand, hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$ has been shown to be effective in sequestering heavy metals, metalloids and radionuclides. The removal mechanism are postulated to occur by coprecipitation or ion exchange. In the new method developed, uranyl is immobilized by homogeneous precipitation with dissolved phosphate and copper released from a synthetic copper-substituted HAP forming the very low soluble meta-torbernite *(Fig. 1)*.

The efficiency of the patented method[2] was demonstrated in batch experiments. The synthetic copper-substituted HAP was contacted with mine waters of various pH and compositions. U elemental concentration in solution was found to decrease strongly after 2 hours of contact and U was precipitated as square shaped grains of meta-torbernite *(Fig. 1)*. The results showed the high reactivity of the prepared Cu-substituted HAP, which was attributed to its poor crystallinity and high specific surface area. This material is promising to be used in passive treatment devices such as permeable reactive barriers for water remediation.

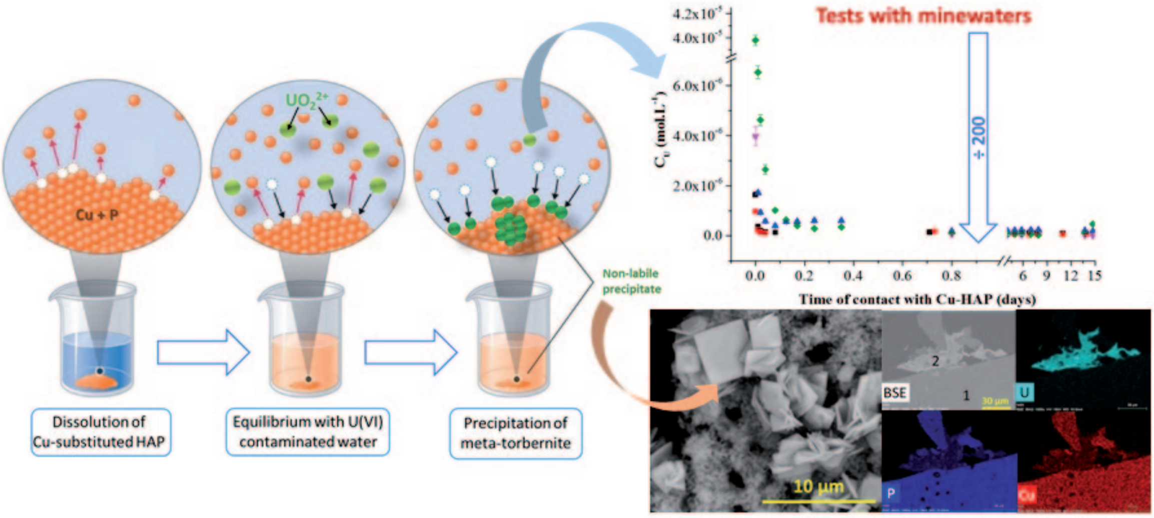


Fig. 1: Principle of the method developed for the immobilization of U(VI) in contaminated water. Evolution of uranium concentration in mine waters contacted with Cu-HAP. SEM micrographs and elemental mapping of the precipitate.

---

[1] Cretaz F., Szenknect S., Clavier N., Vitorge P., Mesbah A., Descostes M., Poinssot C., Dacheux N. – **Solubility properties of synthetic and natural meta-torbernite** – Journal of Nuclear Materials (2013) 442, 195-207.

[2] Szenknect S., Dacheux N., Mesbah A., Descostes M., Ziouane Y, Maihatchi-Ahamed A. – **Procédé de séparation de l'uranium utilisant une hydroxyapatite dopée au cuivre, procédé de préparation d'une telle hydroxyapatite et hydroxyapatite ainsi préparée** – Brevet Français n°16 58525 (2016).

IN SITU HT-ESEM STUDY OF FLUORITE-TYPE MO_2 (M = Ce, Th, U) MICROSPHERES SINTERING

Clavier Nicolas, Trillaud Victor, Nkou Bouala Galy Ingrid, Dacheux Nicolas, Podor Renaud
Léchelle Jacques (CEA/DEN/DEC/SESC/LM2C)

As a key-step for the elaboration of nuclear fuels, the sintering of UO_2 has been studied for years. If grain growth processes were investigated thanks to experimental works and calculations, the elaboration of necks during the first step of sintering was generally assessed only through numerical models, frequently based on simple configurations (two spherical single crystals in contact). In order to complement such numerical approaches, the elaboration of necks during the sintering of MO_2 microspheres (with M = Ce, Th and U), herein used as model compounds, was experimentally observed by High Temperature Environmental Scanning Electron Microscopy (HT-ESEM).

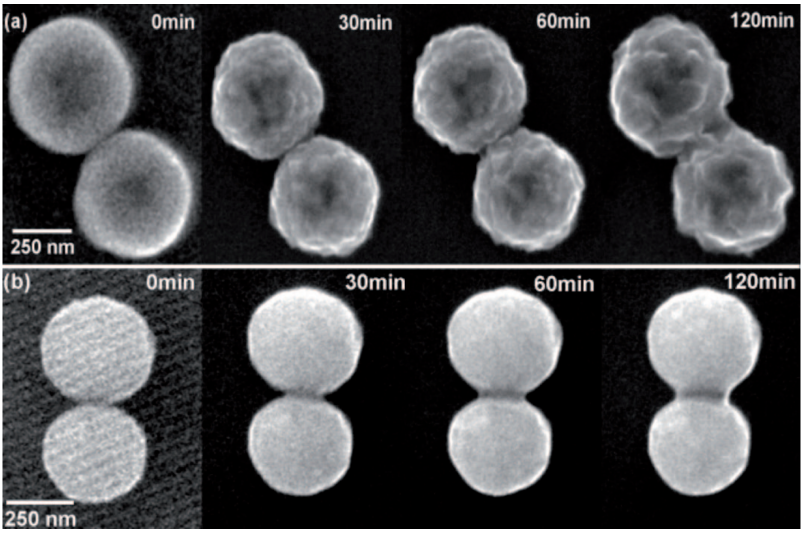


Fig. 1. In situ HT-ESEM observation of CeO_2 microspheres sintering at 1050°C: (a) poly- and (b) single-crystal particles [2].

In a first step, the study of the morphological modifications occurring within a single grain during heat treatment at high temperature (typically in the 1000-1300°C range) led to determine the variation of the number of crystallites included in the polycristalline microspheres and the attached mechanisms[1]. Mechanical rearrangement of the crystallites was generally pointed out for short heating times and associated to low values of activation energies, while solid-state diffusion was found to occur for longer durations. In parallel, the conditions required to reach a spherical single crystal grain was evaluated for all the samples.

The kinetics associated to the evolution of neck, contact angles and centers displacement during the sintering of two microspheres were then evaluated. In this case, the evolution of polycrystalline assemblies and of single crystals was studied in parallel and led to determine the driving diffusion mechanism. The comparison of the results with that supplied by the SALAMMBO model then allowed us to estimate the bias associated to the polycristallinity of the powders or to the existence of mesoporosity within the microspheres[2,3]. Also, in the case of UO_2, preliminary data were acquired regarding to the influence of pO_2 over the kinetics of neck formation during the heat treatment.

More recently, this approach was complemented by in situ HT-TEM observations undertaken on ThO_2 and UO_2 samples. It led to observe the reorientation of elementary crystallites at the atomic scale as well as the motion of atomic planes from the grains to the neck.

---

[1] Nkou Bouala G.I., Clavier N., Léchelle J., Mesbah A., Dacheux N., Podor R. - **In situ HT-ESEM study of CeO_2 nano-ripening : toward a control of nanostructure** - Ceramics International (2015) 41, 14703-14711.

[2] Nkou Bouala G.I., Clavier N., Martin S., Léchelle J., Dacheux N., Favrichon J., Brau H.P., Podor R. - **From in situ HT-ESEM observations to simulation : how does polycristallinity affects the sintering of CeO_2 microspheres** – Journal of Physical Chemistry C (2016) 120, 386-395.

[3] Nkou Bouala G.I., Clavier N., Léchelle J., Monnier J., Ricolleau Ch., Dacheux N., Podor R. - **High-temperature electron microscopy study of ThO_2 microspheres sintering** – Journal of the European Ceramic Society (2017) 27, 727-738.

DIRECT WET-CHEMISTRY ROUTES TOWARDS LANTHANIDE AND ACTINIDE OXIDES

Clavier Nicolas, Manaud Jérémie, Trillaud Victor, Maynadié Jérôme, Mesbah Adel, Podor Renaud, Dacheux Nicolas

Powders used in current nuclear fuel fabrication are mainly issued from dry chemistry routes. In order to increase the control of several physico-chemical properties of the starting compounds, such as cation distribution, grain size, morphology, … novel wet chemistry methods have been developed. They are generally based on the precipitation of low-temperature precursors which are further converted into MO_2 fluorite-type dioxides through heat treatment at high temperature under appropriate atmosphere. Among them, oxalic precipitation[1] can be considered as a reference method owing to the large interest paid to this family of compounds by the community for almost one century. However, the samples obtained generally present a square-shaped morphology *(Fig. 1)* which is hardly suitable for densification. Also, thermal conversion towards the oxide form has been frequently associated to the presence of residual carbon which can further impact the sintering process[1].

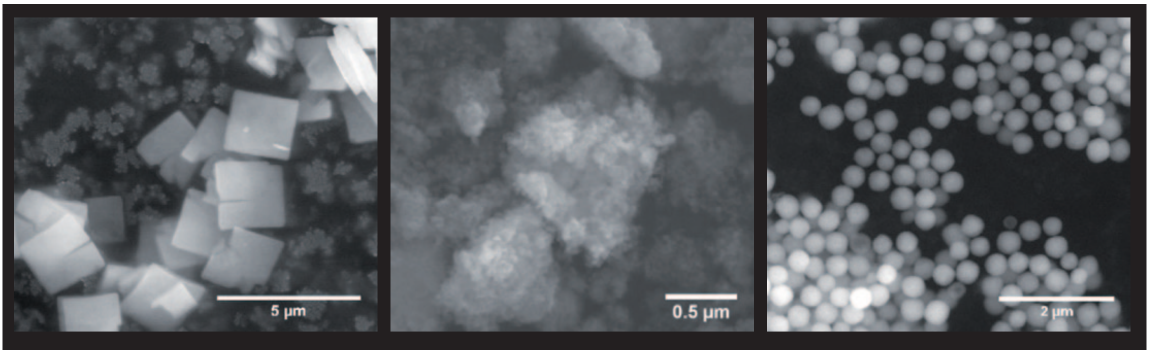


Fig. 1: SEM micrographs of UO_2 powders prepared from oxalic precipitation[1], hydroxide route[2], or precipitated from a mixture of U(IV) and aspartic acid[4].

In order to avoid these drawbacks, original wet chemistry routes were developed to obtain directly actinide (IV) dioxide precipitates. Highly reactive hydrated (U,Ce)$O_2.2H_2O$ powders were obtained from the precipitation of acidic solutions containing cations with ammonia, the resulting powder being later dried under stirring and vacuum[2]. Such method ensured the formation of homogeneous mixed nanoparticles (about 3 nm) which can be directly used for the densification of pellets. Wet chemistry routes were also used to get enhanced control over the final morphology of the powders. In this case, the use of aspartic acid as a precipitating agent and of hydrothermal conditions led to $AnO_2.nH_2O$ sample[3] . For uranium-based compounds, the optimization of operating conditions (in terms of temperature, time, M/L ratio) allowed to prepare monodisperse spherical particles. Also, addition of a mechanical stirring led to control accurately the particles size in the 400-2500 nm range[4]. Finally, studies are currently under progress to investigate the in situ conversion of actinide oxalates. In this framework, the use of mild hydrothermal conditions already yield to the preparation of anhydrous and carbone-free UO_2 powders directly from solution.

---

[1] Martinez J., Clavier N., Ducasse T., Mesbah A., Audubert F., Corso B., Vigier N., Dacheux N. - **From uranium(IV) oxalate to sintered UO_2: Consequences of the powders' thermal history on the microstructure** – Journal of the European Ceramic Society (2015) 35, 4535-4546.

[2] Martinez J., Clavier N., Mesbah A., Audubert F., Le Goff X.F., Vigier N., Dacheux N. - **An Original Precipitation Route toward the Preparation and the Sintering of Highly Reactive Uranium Cerium Dioxide Powders** - Journal of Nuclear Materials (2015) 462, 173-181.

[3] Clavier N., Maynadié J., Mesbah A., Hidalgo J., Lauwerier R., Nkou Bouala G.I., Parrès-Maynadié S., Meyer D., Dacheux N., Podor R. - **Thorium Aspartate Tetrahydrate Precursor to ThO_2 : Comparison of Hydrothermal and Thermal Conversions** – Journal of Nuclear Materials (2016) 487, 331-342.

[4] Trillaud V., Maynadié J., Manaud J., Hidalgo J., Meyer D., Podor R., Dacheux N., Clavier N. - **Synthesis of size-controlled UO_2 microspheres from the hydrothermal conversion of U(IV) aspartate** – CrystEngComm (2018) submitted.

PHOSPHATES MATRICES FOR THE SPECIFIC CONDITIONING OF NUCLEAR WASTEFORMS

Qin Danwen, Mohammed Ruwaid Rafiuddin, Mesbah Adel, Szenknect Stéphanie, Clavier Nicolas, Dacheux Nicolas

Phosphates based ceramics ($REEPO_4$) are often considered as promising "crystalline" matrices for the specific conditioning of tetravalent and trivalent actinides coming from the back-end of the nuclear fuel cycle. Moreover, these materials are also proposed for the disposal of excess plutonium coming from dismantled nuclear weapons. Such interests stem not only from their easy way of fabrication, but also owing to their interesting sintering capability, high chemical durability and good resistance to radiation damage. Among them, monazite (monoclinic $P2_1/n$ structure type) is encountered for light rare-earth elements (LREE) with larger ionic radii (Ln = La – Gd). On the contrary, xenotime (zircon-type structure, tetragonal system, $I4_1/amd$) occurs for heavier elements (Ln = Tb – Lu) and for yttrium. The incorporation of actinides within the structure goes through different substitution mechanisms. For trivalent elements, direct substitution is performed forming $Ln_{1-x}An_xPO_4$ compounds. For tetravalent actinides, owing to the chemical flexibility of such phases, various mechanisms of substitution are followed.

The first consists in coupled substitution: $2\ REE^{3+} \Leftrightarrow Ca^{2+} + An^{4+}$ whereas the second is performed through coupled mixed substitution following $REE^{3+} + PO_4^{3-} \Leftrightarrow (Th,U)^{4+} + SiO_4^{4-}$. In general, such materials are synthesized by solid-state chemistry routes which may lead to some heterogeneous materials. Thus, such routes require the use of grinding steps, which are usually considered as drawback for radioactive materials. Therefore, wet chemistry routes appeared as very interesting processes to improve the cationic homogeneity within the sample and to increase the powder reactivity by the means of higher specific surface areas. In this context, the preparation of the target materials was performed by precipitation or by hydrothermal methods. The use of low temperature precursors such as rhabdophane[1,2] or churchite was particularly considered.

As a recent progress, the dehydration process of the rhabdophane structure was toughly characterized leading to the identification of three successively forms as viewed in Figure 1 for samarium.

Moreover, the incorporation of thorium in $Ln_{1-2x}Ca_xTh_xPO_4.nH_2O$ (Ln = Pr, Nd)[3] was successfully performed. The optimal conditions to prepare pure samples were fixed on the basis of a multiparametric study. Therefore, the thermal conversion into the final monazite-cheralite solid solution was obtained. Regarding to the coupled mixed substitution, solid solutions with general formula $Th_{1-x}Er_x(SiO_4)_{1-x}(PO_4)_x$[4] were prepared. Their thermal stability is actually under investigation in the frame of the X-MAS project (ANR funding).

In the near future, sintering capability and chemical durability of the prepared powders will be examined in order to confirm the suitability of such materials for the specific conditioning of some long-life radionuclides such as minor actinides or excess plutonium coming from dismantled nuclear weapons.

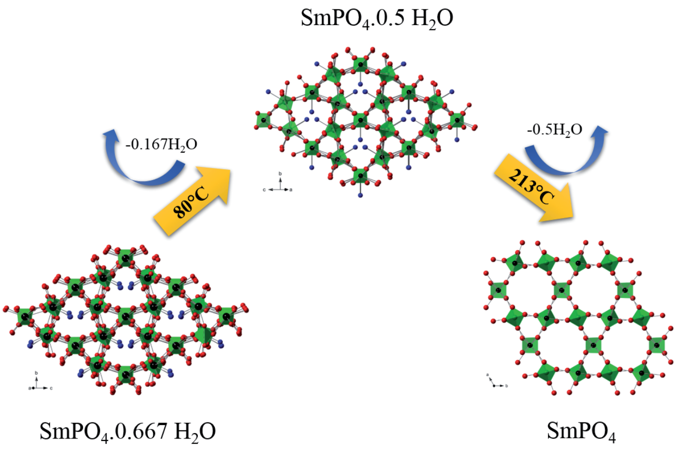


Figure 1. Dehydration scheme of the $SmPO_4.0.667\ H_2O$

[1] Mesbah A., Clavier N., Elkaim E., Gausse C., Ben Kacem I., Szenknect S., Dacheux N. - **Monoclinic Form of the Rhabdophane Compounds: $REEPO_4 \cdot 0.667\ H_2O$** - Crystal Growth & Design (2014) 14, 5090-5098

[2] Mesbah A., Clavier N., Elkaim E., Szenknect S., Dacheux N. - **In pursuit of the rhabdophane crystal structure: from the hydrated monoclinic $LnPO_4.0.667\ H_2O$ to the hexagonal $LnPO_4$ (Ln = Nd, Sm, Gd, Eu and Dy)** - Journal of Solid State Chemistry (2017) 249, 221-227

[3] Qin D., Mesbah A., Gausse C., Szenknect S., Dacheux N., Clavier N. - **Incorporation of thorium in the rhabdophane structure: Synthesis and characterization of $Pr_{1-2x}Ca_xTh_xPO_4 \cdot nH_2O$ solid solutions** - Journal of Nuclear Materials (2017) 492, 88-96

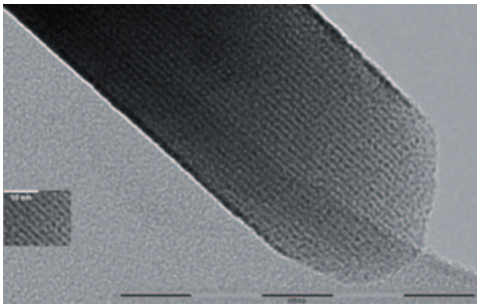
DEVELOPMENT OF SYNTHESIS STRATEGIES FOR ANO_2 BASED NANO-HYBRID MATERIALS

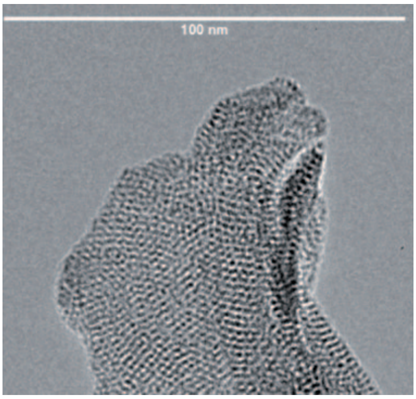
E. Ré, J. Monnier, J. Maynadié, D. Meyer

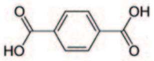
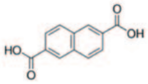
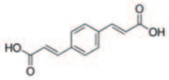
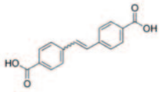
This project deals with the conception of new nano-structured hybrid materials based on nanocrystals of actinide oxides, which can display unusual properties with respect to the single nano-crystalline counterpart. In this way, we are focused our attention on the development of two bottom-up synthesis strategies.

The first one consists in a one-pot strategy derived from the expertise acquired by the team on nanocrystals of actinide oxides synthesis[1] Using a ternary molecular system (dicarboxylic acid, oleylamine, dibenzyl ether), it is possible to obtained nano-sheets displaying lamellar structuration in which UOx nano-lamellae is around 1 nm *(figure 1)*. Moreover, in the nano-sheets, the interlamellar distance could be adjusted in accordance with the length of the employed dicarboxylic acid.

The second strategy, currently explored, is based on the self-assembly of functionalised nanoparticles. This strategy starts with the well-known synthesis of metal-oxide nanocrystals (UO_2, ThO_2 or MO_x) stabilized with oleic acid. Then, the surface of the pre-synthesized nanoparticles is modified using capping agents having reactive pendant functionality (alkyne, azide, ionic moiety). To obtain the final material, the crosslinking of modified nanocrystals could be operated through a click-chemistry step catalysed by Cu(I) or electrostatic interactions. The final goal consists in the formation and the characterization of heterometallic nano-hybrid superlattices.





Dicarboxylic acid				
DFT d_{U-U} (nm)	0.91	1.37	1.62	1.81
TEM (nm)	1.43	1.65	1.83	1.90
SAXS (nm)	/	1.60	2.00	2.67

---

[1] D Hudry et al. «**Thorium/uranium mixed oxides nanocrystals: Synthesis, structural characterization and magnetic properties**» Nano Research, 2014, 7(1), 119-131. D Hudry et al. «**Ultra-Small Plutonium Oxide Nanocrystals: An innovative Material in Plutonium Science**» Chem. Eur. J., 2014, 20, 10431.

SYNTHESIS OF URANIUM OXIDE COMPOUNDS BY SOL-GEL PROCESSES

Zijie Lu, Diane Rébiscoul, Jeremy Causse, Cyrielle Rey, Julien Monnier, Xavier Deschanels

In the framework of generation IV development for nuclear reactors, two different routes involving a sol-gel process are investigated to obtain actinide mixed oxides.

Conversion of actinides nitrate by Solution Combustion Synthesis

Solution combustion synthesis (SCS) involves the self-propagation of an exothermic reactions in a media composed of an organic fuels (glycine, citric acid…) and a metal nitrate dissolved in water. In a first step of the process during the thermal treatment leading to the dehydration of these precursors a gel is obtained, and finally the ignition occurs at very low temperature (~200°C) to produce a white powder composed of actinide oxide *(Figure 1)*. UO_{2+x} and surrogate oxide powders (Gd, Ce…) were successfully synthesized by this technique at temperature about 200°C lower than that of a classical denitration reaction. The process conditions (heating rate, excess of fuel…) impact the characteristics of the final product, i.e. crystallinity of the powders, amount of residual carbon, size of the crystallites, and stoichiometry of UO_{2+x}.

Study of colloidal sol-gel transition for the elaboration of UO_2/ThO_2 materials with controlled and organized mesoporosity

UO_2/ThO_2 materials having an ordered mesoporosity are elaborated either as a model materials to study the impact of the pore size on their dissolution in the context of spent nuclear fuel reprocessing and direct repository, either to elaborate homogeneous UO_2/AmO_2 nuclear fuel (Generation IV). To reach this goal, a colloidal sol-gel template method is used. Our approach consists in the determination of the impact of several experimental parameters on the sol-gel transition and the final materials *(Figure 2)*: the nanoparticles size, the sol stability, the target pore size and the pores organization1. The thermodynamics and kinetics of the nanoparticles formation as well as the interactions between the template molecules, the actinides present in the solution and the nanoparticles in the sol are also investigated (PhD. Zijie Lu).

Figure 1 : Example of actinide surrogate powders Gd_2O_3 obtained by SCS of Gadolinium nitrate/Glycine

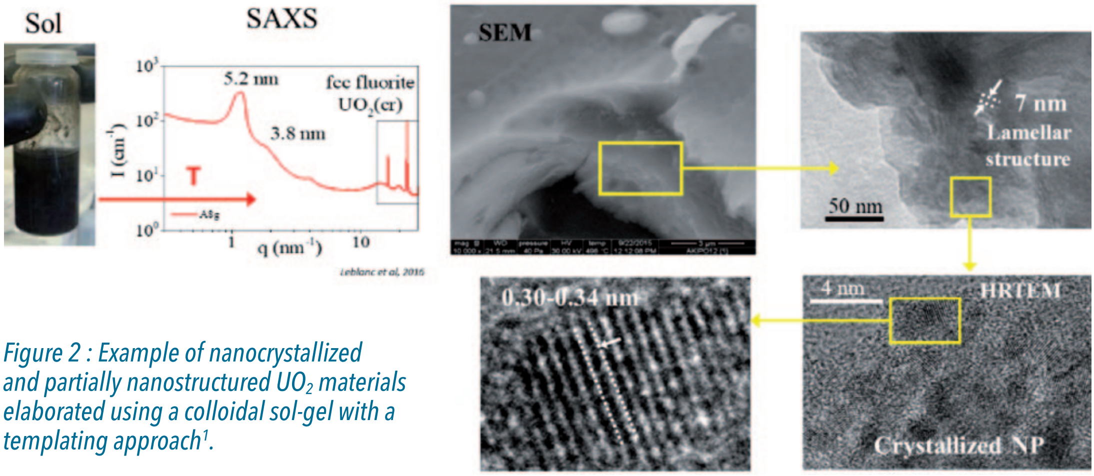


Figure 2 : Example of nanocrystallized and partially nanostructured UO_2 materials elaborated using a colloidal sol-gel with a templating approach[1].

---

[1] Leblanc, M.,Causse, J.,Lu, Z.,Rébiscoul, D. - **Stable uranium sols as precursors for the elaboration of nanostructured nc-UO_2 materials** - Colloids and Surfaces A: Physicochemical and Engineering Aspects (2017) 522, 18-27.

IMPACT OF (Th,Y)O_2 CERAMIC ELECTROLYTE'S MICROSTRUCTURE ON ITS RESISTANCE TO LIQUID SODIUM CORROSION

Clavier Nicolas, Podor Renaud, Dacheux Nicolas
Cherkaski Yanis, Brissonneau Laurent (CEA/DEN/DTN/SMTA/LMCT)

In the framework of the development of the fourth generation nuclear reactor demonstrator ASTRID (Advanced Sodium Fast Reactor for Industrial Demonstration), an electrochemical sensor, allowing accurate and specific measurement of dissolved oxygen in liquid sodium, is currently under development. One critical point of this device is the solid electrolyte, made of yttria-doped thoria. In this context, studies were undertaken to understand the properties of the solid electrolyte in terms of ionic conductivity and the resistance to sodium corrosion according to its microstructure, in order to optimize the conditions of elaboration.

The first part of this work was dedicated to the preparation of sintered $Th_{1-x}Y_xO_{2-x/2}$ ($0.01 \le x \le 0.22$) ceramics with various microstructures. In this aim, the precursors obtained after oxalic co-precipitation and the final oxides were thoroughly characterized on the structural, morphologic and chemical points of view[1]. Furthermore, the densification of the oxide samples was investigated to achieve sintering maps by correlating the average grain size and the relative density values[2]. They further led to identify the optimal sintering conditions required to address the specifications of the electrolyte ceramic. In addition, the electric properties of the ceramics were characterized by impedance spectroscopy, with a maximum of the conductivity observed between 8 and 15 mol.% of yttrium.

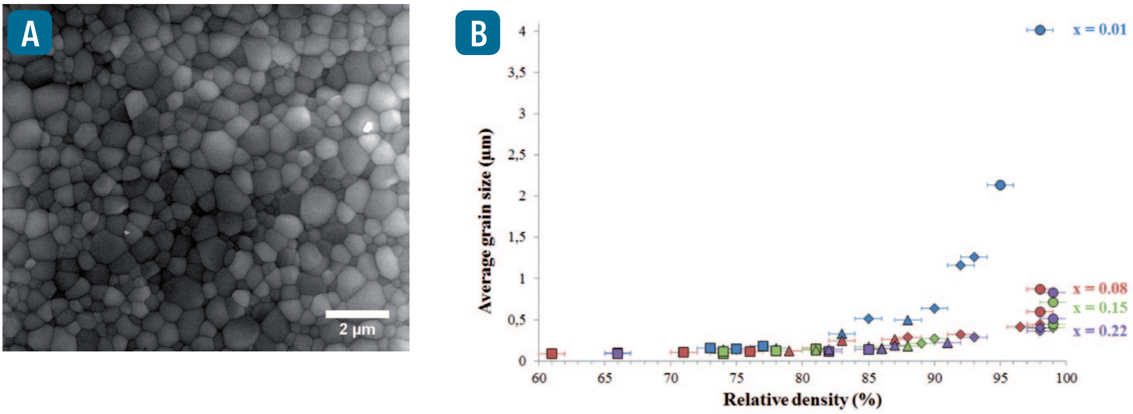


Fig. 1: **A** *SEM observation of $Th_{0.92}Y_{0.08}O_{1.96}$ pellet after sintering (1575°C – 8h)* **B** *Sintering map of $Th_{1-x}Y_xO_{2-x/2}$ solid solutions[2].*

Furthermore, the study of the compatibility of the ceramic with liquid sodium was undertaken at 500°C during several hundred hours. In these experimental conditions, no sign of corrosion was evidenced at the surface of the samples while the fracture showed two different habits (trans- and intergranular) indicating the penetration of sodium through the grain boundaries. Electric characterizations were also undertaken post-mortem and revealed a significant variation of the conductivity, especially for the grain boundary contributions. Finally, similar experiments were performed on samples incorporating impurities on purpose (Al, Zr and Si up to 1 wt.%). While their incorporation only causes a slight change of the microstructure, it led to a deleterious role on the resistance to sodium corrosion for silicon and high contents in zirconium (1 wt.%).

[1] Gabard M., Cherkaski Y., Clavier N., Brissonneau L., Steil M.C., Fouletier J., Mesbah A., Dacheux N. - **Preparation, characterization and sintering of yttrium-doped ThO_2 for oxygen sensors applications** – Journal of Alloys and Compounds (2016) 689, 374-382.

[2] Cherkaski Y., Clavier N., Brissonneau L., Podor R., Dacheux N. - **Densification behaviour and microstructure evolution of yttrium-doped ThO_2 electrolyte ceramics** – Journal of the European Ceramic Society (2017) 37, 3381-3391.

MULTI-PARAMETRIC STUDY OF THE DISSOLUTION KINETICS OF ACTINIDES OXIDES

Cordara Théo, Dalger Thomas, Claparède Laurent, Szenknect Stéphanie, Clavier Nicolas, Mesbah Adel, Dacheux Nicolas

The dissolution of spent nuclear fuels (SNF), performed in concentrated nitric acid solution, is a very complex process due to some chemical and microstructural heterogeneities in the material. As instance, the presence of Fission Products (FP) in various phases contained in SNF can affect the chemical durability of the ceramics during dissolution processes.

In this context, samples of three systems of interest representing fresh UO_2 (reference material)[1], UO_2 doped with FP dissolved in the fluorite structure (lanthanide elements) or incorporated as metallic precipitates (PGM) were prepared by oxalic or hydroxide precipitation then sintered at high temperature. For this large panel of materials, the final microstructure was representative for SNF.

The multiparametric study of the dissolution (macroscopic approach) was developed by varying independently several parameters affecting the normalized dissolution rates (R_L). Not surprisingly, the increase of nitric acid concentration or temperature led to the decrease of the chemical durability of the prepared materials. Chemical composition and heterogeneity are also first-order parameters to be considered. Indeed, the incorporation of lanthanide elements induced a significant increase of the R_L values. However, it remained lower compared to that induced by the presence of PGM, which were associated to the stronger effect. Additionally, significant modification of the preponderant mechanism of dissolution occurred for nitric acid concentration higher than 0.5 $mol.L^{-1}$. More generally, three different and successive steps were identified during the dissolution of UO_2 based ceramics ; the last step being characterized by a strong and continuous increase of R_L values *(Fig. 1)*.

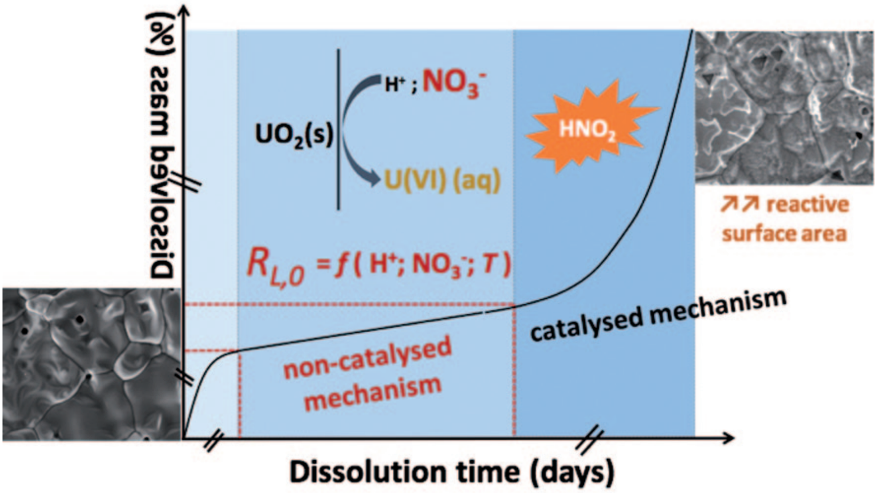


Fig. 1. Schematic representation of the three steps occurring during the evolution of the dissolved mass of UO_2 pellet, $\Delta m(t)$ (%) in nitric acid solutions[1].

A follow-up study was then performed during the dissolution of sintered pellets of $Th_{0.25}U_{0.75}O_2$ in various acidic media in order to evidence the changes occurring in the rate of the limiting step and to establish specific rate laws. The kinetics of the overall dissolution reaction appeared to be first controlled by the oxidation of U(IV) by HNO_3 at the solid/solution interface. Moreover, the increase of the R_L values evidenced after the steady state period was assigned to the simultaneous increase of the specific surface area of the material and of the HNO_2 concentration in solution, which acts as an important oxidative species regarding to tetravalent uranium[2].

[1] Cordara T., Szenknect S., Claparede L., Podor R., Mesbah A., Lavalette C., Dacheux N. - **Kinetics of dissolution of UO_2 in nitric acid solutions : A multiparametric study of the non-catalyser reaction**– Journal of Nuclear Materials (2017) 496, 251-264.

[2] Dalger T., Szenknect S., Tocino F., Claparede L., Mesbah A., Moisy P., Dacheux N. - **Kinetics of dissolution of $Th_{0.25}U_{0.75}O_2$ sintered pellets in various acidic conditions** – Journal of Nuclear Materials (2018) 510, 109-122.

OPERANDO MONITORING OF THE SOLID/LIQUID INTERFACE DURING DISSOLUTION TESTS

Cordara Théo, Dalger Thomas, Bertolotto Solène, Claparède Laurent, Szenknect Stéphanie, Le Goff Xavier, Favrichon Julien, Podor Renaud, Dacheux Nicolas

The operando monitoring of evolving solid / solution interface was developed in order to improve the overall understanding on the dissolution mechanisms involved for different systems such as UO_2, UO_2 incorporating lanthanides or PGM elements. This work was particularly focused on the precise description of the pellets microstructural evolution.

The microscopic study of the dissolution of UO_2 in HNO_3 1 mol.L^{-1} at 60°C revealed a relatively homogeneous dissolution of the surface of the pellet in agreement with the existence of preponderant dissolution mechanism controlled by the oxidation of uranium (IV) to uranium (VI). On the contrary, preferential dissolution zones located at the grain boundaries were observed for samples doped with trivalent lanthanide elements. This phenomenon was assigned to the possible accumulation of lanthanides in such zones, leading to the decrease of the chemical durability[1]. The dissolution of UO_2 + 3 mol% of PGM ceramics in 0.1 mol.L^{-1} HNO_3 at 60°C also exhibited preferential dissolution zones located near the formed metal particles. This result was connected to the existence of nitrogen species at the UO_2/PGM interphase, catalyzing the oxidative dissolution of the ceramics. In more aggressive medium (HNO_3 1 mol.L^{-1}, T = 60°C), a massive and homogeneous dissolution of the grains was observed, underlining a mechanism change for nitric acid concentrations higher than 0,5 mol.L-1. In such media, the presence of the PGM particles did not significantly affect the microstructural evolution.

The 3D reconstruction of the surface of dissolved ceramics allowed to access the normalized dissolution rate (R_L) of preferential dissolution zones (e.g. grain boundaries) and to quantify the contributions of these zones on the overall dissolution progress (*Fig. 1* for UO_2 + 3 mol% PGM). The obtained results suggested that, at the beginning of the dissolution progress, the R_L value was essentially controlled by the dissolution of the grain boundaries. This was consistent with the potential accumulation of reactive species catalyzing the dissolution reaction in the more confined space created between the grains.

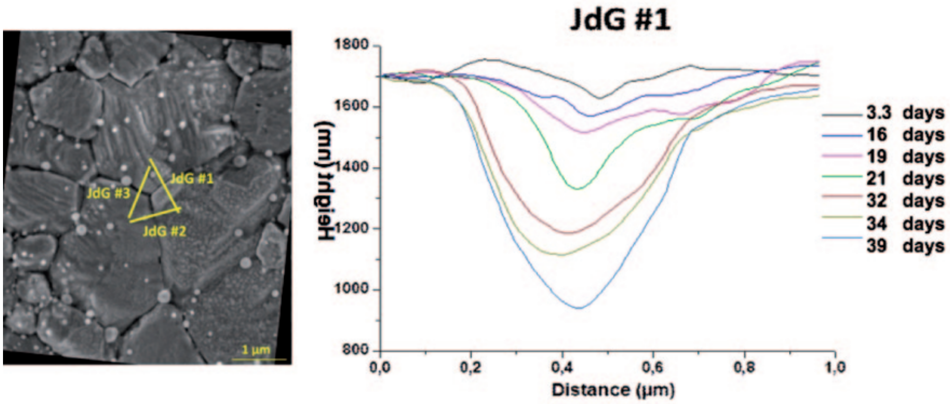


Fig. 1. Evolution of the height profiles perpendicular to a grain boundary obtained during the dissolution of sintered pellet of UO_2 + 3 mol% PGM in 0.1 mol.L^{-1} HNO_3 at 60 ° C.

---

[1] Horlait D., Claparede L., Tocino F., Clavier N., Ravaux J., Szenknect S., Podor R., Dacheux N. - **Environmental SEM monitoring of $Ce_{1-x}Ln_xO_{2-x/2}$ mixed-oxide microstructural evolution during dissolution** – Journal of Materials Chemistry A (2014) 2, 15, 5193-5203.

SONOCHEMISTRY OF ACTINIDES IN SOLID/LIQUID HETEROGENEOUS SYSTEMS

M. Virot, E. Dalodière, T. Dumas (CEA/DEN/DMRC), P. Moisy (CEA/DEN), S. I. Nikitenko

In heterogeneous systems, acoustic cavitation goes with strong physical effects such as erosion of surfaces, grain fracture, depassivation, increase of mass transfer and decrease of diffusion layers. The chemical transformation of sonicated media coupled to specific activation of surfaces could be promising for current and future nuclear fuel reprocessing. Within this frame, the behavior of actinide oxides is studied in collaboration with DMRC department (Atalante facility, Marcoule). [1]

PuO_2, which is an important material for current and future nuclear fuel, is very refractive towards dissolution and is reprocessed in concentrated and boiling nitric acid with HF, or in the presence of strong oxidizing agents (e.g., Ce(IV) or Ag(II)). These routes nevertheless suffer from some drawbacks such as low dissolution rates, equipment corrosion, compatibility with nuclear industry, etc. Recent studies showed that the reductive dissolution of PuO_2 can be considered under ultrasound irradiation with milder conditions. Quantitative dissolutions of PuO_2 was observed at 20 kHz (Ar, 33°C, 0.35-0.70 W mL-1) in 0.5-1.0 M HNO3 / 0.1 M $[N_2H_5NO_3]$ / 1-3 M HCOOH in the presence of Ti particles as a generating source of reductive species. [2] Cavitation enables the depassivation of Ti surface usually strongly passivated in nitric solutions and leads to the generation of intermediate Ti(III) reductive species. Dissolution rates and yields can be improved with injection of dilute NH4F or HF aliquots during sonication to favor Ti chemical depassivation *(Fig 1.a.)*.

Fundamental understanding of Pu colloid formation plays nowadays a critical role in An chemistry due to environmental and industrial issues. We demonstrated that the extended sonication of PuO_2 under reducing atmosphere leads, after centrifugation to remove PuO_2 particles that did not react, to the formation of very stable intrinsic Pu colloidal suspensions. [3] The Vis-NIR absorption spectra measured on sonolytic and hydrolytic Pu colloids indicate some structural similarities and significant differences, including a strong Mie scattering for the sonolytic colloid attributed to the presence of larger colloids *(Fig 1.b.)*. Thorough study using XAFS, NEXAFS and HR-TEM allowed us to describe these colloids as stable suspensions of core-shell nanoparticles composed of crystalline PuO_2 core covered by hydrolyzed Pu(IV) moieties responsible for their high stability. [3]

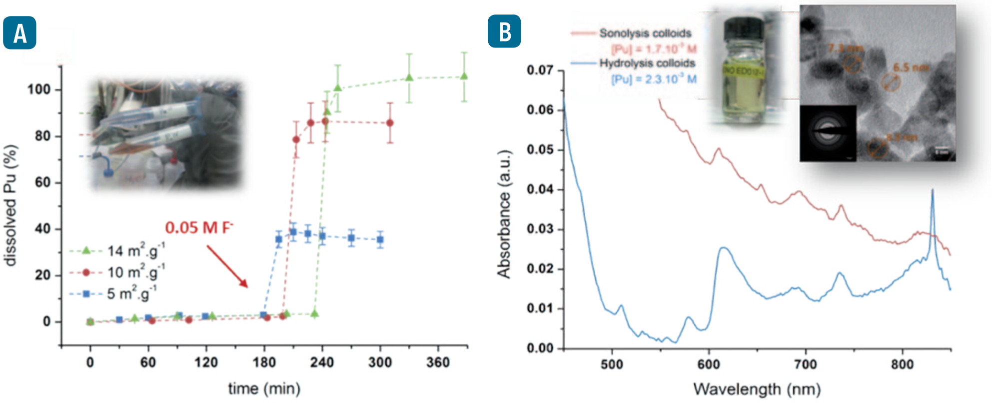


Fig. 1: **A** *Sonochemical (20 kHz, 0.45 W mL^{-1}, Ar, Ti 325 mesh, 35 °C) and reductive dissolution of PuO_2 (S_{BET}= 5, 10, 14 m^2g^{-1}) in 0.5 M HNO_3/2 M HCOOH/0.1 M HN* **B** *UV-Vis absorption spectra of hydrolytic and sonolytic Pu colloids (inset: sonolytic colloids, and HR-TEM picture of the crystalline particles).*

[1] Virot M., Chave T., Morosini V., Pflieger R., Venault L., Moisy P., Nikitenko S. I. **Sonochemistry of Actinides**, Actinide Research Quarterly (2016) 67.

[2] Beaudoux X., Virot M., Chave T., Leturcq G., Jouan G., Venault L., Moisy P., Nikitenko S. I. **Ultrasound reductive dissolution of CeO_2 and PuO_2 in the presence of Ti particle**s, Dalton Transactions, 45 (2016) 8802-8810.

[3] Dalodière E., Virot M., Morosini V., Chave T., Dumas T., Hennig C., Wiss T., Dieste Blanco O., Shuh D. K., Tyliszczak T., Venault L., Moisy P., Nikitenko S. I. **Insights into the sonochemical synthesis and properties of salt-free intrinsic plutonium colloids**, Scientific Reports (2017) 43514.

RADIATION EFFECTS IN INNOVATIVE MATERIALS FOR NUCLEAR WASTE PACKAGING

X. Deschanels, Y. Lou, S. Dourdain, C. Rey, J. Causse, G. Toquer, D. Rebiscoul, A.M. Seydoux-Guillaume, A. Mesbah, S. Peuget***

** CNRS, Université Clermont Auvergne, IRD, UJM, Laboratoire Magmas et Volcans, F-63000 Clermont-Ferrand, France,*
***CEA Marcoule, DEN/DE2D/LMPA*

An important task of nuclear industry is to find suitable and sustainable ways to dispose nuclear wastes. For many of the existing processes, the last step is to stabilize the waste in a matrix, which can be a simple coating material (bitumen, cement for low and intermediate level waste in France) or the radionuclide is incorporated into the network of the host material (R7T7 glass for high-level waste). In all case, the final waste-form is subjected to intense irradiations, which are the consequence of the disintegrations (alpha, beta gamma) associated with the presence of radionuclides. To simulate these damage, we have used external irradiations. These last years, two materials have been studied at ICSM by these technique.

The first concerns Monazite ($LaPO_4$) which a promising mineral for the immobilization of Pu and minor actinides. Previous results[1] have demonstrated the ability of this structure to maintain a crystalline state despite high radiation damage levels. However, the low critical temperature (180°C), above which amorphization cannot be achieved in monazite under ion irradiation, does not explain the strong radiation resistant to amorphization of actinide-doped monazite (natural or synthetic samples). For that, synthetic polycrystals of $LaPO_4$-monazite were irradiated sequentially and simultaneously with alpha particles (He) and gold (Au) ions. The use of Au^{2+} ions at 1.5 MeV and He^+ ions at 160 keV allows respectively, the simulation of the effect of the recoil nucleus and the α-particle released in α-decay In situ irradiation experiments were performed at room temperature conditions on the JANNuS-Orsay/SCALP platform, which couples two accelerators with a Transmission Electron Microscope. Our results demonstrate experimentally for the first time in monazite, the existence of the defect recovery mechanism, called alpha-healing, acting in this structure due to electronic energy loss of alpha particles, which explains the better damage resistance (amorphization, swelling) of actinide doped monazite compared to other mineral matrices[2].

The second concerns the use of silica mesoporous material for the encapsulation of nuclear wastes. The so-called "separation-conditioning"[3] strategy, which consists of implementing a functionalized silica porous matrix for the radionuclide sorption, is an interesting alternative. Such matrix could even act as a long term conditioning matrix, after porosity closure, in order to ensure a durable confinement. During its working process and with the presence of radionuclide, the mesoporous structure will be exposed to self-irradiation. This is why it's important to know the structure evolution under such conditions. For this purpose, mesoporous silica thin films deposited on Si-substrate (e~100nm) were irradiated by swift ions, especially Au ions. Porous characteristics of such films were obtained from the X-rays reflectivity measurements (XRR). Ballistic processes (Au ions) lead to a total compaction of the mesoporous structure for a dose of about ~10 keV/nm^3 (~1.4 dpa)[4,5]. Works are in progress in the frame of the ANR project AUTOMACT to have a better understanding of this compaction process.

[1] Deschanels, X.; Seydoux-Guillaume, A. M.; Magnin, V.; Mesbah, A.; Tribet, M.; Moloney, M. P.; Serruys, Y.; Peuget, S., **Swelling induced by alpha decay in monazite and zirconolite ceramics: A XRD and TEM comparative study**. Journal of Nuclear Materials 2014, 448 (1-3), 184-194.

[2] Seydoux-Guillaume, A. M.; Deschanels, X.; Baumier, C.; Neumeier, S.; Weber, W. J.; Peuget, S., **Why natural monazite never becomes amorphous: Experimental evidence for alpha self-healing**. American Mineralogist 2018, 103 (5), 824-827.

[3] Makowski, P.; Deschanels, X.; Grandjean, A.; Meyer, D.; Toquer, G.; Goettmann, F., **Mesoporous materials in the field of nuclear industry: applications and perspectives**. New Journal of Chemistry 2012, 36 (3), 531-541

[4] Lou, Y.; Dourdain, S.; Rey, C.; Serruys, Y.; Simeone, D.; Mollard, N.; Deschanels, X., **Structure evolution of mesoporous silica under heavy ion irradiations of intermediate energies**. Microporous and Mesoporous Materials 2017, 251, 146-154

[5] Lou, Y.; Toquer, G.; Dourdain, S.; Rey, C.; Grygiel, C.; Simeone, D.; Deschanels, X., **Structure evolution of mesoporous silica SBA-15 and MCM-41 under swift heavy ion irradiation**. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 2015, 365, 336-341

SOFT CHEMISTRY ROUTES FOR CARBIDES SYNTHESIS

Hélène Arena, Moustapha Coulibaly, Guilhem Arrachart, Adel Mesbah, Xavier Deschanels

Two soft chemistry approaches (colloidal and molecular routes) were used to synthesize silicon carbide powders[1]. These methods have been implemented for the synthesis of others carbides (TiC, ZrC, UC) and composite[2] (SiC-TiC).

Basically, the "colloidal route" consists in the carbothermal reduction (1) of a parent oxide (colloidal or micrometric powders) by sugar (sucrose, cyclodextrin…). The "molecular route" *(Fig. 1)* is based on an intimate mixing of metal oxide precursors and carbon source during a gelling step. In the case of composite materials, capping agents (citric acid, carboxylic acids…) can be used to modify the reactivity. After the pyrolysis of the carbohydrate (carbon source) under inert atmosphere at temperature below 800°C, the carbothermal reduction of the oxides can be achieved at high temperature (1000 and 1450 °C) by the following reaction:

$$MO_2(s) + 3C(s) = MC(s) + 2\,CO(g) \qquad (1)$$

From both routes, carbide powders (M : Si, Ti, Zr, Hf, Si/Ti) with a high yield of submicrometric particles were successfully synthesized. Nanocomposite SiC–TiC, SiC and TiC powders, synthesized by the molecular route, were densified up to 90% by Spark Plasma Sintering. The spectral reflectance of the pellets was measured in the range of 0.25 to 25 um to evaluate their optical selectivity. The reflectance was found to increase in the whole wavelength range, with the increase in the density. Titanium carbide presents the highest optical selectivity, which is characterized by a high absorbance (α) in the UV-visible region and a low emittance (ε) in the infrared range. This feature is at the origin of many studies on these materials where they were expected to play the role of absorber in a Concentrating Solar Power plant (CSP). However, these materials present high sensitivity to oxidation due to the large amount of TiC, and it's necessary to optimize the TiC fraction in regard to the oxidation/selectivity properties. In collaboration with PROMES Odeillo, IEM Montpellier, SPCTS Limoges, and CRM2 Nancy, the project CARAPASS, supported by the French National Research Agency, aims to study these aspects.

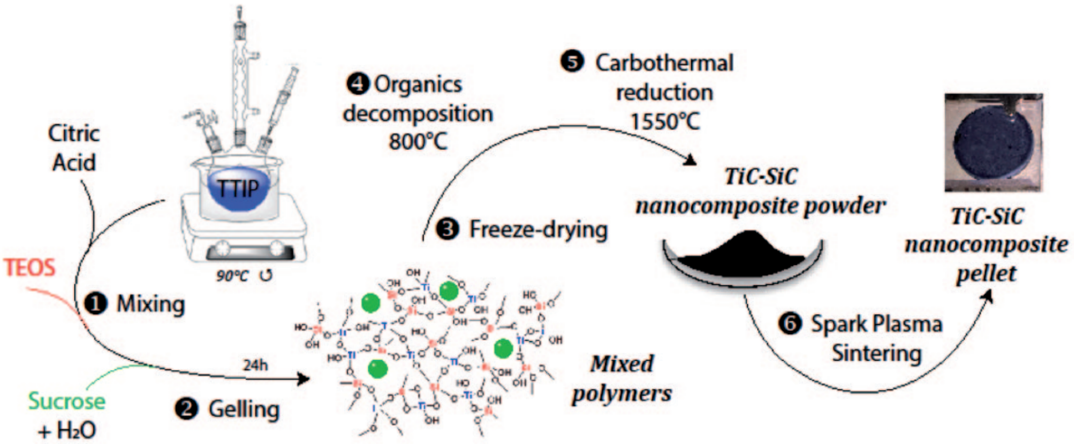


Figure 1: Reaction scheme of the molecular route

---

[1] X. Deschanels, D. Herault, G. Arrachart, C. Rey, A. Grandjean, G. Toquer, R. Podor, G. Cerveau, T. Zemb, R. Corriu **"Comparison of two soft chemistry routes for the synthesis of mesoporous carbon/b-SiC nanocomposites"** Journal of Material Science (2013) 48:4097–4108.

[2] M. Coulibaly, G. Arrachart, A. Mesbah, X. Deschanels **"From colloidal precursors to metal carbides nanocomposites MC (M=Ti, Zr, Hf and Si): Synthesis, characterization and optical spectral selectivity studies"** Solar Energy Materials and Solar Cells 143 (2015) 473-479.

[3] H. Aréna, M. Coulibaly, A. Soum-Glaude, A. Jonchère, A. Mesbah, G. Arrachart, A. Maitre, N. Pradeilles, X. Deschanels **"Carbide nanocomposite TiC –SiC for bulk solar absorbers applications: effect of the density and the surface roughness"** accepted to Solar Energy Materials and Solar Cells

SONOCHEMICAL SYNTHESIS OF NANOMATERIALS FOR ENERGY AND ENVIRONMENT

T. Chave, A. F. Sierra Salazar, C. Cau, H.-P. Brau, S. I. Nikitenko,
P. Lacroix-Desmazes (ICG-Montpellier), A. Ayral (IEM, Montpellier), V. Huela (ICG-Montpellier)

Sonolysis of water leads to the splitting of H_2O molecules and the formation of H atoms and OH radicals which can further recombine into hydrogen and hydrogen peroxide respectively. In situ formed species can be considered in order to initiate chemical reactions, especially reduction of noble metal without addition of further reagents. Ultrasonic irradiation at room temperature was thus considered for the preparation of catalysts through the sonochemical deposition of Pt nanoparticles on the surface of polystyrene beads and their transfer into a sol-gel derived porous silica matrix after the removal of the organic template (Fig. 1). The innovative method developed in our laboratory clearly demonstrated its ability to synthesize catalysts with tuned hierarchical porosity, high specific surface area and controlled active site localization and dispersion. For instance, our Pt/SiO_2 tailored catalysts exhibit hierarchical porosity with high specific surface area around 600 $m^2.g^{-1}$ and show good activity and very good selectivity during selective hydrogenation of choloronitrobenzene into chloroaniline compared to reference catalyst. [1]

Ultrasonic cavitation can be applied in a wide range of experimental conditions and even during hydrothermal treatment. The coupling of ultrasound with high temperature and autogenic pressure can offer an opportunity to obtain principally new catalysts. This how, we have developed, for the first time, simple, easily scalable and environmentally friendly synthesis of stable Ti@TiO2 core-shell nanoparticles exhibiting photocatalytic activity in hydrogen production under Vis/NIR light irradiation without any noble metals. [2] Stable to oxidation core-shell $Ti@TiO_2$ nanoparticles have been obtained by the simultaneous actions of ultrasound and hydrothermal treatment at 200°C on air-passivated titanium metal nanoparticles in pure water. The obtained material is composed of quasi-spherical Ti particles (20-80 nm) coated by 5-15 nm crystals of defect-free anatase with small amounts of rutile. In contrast to pristine TiO_2, the $Ti@TiO_2$ nanoparticles extend the photo response from UV to NIR light region due to the light absorption by nonplasmonic Ti core. In $MeOH\text{-}H_2O$ solutions, the $Ti@TiO_2$ nanoparticles exhibit the strongest catalytic activity in H_2 formation under the joint effect of Vis/NIR light and heat. Isotopic study using MeOH-D2O solutions suggested the reaction mechanism involving electron holes accumulation in semiconducting TiO_2 shell via charge separation and multiple charge-transfer steps that follow Ti interband transition.

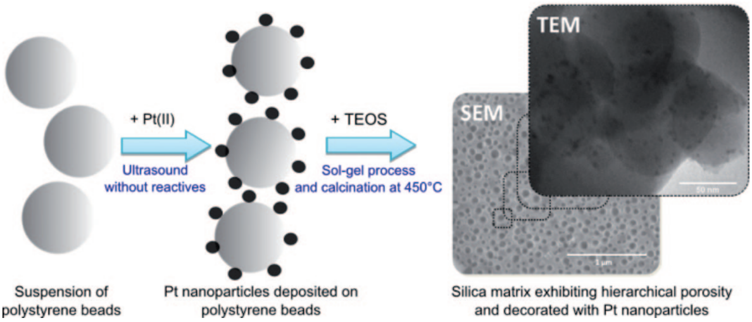


Fig. 1: Schematic representation of the platinum nanoparticle deposition on the polystyrene beads and their transfer within a porous silica matrix. TEM and SEM scale bars are respectively 50 nm and 1 μm.

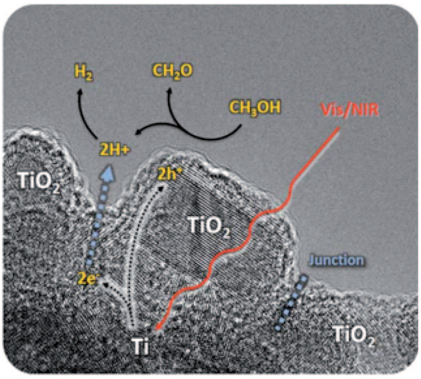


Fig. 2: HRTEM image of $Ti@TiO_2$ and suggested mechanism of H_2 photo-catalytic production in $MeOH\text{-}H_2O$ mixture.

[1] Sierra Salazar A.F., Chave T., Ayral A., Nikitenko S.I. et al. **Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis; sonochemistry, and sol-gel process** – I. Material Preparation, Microporous and Mesoporous Materials, 234 (2016) 207-214.
[2] Nikitenko S.I., Chave T., Cau C., Brau H-P., Flaud V. **Photothermal hydrogen production using noble metal-free Ti@TiO2 core-shell nanoparticles under visible**-NIR light irradiation, ACS Catalysis, 5 (2015) 4790-4795.

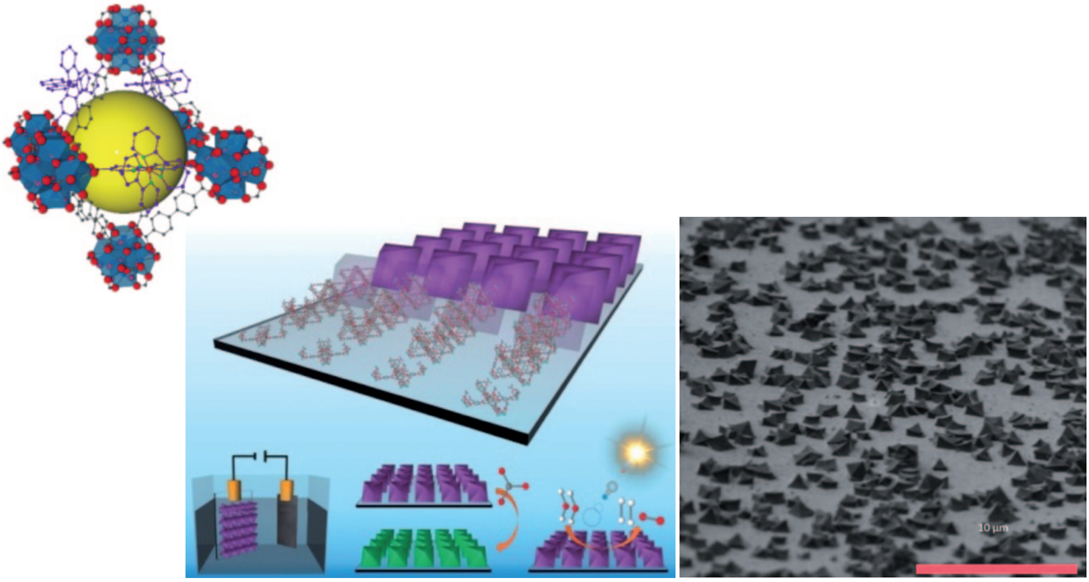
ORIENTATED GROWTH OF PHOTOACTIVE METAL-ORGANIC FRAMEWORK ON CONDUCTIVE SUPPORT

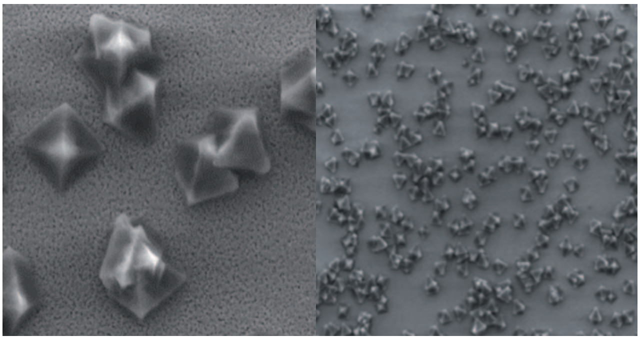
G. Genesio, J. Maynadié, M. Carboni, D. Meyer

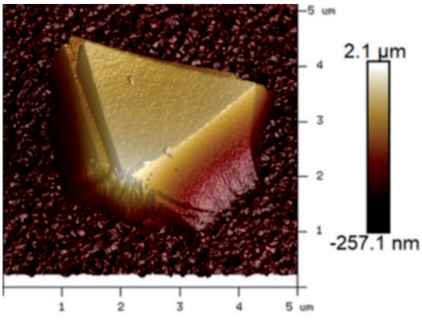
Our interest is to develop a functionalization method of transparent conductive surfaces (Transparent Conductive Oxide) by hybrid multifunctional materials, Metal-Organic Frameworks (MOFs). Different properties are provided within the MOF by adding different photosensitive and catalytic units[1]. The development of such materials is in its infancy and they have been mainly developed as crystalline powder. However, the development of these MOFs onto a solid support is challenging but also essential toward obtaining a technologically advanced device[2].

From a Zirconium material, it was possible to obtain multifunctional systems by changing components directly during the synthesis or by post synthesis modifications. It has been possible to control the growth of materials on the support by direct in situ solvothermal synthesis and to obtain a monodisperse layer of crystals well anchored to the TCO supports. Photodegradation of methylene blue (organic pollutant) has been performed to validate their photoreactivity.

The methodology developed with the Zirconium based MOF has been implemented successfully in a similar compound to include higher photosensitizer components and with titanium-based MOFs. It shows the portability of the strategy towards other types of MOFs. They were used in CO_2 photo-reduction (in collaboration of the College de France) where selectively of formate production was observed.







---

[1] R. Navarro Amador, M. Carboni, D. Meyer «**Sorption and photodegradation under visible light irradiation of an organic pollutant by a heterogeneous UiO-67-Ru-Ti MOF obtained by Post-Synthetic Exchange**», RSC Advances, 2017, 7, 29, 195-200

[2] G. Genesio, J. Maynadie, M. Carboni, D. Meyer «**Recent status on MOF Thin Films on Transparent Conductive Oxides substrates (ITO or FTO)**», New J. Chem, 2018, 42, 2351-2363 (cover : 42, 2326)

COLLOIDAL PHYSICAL CHEMISTRY TOWARDS ELECTROPHORETIC DEPOSITION

S. Shehayeb, P. Alastuey, X. Deschanels, G. Toquer

This theme deals with the electrophoretic deposition (EPD) which is known to be an important tool for the fabrication of wide range of materials[1] but this time extended to the nanoscale. This final target is to control, through a bottom-up approach, the formation of nanostructured material associated with selective optical properties designed for photothermal solar collectors. These studies are focused first on stable charged colloidal dispersion (by adding charging agents acting also as electro-steric stabilizers) which is electrodeposited on substrate with tunable thickness, density and morphology.

In this way, we have performed a home-made cell dedicated of the accurate control of an electric field coupled with a three electrodes system in order to control independently the electric field from the current. Nanoparticle electrophoretic deposition (NEPD) method is developed here to understand the mechanisms and the yield rate deposition of thin film[2] based on nanoparticles (SiO_2, CuO, SWCNT). The coating on the working electrode surface is based on the migration of charged particles in a polar medium under an electric field.

This step implies necessary some physical-chemical conditions in order to reach an efficient electrophoretic mobility (*i.e.* nanoparticle Zeta potential) characterized by laser Doppler velocimetry and also a quite monodisperse system (studied by SAXS and/or DLS). Nanoparticles at the vicinity of the working electrode are expected to be sufficiently fixed due to short range attractive Van der Waals interactions.

Further, nanoparticles coagulate *(see figure 1)* and the rate of deposition depends mainly on the nanoparticle concentration, deposition time and electric field magnitude. Different kinds of coating are obtained by varying different EPD parameters (voltage type and range, deposition time) to control the final thickness film and also the morphology, which are the main keys to tune and optimize the final optical properties[3].

During NEPD, the electric field strength is the driven force promoting particle packing, affecting thereby the film density and the final thickness but the post-deposition drying process seems also to be a crucial step for the film adhesion. The structure (*i.e.* density) and the morphology (*i.e.* thickness and roughness) of the films *(see figure 2)* are analyzed through energy-dispersive X-ray spectroscopy coupled with the X-film software and scanning electron microscopy respectively[4]. Selective optical properties of films are analyzed by reflectance spectra of the UV-Vis-NIR and by Fourier transform InfraRed (FTIR) spectroscopy [3]. From a fundamental point of view, we have started a recent collaboration with the National University of Tucumán to investigate deeply the dielectric properties of the coatings from impedance measurements to follow the effective electric field drop occurring during EPD, which is crucial to better understand and predict the kinetic yield.

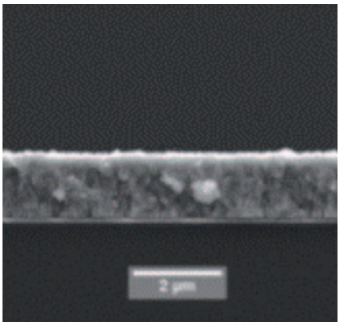


Figure 1 :
SEM (cross-section) image of CuO/PEI coating

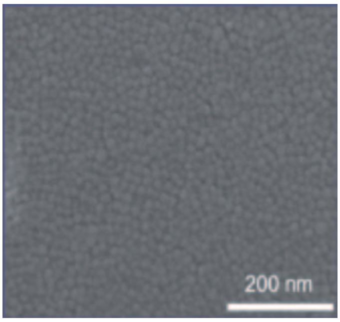


Figure 2 :
SEM (top-view) image of SiO_2 coating

[1] Zhitomirsky I. -**Cathodic electrodeposition of ceramic and organoceramic materials. Fundamental aspects**- Advances in Colloid and Interface Science (2002), 97 (1-3), 279-317

[2] Charlot A., Deschanels X., Toquer G. -**Submicron coating of SiO_2 nanoparticles from EPD**-Thin Solid Films (2014), 553, 148-15

[3] Shehayeb S., Deschanels X., .Karame I., Ghannam L., Toquer, G. -**Spectrally selective coatings obtained from electrophoretic deposition of CuO nanoparticles**- Advances in Colloid and Interface Science (2002), 97 (1-3), 279-317

[4] Shehayeb S., Lautru J., .Karame I., Ghannam L., Odorico M., Deschanels X., Toquer, G. –**Thin polymeric CuO film from EPD designed for low temperature photothermal absorbers-Submitted to Electrochimica Acta** (2018)

USE OF SUPERCRITICAL CO_2 AS SOLVENT FOR NANOMATERIALS ELABORATION

Susan Sananes Israel, Diane Rébiscoul, Guillaume Toquer, Jérémy Causse

Supercritical carbon dioxide (SC CO_2) is used to functionalize the surface of silica for the elaboration of materials with possible applications in the selective ion extraction. Our scientific approach is to determine the morphology and the structure of grafted alkoxysilanes as a function of the functional head groups (SH, NH_2, I, $PO(OH)_2$) on silica planar surface. The impact of the nanoconfinement on the functionalization is also studied using silica nanochannels and highly ordered mesoporous silica. In order to determine their durability for decontamination application, the evolution of these functionalized silica materials in various aqueous solutions (pH, acids and bases nature) is also characterized.

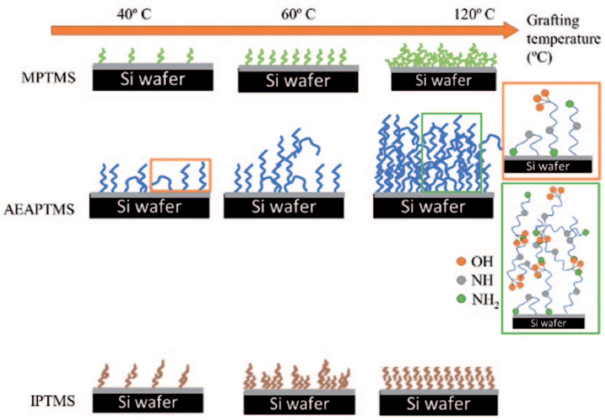


Figure 1:
Schematic representations of the morphology of grafted layers of MPTMS (top), AEAPTMS (middle) and IPTES (bottom) as a function of the grafting temperature[1]*.*

Keeping in mind that systems in supercritical solvent are always difficult to characterize, due to the fact that autoclave cells have to be used in pressure and temperature conditions above critical point (31°C, 73 bars for CO_2), our team has developed specific cells allowing SAXS measurements in this unconventional solvent. At this moment, these cells have been used to assess aggregation and size of ligands designed for extraction of metal of interest from solid matrices[2] through collaborations with Montpellier University or CEA/DEN/DE2D/LPSD (Laboratoire des Procédés Supercritiques et Décontamination).

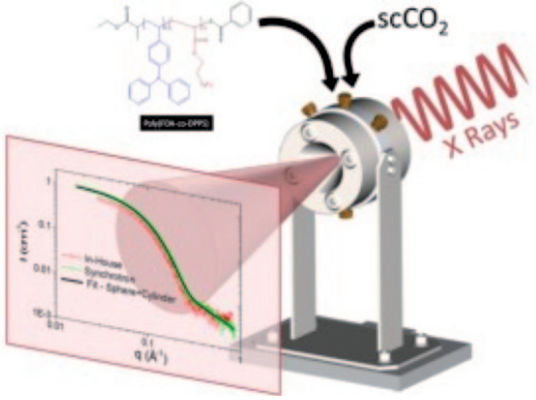


Figure 2:
In-situ SAXS cell for a use in supercritical CO2 (scCO2) solvent.

The future works on this topic will concern the use of this specific cell during grafting process of porous materials. The main idea is to follow the kinetics of ligands grafting in this non-conventional solvent with in-situ SAXS measurements. To the best of our knowledge, this has never been reported yet in literature.

---

[1] Sananes Israel, S. Rébiscoul, D. Odorico, M., Flaud, V. Ayral, A. - **Surface properties of alkoxysilane layers grafted in supercritical carbon dioxide** – submitted to Langmuir.

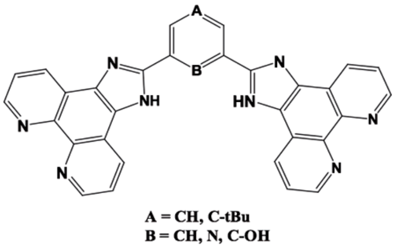
[2] Gasc, F., Corso, B., Lacroix-Desmazes, P., Causse, J., J. Supercrit. Fluids, 114, (2016), 26-31.

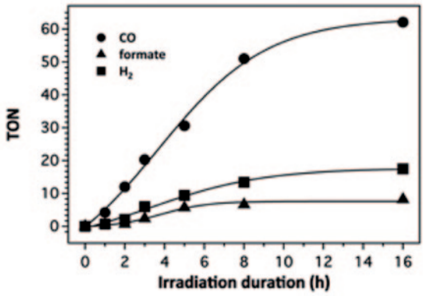
CO$_2$ REDUCTION BY Ru-Co MOLECULAR SPECIES

V. Goudy, J. Maynadié, x. Le Goff, D. Meyer
X. Wang, M. Fontecave (Collége de France)

Main aims of these studies are to determine molecular properties important for charge transfer and charge separation in a molecular species as preliminary studies for a transposition to hybrid solids.

As a first step we have developed molecular bimetallic species containing a photosensitive element (Ru or Ir) and a catalyst (d-element) to get their photophysical (spectra, lifetime,…) and electrochemical properties. The organic ditopic ligands (DIP) develop for this project display a delocalised electronic pi-system based on nitrogen containing aromatic rings attached to a central aryl core *(Figure 1)*. Several systems containing Ru and Ru-Co were synthetised and some basic characteristics (NMR, UV-Vis, voltammograms…) were collected[1]. These bimetallic species are constructed in order to be used as precursor of high ordered matter.





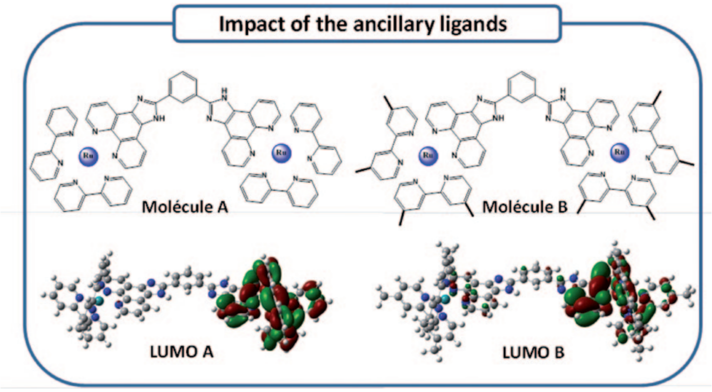


Figure 1: Studied DIP ligands, CO$_2$ photoreduction and related TD-DFT calculation.

Combined experimental and theoretical structure–properties studies of DIP based mononuclear and dinuclear ruthenium(II) complexes have shown the importance not only of the electronic structure and the rigidity of the DIP ligand but also of the pi-accepting properties of the ancillary ligands. The electrochemical behaviour and the photophysical properties of the ruthenium dinuclear complexes show that this kind of compounds has two independent photosensitive metal centres whatever the nature of the central aryl core. They are likely to transfer two electrons simultaneously under irradiation.

Photochemical investigations have allowed to identify a Ru-Co complex showing the best catalytic photoreduction of CO$_2$ activity for a non- noble metal based system published so far *(figure 1)*[2].

---

[1] V. Goudy, J. Maynadié, X. Le Goff, D. Meyer, M. Fontecave, «**Synthesis, electrochemical and spectroscopic properties of ruthenium(II) complexes containing 2,6-di(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)aryl ligands**», New J. Chem., 2016, 40, 1704-1714.
[2] X. Wang, V. Goudy, G. Genesio, J. Maynadié, D. Meyer, M. Fontecave - « **Ruthenium–cobalt dinuclear complexes as photocatalysts for CO$_2$ reduction**» - Chemical Communications (2017) 53, 5040-5043.

METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

MÉTHODOLOGIE ET THÉORIES POUR LA CHIMIE SÉPARATIVE

METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

Via the refinement of experimental tools (microscopies, radiation scattering, spectroscopies) and multi-scale predictive modelling (supramolecular, mesoscopic and colloidal).

METHODOLOGIES ET THEORIES POUR LA CHIMIE SEPARATIVE

Via le perfectionnement d'outils expérimentaux (microscopies, diffusion du rayonnement, spectroscopies) et la modélisation prédictive multi-échelle (supramoléculaire et colloïdale).

MULTI-SCALE MODELING OF ELECTROLYTE AQUEOUS SOLUTIONS: FROM ATOMS TO MASS ACTION LAW

M. Duvail, T.-N. Nguyen, A. Villard, J. J. Molina (Fukui Institute for Fundamental Chemistry, Kyoto Univ., Japan), P. Turq (PHENIX, UPMC), Ph. Guilbaud (DEN/DMRC-CEA Marcoule), J.-F. Dufrêche

The study of electrolytes in solution has relied heavily on computer simulations that allowed for better understanding their microscopic and macroscopic properties, complementing the available experimental techniques. We attempt to develop a unified (consistent) multi-scale description of electrolyte solutions based on: (I) molecular dynamics simulations in order to access the structural and thermodynamics properties of ions in solution, and (II) implicit solvent Monte-Carlo simulations to determine the ion activities from the solvent averaged potentials issued from MD simulations. This coarse-grained technique has proved its efficiency for fine-tuning atomic force fields to experimental data. This approach has been therefore used to describe the thermodynamics properties of molecular ions in aqueous solutions. The description of the thermodynamics properties of such ions is more complex than the monoatomic ones because of their molecular character. First[1], we focused on the uranyl chloride UO_2Cl_2 electrolytes in aqueous solution in order to reduce the complexity of the system since only the uranyl cation is molecular. Directly from the UO_2^{2+} – Cl– potential *(Fig. 1)*, we calculated association constant in agreement with the experimental one, as well as osmotic coefficients *(Fig. 2)* that have been calculated using our coarse-grained approach.

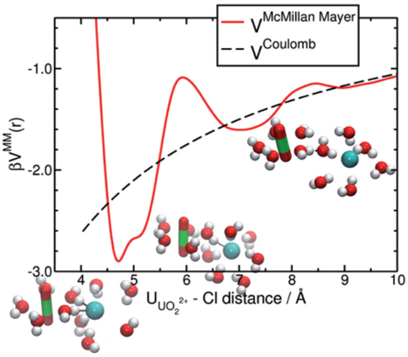


Figure 1: UO_2^{2+}—Cl— McMillan-Mayer potential profile. Characteristic snapshots of hydrated UO_2Cl^+ complexes are also shown. Uranium is in green, chloride in cyan, oxygen atoms in red, and hydrogen atoms in white.

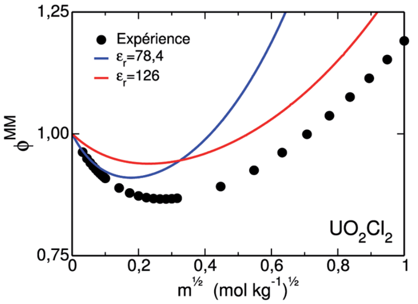


Figure 2: Osmotic coefficients in the McMillan-Mayer frame of reference for UO_2Cl_2 obtained experimentally (circles) and from coarse-grained atomistic simulations (lines) as a function of the square root of the concentration.

In parallel, a polarizable force field for describing the sulfate anion SO_4^{2-} has been developed in order to reproduce its structural and thermodynamics properties in aqueous solution. Potentials of mean force of sulfate electrolytes, i.e., $MgSO_4$, $EuSO_4$+, and UO_2SO_4, have been calculated allowing for calculating pair association constants in very good agreement with the experimental ones. Moreover, we pointed out that for electrolytes composed of monoatomic cations (Mg^{2+} and Eu^{3+}) the Contact Ion Pair configuration contributes the most for the association, whereas it is the Solvent Shared Ion Pair in the case of the purely molecular electrolyte (UO_2SO_4) *(Fig. 3)*.

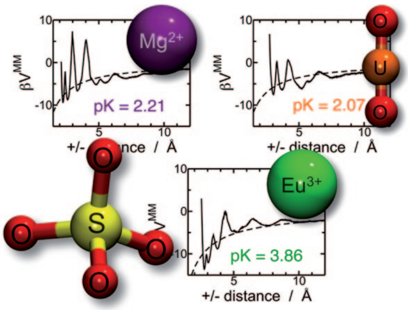


Figure 3: Schematic representation of the sulfate electrolytes association properties calculated from classical molecular dynamics using explicit polarization: $MgSO_4$, UO_2SO_4 and $EuSO_4$+.

---

[1] Nguyen T.-N., Duvail M., Villard A., Molina J. J., Guilbaud Ph., Dufrêche J.-F. – **Multi-Scale Modelling of Uranyl Chloride Solutions.** – The Journal of Chemical Physics (2015) 142, 02450.

[2] Duvail M., Villard A., Nguyen T.-N., Dufrêche J.-F. – **Thermodynamics of Associated Electrolytes in Water: Molecular Dynamics Simulations of Sulfate Solutions.** – Journal of Physical Chemistry B (2015) 119, 11184-11195.

A NEW TOOL FOR THE CALCULATION OF ACTIVITY OF SOLUTIONS BY SIMULATING OSMOTIC EQUILIBRIA

M. Bley, M. Duvail, Ph. Guilbaud (DEN/DMRC-CEA Marcoule), J.-F. Dufrêche

Understanding solvent-extraction-based purification and recycling approaches requires detailed information on different thermodynamic equilibrium properties of phases. Here, a new theoretical method is presented for predicting osmotic equilibria and activities, where a bulk liquid phase and its corresponding vapor phase are simulated by means of molecular dynamics using explicit polarization.

This multi-scale approach based on the thermodynamic interpretation of the time-averaged density profiles from MD simulations of vapor-liquid interfaces is in principle similar to the experimental isopiestic approach for aqueous solutions.

This method has been first applied to aqueous solutions of dysprosium nitrate [$Dy(NO_3)_3$] at different concentrations in order to determine the activity coefficients of the solutes *(Fig. 1)* [1].

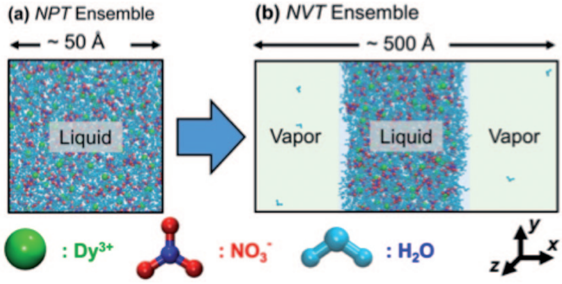


Figure 1: Representation of the MD simulations of (a) a bulk liquid phase and (b) a simulation box representing a liquid-vapor interface.

Then, using the same approach osmotic and activity coefficients of three aqueous electrolyte solutions with cations of similar ionic radius, but different charges ($NaNO_3$, $Ca(NO_3)_2$, and $Eu(NO_3)_3$), have been described by molecular dynamics with the help of the osmotic equilibrium method up to high concentration[2]. The densities of the liquid bulk calculated and the osmotic and activity coefficients obtained for the three different nitrate salts are in very good agreement with the experimental results *(Fig. 2)*.

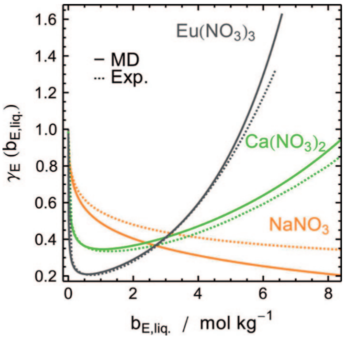


Figure 2: Experimental (dashed lines) and simulated (solid lines) salt activity coefficients for aqueous solutions of $NaNO_3$, $Ca(NO_3)_2$, and $Eu(NO_3)_3$.

Such an approach has been then extended for simulating phase diagrams of binary water/ethanol mixtures[3]. MD simulations of water/ethanol mixtures have been conducted at different ethanol concentrations *(Fig. 3)*. The activities in the liquid phase have been calculated at a given composition, providing a good agreement with the experimental data. An azeotropic point was calculated for an excess concentration at 87 wt% of ethanol compared to the experimental value of 95.5 wt% *(Fig. 4)*.

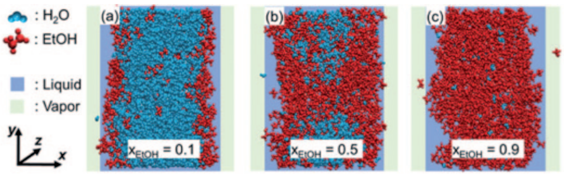


Figure 3: Snapshots representing the liquid phase in contact with vapor phases for different ethanol mole fractions.

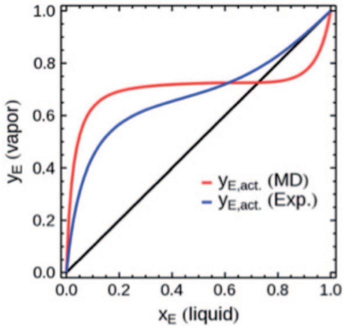


Figure 4: Ethanol gas phase mole fraction y_E as a function of the ethanol mole fraction in the liquid phase x_E.

[1] Bley M., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Simulating Osmotic Equilibria: A New Tool to Calculate Activity Coefficients in Concentrated Aqueous Salt Solutions** – Journal of Physical Chemistry B (2017) 121, 9647-9658.

[2] Bley M., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Activity Coefficients of Aqueous Sodium, Calcium, and Europium Nitrate Solutions from Osmotic Equilibrium MD Simulations.** – Journal of Physical Chemistry B (2018) 122, 7726-7736.

[3] Bley M., Duvail M., Guilbaud Ph., Penisson Ch., Theisen J., Gabriel J.-Ch., Dufrêche J.-F. – **Molecular simulation of binary phase diagrams from the osmotic equilibrium method: vapour pressure and activity in water-ethanol mixtures.** – Molecular Physics (2018) 116, 2009-2021

STRUCTURES OF SOLUTIONS RESOLVED AT MOLECULAR AND SUPRAMOLECULAR SCALES: DEVELOPMENTS OF POLARIZABLE FORCE FIELDS FOR MOLECULAR DYNAMICS

M. Duvail, A. Coste, O. Diat, J.-F. Dufrêche, Th. Dumas, A. Paquet, L. Berthon, Ph. Guilbaud (DEN/DMRC- CEA Marcoule), A. Poulesquen (DEN/DE2D-CEA Marcoule)

Molecular dynamics (MD) simulations coupled with experiments, such as EXAFS and SWAXS techniques, are methods of choice to access the structural, dynamic, and thermodynamic properties of ions in solutions. However, force fields for molecular dynamics have to be developed as accurately as possible in order to reproduce all the experimental solvation properties.

Recently, we proposed a new polarizable force field for describing the UO_2^{2+} solvation by means of classical molecular dynamics in both aqueous and solvent extraction phases[1,2]. This new force field, that has been improved compared to our previous force field[3], provides structural hydration properties in very good agreement with the EXAFS experiments.

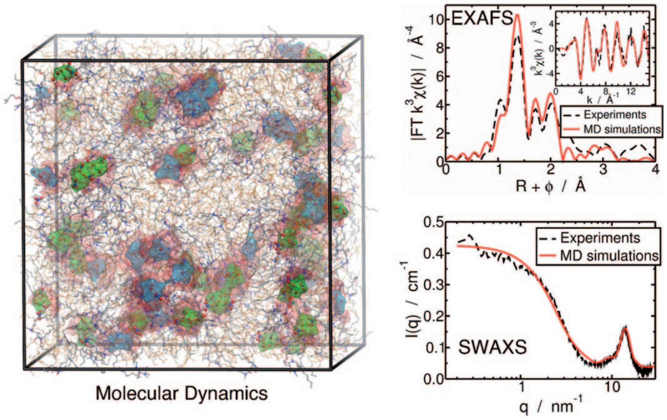


Figure 1: Combined MD/EXAFS/SWAXS approach.

The transferability of the UO_2^{2+} force field has also been tested on solvent extraction phases containing uranyl nitrate salts with DMDOHEMA molecules in n-heptane. The good agreements between MD simulations and SWAXS and EXAFS experiments comfort us on the reliability of the force field developed here for describing the solvation structure of the UO_2^{2+} cation in solvent extraction phases at both the molecular (EXAFS) and supramolecular (SWAXS) scales *(Fig. 1)*.

Such an approach coupling both MD simulations with WAXS experiments has also been used for studying concentrated NaOH aqueous solutions from diluted systems to 10 mol L^{-1}.[4] A new polarizable force field has been therefore developed for describing the OH– anion in aqueous solutions by means of classical MD simulations. This new OH– polarizable force field gives an accurate description of the molecular structures of alkali media *(Fig. 2)*. We also calculated a small association constant for the Na^+–OH– Contact Ion Pair (K = 0.1 L mol^{-1}) that is in agreement with the experiments.

Combining molecular dynamics with scattering techniques such as EXAFS and SWAXS points out its efficiency for providing realistic pictures of electrolyte salts solvation that is a first needed step to access their thermodynamical properties.

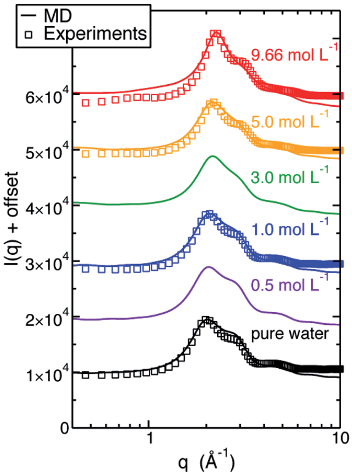


Figure 2: Comparison between theoretical results (lines) and experimental (square) WAXS intensities.

---

[1] Duvail M., Dumas Th., Paquet A., Coste A., Berthon L., Guilbaud Ph. – **UO_2^{2+} Structure in Solvent Extraction Phases Resolved at Molecular and Supramolecular Scales: A Combined Molecular Dynamics, EXAFS and SWAXS Approach.** – Inorganic Chemistry (2018) submitted.

[2] Lahrouch F., Chamayou A.-C., Creff G., Duvail M., Hennig Ch., Lozano Rodriguez M. J., Den Auwer Ch., Di Giorgio Ch. – **A Combined Spectroscopic/Molecular Dynamic Study for Investigating a Methyl-Carboxylated PEI as a Potential Uranium Decorporation Agent.** – Inorganic Chemistry (2017) 56, 1300-1308.

[3] Nguyen T.-N., Duvail M., Villard A., Molina J. J., Guilbaud Ph., Dufrêche J.-F. – **Multi-Scale Modelling of Uranyl Chloride Solutions.** – The Journal of Chemical Physics (2015) 142, 024501.

[4] Coste A., Poulesquen A., Diat O., Dufrêche J.-F., Duvail M. – **Investigation of the Structure of Concentrated NaOH Solutions: Development of a Polarizable Force Field For the OH– Anion.** – The Journal of Chemical Physics (2018) submitted.

ORGANIC PHASES MODELING FOR THE LIQUID-LIQUID EXTRACTION: A MOLECULAR APPROACH

M. Duvail, S. Van Damme, Y. Chen, Ph. Guilbaud (DEN/DMRC-CEA Marcoule), J.-F. Dufrêche

Most of efficient methods known for separating ions are based on equilibria between complex fluids, typically between aqueous and organized organic phases. Understanding the thermodynamics in both phases is therefore a crucial issue in order to optimize the separation processes. Although the aqueous solutions are nowadays well described, a lack remains in understanding the thermodynamics properties of ions in organic phases. Indeed, it is well known that ions migrate from the aqueous to the organic phase thanks to surfactant or extractant molecules in the organic phase, and then are captured in reverse micelles or aggregates. Modeling such processes remains quite difficult since many phenomena are involved: complexation, solvation, electrostatic interactions, polarization forces, etc.

The main goal of this study is to understand the various effects (solvation, electrostatic and van der Waals forces, entropy) that drive the transfer of lanthanide salts ($Ln(NO_3)_3$) from an aqueous phase to an organic organized phase thanks to the DMDOHEMA molecule (noted L)

$$[Ln(NO_3)(H_2O)x{-}1L_4](org) + H_2O(org) = [Ln(NO_3)(H_2O)xL_4](org) \qquad \text{with } x = 1 \text{ to } 5$$

First, we focused on association pathways of water molecules in reverse micelles containing lanthanum nitrate $La(NO_3)_3$ salts and DMDOHEMA extractant molecules in *n*-heptane[1]. In order to investigate quantitatively the stability of such aggregates as a function of the number of water molecules, umbrella sampling molecular dynamics (MD) simulations have been performed. This work demonstrates that the stability of such aggregates in the organic phase, composed of a polar core and an apolar ring, is clearly a compromise between the curvature properties of the ligand molecules (number of ligands and the shape) and the structural properties inside the polar core, i.e., number of water molecules, H-bond between the species *(Fig. 1)*.

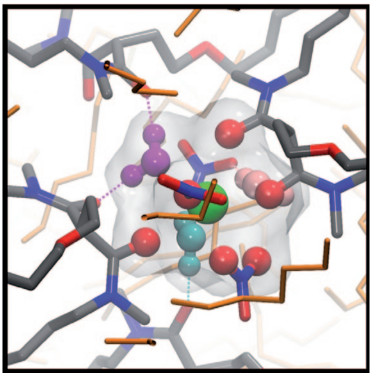


Figure 1: Snapshot obtained from MD simulations representing an aggregate of $La(NO_3)_3L_4(H_2O)_3$ in n-heptane with colored water molecules: WAT0 (pink), WAT1 (cyan), and WAT2 (purple) where the number after WAT corresponds to the number of DMDOHEMA molecules H-bonded to the water molecule. For the illustration, La^{3+} is colored in green, oxygen atoms are in red, nitrogen atoms are in blue, carbon atoms are in black, and hydrogen atoms are in white. n-Heptane molecules are colored in orange.

Then, in order to quantify these curvature properties, umbrella-sampling MD simulations of aggregates in explicit (described at the molecular level) and implicit (described by its dielectric constant) solvents have been performed[2]. This pointed out that it is crucial to take into account explicitly the solvent in order calculate accurate physicochemical properties.

Furthermore, coupling both molecular and mesoscopic modeling based on the microemulsion theory proved that such aggregates behave like microemulsions *(Fig. 2)*.

The combination between small size of the polar core and high rigidity of the interface may explain the strong stability of such aggregates in organic phases, and therefore, why such extractant is used in the liquid–liquid separation processes.

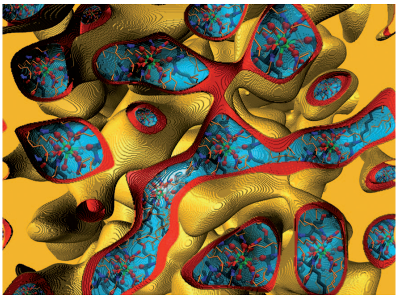


Figure 2: Representation of the microemulsion coupled with MD simulations. For the illustration, water is blue, oil is yellow and the surfactant is red.

[1] Chen Y., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Stability of Reverse Micelles in Rare-Earth Separation: a Chemical Model Based on a Molecular Approach**. – Physical Chemistry Chemical Physics (2017) 19, 7094-7100.

[2] Duvail M., Van Damme S., Guilbaud Ph., Chen Y., Zemb Th., Dufrêche J.-F. – **The Role of Curvature Effects in Liquid–Liquid Extraction: Assessing Organic Phase Mesoscopic Properties From MD Simulations**. – Soft Matter (2017) 13, 5518-5526.

SUPRAMOLECULAR AND MESOSCALE MODELING OF LIQUID-LIQUID EXTRACTION OF RARE EARTH SALTS

A. Karmakar, M. Bley, S. Gourdin-Bertin, M. Duvail, B.Siboulet, J.-F. Dufrêche, Th. Zemb

The recycling of rare earth elements and the understanding of nuclear waste management based on liquid-liquid extraction systems is important for the success of present and future technologies. It is crucial to identify and to understand the motors of selectivity and efficiency of such hydrometallurgical approaches[1]. One essential aspect is the understanding of the aggregation processes in organic solvent phases in contact with an aqueous electrolyte solution[2].

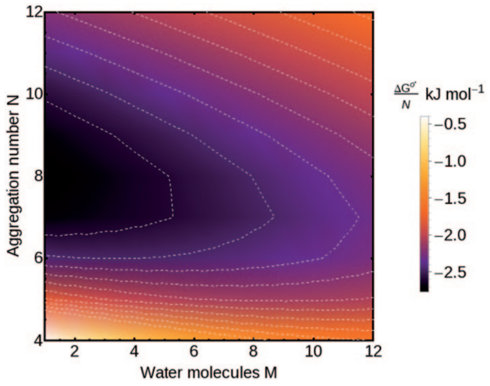


Figure 1: Calculated standard Gibbs energy ΔGo° potential surface.

First, we introduced a minimal model for the case of W/O solubilization of badly soluble compounds present in an excess phase by reverse aggregates in chemical equilibrium with its single compounds[3]. Such a simple model is crucial for obtaining predictive parameters for modeling the separation chemistry systems. The standard Gibbs free energy of aggregation and the concentration of the corresponding aggregate have been calculated within a multiple-equilibria approach for a set of aggregate compositions of M water and N amphiphilic extractant molecules *(Figs. 1 and 2)*.

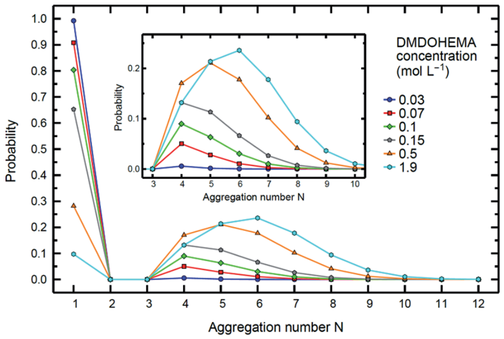


Figure 2: Probabilities of finding aggregates with a given aggregation number calculated for different concentrations of extractant in the organic phase.

This thermodynamic model allows for capturing the complete concentrations of free and aggregated extractant species as well as the favored aggregation numbers, the polydispersity, the activity of the organic solvent.

In an attempt of understanding the relation between the extraction and the complexation free energies in the case of lanthanide salt ($Eu(NO_3)_3$)–containing reverse micelles, another thermodynamics model combining supramolecular chemistry and mesoscale has been developed[4], where we took into account the fundamental property of weak aggregation: the aggregates are equilibrated by constant exchange of ligands, so the polydispersity in the aggregates is described using general theories of surfactant self-assembly. This multi-scale approach allows for reducing largely the number of parallel apparent equilibria currently used for dimensioning extraction devices *(Fig. 3)*.

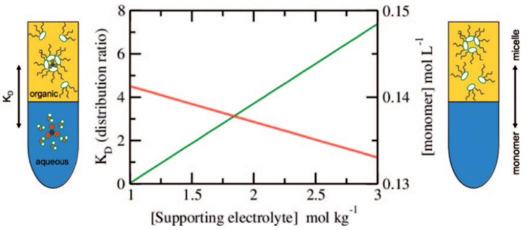


Figure 3: Distribution coefficient and concentration of free monomer in the organic solution as a function of the concentration of supporting electrolyte present in the aqueous phase.

[1] Zemb Th., Bauer C., Bauduin P., Belloni L., Déjugnat Ch., Diat O., Dubois V., Dufrêche J.-F., Dourdain S., Duvail M., Larpent Ch., Testard F., Pellet-Rostaing S. – **Recycling Metals by Controlled Transfer of Ionic Species between Complex Fluids: En Route to "Ienaics".** – Colloid and Polymer Science (2015) 293, 1-22.

[2] Dufrêche J.-F., Zemb Th. – **Effect of Long-Range Interactions on Ion Equilibria in Liquid-Liquid Extraction.** – Chemical Physics Letter (2015) 622, 45-49.

[3] Bley M., Siboulet B., Karmakar A., Zemb Th., Dufrêche J.-F. – **A Predictive Model of Reverse Micelles Solubilizing Water for Solvent Extraction.** – Journal of Colloid and Interface Science (2016) 479, 106-114.

[4] Karmakar A., Duvail M., Bley M., Zemb Th., Dufrêche J.-F. – **Combined Supramolecular and Mesoscale Modelling of Liquid-Liquid Extraction of Rare Earth Salts.** – Colloids and Surfaces A: Physicochemical and Engineering Aspects (2018) 555, 713-727.

COLLOIDAL MODEL FOR THE PREDICTION OF NUCLEAR WASTE/RARE EARTH EXTRACTION PROCESSES

M. Špadina, S. Gourdin-Bertin, Th. Zemb, J.-F. Dufrêche, K. Bohinc (Univ. of Ljubljana, Slovenia)

We develop a minimal model for the prediction of solvent extraction. We consider a rare earth extraction system for which the solvent phase is similar to water-poor microemulsions. All physical molecular quantities used in the calculation can be measured separately. The model takes into account competition complexation, mixing entropy of complexed species, differences of salt concentrations between the two phases, and the surfactant nature of extractant molecules. We consider the practical case where rare earths are extracted from iron nitrates in the presence of acids with a common neutral complexing extractant. The solvent wetting of the reverse aggregates is taken into account via the spontaneous packing. All the water-in-oil reverse aggregates are supposed to be spherical on average.

The minimal model captures several features observed in practice: reverse aggregates with different water and extractant content coexist dynamically with monomeric extractant molecules at and above a critical aggregate concentration (CAC). The CAC decreases upon the addition of electrolytes in the aqueous phase. The free energy of transfer of an ion to the organic phase is lower than the driving complexation. The commonly observed log–log relation used to determine the apparent stoichiometry of complexation is valid as a guideline but should be used with care. The results point to the fact that stoichiometry, as well as the probabilities of a particular aggregate, is dependent on the composition of the entire system, namely the extractant and the target solutes' concentrations. Moreover, the experimentally observed dependence of the extraction efficiency on branching of the extractant chains in a given solvent can be quantified. The evolution of the distribution coefficient of particular rare earth, acid, or other different metallic cations can be studied as a function of initial extractant concentration through the whole region that is typically used by chemical engineers. For every chemical species involved in the calculation, the model is able to predict the exact equilibrium concentration in both the aqueous and the solvent phases at a given thermodynamic temperature[1].

For acidic extractant (HDEHP), multiple extraction regimes were identified. Each of these regimes is controlled by the formation of different species in the solvent phase, ranging from multiple metal cation filled aggregates (at the low acid concentrations in the aqueous phase), to the pure acid filled aggregates (at the high acid concentrations in the aqueous phase). These results are contrary to a long-standing opinion that liquid-liquid extraction can be modelled with only a few species.

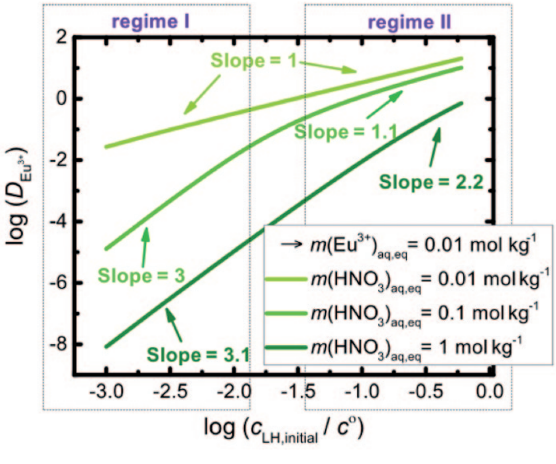


Figure 1: Distribution coefficients as functions of extractant for different conditions. The figure exhibits the difficulty to apply a slope method to get stoichiometries of complexes in solvent extraction

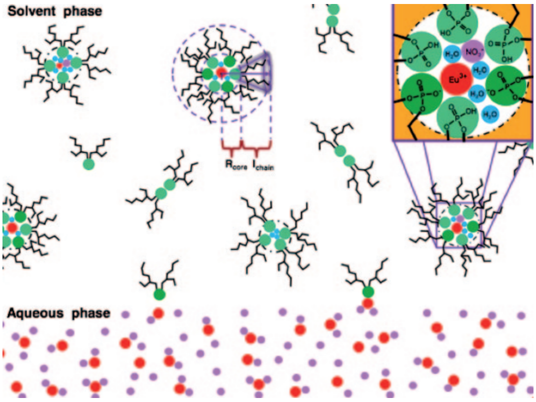


Figure 2: Colloidal modelling of solvent extraction

---

[1] Špadina M., Bohinc K., Zemb Th., Dufrêche J.-F. –**Multicomponent Model for the Prediction of Nuclear Waste/Rare-Earth Extraction Processe Extraction.** – Langmuir (2018) 34, 10434-10447.

IONS AT LIQUID-SOLID INTERFACES

B. Siboulet, S. Hocine, M. Duvail, J.-F. Dufrêche, R. Hartkamp, B. Coasne (ICG & MIT)

The description at the atomic level of the ions at the interface is a fundamental topic but it has very direct applications, which are also in the scope of LMCT.

The condensation of ions in the Stern layer can be studied by molecular dynamics. In the case of charged silica interfaces we have determined the surface-ion interaction: namely, the McMillan-Mayer mean force potentials between a charged oxygen site and a lithium or cesium cation[1].

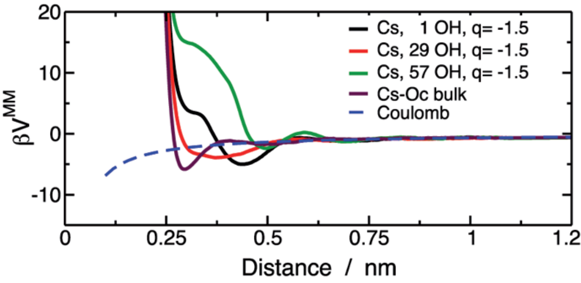


Figure 1: Cs–Oc McMillan-Mayer potentials calculated for different OH surface densities.

It appears that Contact Ion Pairs (CIP) are the building blocks of the Stern layer. The adsorption specificity of the ions can be reproduced and justified by the simulation *(Fig. 1)*. It is interesting to note that high activation energies for desorption but also for adsorption cause a relaxation time sometimes much larger than the feasible simulation times. A new image of the Stern layer appears: it is not a continuous layer but a set of ionic pairs. Treatments of such systems with localized surface charges require three-dimensional models, while existing models are one-dimensional.

Molecular dynamics allow the simulation of electro-osmotic phenomena[2,3]. The results can be compared to standard mesoscopic models such as Smoluchowski model for zeta potential or Bikerman for surface conductivity.
In the simulation, the flow of an aqueous solution of cesium chloride confined in a charged amorphous silica channel is generated by an electric field *(Fig. 2)*. The traditional interface model, which is the electrical double layer, including a Stern layer and a diffuse charge layer, a solvent stagnant layer and an ionic conduction in the stagnant layer, must be reconsidered.

Simulations indicate that there is no stagnant layer, no conduction layer in the Stern layer, and no Helmholtz outer layer. The description of the interface as we present the simulations is simple. It is sufficient to distinguish between the ions in contact with the surface and the ions separated from the surface by at least one molecule of water to distinguish the sources of both conduction and electro-osmosis. The mobility of the ions very close to the surface is very small, so that the surface conductivity formulas are valid only at low concentrations. Indeed, we show that the surface conduction is negative at high concentration and that the Bikerman formula is only valid at low concentration.

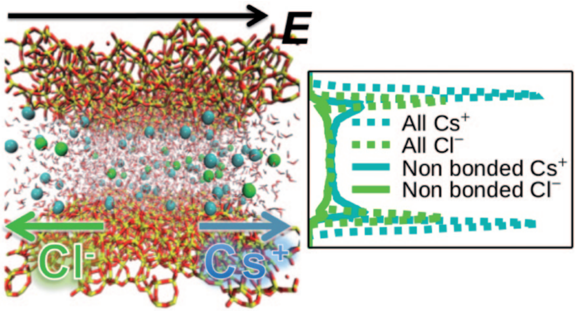


Figure 2: Electro-osmosis of a CsCl solution in a planar silica nanochannel.

---

[1] Hocine S., Hartkamp R., Siboulet B., Duvail M., Coasne B., Turq P., Dufrêche J.-F. – **How Ion Condensation Occurs At a Charged Surface: a Molecular Dynamics Investigation of the Stern Layer for Water-Silica Interfaces.** – Journal of Physical Chemistry C (2016) 120, 963-973.
[2] Hartkamp R., Siboulet B., Dufrêche J.-F., Coasne B. – **Ion-Specific Adsorption and Electroosmosis in Charged Amorphous Porous Silica**. – Physical Chemistry Chemical Physics (2015) 17, 24683-24695.
[3] Siboulet B., Hocine S., Hartkamp R., Dufrêche J.-F. – **Scrutinizing Electro-Osmosis and Surface Conductivity with Molecular Dynamics.** – Journal of Physical Chemistry C (2017) 121, 6756-6769.

LIQUID/SOLID INTERFACES FOR DECONTAMINATION

A Villard, B. Siboulet, A Grandjean, G. Toquer, J.-F. Dufrêche

High specific surface materials allow specificity in adsorption and liquid decontamination. We have considered the case of sodium-strontium exchange.

We used sodium for this nonatitanate powder, to which is added nitrate strontium and acetate sodium mixture[1]. We have examined jointly experiments and mesoscopic models *(Fig. 1)*. Experiments show that adsorption is quantitative. The excess Gibbs free energy has been modeled by various models (ideal, 2D Coulomb, regular solution model) for the solid phase. We find that the free energy of the solid phase is controlled by short-range interactions rather than long-ranged Coulombic forces. The selectivity is the consequence of a competition between the liquid and solid phases: both phases prefer strontium rather than sodium but the solid contribution is predominant.

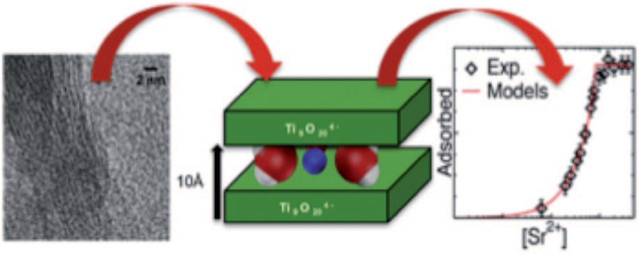


Figure 1: Combined experimental and mesoscopic modeling approaches used for the sodium nanotitanate.

We have also studied the sorption mechanism in more details. Sodium nonatitanate powder is a layered material. We have modeled the sorption mechanism of this material at the solid-liquid interface.
In particular, the ion-exchange mechanism was not entirely known and especially the role of the pH on sorption properties. To investigate this latter, the solid was first equilibrated with inert acidic and base (nitric acid and triethylamine) for which the co-ions nitrate and triethylammonium do not penetrate the solid. The exchange between proton or divalent ions (strontium or calcium), and the sodium initially located in the sodium nonatitanate, were characterized through capillary ionic chromatography and conductivity experiments. To understand and explain the sorption properties, we modeled the equilibrium constant of different exchange reactions as a function of the solution pH. The equilibrium constants of the strontium/sodium and the calcium/sodium exchange have been obtained. We have shown the important role of the pH on the sorption rate of the strontium and moreover the hydrolysis rate of the sodium nonatitanate is calculated. We found that one eighth of sodium is spontaneously hydrolysed in aqueous phase whereas seven-eighths are exchanged by different divalent cations (strontium or calcium). Strontium and calcium exhibit similar exchange curves and competition with the proton adsorbed is modeled with global equilibrium constant. The prediction is in agreement with the conductivity experiments and the global extraction isotherms[2].

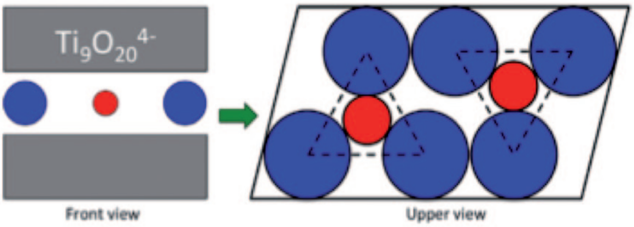


Figure 2: Representation of triangular geometry of the sodium hydrate in porous media, the blue and red spheres are water molecules and sodium ions, respectively.

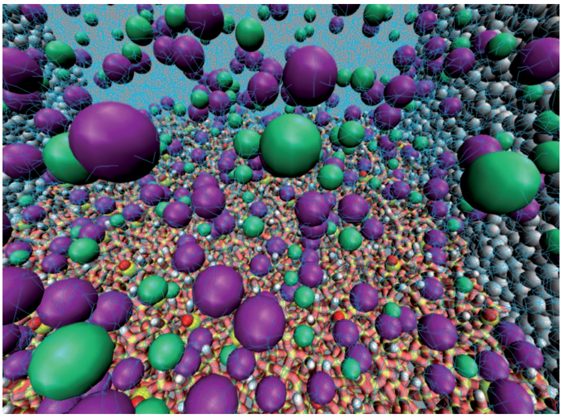
---

[1] Villard A., Siboulet B., Toquer G., Merceille A., Grandjean A., Dufrêche J.-F. – **Strontium Selectivity in Sodium Nonatitanate Na4Ti9O20·xH2O.** – Journal of Hazardous Materials (2015) 283, 432-438.

[2] Villard A., Toquer G., Siboulet B., Trens Ph., Grandjean A., Dufrêche J.-F. – **Sorption pH Dependance of Strontium/Calcium by Sodium Nonatitanate.** – Chemosphere (2018) 202, 33-39.

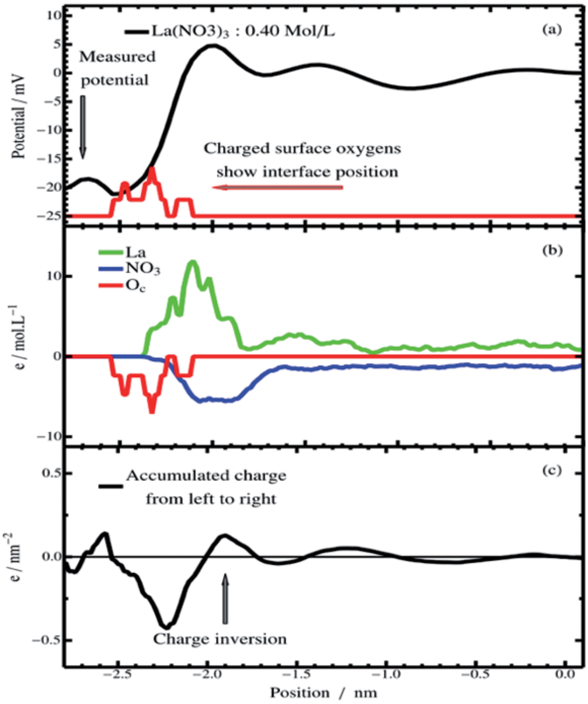
IONS AT INTERFACES FOR NANOTECHNOLOGY

N. Clément (Univ. Lille), B. Siboulet, J.-F. Dufrêche



Despite being ubiquitous in the fields of chemistry and biology, the ion-specific effects of electrolytes pose major challenges for researchers. A lack of understanding about ion-specific surface interactions has hampered the development and application of materials for bio-chemical sensor applications.

Here[1], we show that scaling a silicon nanotransistor sensor down to ~25 nm provides a unique opportunity to understand and exploit ion-specific surface interactions, yielding a surface that is highly sensitive to cations and inert to pH. The unprecedented sensitivity of these devices to Na^+ and divalent ions can be attributed to an overscreening effect via molecular dynamics. The surface potential of multi-ion solutions is well described by the sum of the electrochemical potentials of each cation, enabling selective measurements of a target ion concentration without requiring a selective organic layer. We use these features to construct a blood serum ionogram for Na^+, K^+, Ca^{2+} and Mg^{2+}, in an important step towards the development of a versatile, durable and mobile chemical or blood diagnostic tool. Combination of molecular simulations and classical DFT calculations show that the sensibility of the captor is magnified by the small size of the device. A specific response is obtained and the final device compares well with the existing sensors but with a much lower size.



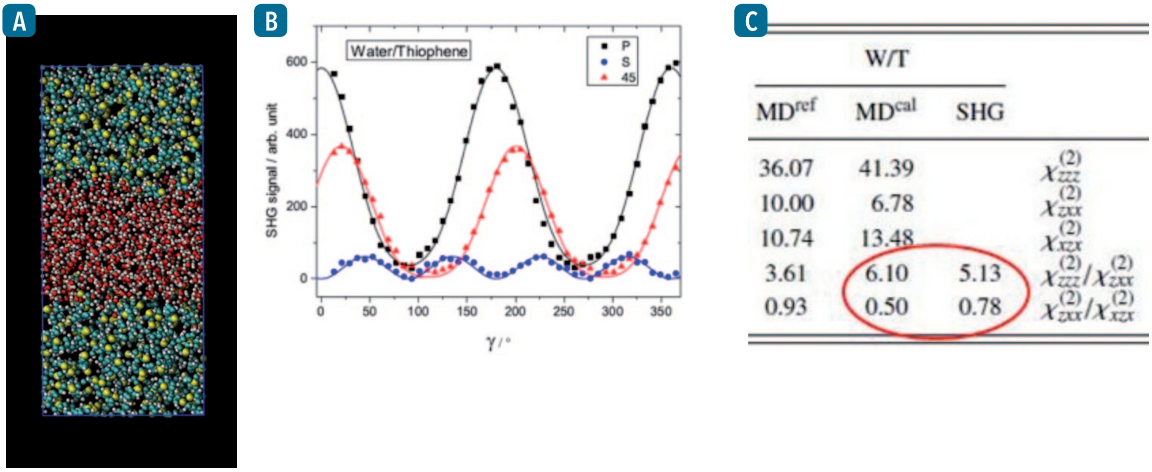
---

[1] Sivakumarasamy R., Hartkamp R., Siboulet B., Dufrêche J.-F., Nishiguchi K., Fujiwara A., Clement N. – **Selective Layer-Free Blood Serum Ionogram Based on Ion-Specific Interactions with a Nanotransistor.** – Nature Materials (2018) 17, 464-470

LIQUID/LIQUID INTERFACE OR INTERPHASE IN A SOLVENT EXTRACTION PROCESS

Girard Luc, Pham Thanh, Scoppola Ernesto, Dufrêche Jean-Francois, Fragneto Giovanna (ILL-Grenoble) and Diat Olivier

Among the many solvent extraction technologies, those used for metal recovering are quite challenging due to the poor solubility of inorganic ions in oils. Metal extraction thus requires the use of lipophilic extractant molecules to complex the cations and to solubilize the complex in the oil phase. In practice, there is a trade-off between selectivity, kinetics and efficiency, in keeping with energy cost constraints, enthalpic and entropic. Despite all the attention solvent extraction has received especially in studying the ion speciation on the aqueous side and the mesoscopic structuration in the oily part, however, the molecular structure of the liquid/liquid (LL) interface remains quite elusive and, as a result, the mechanisms of complexes (ion + extractant molecules + counterions) formation and transfer, that influence the kinetics of extraction, are not well understood. Ion-extraction can be referred to as a diffusion-limited or a reaction-limited process depending on how high is the energy barrier at the LL interface. To tackle this highly challenging problem, we buckle down by seeking for coherent structural information of the interface at the nanometer scale, at equilibrium first. The initial step was to use X-ray AND neutron reflectivity techniques (with a specific development of sample cells) to show the evolution of the interfacial structure and to determine the ion potentials at the LL interface[1]. In parallel, the second harmonic generation (SHG) signal was recorded from the LL interface during an ion transfer highlighting some intense intensity fluctuations. The SHG is indeed a very promising and specific technique to study LL interface static and dynamic evolution in a solvent extraction process. However, the quantification of this signal is not so simple and a deep analysis of the second order susceptibility components is required. A preliminary work with the LMCT has been dedicated to a molecular dynamic approach on a simple LL interface, without ligand molecules, to demonstrate how it is possible to correlate the interfacial structure and its evolution with the variation of the SHG signal - see figure[2]. This approach will be extended with ligands. Now, studies in progress are dedicated to the use of synthesized "chromophoric" extractant, as a useful probe for SHG and simulate via MD the interfacial structure (collaboration with the DEN department and then a theoretical development at the quantum level will be initiated with the support of CEA bottom-up program in collaboration with the LMCT team and ENS Paris.



	W/T		
MD^{ref}	MD^{cal}	SHG	
36.07	41.39		$\chi^{(2)}_{zzz}$
10.00	6.78		$\chi^{(2)}_{zxx}$
10.74	13.48		$\chi^{(2)}_{xzx}$
3.61	6.10	5.13	$\chi^{(2)}_{zzz}/\chi^{(2)}_{zxx}$
0.93	0.50	0.78	$\chi^{(2)}_{zxx}/\chi^{(2)}_{xzx}$

fig. **A** *side view of a MD simulation box at equilibrium of Thiophene/Water (T/W) interfaces.* **B** *Polarization curves obtained from T/W interface via SHG.* **C** *Comparison of the two second order susceptibilities components obtained from a calculation using the molecular distribution obtained from the MD simulation and those determined experimentally.*

---

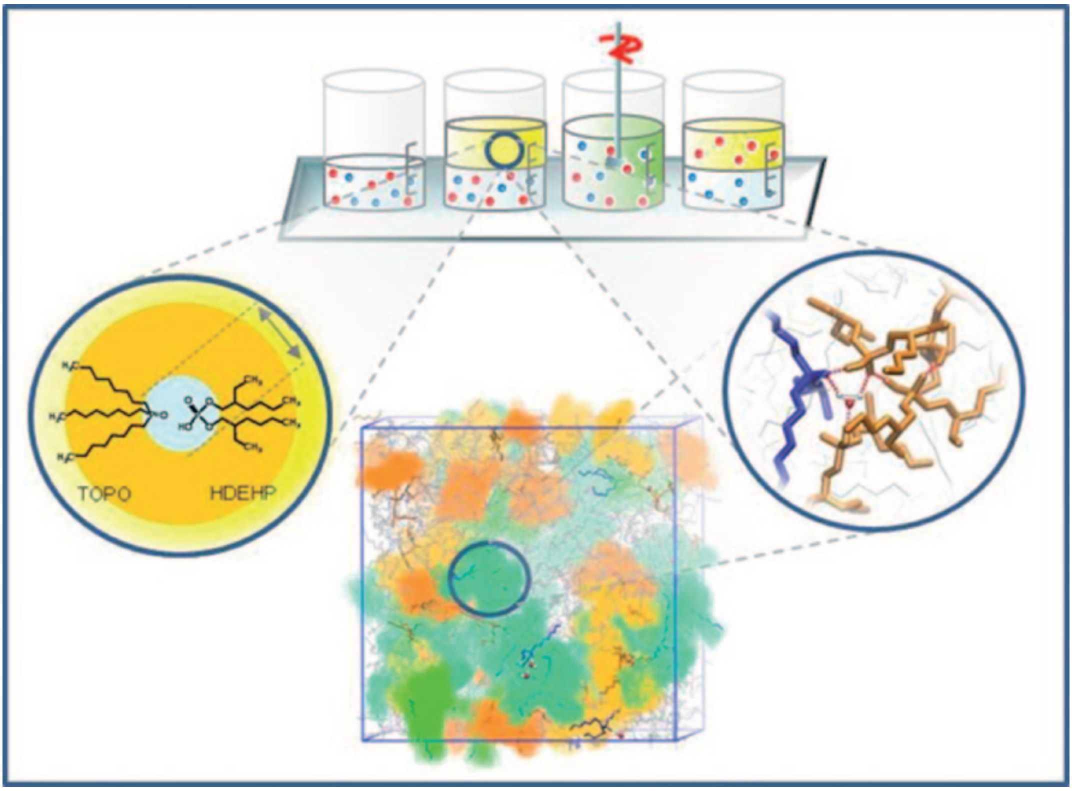
[1] Scoppola E., Watkins E.B., Campbell R.A., Konovalov O., Girard L., Dufrêche J-F., Ferru G., Fragneto G., Diat O. - **Solvent extraction: Structure of the liquid/liquid interface containing a diamide ligand** - Angewandte Chemie Int. ed. (2016) 55(32) 9326.

[2] Pham T.T., Jonchere A., Dufrêche J-F., Brevet P-F., Diat O. - **Analysis of the second harmonic generation signal from a liquid/air and liquid/liquid interface** - Journal of Chemical Physics (2017) 146, 144701.

ORIGIN OF SYNERGY IN HDEHP/TOPO SOLVENT EXTRACTION SYSTEM: AN INTRINSIC LIGANDS PROPERTY?

O. Pecheur, J. Rey, S. Dourdain, S. Pellet-Rostaing,
D. Guillaumont, P. Guilbaud, L. Berthon, M-C. Charbonnel (CEA-Marcoule), F. Testard (CEA-Saclay)

Among the proposed mechanisms to predict and understand synergism in solvent extraction, the possibility of a pre-organization of the mixture of extractant molecules has been considered. Whether involving synergistic aggregation as for solubilisation enhancement with reverse micelles, or favored molecular interaction between the extractant molecules, the evaluation of this hypothesis requires the characterization of the aggregates formed by the extractant molecules at different scales. We investigated the HDEHP/TOPO couple of extractant with methods going from vibrational spectroscopy, ESI-MS spectrometry to vapor pressure osmometry and neutron and X ray scattering to cover both molecular and supra molecular scales. These experimental methods were confronted to DFT calculations and molecular dynamics calculations allowing a rationalization of the results through the different scales[1]. Performed in the absence of any cation, this original study is expected to allow a de-correlateion of the mechanisms at the origin of synergy: it appears that no clear preorganization of the extractants can explain the synergy and therefore that the synergistic aggregation observed in the presence of cations is rather due to a chelation mechanism than to intrinsic properties of the extractant molecules.



---

[1] O. Pecheur, S. Dourdain, D. Guillaumont, J. Rey, P. Guilbaud, L. Berthon, M.C. Charbonnel, S. Pellet-Rostaing, F. Testard - **Synergism in HDEHP/TOPO liquid-liquid extraction system: an intrinsic ligands property?** - J. Phys. Chem. B (2016). 120, 10, 2817-2823.

HOW WATER AND IONS PROPERTIES IN NANOCONFINEMENT IMPACT THE EVOLUTION OF MESOPOROUS MATERIALS?

Diane Rebiscoul, Markus Baum, Samuel Tardif, Francois Rieutord (CEA-Grenoble), Kunyu Wang, Bertrand Siboulet, Jean-Francois Dufrêche

The prediction and the understanding of materials behavior regarding their interactions with aqueous solution in the fields of building, geochemistry, membranes, nuclear wastes… requires the use of modelling. Such modelling is based on thermodynamic models and rate laws. However, most of these materials are completely or partially nanoporous such as cementitious materials, geopolymers, biominerals, clay materials, secondary minerals, amorphous nanoporous alteration layer of glasses… They consist of a set of confined media having a complex form, filled with water and ions which for these thermodynamic models and rate laws are not validated. Indeed, the processes occurring in their porosity of few nanometers such as ions sorption, phase's precipitation, pore wall dissolution and dissolved species recondensation or electrolyte diffusion differ from that of dense and planar materials in contact with aqueous solution. Since this nanoporosity accounts for a non-negligible proportion of the total porosity of many of these systems, there is a real impact on their macroscopic behavior.

The main objective of this topic is to bring some fundamental data about the processes occuring in silica nanoconfinement. To reach this goal, we used an original approach, consisting in the use of electrolyte solutions having ions with various kosmotropic property XCl_2 (X = Ba, Ca, Mg) confined in model systems such as two parallel and planar silica surfaces spaced of few nm (nanochannels) and concave silica surfaces (highly ordered mesoporous silica materials) (PhD M. Baum). Using various characterization techniques such as Hard X-ray reflectivity, quasi-elastic neutron scattering, infrared spectroscopy and atomistic modelling (ICSM/LMCT), the water and ions behavior in these model confined silica systems[1] are determined and related to the processes driving the evolution of silica mesoporous materials in aqueous solutions *(Figure 1)*.

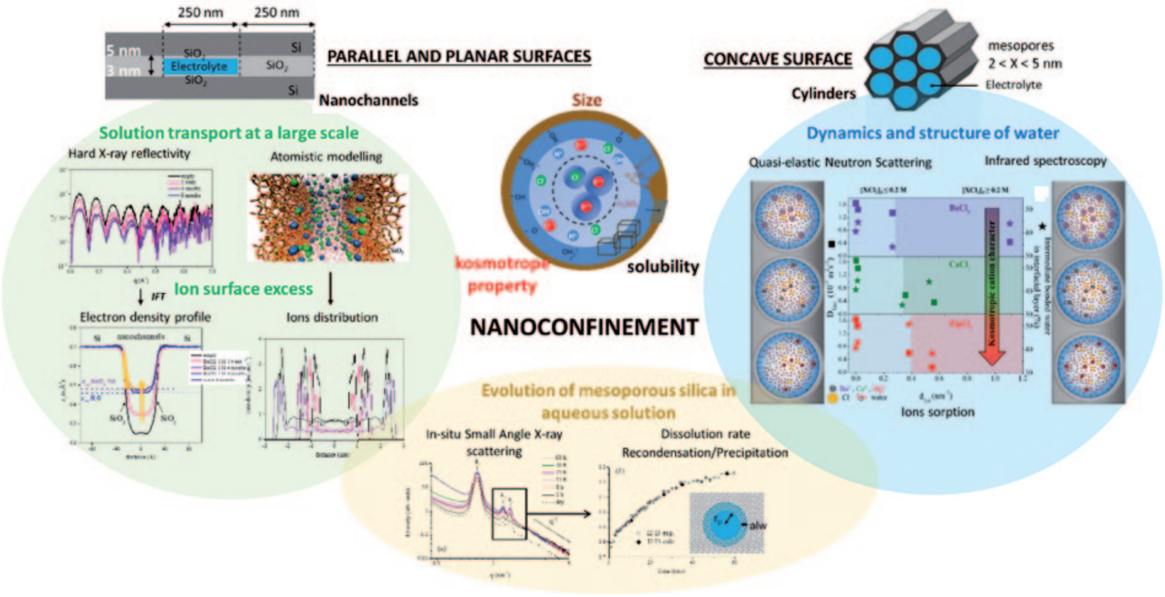


Figure 1: Scientific approach used to study the physical and chemical properties of nanoconfined water in presence of ions.

[1] Baum M., Rebiscoul D., Juranyi F., Rieutord F. – **Structural and Dynamical Properties of Water Confined in Highly Ordered Mesoporous Silica in the Presence of Electrolytes** – Journal of Physical Chemistry (2018) 122 (34), 19857-198.

STUDY OF CAVITATION PRODUCED IN NON-CLASSICAL CONDITIONS

L. Parizot, T. Chave, S. I. Nikitenko
H. Dutilleul, M.E Galvez, P. Da Costa (UPMC)

The acoustic cavitation generated by ultrasound is a renowned approach applied in various field of research ranging from the synthesis of nanomaterials to the treatment of wastewaters. Recently a new way to produce cavitation bubble, based on shock, has merged and is now under investigations and compared to ultrasonic cavitation. This innovative approach generates cavitation by mechanical impact of a piston on the water surface in a low pressure reactor as depicted in *Fig. 1*. [1]

The characterization of this reactor indicate that impact cavitation is different from ultrasonic cavitation mainly because of the multi-frequency pressure wave produced by the shock with pressure ranging from 20 mbar at the initial stage and up to 50 bars at the impact.

The most appropriate model to describe this phenomenon is the Water Hammer which gives a relation between the pressure at the impact, the speed of the piston and the fraction of gas thanks to the Joukovski's equation. Obtained results verify this linear relation in our domain of study. Moreover, the bubble visualization by fast camera gives us information onto the large diversity of bubble radius ranging from 0.01 to 2.8 mm depending on the height of the piston and initial pressure.

Besides this physical aspect, the chemical activity generated within this shock induced reactor was assessed by the measurement of HO• radicals using terephtalic acid dosimetry. Formation of HO• radicals was observed and even if the radical formation rates are fold lower than the ones obtained under ultrasonic irradiation, these results confirm the occurrence of the cavitation phenomenon under mechanical impact and for the first time the in situ generation of active species.[2]

Moreover, the impact intensity observed during each impact leads to very strong mechanical effects that would certainly be of great interest to enhance heterogeneous systems implying powdered catalysts for instance.

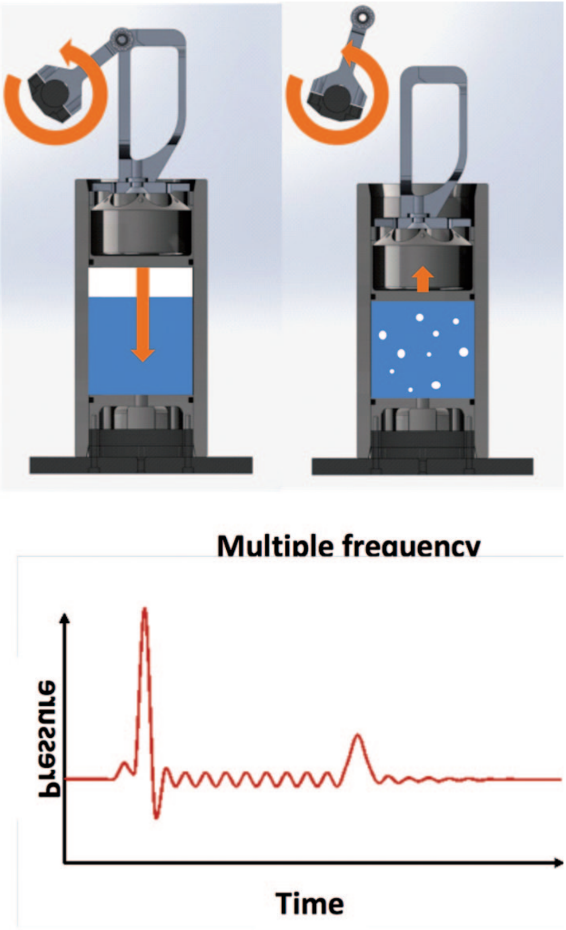


Fig. 1: Schematic representation of the shock induced reactor and the generated pressure wave within the liquid.

[1] Dutilleul H., Partaloglu A., Da Costa P., Galvez M.E. **Shock-induced cavitation as a way of accelerating phenol oxidation in aqueous media** - Chemical Engineering and Processing: Process Intensification, 112 (2017) 47-55.
[2] Parizot L., Dutilleul H., Galvez M.E., Chave T., Da Costa P., Nikitenko S. I. **Shocked-induced cavitation physical and chemical characterization**, Ultrasonics Sonochemistry, 2018 (ESS16 special issue – article in progress).

CHARACTERISATION OF THE PLASMA FORMED DURING ACOUSTIC CAVITATION IN WATER

R. Pflieger, R. Ji, T. Ouerhani, M. Virot, S.I. Nikitenko

Sonoluminescence (SL) is the emission of UV-visible light triggered by the violent collapse of microbubbles generated in liquids submitted to ultrasonic irradiation. This violent collapse leads indeed to extreme conditions in the bubbles (T>5000 K) which are the source for the sonochemical reactions, in particular through the formation of radicals (e.g. H• and HO• in water). Hence, a better understanding of the conditions reached in the bubbles would allow an optimization of the sonochemical reactions. These conditions are probed by measuring the SL spectrum by means of a spectrograph coupled to a CCD camera.

In well-chosen conditions, SL spectra bear emissions of excited species which can be fitted to estimate characteristic temperatures of the plasma.[1] For instance, emissions of NH* and OH* in ammonia solutions saturated with Ar correspond to vibrational temperatures of 8000 K (± 1000K) at 20 kHz (low frequency) and 12000 K (± 2000K) at 359 kHz (high frequency, HF).[2] Frequencies in between, so to say intermediate ones (~100 kHz), are poorly characterized. Spectroscopy of SL (Fig. 1) showed that they present intermediate properties and share for instance the ability of HF bubbles to dissociate O_2 and N_2 molecules.[3]

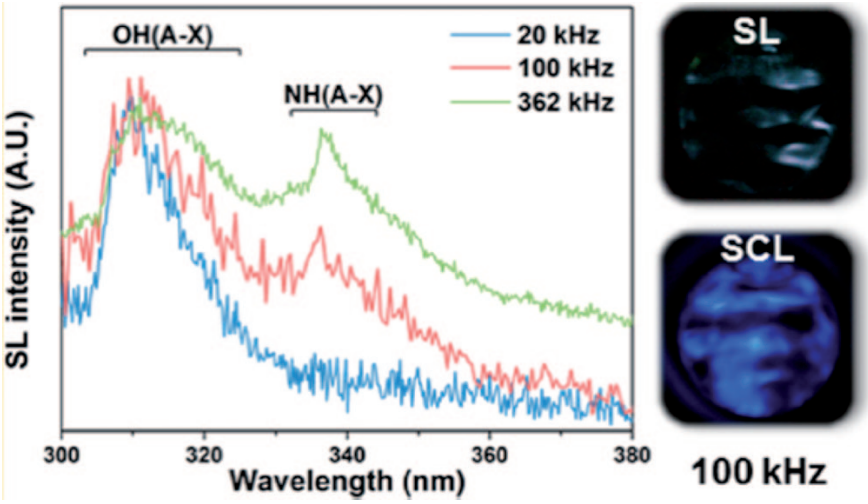


Fig. 1: Left: SL spectra of water submitted to 20 kHz (blue, 33 W), 100 kHz (red, 40 W) and 362 kHz (green, 43 W) at 18°C under Ar / 20 vol%N_2 flow. Right: photos of SL and sonochemiluminescence (SCL) at 100 kHz under Ar.

Acquisition of spectra with higher spectral resolution and their simulation with existing spectroscopy softwares allowed us to underline the lacks of existing softwares. In particular they are not adapted to high pressure plasmas like the one formed in cavitation bubbles.[1] In such a case, more broadening sources of the emissions lines have to be taken into account, in particular broadening by neighboring charged species (so-called Stark effects). The development of an approach to better characterize such high-pressure plasmas is the core of a collaboration with the Jean Lamour Institute in Nancy.[4]

[1] S. I. Nikitenko, R. Pflieger, **Toward a new paradigm for sonochemistry: Short review on nonequilibrium plasma observations by means of MBSL spectroscopy in aqueous solutions**, Ultrasonics Sonochemistry, 35 (2017) 623-630.
[2] R. Pflieger, T. Ouerhani, T. Belmonte, S.I. Nikitenko, **Use of $NH(A^3\Pi-X^3\Sigma^-)$ sonoluminescence for diagnostics of nonequilibrium plasma produced by multibubble cavitation**, Physical Chemistry Chemical Physics, 19 (2017) 26272-26279.
[3] R. Ji, R. Pflieger, M. Virot, S.I. Nikitenko, **Multibubble Sonochemistry and Sonoluminescence at 100 kHz: The Missing Link between Low- and High-Frequency Ultrasound**, Journal of Physical Chemistry B, 122 (2018) 6989-6994.
[4] T. Belmonte, H. Kabbara, C. Noel, R. Pflieger, **Analysis of Zn I emission lines observed during a spark discharge in liquid nitrogen for zinc nanosheet synthesis**, Plasma Sources Science & Technology, 27 (2018) 074004.

IN SITU ESEM STUDY OF THE SOLID STATE REACTIVITY OF COATINGS AND THIN FILMS

Podor R., Lautru J., Ravaux J. – Song B., Cooper S. J. Brandon Nigel P. (Imperial College) – Teisseire J., Gozhyk I. (UMR 125 CNRS/Saint Gobain) - Jupille J., Lazzari R. (INSP, France)

During the last few years, an increasing research effort has been dedicated to the solid-state dewetting of metallic thin films. It is identified as a potential way to produce at will metallic structures for numerous applications but it can also be an unexpected process for specific applications. However, for each application, the control of the morphology obtained through dewetting is crucial. In this respect, the understanding of the physical phenomena driving dewetting in polycristalline films has been greatly improved. The role of grains has been underlined[1], new diffusion pathways have been identified and the role of crystalline orientation in anisotropic materials has been explored. In the present study, the dewetting of metallic thin layers will be investigated through in situ and real time HT-ESEM.

- Solid-state dewetting of polycrystalline silver thin films was investigated in different annealing atmospheres: secondary vacuum or oxygen-rich (partial pressure 400 Pa) environment *(Fig. 1)*. A model where oxygen plays a key role is proposed to explain the very different observed morphologies; oxygen favours hole creation and isotropic hole propagation as well as grain selection. But, whatever the atmosphere, dewetting does not proceed through the propagation of a rim but instead involves the growth of specific grains and shrinkage of others[2].
- The isothermal dewetting behaviour of 40 nm Ni thin film on the yttria-stabilized zirconia substrate has been investigated with a controlled gas mixture *(Fig. 2)*[3]. Indeed, during the fuel cell operation, the solid-state dewetting of the nickel leads to significant changes in electrode morphology that deteriorates its electrochemical performances. The material degradation was observed and quantified though the determination of Triple Phase Boundary density. The coupling of morphological statistics and electrochemical performance degradation enabled qualitative discussion of the observed processes.

These new developments will be later used to study the lifetime limits of coatings and thin films used in the nuclear industry (UO_2 thin films, coatings on superalloys).

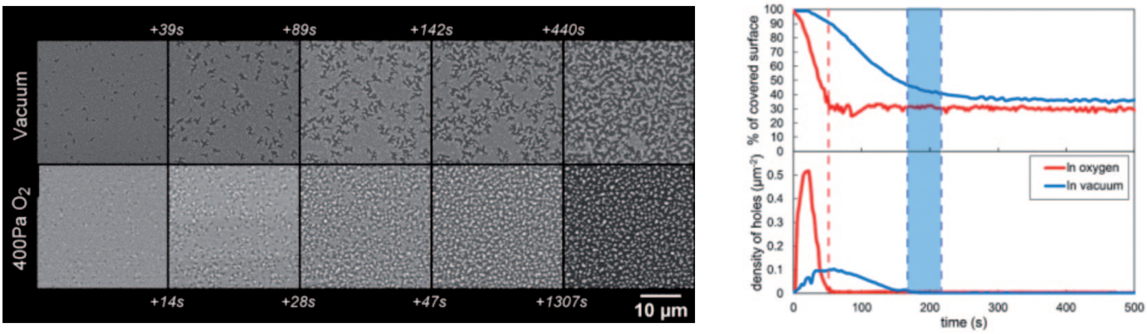


Fig. 1. (a) Snapshots of a 40 nm silver layer dewetting in vacuum and 400Pa O_2 at 350 °C. (b) Data extracted from image series.

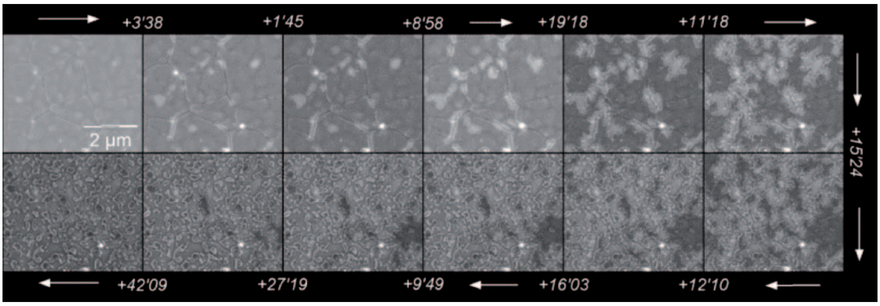


Fig. 2. Snapshots of a 40 nm silver layer dewetting in the controlled gas mixture at 575°C. The direction of the arrows indicates increasing time scale.

---

[1] Jacquet P. et al - **Grain growth : key in understanding silver solid-state dewetting** – Scripta Materialia (2016) 115, 128-132

[2] Jacquet P. et al - **On the influence of oxygen on solid-state dewetting of polycristalline silver thin films** – Acta Materialia (2018) 143, 281-290.

[3] Song B. et al - **In-situ imaging and microstructural-electrochemical quantification of Ni dewetting in novel 2D Ni-YSZ electrodes for solid oxide fuel cells** – Submitted

SrO SURFACE PRECIPITATION ON SOFC CATHODES

*Podor Renaud, Niania Mathew *, Britton T. Ben *, Skinner Stephen J. * and Kilner John A. **
** Department of Materials, Imperial College London, London SW7 2AZ, UK*

Solid oxide fuel cells (SOFC) convert gaseous fuels, e.g. H_2, into electricity through an electrochemical process. Their conversion efficiencies are not limited by the Carnot cycle and pollution levels in the exhaust gas are significantly lower than that of traditional technologies. SOFC cathode materials require a very precise balance of material properties in order to function at operating temperatures (~600 – 800°C). A number of systems fulfil the requirements, but there are numerous challenges these materials face during manufacture and operation. Of particularly concern is the negative impact secondary phase formation at the surface has on the reduction of oxygen. In a large number of perovskite systems used for SOFC cathodes the A-site is occupied by lanthanum (La^{3+}) and it is often doped with strontium (Sr^{2+}) to introduce oxygen vacancies, which generates ionic conductivity, and electronic species leading to mixed conductivity, essential for operation as an SOFC cathode. However, due to the particular crystal-chemistry of these materials, surface precipitation of SrO is favored and this yields to a continuous degradation of the cathodic material.

Continuous surface precipitation was observed on polished $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) ceramics using high temperature environmental scanning electron microscopy (HT-ESEM) up to 1000°C[1]. Several experiments were performed under different atmospheres: vacuum, 300 Pa O_2, H_2O and air. A characteristic image series recorded under water vapor is reported on Fig. 1. The surface precipitation phenomenon can be clearly observed. The composition of the precipitates determined from the X-ray maps recorded on samples cooled at room temperature is SrO. The evolution of the surface occurs in three distinct stages: (1) rapid growth of precipitates on grain boundaries, at defect points as well as at the centre of the grains, (2) agglomeration of the precipitates due to surface transport phenomena and (3) Continuous coarsening during the heat treatment. It is clear that at the beginning the precipitation process, the SrO precipitates appear to grow with crystallographic direction as, within each grain, they tend to orientate themselves in a similar direction. It is also clear that the initiation of the SrO precipitation and the density of the precipitates depend on the LSCF grain orientations. When comparing the EBSD maps with the HT-ESEM images *(Fig. 2a)*, it is obvious that the precipitation process and grain growth are directly linked with the grain orientations and presence of twinning inside the grains *(Fig. 2bcd)*. Twin planes exist in many grains. Average twin plane width measured across a particular grain *(Fig. 2b)* is very close to the average particle width (measured centre to centre). This result suggests that twin planes in this orientation are fast diffusion pathways. Other grains display homogenous precipitate growth across the grain surface and it is predicted that knowledge of the twin habit plane can be used to describe why these grain orientations display different behavior.

From these new data sets, a very precise and original description of the surface precipitation has been proposed[2].

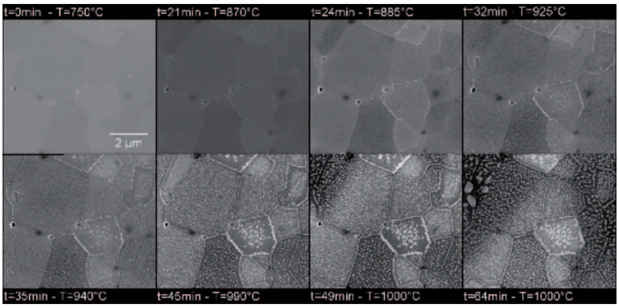


Fig. 1. HT-ESEM micrographs of a SrO precipitation on a polished $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ surface observed at high temperature in the ESEM under 300Pa of water vapor.

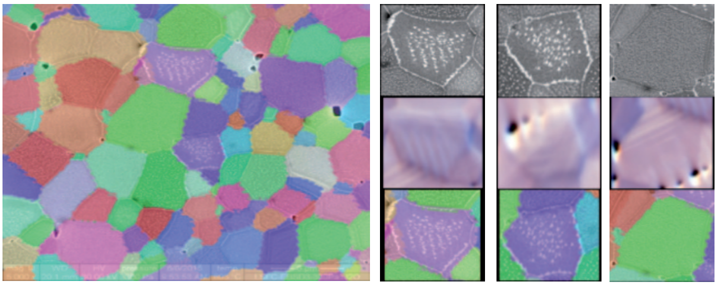


Fig. 2a) EBSD data matched with HT-ESEM data. 2bcd) Correlations between the HT-ESEM, Argus and EBSD images determined for 3 specific grains.

[1] Niania M. et al - **in-situ surface analysis of SOFC cathode degradation using high temperature environmental scanning electron microscopy** - ECS Transactions (2015) 68(1), 665-670.

[2] Niania M. et al - **In-situ study of strontium segregation in LSCF in ambient atmospheres using HT-ESEM** - Journal of Materials Chemistry A (2018) 6, 14120-14135.

CONTRIBUTION OF IN SITU HIGH TEMPERATURE ESEM TO THE STUDY OF MATERIALS' OXYDATION

Podor R., Lautru J., Ravaux J., Odorico M. – Perez T. Mathieu S. (Univ. Lorraine) - Mehedi Hassan Al., Jourdain V. (L2C, Montpellier) – Gasparrini C., Lee W. (Imperial College, UK)

The Environmental Scanning Electron Microscope associated with a high temperature device is a tool that is particularly well adapted to the study of materials' oxidation. The high temperature behavior of several materials has been studied with different research teams over France and Europe. These materials are as different as uranium carbide[1], simplified Ni-base alloys[2] and carbon nanotubes[3] that can be respectively classified as 3D, 2D and 1D materials regarding their oxidation behavior.

- UC exhibits a very specific oxidation behavior that is characterized by an exponential swelling followed by a fast sample expansion *(Fig. 1)*.
- Simplified Ni-base alloys are oxidized according to a parabolic law. The growth of a Cr_2O_3 surface layer containing $MnCr_2O_4$ spinel crystals has been characterized *(Fig. 2)*.
- We have determined that the oxidation of single wall carbon nanotubes begins locally probably where structural defaults are present *(Fig. 3)*.

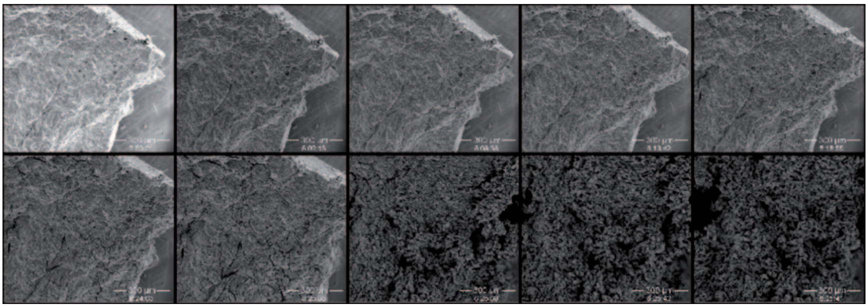


Fig. 1. Image series showing the UC oxidation at T=575°C, P_{O2}=10Pa.

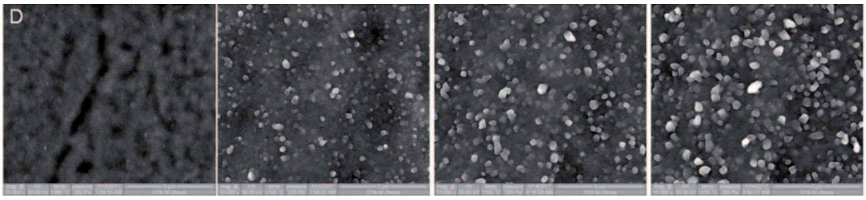


Fig. 2. Image series showing the formation of $MnCr_2O_4$ spinel crystals during the oxidation of a Ni-30Cr + 1.5wt%Mn alloy at T=1000°C, P_{air}=200Pa.

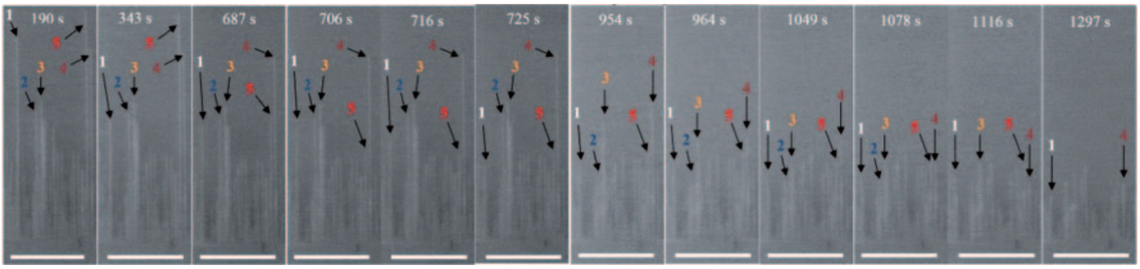


Fig. 3. Image series showing the oxidation of SWCNT at T=480°C, P_{O2}=11Pa

[1] Gasparrini C. et al - **Oxidation of UC: An in situ high temperature environmental scanning electron microscopy study** –Journal of Nuclear Materials (2017) 494 127-137

[2] Perez T. et al - **In situ oxide growth characterization of Mn-containing Ni-25Cr (wt%) model alloys at 1050 °C** –Oxidation of Metals (2018) 89(5-6) 781-795

[3] Mehedi H.A. et al - **Increased chemical reactivity of single-walled carbon nanotubes on oxide substrates: In situ imaging and effect of electron and laser irradiations** –Nano Research (2016) 9(2) 517-529

DEVELOPMENT OF NEW METHODS TO STUDY THE DISSOLUTION / CORROSION OF MATERIALS

Podor Renaud, Szekneckt Stéphanie,Le Goff Xavier, Favrichon Julien, Odorico Michael, Claparède Laurent, Cordara Théo, Dacheux Nicolas

The understanding of chemical durability of spent nuclear fuels is a key issue to improve their reprocessing. The influence of well identified parameters such as temperature, acidity and the composition of the dissolution medium were already examined using batch experiments ledding to a multiparametric expression of the macroscopic dissolution rate. However, the effect of other parameters associated with the microstructure of the dense material, such as crystallite size, grain size, porosity and homogeneity on the dissolution process are less studied, mainly due to the fact that their impact leads to local modifications of the dissolution rate, which are hardly evidenced without specific methods. Generally, the use of surface characterization techniques as atomic force microscopy (AFM), environmental scanning electron microscopy (ESEM), grazing incidence X-Ray Reflectivity (GI-XRR), and light optical microscopy methods, allows tracking the microstructural evolution of the solid/solution interface, identifying various rate contributors and even determining local dissolution rates[1].

In this context, a specific effort was made at the ICSM in order to take advantage of the capabilities of the ESEM. The microstructural evolution of the surface of a ceramic was monitored in operando by recording series of images of a same zone. After a first dissolution step, the sample was simply rinsed with deionized water to avoid the presence of acid vapor in the ESEM chamber and to stop the dissolution. Then, ESEM micrographs were recorded under environmental conditions, which preserved the hydration state of the sample surface. Then, sample was placed in the dissolution medium for another step of dissolution and images were regularly recorded *(Fig. 1a)*. In parallel, a software is under development to extract semi-automatically the data of interest from the series of images (number and size of corrosion pits, location of the defects, etc).

The 3D reconstruction of the surface of the sample can also be achieved from tilted ESEM images *(Fig. 1b)* using the MEX software[2]. After validation of this method by comparing reconstructed surfaces with AFM images of the same zone, 3D height map series are recorded to characterize precisely the local volume of dissolved matter and to evaluate local dissolution rates.

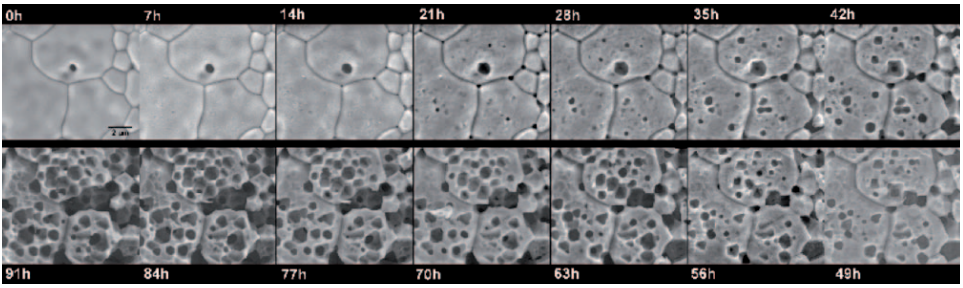


Fig. 1: ESEM observation of (U, Th)O_2 dissolution in 2M HNO_3 at 90°C b) 3D reconstruction of the sample surface using tilted ESEM image series and MEX Software.

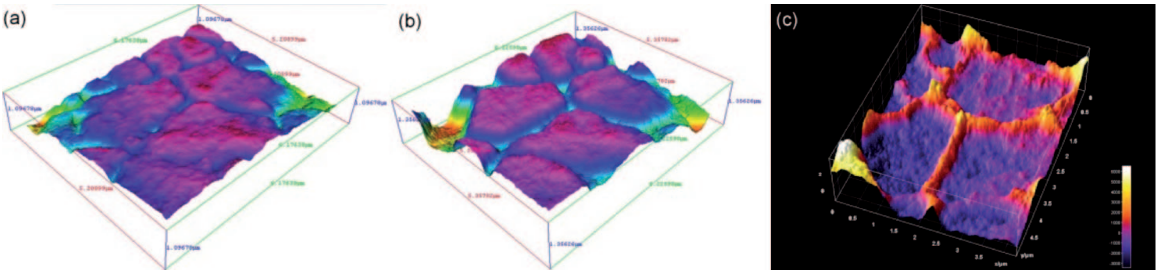


Fig. 2. a, b)3D reconstruction of the sample surface using tilted ESEM image series and MEX Software after 645 h (a) and 287 h (c) of dissolution. c) 3D view of the difference of these surfaces.

---

[1] Szenknect S. et al. - **Monitoring the microstructural evolution of Nd2Zr2O7 pyrochlore during dissolution; implications regarding the evaluation of the chemical stability** – J. of Nuclear Materials (2017) 496, 97-108.

[2] Ji R. et al. - **Controlled «Golf Ball Shape» structuring of Mg surface under acoustic cavitation** - Ultrasonics Sonochemistry (2018) 40(A), 30-40.

CELDI : A NEW TOOL FOR THE DIRECT STUDY OF MATERIALS' CORROSION AND DISSOLUTION

Salacroup Johann, Podor Renaud, Brau Henri-Pierre, Ravaux Johann,
Candeias Antoine, Szekneckt Stéphanie

In numerous scientific fields such as life, materials and Earth sciences, or quality controls of industrial processes, there is a growing interest for the direct observation - at the submicroscopic scale - of processes occurring at solid / liquid and solid / gas interfaces. So far, only few experimental cells were designed to address this challenging issue. Most of them are devoted to a specific use in Transmission Electron Microscopy (TEM) and are not suitable for observation of large (or thick) samples and the other cells designed to be used in a Scanning Electron Microscope (SEM) chamber do not allow fluid flow.

To address this issue, a dedicated device was developed according to the following requirements:

1) The sample holder must be suitable for large samples.
2) The device must allow the renewal of the fluid through a continuous flow.
3) The device should be sufficiently efficient and secure to be used in any type of conventional SEM.
4) The device should be easy to implement and user friendly. An easy-to-use tool *(Fig. 1)* was recently tested and patented[1]. This project has been supported by the SATT AxLR. It will be commercialized by the NewTEC company located in Nimes during the first months of 2019.

For the proof of concept, it was used to perform in situ experiments during which series of images was recorded with a SEM, using the back scattered electron detector, high vacuum in the SEM chamber and e-beam acceleration voltage of 30kV. Several images recorded in situ during the dissolution of a $Ce_{0.2}Nd_{0.8}O_2$ ceramic are reported on Fig. 2a. The time between two images can be as low as 20s and the achieved resolution is in the order of a few tens of nanometers. From the image series, local parameters that are characteristic of the material's dissolution can be easily extracted *(Fig. 2b)*. The growth of NaCl crystals was also observed directly from a supersaturated solution. Experiments that last many hours were performed: the liquid system that is inside the stage always remained isolated from the SEM chamber during the complete experiment. 1M acidic and 1M basic liquids can be used[2].

The CelDi tool will be useful for the study of the dissolution and corrosion of materials. It also offers interesting opportunities for the direct observation of coating formation from liquids and gases. It will be possible to integrate a specific and fast BSE detector in combination with the stage, and work is under progress to develop automatized image processing through dedicated software.

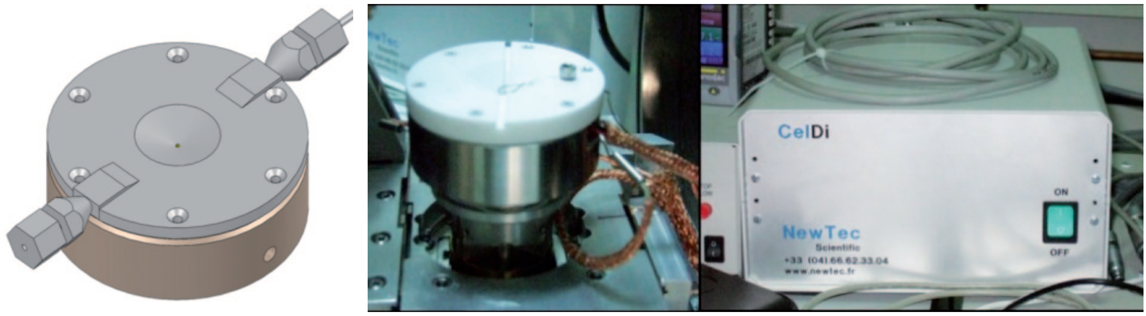


Fig. 1: Artist view of the CelDi tool and pictures of the tool that has been built.

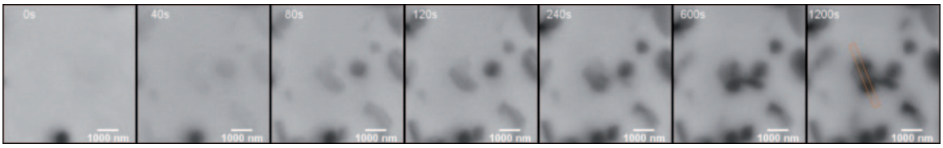
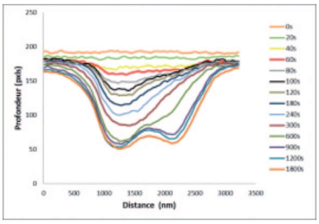


Fig. 2. a) Image series recorded during the dissolution of a $Ce_{0.2}Nd_{0.8}O_2$ ceramic in HCl 0.1M for 1200s. c) Height profile series extracted from the image series along the orange line drawn in the picture '1200s'.



---

[1] Podor R. et al. - **Cellule de suivi de réaction solide-liquide ou solide-gaz pour microscope électronique à balayage** - Patent n° FR 15 59465 (05/10/2015)

[2] Salacroup J. et al. - **CelDi: Development of an advanced solid / fluid reaction stage for SEM** – Microscopy and Microanalysis (2016) 22(S5), 76-77.

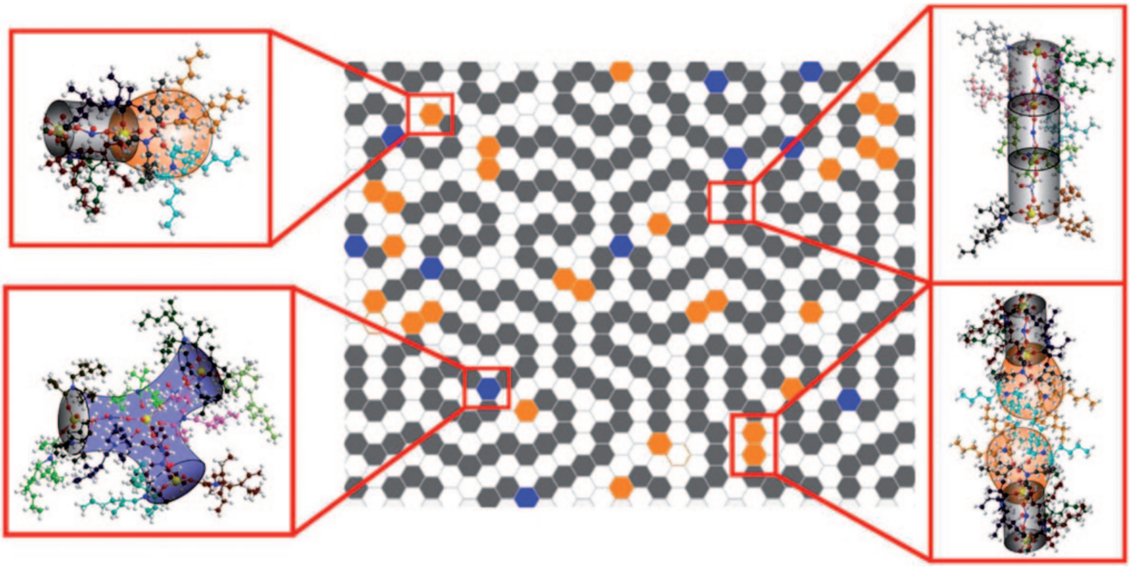
A MINIMAL THERMODYNAMIC MODEL PREDICTING DIRECT AND REVERSE GIANT MICLLE VISCOSITY

Maximilian Pleines, Th. Zemb, (ICSM)- Jean Duhamet , W. Kunz (Université de Regensburg)

The viscosity increase of the organic phase when liquid-liquid-extraction processes are intensified in order to extract more metal per acid effluent causes difficulties for processes on industrial scale. We have analyzed this problem for the example of the family of N,N-dialkylamides with different topologies of the hydrocarbon chain in presence of uranyl experimentally.

We present a minimal model present at nanoscale based on contact-points, end-caps and rigid w/o cylinder coexistence *(see fig.1)* that requires only measurable input parameters such as spontaneous curvature and chain flexibility allows to rationalize all the experimental values observed. Based on modeling the phenomena on molecular, mesoscopic and macroscopic scale, we predict qualitative trends in viscosity variation observed when cation content is increased. The model explains why some molecules behave "better" than others and the moderate effect of diluent formulation[1]. This new model is a further step towards knowledge-based formulation of extracting microemulsions with moderate viscosity increase.

Surprisingly, the model also applies in the o/w case: in the domain of the and body care, the viscosity increase linked to additives has to be increased as much as possible with low solute concentration. Instead of an increase that should be avoided, a viscosity peak is obtained and searched for: our model initially tailored for hydrometallurgy appeared to be robust enough to predict the variation of the viscosity peak as well with electrolytes or fragrances[2]. Moreover, aqueous phase instability is important when detergents are combined in formulation for laundry. In the case of nonionic surfactants with different branching of the chains, the same model explains for the first time quantitatively the variation of temperature of usage in detergency for molecules that are isomers in branching of the alkyl chain only[3].



[1] Pleines M., Hahn M., Duhamet J. and Zemb T. ; **A minimal model leading towards a new formulation principle for extracting microemulsions** ;J. of surfactants and detergents (2018) in press

[2] Pleines M. et al. **Prediction of the viscosity peak of giant micelles in the presence of salt and fragrances**, submitted (submitted September 2018)

[3] Pleines M., Kunz W. and Zemb T. ;**Understanding and predicting of the clouding Phenomenon by Spontaneous and Effective Packing concepts** (submitted August 2018)

INTERNATIONAL PROJECTS

PROJECT: RARE EARTH EXTRACTION AND RECYCLING WITH LOW HARMFUL EMISSIONS (2013-2018)

P.I.: Thomas Zemb (Marcoule), co-P.I. : Jean-Christophe Gabriel (Grenoble)
Scientific Advisor: Helmuth Möhwald, Secretary: Aline Leprou-Taconet

Aim of the project: recycling rare earth elements (REE) is a matter of strategic independence for Europe, hence to urgently find processes taking better account of environmental and economic issues. Currently *THERE IS NO SUCH INDUSTRIAL PROCESS AVAILABLE*[1] and there is no waste recycling for rare earth elements at all. Moreover, 97% of the mining operations are performed in China, hence representing a major Damocles' Sword for the rest of the world's economy.

Our objective is on one hand to develop the fundamental understanding involved in the processing complex fluids (both experimental and theoretical) and on the other hand to use predictive modelling, accelerated determination of phase diagrams as well as free energies of transfer in order to be able to develop new, cost effective and environmentally friendly REE recycling processes.

We will achieve this:

(WORK-PACKAGE 1) by enabling, for the first time ever, a fast and efficient measurement of free energy of mass transfer of five to ten elements between an aqueous solution and a water-poor microemulsion. Thus, it will be possible to explore and master an extensive number of process formulations;

(WORK-PACKAGE 2) develop predictive models of ion liquid-liquid separation including the effect of long-range interactions between metal cations and micelles;

(WORK-PACKAGE 3) by using the experimental results and prediction tools developed, we will design an advanced & environmentally friendly process formulations;

(WORK-PACKAGE 4) by enhancing the extraction kinetics and selectivity, by implementing a new, innovative and selectively triggered triggering cation exchange process step.

Furthermore, this new understanding of mechanisms involved in selective ion transfer should be applicable to optimize knowledge-based processes that are economically, ecologically and sociologically acceptable to other unresolved problems such as heavy metals, hormones, or drug contamination in drinkable water as well as open new recycling possibilities and pave the way to economic recovery of metals from a very rapidly growing "mine", i.e. the diverse metal containing "wastes" generated by used Li-ion batteries, super-capacitors, wind turbines, supported catalysts and fuel cells.

The group actively involved in the REE-CYCLE project (November 2016 from top, left to right): J. Theisen, M. Bley, S. Gourdin, Alla Malinennko, J.-F. Dufrêche, M. Spadina, O. Diat, S. Pellet-Rostaing, M. Duvail, C. Penisson, R. Laucournet, D. Meyer, J. Duhamet, A. Leprou, S. Charton, D. Alpe-Conchyand in the first row: Helmuth Möhwald, Thomas Zemb (Principal investigator) and Jean-Christophe P. Gabriel (co-Principal Investigator)

---

[1] European Union's 7th Framework Program (FP/2007-2013)/ERC Grant Agreement N° [320915] "REE-CYCLE" from proposal submitted by Thomas Zemb and Jean-Christophe Gabriel in February 2012.

EN MÉMOIRE DU PROFESSEUR HELMUT MÖHWALD

Helmuth Möhwald, Pr Dr honoris causa de Montpellier, Prix Humbold Gay Lussac en Chimie Séparative, était membre du Comité d'Orientation Scientifique de Balard et a présidé le dernier « visiting committee » du CEA consacré à la Chimie en 2009.

Retraité de sa fonction de Directeur-fondateur de l'Institut Max Planck « Colloïdes et Interfaces » de Potsdam depuis février 2017, Helmuth Möhwald était actif à temps partiel à Marcoule et à Grenoble sur le projet Européen de recyclage de terres rares « REE-cycle » (action transverse CEA-DRF/DEN/DRT). Il était membre du conseil scientifique du labex Chemisyst de Montpellier ainsi que du Labex CSC de Strasbourg.

Ses travaux personnels dans l'auto-assemblage sur des surfaces, de l'ordre de 500 articles et cinquante brevets, sont cités plus de dix mille fois par an dans le Web of Science. La partie « engineering » de ses travaux porte sur la lubrification dans l'espace et le transport des radicaux en cristaux liquides. Il restera dans l'Histoire des Nanosciences comme ayant été l'unificateur des équations d'état en 2D et 3D des mélanges de lipides et de polymères. On lui doit aussi la méthode de dépôt de monocouches de charges alternées sur des surfaces (Layer-by-Layer) qui ont conduit à de nombreuses applications allant de la pharmaco-technique à la protection auto-réparatrice contre la corrosion.

Il a été un éditeur-fondateur de la revue ACS-nano, qui s'est hissée très vite dans les dix meilleurs journaux généralistes et le trio de tête en nanosciences. Depuis 2009, il venait régulièrement comme lauréat Humboldt-Gay Lussac et ensuite comme conseiller scientifique actif à l'ICSM pour travailler sur la modélisation d'expériences d'extraction liquide-liquide par micro-émulsions et diriger des étudiants à l'ICSM à Marcoule, la dernière fois en novembre 2017.

La «life-time Awards colloïdes et interfaces», qui est attribuée tous les trois ans sur nomination ouverte internationale, a été votée en décembre dernier et lui a été remise lors du congrès mondial IACIS à titre posthume à Rotterdam en mai dernier.

WORK-PACKAGE 1
JEAN-CHRISTOPHE GABRIEL

A NEW FAST REAL-TIME AND ON-LINE ANALYTIC TOOL TO DETERMINE PHASE DIAGRAMS AND ION EQUILIBRIA

With Johannes Theisen, Christophe Penisson, Asmae El Mangaar and Jean-Christophe P. Gabriel in Grenoble; Julien Rey, Véronique Dubois, Jean Duhamet in Marcoule.

We have developed a mini-fluidic device (fluxes with a few ml/hour) containing a membrane and allowing exchange between phases of known concentrations varying slowly with time. This work included some research on nanoporous materials as potential membrane[2]. Real-time variation of pH, temperature, solvent's chemical activity coefficient via vapour pressure measured by infrared adsorption as well as the composition for up to five rare earths together with a background cation (iron) allow determination of the free energy of transfer. The device is shown in figure 1 and a typical result obtained from time-dependant X-ray fluorescence analysis of the flow out is shown in figure 2.

A "competition experiment" is performed with five rare earths in the presence of excess iron in the water phase containing nitric acid. The outgoing solvent phase is analysed by X-ray fluorescence in parallel with the output water phase. Constrained fitting of the XRF data allow an evaluation of the free energy of transfer. One equilibrium data point in a phase diagram per hour can be investigated using 10-100 microliter/mn flow rates[3].

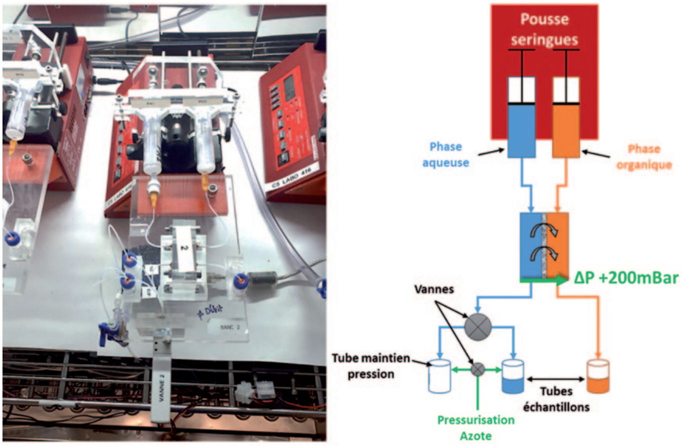


Figure 1: the first PMMA based microfluidic card with cation exchange through a membrane, and designed for real time experiment and on-line analysis of ion content and solvent activity: channel diameter 0.2 mm, first successful systematic usage in May 2018 (source Master report Asmae El Mangaar - August 2018).

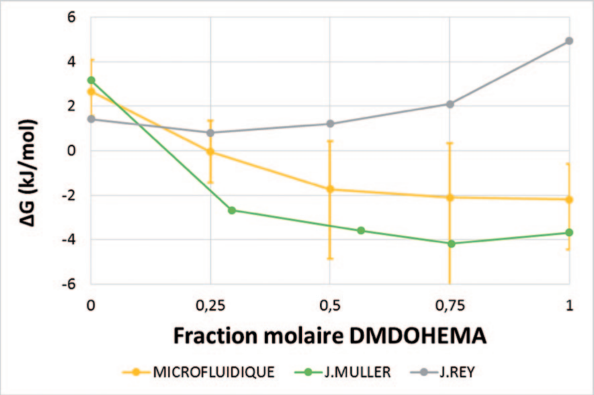


*Figure 2: Confirmation by microfluidics of a colloidal synergy term of the order of 2KbT (*10 in distribution coefficient for a mole-fraction of 0.5 due to the entropic origin. Data obtained in a few hours by microfluidics are compared to the experiments by Julien Rey using a classical batch method at lower pH and the results obtained in 3M Lithium nitrate to screen all effects linked to electrostatic charges by J. Muller (source: phD of Christophe Penisson, Grenoble 2018)*

---

[2] Davidson, P., Penisson, C. , Doru, C. , Gabriel, J.C.P. **Isotropic, nematic, and lamellar phases in colloidal suspensions of nanosheets.** Proc. National. Acad. Sc. 201802692 (2018).

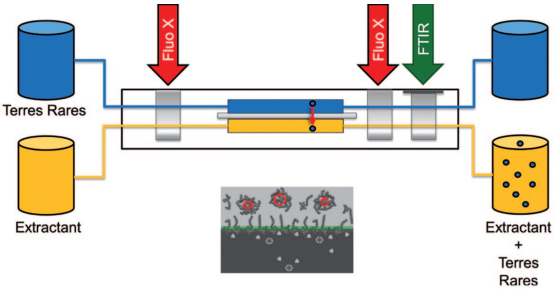
[3] Johannes Theisen, Christophe Penisson, Julien Rey, Thomas Zemb, Jean Duhamet and Jean-Christophe P. Gabriel,**" Effects of Porous Media on Extraction Kinetics: Is the Membrane Really a Limiting Factor"**,submitted Oct. 2018.

WORK-PACKAGE 1
JEAN-CHRISTOPHE GABRIEL

ON-LINE MEASUREMENT OF ELECTROLYTE EQUILIBRIA AND SOLVENT ACTIVITY DURING LIQUID-LIQUID EXTRACTION

With Johannes Theisen, Christophe Penisson, in Grenoble; Jean Duhamet and Thomas Zemb in Marcoule.
In collaboration with Boris Mizaikoff (Ulm Univ.)

Quantitative determination the free energy of transfer of species between water and solvent by microfluidics require to measure in situ at entry and at exit of the microfluidic device (as shown in the figure to the left) of the concentration of ions and of the solvent activity. The later is measured by integrated hollow waveguide FTIR[4]. Electrolyte concentrations (as rare earths and iron cations) are obtained via X-ray fluorescence, a non-destructive method that allows routinely determining concentrations as mM/l present on a surface that is illuminated by a collimated X-ray source. We have developed special algorithm of the collected data containing superposed adsorbtion lines that take into account the conservation of total number of species between input and output. This allows, for the first time, to determine the cation distribution factor and hence free energy of transfer with a precision of a few tenths of kJ/Mole[5].



In extraction processes, electrolyte up-take or stripping is always associated to reorganisation of the aggregates of complexing molecules present in the solvent phase. A general model free measurement of this effect is the determination of solvent's vapour pressure. The device *(figure 2)* is able to detect variations down to the percent of typical solvent activity (via Gibbes-Duhem relations)[6,7].

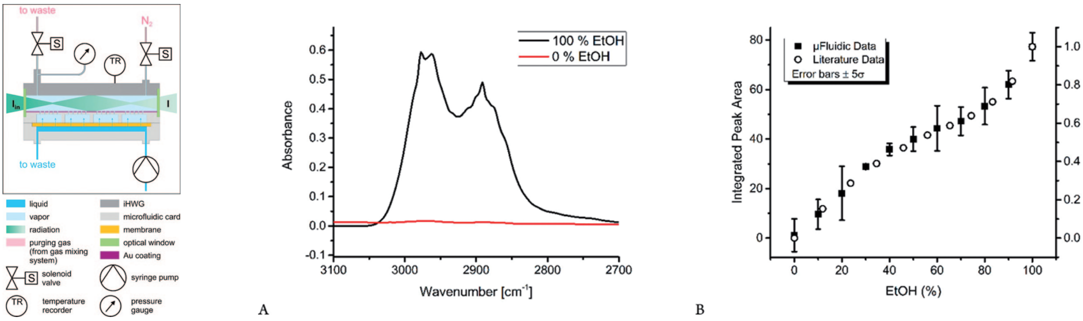


Figure 2 (left side): principle of operation of the on-line measurement of solvent activity by IR adsorption (middle): Absorbance signal obtained for 100% ethanol and 0% ethanol (right: values obtained for the ethanol activity in the vapour phase in equilibrium with ethanol/water mixtures: comparison of the values measured and obtained by head-space chromatography. Note that these values can also be obtained via molecular dynamics[8].

[4] Patent application EP17198247.3, **Apparatus for the measurement of chemical activity coefficients of gas phase species in thermodynamic equilibrium with liquid phase**, Gabriel, J.C.P. Theisen, J., Penisson, C., Zemb, T., Mizaikoff, M. B., Wilk M. A., Kokoric, M.V.

[5] Christophe Penisson ; **Etudes thermodynamiques de fluides comlexes par un dispositif de caractérisation microfluidique intégré,** phD Thesis, Université Grenoble-ALpes (September 2018).

[6] Kokoric V., Theisen J., Wilk A., Penisson C., Bernard G., Mizaikoff B. and Gabriel JCP. ; **Determining the Partial Pressure of Volatile Components via Substrate-Integrated Hollow Waveguide Infrared Spectroscopy with Integrated Microfluidics** (2018) Anal. Chem. 2018, 90, 4445−4451.

[7] Penisson, C., Wilk, A., Theisen, J., Kokoric, V., Mizaikoff, B., Gabriel, J.C.P., **Water activity measurement of NaCl/H2O mixtures via substrate-integrated hollow waveguide infrared spectroscopy with integrated microfluidics.** Biotech, Biomaterials, and Biomedical: TechConnect Briefs 198-201 (2018), CRC Press, ISBN 978-0-9988782-4-9. Proceeding of Nanotech 2018, May 13-16, 2018 Anaheim, CA, USA.

[8] Michael Bley M., Duvail M., Guilbaud Ph., Penisson P.,Theisen J, Gabriel JCP & Dufrêche JF **Molecular simulation of binary phase diagrams from the osmotic equilibrium method: vapour pressure and activity in water–ethanol mixtures**, Molecular Physics, 116, pp. 2009-2021 (2018).

WORK-PACKAGE 2

JEAN-FRANÇOIS DUFRÊCHE

TOWARDS PREDICTIVE MODELLING OF THE FREE ENERGY OF TRANSFER OF LANTHANIDES IN THE PRESENCE OF ACIDS

With Magali Duvail, Simon Gourdin, Bertrand Siboulet, Michael Bley and Thomas Zemb

The aim of WKP 2 is to develop predictive models for the relation between free energy of supramolecular complexation that is the driving force for extraction and stripping and the observed free energy of transfer between an aqueous and a liquid phase. Classical methods imply dozens of parameter for the seventeen different classes of extraction mechanisms used industrially. Separating colloidal from supra-molecular scale requires to abandon the notion of stoechimetry of complexes, and treat all solvent solution as dispersed media with known area of polar/apolar contact and curvature.

We have first established predictive models for the stability polar aggregate volume in different regions of the ternary phase diagrams[9] (Duvail, Dufrêche, Arleth, & Zemb, 2013). This required to move from a molecular modelling to meso-scale modelling of polar core, head-group distributions and solvent via Gaussian random waves *(figure 1)*, for which an expression of the entropy is now available[10]. Then, the fixed stoechiometry of each aggregate by a map of probability of presence with tow coordinates : the number of water molecules per aggregate and the number of extrctant per aggregate. Up to now, this calculation could only be made explicitely when approximating all agregates as spherical unconnected polar cores[11] *(figure 2)*.

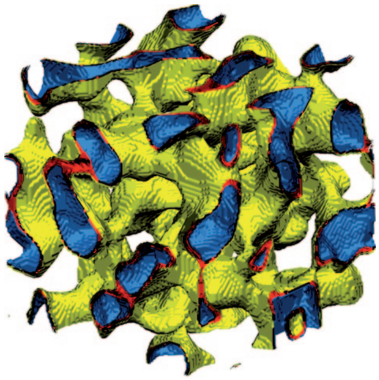


Figure 1: a concentrated solution of extractants represented at the meso-scale. "Hydrophobic" domains (solvent, chains of extractants, modifiers are shown in yellow), ions, water, acids are shown in yellow; polar heads of extractants are shown in red and all water-soluble species are shown as a homogenous blue volume. The snapshot in thermodynamic equilibrium shown on the left has a scale of 10 nm.

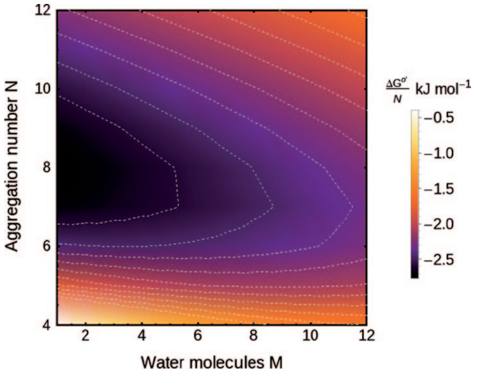


Figure 2: a typical probability map for w/o weak aggregates. The color gives the free energy of aggregation in kJ/Mole for any aggregate with four molecules or more determining an "inside" volume containing polar head-groups as well as M water molecules. All aggregates are supposed to be spherical and the curvature energy given by the intrinsic flexibility of the interface in a given more or less "penetrating" solvent wetting the chains protruding from the aggregate[12].

---

[9] Duvail, M., Arleth, L., Zemb, T., & Dufrêche, J.-F. **Predicting for thermodynamic instabilities in water/oil/surfactant microemulsions: A mesoscopic modelling approach**. The Journal of Chemical Physics, (2015) 140, 164711.

[10] Marčelja, S. **Entropy of level-cut random Gaussian structures at different volume fractions**. (2017) Physical Review E, 96(4). Page 042147

[11] Bley, M., Siboulet, B., Karmakar, A., Zemb, T., & Dufrêche, J.-F. (2016). **A predictive model of reverse micelles solubilizing water for solvent extraction**. Journal of Colloid and Interface Science, 479, pp.106–114.

[12] Duvail, M., van Damme, S., Guilbaud, P., Chen, Y., Zemb, T., & Dufrêche, J.-F. **The role of curvature effects in liquid-liquid extraction: assessing organic phase mesoscopic properties from MD simulations** (2017)Soft Matter, 13 pp.5518–5526.

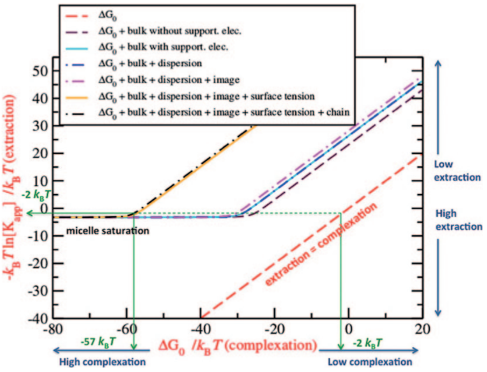
WORK-PACKAGE 2
JEAN-FRANÇOIS DUFRÊCHE

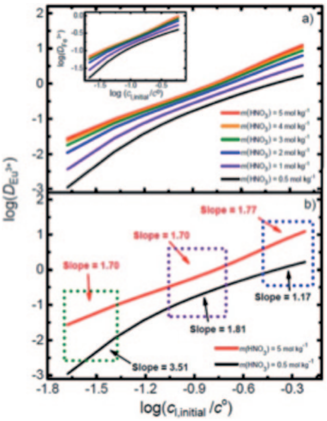
RELATING THE FREE ENERGY OF TRANSFER AND SUPRAMOLECULAR COMPLEXATION VIA COLLOIDAL INTERACTION

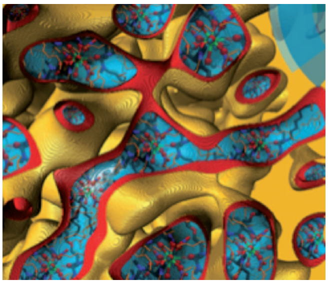
With Magali Duvail, Simon Gourdin, Bertrand Siboulet, Michael Bley, Anwesa Karmakar and Thomas Zemb

The equilibrium distribution coefficient of any electrolyte between an aqueous phase and a solvent phase reflects the free energy of transfer of the electrolyte. The free energy of transfer can be modelled as an isotherm on a flexible divided surface. The effective free energy of transfer is the difference between (I) the supramolecular complexation free energies driving towards the phase containing the "complexing" molecules and (ii) the mechanisms quenching this transfer. The latter are mainlu the entropy due to the confinement/reorganisation of solvent molecule nanostructure and electrostatic effect mainly (treated, if volumes are not taken into account, as mass action law). A typical result of a self-consistent evaluation of the interplay between these factors is shown figure 1 on the left, showing a job-diagram linking complexation to extraction[13]. Since we need to avoid explicit description of each of the dozens of coexisting aggregates that are needed to apply competing equilibrium models, all the paolr cores need to be treated as droplets contained in a flexible film. This allows making explicit calculation, knowing only a few physical quantities describing weak aggregation of extractants. One first success of this liquid droplet approach of the polar cores of all aggregates, supposed to be perfect spheres, is shown on the figure below (to the left). The classical method used to determine an apparent stoechiometry is to make log log-log plots of extraction versus the electrolyte content. However, calculation shows that this apparent stoechiometry results form an average of a large population of different aggregates, and thus varies significantly with the pH for instance: the log-log plot procedure gives only indicative values[14]. Considering that all complexes including co-extracted species and all adducts is only a rough approximation.

Quantitative estimation of the free energy of transfer requires modelling solvent phase via Gaussian random waves with two level cuts: the "inside" is a low dimensional ionic liquid while the oily phase (represented in yellow below to the right) is a solution of solvent and the un-associated "monomers" of the extracted molecules[15].







---

[13] a) Dufreche, J. F., & Zemb, T. **Effect of long-range interactions on ion equilibria in liquid–liquid extraction.** (2015) Chemical Physics Letters, 622, 45–49. b) Karmakar A. , Duvail M., Bley M., Zemb T., Dufrêche J.F. ; **Combined supramolecular and mesoscale modelling of liquid-liquid extraction of rare earth salts I** (2018) Vol : 555 Pages: 713-727.

[14] Spadina, M., Bohinc, K., Zemb, T., & Dufrêche, J.-F. ; **Multicomponent Model for the Prediction of Nuclear Waste/Rare-Earth Extraction Processes.** (2018) Langmuir vol 34-35, pp. 10434–10447.

[15] M Duvail M., van Damme S., Guilbaud P., Chen YS, Zemb T. and Dufrêche J.F. ; **The role of curvature effects in liquid-liquid extraction: assessing organic phase mesoscopic properties from MD simulations** Soft Matter Vol: 13 pp: 5518-5526.

WORK-PACKAGE 3
JEAN DUHAMET

OPERATING NEW PERTRACTION DEVICES INTENSIFIED BY ULTRA-SOUND FREQUENCY INTERFACIAL EXCITATION

With Ousmane Syll, Julien Rey, Stéphane Pellet-Rostaing

The aim of this work-package is to introduce a pertraction method with materials and dimensions close to real applications. Pertraction, an intricate combination of permeation through a filter and extraction at a liquid-liquid interface, is ideally suited for intensification via Ultra-sound triggering for instance.

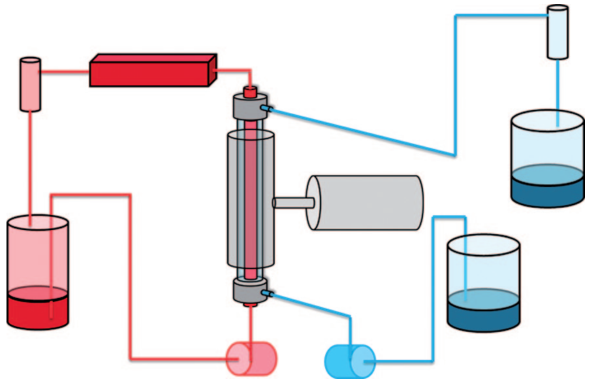


Figure 1: the pertraction device assembled for testing new extractant formulations under excitation at Ultra-sound specific frequencies (grey cylinder) The extracting oil phase (red) circulates through the inside of a cylindrical tube that is separated by a membrane from the water phase (blue) containing the alt (Neodymium nitrate) to be extracted. The grey cylinder arranged horizontally to the concentric tubes represents the ultrasonic transducer.

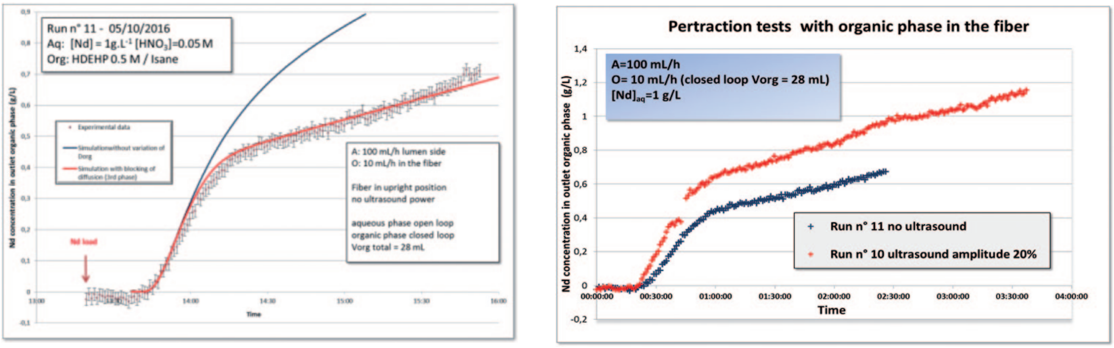


Figure 2 : (left) a typical curve of extraction from a feed circulating outside the pertraction tube towards an oil extractant phase located inside. Pore size is 200 nm; length of pertraction tube is of the order of 270 mm; tube thickness 2mm. The water-poor microemulsion wets the inside of the pertraction tube, and the ions circulate on the outside. (right) :Comparison between experimental data and modelling: a good fit is obtained by taking into account the third phase formation.

On figure 2, it can be seen that after a time to feed the device, there is initially an increase of extracted ion concentration in solution in a manner as expected for a diffusion controlled process. The curve transits further into a linear increase at later times. This effect can be understood, if a "third phase" with lower permeation by ions forms inside the nanopores of the membrane. This process has been modelled with realistic diffusion coefficients and thicknesses of a third phase film (left) By applying ultrasound (right), the rare earth transfer process can be accelerated, but qualitatively the shape of the curve is maintained. These findings open many doors to further increase the rate of extraction, e.g. by optimizing size and wettability of the membrane, varying extractant concentration and oil[16].

---

[16] Duhamet J., Moehwald H., Pleines M. & Zemb T; **Self-Regulated Ion Permeation through Extraction Membranes** » Langmuir 33, 9873–9879 (2017).

WORK-PACKAGE 4

STÉPHANE PELLET-ROSTAING

IMAGINE, SYNTHETIZE AND IMPLEMENT NEW FORMULATION BASED ON SYNERGY AND BI-FUNCTIONAL MOLECULES IN ENGINEERED SOLVENTS

With Julien Rey, Maximilian Pleines, Tobias Lopian, Sandrine Dourdain, Véronique Dubois

The aim is to find new formulations based on synergy as well as bifunctional molecules in order to propose new ion separation methods using knowledge-based approach of the commonly used "synergy" at specific ratio of extractants with complementary properties. This means also validation and control of classical "well-known" extracting systems using TODGA or combination of monoamides, succinates and phosphate-based extractants in formulated "diluents". In a first step, microstructuration as droplets or bicontinuous nanostructures involved in known recipes with synergistic behaviour local must be determined via collaboration with DEN/DMRC , in order to model the first shell important in supra-molecular aspects as well as colloidal scale organisation *(figure 1)*. Figure 2 illustrates the important difference between complexation free energy and salt transfer free energy from water phase to the oil phase that contains w/o oligomeric aggregates[17]. The decomposition into these terms allows to identify the mixing entropy term responsible for synergy, *(see figure 3)* .

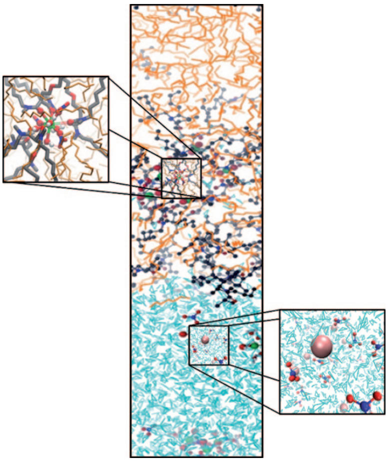


Figure 1: The classical "complexation" term at supramolecular scale involves interaction of the lanthanide and counter-ions to be with first neighbours: water in the oil phases and comlexing molecules shown . Strong effects in favour of the aqueous phase compete with the extraction: these contain ion-specific, local organisation at meso-scale and polarisation terms that can only be modelled at colloidal/nano/meso- scale (right side). Figure and modelisation (Philippe Guilbaud).

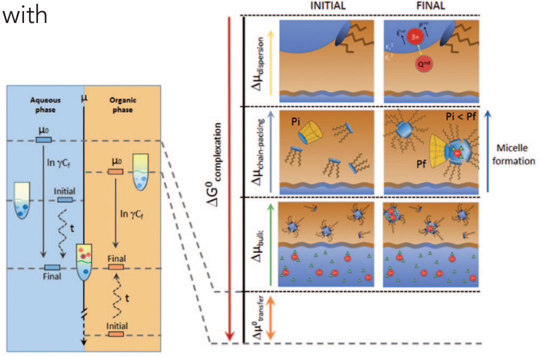


Figure 2: Decomposition of the free energy of transfer in its components[18]. From top to bottom: electrostatic effects, solvent and extractant film reorganization and entropy of mixing related to the confinement of the species in the polar cores of the aggregates present in the solvent phase. The free energy of transfer observed is shown in orange.

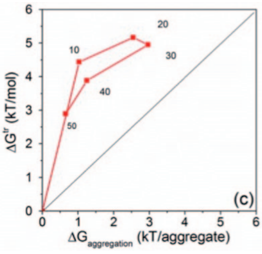


Figure 3: the free energy of transfer measured for europium $\Delta G''$ versus the free energy of aggregate formation $\Delta G''$ measured via the chemical potential of coexisting pseudo-phases. The total concentration of extractant is kept constant while the mole fraction of the uncharged extractant expressed in % is shown as numbers. Points located along the diagonal would present no synergy while points above the diagonal demonstrate cooperative synergy of about $2k_BT$ per molecule that is NOT the combination of individual molecule properties, but an entropic effect[19].

[17] Rey J., Bley M., Dufrêche J.F. ; **Thermodynamic Description of Synergy in Solvent Extraction: II Thermodynamic Balance of Driving Forces Implied in Synergistic Extraction** ; (2017) Langmuir vol 33 pp 13168-13179

[18] Zemb T., Bauer C., Bauduin P et al .;.-**Recycling metals by controlled transfer of ionic species: en route to ienaics**- Colloid Polym. Sci. 293(1) 2015, 1 – 22

[19] Rey J., Dufrêche J.F, Dourdain S., Berthon L., Pellet-Rostaing S. and Zemb T. -**Thermodynamical Description of Synergy in Solvent Extraction: I – Enthalpy of Mixing At the Origin of Synergistic Aggregation**- Langmuir 2016, Vol: 32 pp : 13095-13105

WORK-PACKAGE 5 (STARTED IN 2016)
THOMAS ZEMB

A CONFOCAL FABRY PEROT INTERFEROMETER ACTING ON AN OIL DROPLET DIAMETER

With Johannes Theisen, Julien Rey, Maximilian Pleines, Jean-Christophe P. Gabriel and Thomas Zemb in collaboration with Mario Corti, Paola Brocca and Laura Cantu (University Milano).

The aim of this WP of the REE-CYCLE project, unexpected at the beginning of the REE-CYCLE project, aims to direct observation of surface waves generated upon mechanical or electrical excitation at the surface of a droplet containing extractants molecules and a solvent (diluent). The droplet is typically 1 mm size and floats in a reservoir at fixed pH and containing rare earths and background salt. Surface wave amplitudes can be detected with as low amplitudes than one nanometer, with frequencies close to 100 Hz.

This break-through is made possible by a newly developed device based on confocal Fabry-Perot for measuring nanometer amplitude resonance surface waves on an extractant emulsion droplet. The device is a combination of Fabry-Perot confocal interferometry used in variable frequency mode under electrical excitation. The figure 1 below shows the millimeter-sized droplet of oil-soluble complexing agent extractant used as interferometer.

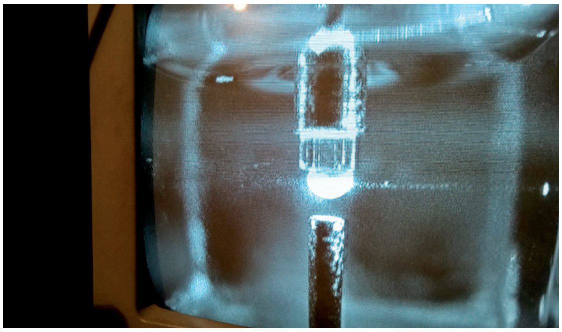


Figure 1: A droplet of typically 1 mm diameter containing a concentrated solution of surface-active extractant is contacted with a solution of high concentration of lanthanide nitrates in nitric acid. The beam crosses the aqueous phase in which some mixed aggregates of slightly water-soluble complexant produce ion oligomers: in the oil droplet, large colloidal aggregates produce scattering. Fabry-Perot confocal interferometry is done in the reflection mode, close to the drop equator, under excitation of a vertical electric field of 5 V/cm in the vertical direction, sweeping in the range 50-250 Hz.

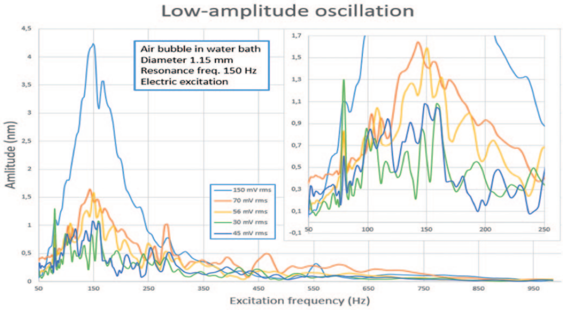


Figure 2: Surface modes of droplets, shown as nanometer amplitude versus electrical excitation frequency. Single shot signal-to-noise ratio = 2 validated for a field of 45 mV/1.5mm = 30 V/m, yielding amplitude of 0.7 nanometre for the surface waves that can be detected in a single shot without accumulation ?

Raw data set are obtained -as shown in figure 2- as an amplitude of the surface wave - known from the known wavelength of the laser used- as well as the local intensity of part of the falling on a photodiode and selected via a lock-in amplifier. The first experiment performed with this new ultra-sensitive instrument was to investigate the surface waves produced when "recognized" Europium ions are present in the water reservoir and the ily droplet is covered by an extractant molecule. The unexpected formation of a thin solid crust (few mm) of third phase with lyotropic liquid crystal has been detected[20].

---

[20] Corti M., Raudino A., Cantu L., Theisen J. Pleines M. and Zemb T. ; **Nanometric Surface Oscillation Spectroscopy of Water-Poor Microemulsions** ; (2018) Langmuir vol pp 8154-8162.

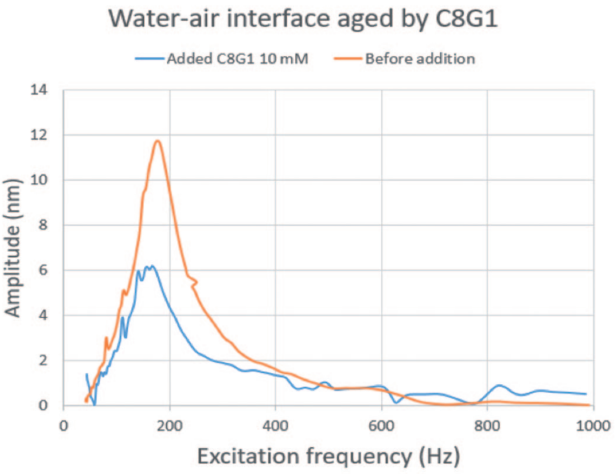


Figure 3: Sensitivity to the presence of a common protein membrane solubilizer (octylglucoside) on the surface of a bubble: one molecule per nm² induces a downshift of the resonance with an increase of relaxation producing FWHM broadening from Q = 0.6 to Q′ = 0.75 (10 mM C8G1) ; curve in orange : no octylglucoside, and in blue : with octylglucoside.

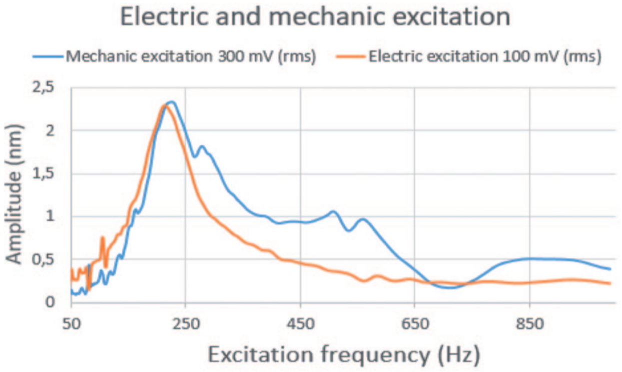
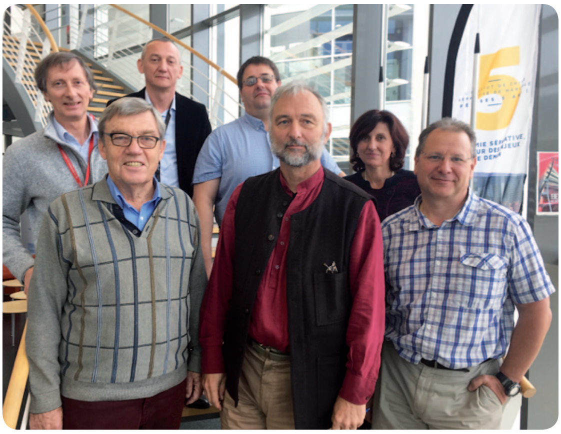


Figure 4: Reciprocity of Onsager coefficients: the same bubble is excited either with electrical excitation produced by the electrodes, or by mechanic excitation via a piezo-electric device located in the bottom of the cell. The main excited mode is te same, but other modes are excited also by echo of the sound on the sample reservoir. Measurement of the hydrostatic pressure and the electrical field of same frequency responsible of the same surface wave amplitude would provide unique information about the energy needed to produce the waves, and therefore the first direct verification (and exploitation) of Onsager reciprocity principle.

Figure 5: Multi-disciplinarity of the team leaders associated ***in the Rare Earth recycling without harmful emissions project :***
(l-r): Jean Duhamet (chemical engineering), Helmuth Môhwald (physical chemistry of interfaces), Stéphane Pellet-Rostaing (functional self-assembled separation chemistry), Jean-François Dufrêche (statistical physical chemistry), Thomas Zemb (colloidal physical chemistry), Dominique Alpe-Conchy (administration and human resources), Jean-Christophe P. Gabriel (material science and analytical chemistry).



ASSOCIATED TO WORK-PACKAGE 4
STÉPHANE PELLET-ROSTAING

HYDROTROPES : IN BETWEEN CO-SOLVENTS AND SURFACTANTS ?

Th. Zemb, O. Diat, D. Horinek, W. Kunz (Université de Regensburg) and E. Leontidis (Cyprus Uni)

Hydrotropes constitue a class of molecules that do not form micelles by themselves, but solubilize insoluble solutes in water when formulated above a typical concentration of 10%w called « minimal hydrotrope concentration » MHC. Hydrotropes are used industrially in formulation since more than hundred years. Ionic as well as non-ionic components show hydrotropic properties[1]. The archetype is ethanol. A peculiarity of ternary or quaternary solutions containing hydrotropes is that there is no macroscopic phase boundary separating structured and non-structured solutions : hydrotropes are a case of weak-aggregation, i.e. all cases where the average free energy linked to aggregation is less than k_BT^2. Two special issues of current opinion of colloid and interface science assembling current knowledge about this case, intermediary between surfactants and co-solvents have been edited by Werner Kunz and Thomas Zemb (12 reviews on hydrotropes and weak aggregation to be found in these COCIS issues published in 2016 and 2017.

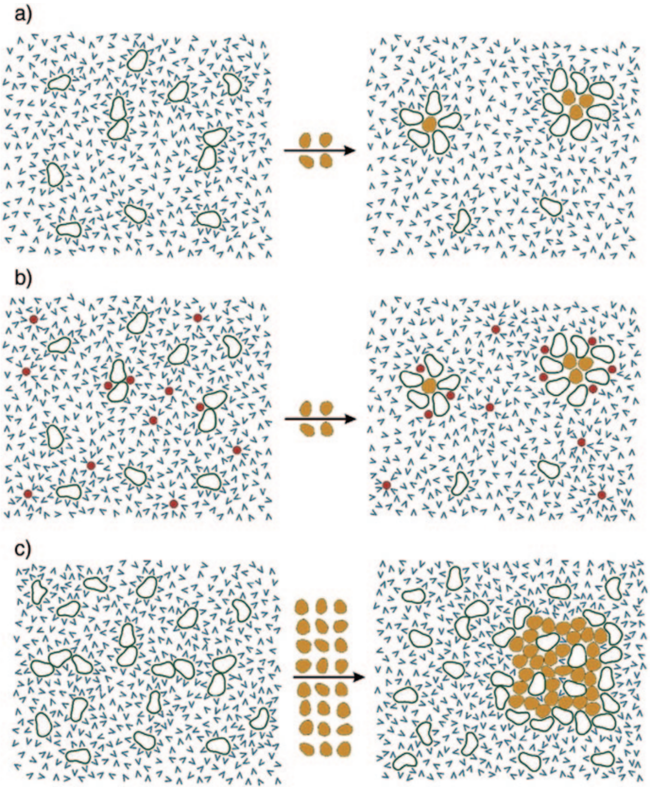


Figure 1: the different regimes of solubilisation linked to the presence of an hydrotrope :
a) the hydrotrope does not form lrage aggregates by itself, but those are nucleated by the presence of a solute and the phenomenon of preferential adsorption ;
b) in the case of ionic hydrotropes, alias antagonistic salts , the entropy of the counter-ion plays a significant role ;
c) in the presence of large quantities of solutes, a water-rich and water-poor large aggregates coexist and can be considered as pseudo-phases, with equality of chemical potential of each component netween the two media in equilibrium while the hydrotrope accumulates also at the interfac between pseudo-phases, thus behaving as a weak surfactant.

---

[1] Kunz, W., Holmberg, K., & Zemb, T. (2017). **Hydrotropes.** Current Opinion in Colloid & Interface Science, 22, 99–107.

[2] Zemb, T., & Kunz, W. (2016). **Weak aggregation: State of the art, expectations and open questions**. Current Opinion in Colloid & Interface Science, 22, 113–119.

LABORATOIRE INTERNATIONAL ASSOCIE
L.I.A. CNRS-MPG «RECYCLING» 2014-2017

Scientists participant to the LIA « RECYCLING » 2014-2017:

- *in Potsdam: Helmuth Möhwald (deceased March 2018), Peter Fratzl (from 2016), Hans Riegler, Luca Bertinetti*
- *in Marcoule and Saclay: Thomas Zemb, Olivier Diat, Michael Odorico, Sophie Charton, Damien Féron, Florence Lequien*
- *PhD students involved:*
  - *Marie Jehannin (co-tutelle Montpellier-Potsdam, 2012-2015): Oxalic precipitation in coalescing droplets: study of the role of coalescence on mixing and nucleation of ceramic precursors*
  - *Virginie Soulié (co-tutelle Montpellier-Potsdam, 2012-2015): Drying of droplets containing soidum chloride and consequences for further corrosion mechanisms on steel*
  - *Aurelio Barbetta (co-tutelle Montpellier-Potsdam, 2013-2017, Labex Chemisyst F/G stipendium): Thermodynamics of water absorption in model structured molecular systems including analogues of hemicelluloses, crystalline cellulose and lignin*
- *Engineers and technicians: Joseph Lautru (Marcoule) and Anne Heilig (Potsdam)*

The RECYCLING project between CNRS/INC and MPG/MPIKG has as original goal linking spectrometry and chemical reactivity in complex fluids induced by ultra-sound, and its application to control movement of ions in colloidal solutions and porous nanomaterials (2009-2012). Special attention is now more focused on separation chemistry to fluids containing metals as ions, nano- or microparticles, with the general aim of applications related to separation and recycling and material life-time extension. The central contractual scientific objectives of the LEA "RECYCLING" for the four years period 2014-2017 are focused on five topics:

1. Droplet coalescence under reactive conditions: we aim to develop quantitative characterization and predictive modeling based on first principles during the contact of two sessile droplets containing surface active and reactive species, coupling of Marangoni effects, bulk flow reactivity producing mechanical turbulence.

2. Metallic corrosion development during drying-wetting cycles by aerosols containing sodium chloride: nanoscience approach to the thermodynamics and hydrodynamics on the three phase contact line between soluble ionic solid, under-saturated solution and partially oxidized metal.

3. Develop atomic force microscopy at an active oil-solvent interface, *i.e.* with respect to hydrometallurgy, *i.e.* when cations are selectively exchanged between an aqueous and organic solvent containing oil-soluble ion specific species.

4. Make use of the ion specific ultra-sound adsorption to excite oil/water interfaces and trigger transfer of ionic or colloidal species. The experiment will involve non linear optical caracterisation of reflection at liquid-liquid interface and ellipsometry. The theory will involve evaluation of the potential wave associated to the macroscopic interface, as well for ions as for nanoparticles crossing the interface. The key initial observation was that ultrasound can be used to enhance the phase transfer between oil and water phase and thus also to dissolve ions[1].

5. Study the specific salt effects on interaction between wood cell wall *i.e.* cellulose-crystalline material in contact with a ternary gel lignin-soluble cellulose and water. This includes direct measurement of osmotic pressure due to concentration gradients of metal ion with respect to the solution in which wood cell wall is immersed (or atmosphere at controlled humidity). This study covers in the unified approach free energy of chemical, colloidal and mechanical energy as introduced by Fratzl and Bertinetti in terms of "master equation". This has a wide domain of application as knowledge-based treatments of wood against (or in favor) of swelling/deswelling under osmotic stress and material life-time improvement.

---

[1] Key initial reference originating from initial LEA CNRS-MPG « SONO »: G. Toquer, T. Zemb, D.G. Shchukin, H. Möhwald: **"Ionic Physisorption of Bubbles induced by pulsed Ultrasound"** PCCP 12 (2010) 14553

RECYCLING TASK 1

COALESCENCE OF DROPLETS IN REACTIVE CONDITIONS

M. Jehannin (DTEC/ICSM), H. Riegler, S. Charton, Th. Zemb

Surprisingly, two droplets of completely miscible liquids can remain separated for some seconds up to minutes after their contact. This non-coalescence behavior can be explained by a surface tension gradient between the liquids of the two drops. The gradient creates a Marangoni flow which competes with the capillary forces and may delay the coalescence of the droplets. Yet, coalescence and non-coalescence of inert sessile droplets is well understood. However, when reactants are dissolved in both droplets, the system gets more complicated. Indeed, the reaction modifies locally the chemical concentrations, thus influencing the surface tension gradient and the Marangoni flow. This research study on coalescence of reacting droplets is led in a coupled way, both at CEA Marcoule (DEN/DTCD), for which this topic is a key issue for a recently patented process, and at MPIKG (Max Planck Institute of Colloids and Interfaces), which studied coalescence of sessile inert drops. The interplay between a precipitation reaction and the immediate coalescence of sessile drops is investigated. We have found that the combination of a Marangoni flow with a fast reactive process could lead to a periodic pattern of alternating black and colorless stripes. Moreover, the stripe formation is reversible, depending on the surface tension gradient that can be set by adding an surface-active molecule[1].

Two drops, one containing cerium nitrate and the second one containing oxalic acid, are deposited on a silica surface at some distance from each other. In the range of concentrations used, cerium nitrate and oxalic acid are soluble in the solvent, whereas the reaction product, namely cerium oxalate, is insoluble in aqueous solution. Three behaviors were observed *(Figure 2)*. At low oxalic excess, light scattering precipitates are obtained, at high oxalic excess, a transparent domain of precipitates is observed above the high surface tension drop. At intermediate cerium nitrate concentration, a periodic arrangement of the two states is observed.

Marangoni flow is known to occur in the surface layer of the high surface tension drop. The exact thickness of this layer is not known yet. We attempted to address this point by studying the location of the precipitation process. Assuming the reaction height represents the width of the Marangoni layer, we probe, using confocal microscopy, on in-situ coalesced droplets, the vertical position of the first detected crystal. Growth rates (typically minutes) are slow as compared to the coalescence and nucleation processes (typically seconds). The transparent and scattering light areas, recorded by the top view camera *(illustrated by Figure 1, top)* are due to nanoparticles having different light diffraction properties

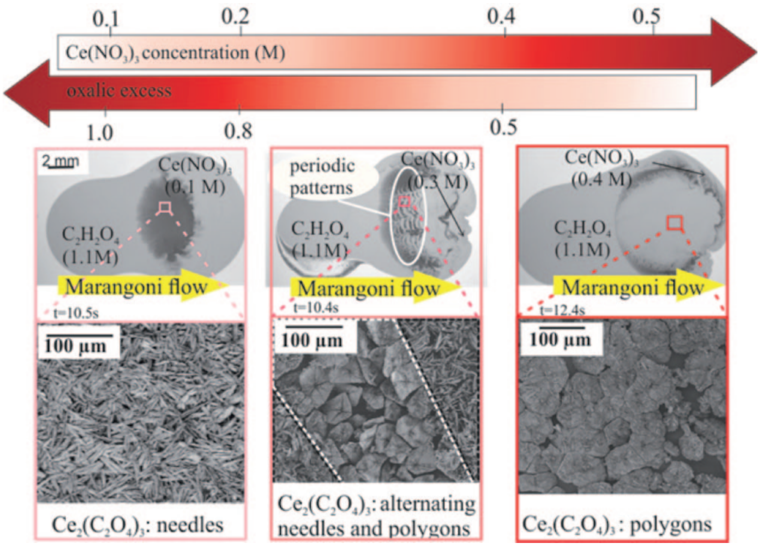


Figure 1 : Top: Coalescence of sessile drops for different initial concentration of cerium nitrate at a constant surface tension difference ($\Delta\gamma$=3mN/m). The Marangoni flow is directed from the oxalic acid drop over the cerium nitrate one. Three behaviors are observed. Bottom: SEM images of the corresponding resulting cerium oxalate morphologies, namely: needles (left), polygons (right) and, for intermediate oxalic excess, alternation of both morphologies (middle).

[1] Jehannin, M.; Charton, S.; Möhwald, H.; Karpitschka, S.; Riegler, H.and Zemb, Th., **«Periodic precipitaion patterns during coalescence of reacting sessile droplets"** . (2015) Langmuir, 31,11484-11490

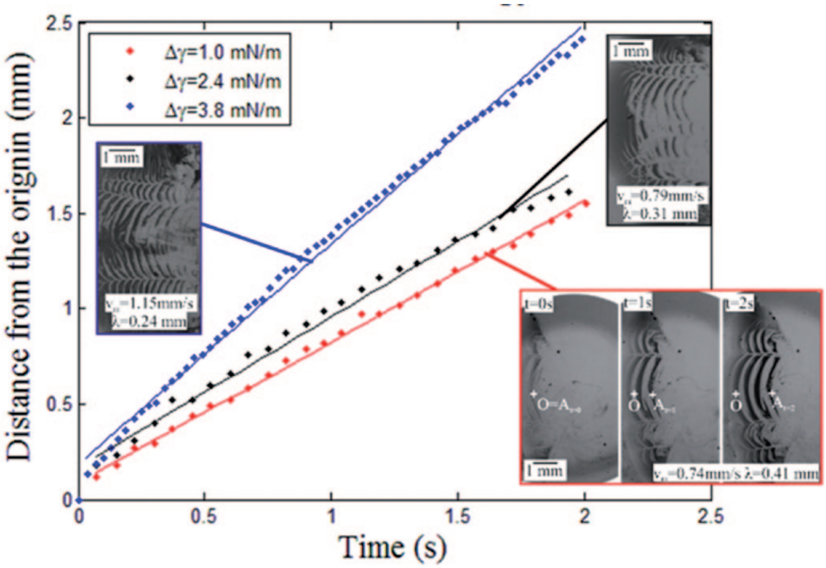


Figure 2 : Distance from the origin evolution in time during fringes formation at different surface tension gradient $\Delta\gamma$. The oxalic excess (0,6M) and the average contact angle ($\theta a=9+0.5°$) are identical for all experiments. The Marangoni flow speed, vM, increases with the surface tension gradient whereas the wavelength of the periodic pattern, λ, decreases.

Now that we elucidated the nature of the fringes, we aim to identify the phenomena responsible for their formation. It is likely that this oscillatory behavior is due to a competition or a feedback between at least two mechanisms, which could be the convection and/or the diffusion (i.e. transport mechanisms) and/or the chemical reaction. Preliminary results indicate that, for a given contact angle, the higher the surface tension difference, the higher the Marangoni flow speed, and the lower the wavelength *(Figure 2)*. The knowledge of the parameters mainly influencing the fringes characteristics is the first step of the development of a numerical model, which would enable sensitivity analysis.

To conclude, the coalescence of droplets is investigated in reacting conditions. In our case study, sessile drops containing cerium nitrate and oxalic acid, the coalescence can lead to three precipitation behaviors depending on the initial oxalic excess. Surprisingly, at intermediate oxalic excess periodic patterns are created. Whatever the behavior, the produced solid particles (after drying) are observed to have identical crystallographic structures but different morphologies, namely polygons or needle morphologies. The periodic patterns correspond to alternating polygons and needles. Currently, we aim to understand the periodic pattern formation by identifying the controlling parameters. This work will enable the development a theoretical model for the coalescence of reactive droplets: an efficient way towards that goal is to investigate the effect of differences in surface tension between droplets as well as the effect of moving form binary solutions to ternary complex fluids, such as ultra-flexible microemulsions[2].

[2] Jehannin, M.; Charton, S.; Corso, B. Möhwald, H.; Riegler, H.and Zemb, Th., «**Structured solvent effects on precipitation of organized cerium oxalate microparticles** (2017) Colloid & Polymer Science, vol 295}({10}), pp.1817–1826

SALT-INDUCED MARANGONI FLOW IN EVAPORATING SESSILE DROPLETS

V. Soulié (DEN/DPC/ICSM), H. Riegler, Ph. Prené, D. Feron, H. Moewald, Th. Zemb

The evaporation behavior of a sessile drop is rather complicated because of the subtle issues arising from its description such as the non-uniform evaporative flux. The evaporation at the contact line region is enhanced, which induces a capillary flow towards the edge (leading to the «coffee-ring» effect [1]). For complex fluids the evaporation behavior becomes even more complex, because the non-uniform evaporative flux will lead to an inhomogeneous distribution of the fluid constituents within the drop. This can induce a surface tension gradient, which in turn may lead to a Marangoni flow [2] in addition to the capillary flow.

We study the evaporation of sessile drops from aqueous sodium chloride solutions on solid planar surfaces. The diverging evaporative flux locally enriches NaCl at the droplet edge *(Figure 1.a)*. Since chaotrope salts are depleted from the air-water interface, the surface tension locally increases in the edge region. This can lead to a Marangoni flow in the same direction as the capillary flow, i.e. towards the contact line. Diffusive dilution resulting from the salt concentration gradient will reduce the evaporation-induced gradient *(Figure 1.b)*. We investigate how the flows within the drop and, in particular the Marangoni flow along its surface, are related and affected by: (I) the initial NaCl concentration, (II) the contact angle, (III) the drop size and (IV) the evaporation rate. To this end the shape and the contact angle of the drop are analyzed by simultaneous optical imaging from the top and the side [3], and the liquid flow is studied by particle tracking velocimetry (PTV) with polystyrene particles.

We find that the flow behavior is strongly affected by the initial NaCl concentration. At low initial NaCl concentrations, PTV experiments reveal only a flow towards the contact line. This may arise from the capillary flow compensating for the local evaporative losses, possibly increased by a Marangoni flow component. Thus, capillary and Marangoni flows both favor the formation of a coffee-stain deposit *(Figure 1.b)*. However, above 10^{-3}M NaCl, the surface tension gradient respectively Marangoni flow leads to such a strong flow towards the drop edge, that the capillary pressure in this region increases. Therefore, the compensating capillary flow is now directed inward and we observe a convection roll near the drop edge. This circulating flow can lead to a more uniform salt deposition or a wider coffee-ring, depending on the initial NaCl concentration *(Figure 1.c)*. Experiments reveal that the flow patterns are also affected by the ambient vapor pressure, the drop size and contact angle.

To conclude, the flow behavior of an evaporating drop of a saline solution is dominated by a solely outward flow (combination of Marangoni and capillary forces) at low salt concentrations. At high salt concentrations, the flow behavior changes drastically and is governed by compensating Marangoni and capillary flows that lead to convection rolls[1].

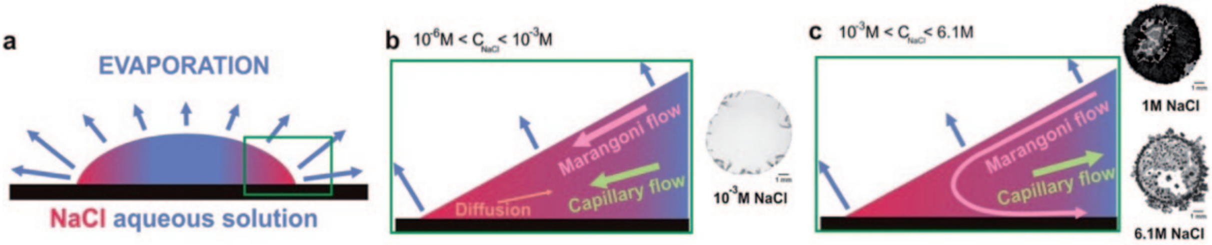


Figure 1: (a) Evaporation behavior of a sessile droplet from aqueous sodium chloride solutions. Locally varying evaporation rate and resulting concentration gradient: below (b) or above (c) 10^{-3}M NaCl. Typical microscopy images of the final deposit patterns from droplets of 10^{-3}, 1 and 6.1M NaCl on silica wafers at T = 25°C and RH = 0%.

---

[1] Soulie, V.; Karpitschka, S.; Lequien, F.; Prene, P.; Zemb, T.; Moehwald, H.; Riegler, H., **«The evaporation behavior of sessile droplets from aqueous saline solutions.»** Phys Chem Chem Phys 2015, 17 (34), 22296-22303.

RECYCLING TASK 2

PITTING CORROSION OF IRON UNDER A SESSILE DROPLET FROM AQUEOUS SALINE SOLUTIONS

V. Soulié (DEN/DPC and CEA/ICSM), H. Riegler, Ph. Prené, D. Feron, H. Möhwald, Th. Zemb

The corrosion process induced by evaporation of sessile droplets from aqueous sodium chloride solutionson planar iron surfaces was quantitatively investigated. The spatial distribution of the salt inside the evaporating sessile droplet, which is influenced by the initial salt concentration in the droplet bulk, is correlated to the localization of the anodic and cathodic reactions at the electrolyte-metal interface over the footprint droplet area. At low salt concentration the inverse of the classical well-accepted Evans model is observed: the anode area is established near the three-phase contact line region. Increasing salt concentration leads to a more uniform pitted sessile droplet: we observed locally anodic and cathodic areas over the droplet surface at the metal-electrolyte interface, where local variations in chloride concentrations takes place if the salt concentration reaches a threshold value, experimentally determined by an optical set-up *(figure 1)*.

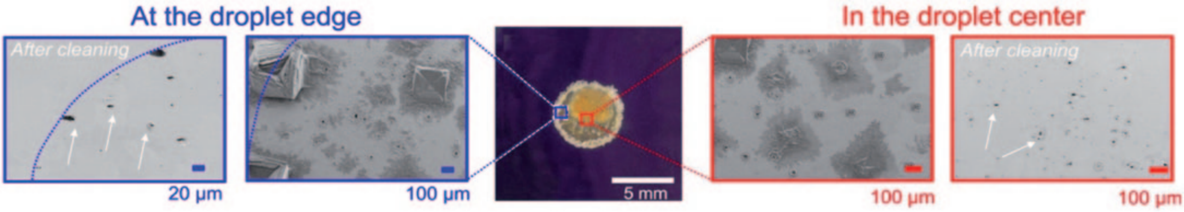


Figure 1: Microscopy image of an iron surface, onto which an aqueous sessile droplet from 1M NaCl (10 µl, contact angle 15.2°) was deposited, after complete evaporation with a relative humidity RH of 40% at T = 23°C. The two insets show SEM micrographs of two different locations on iron corroded under evaporating NaCl sessile droplets: at the droplet edge and in the droplet centre. The white arrows indicate the presence of pit[1]

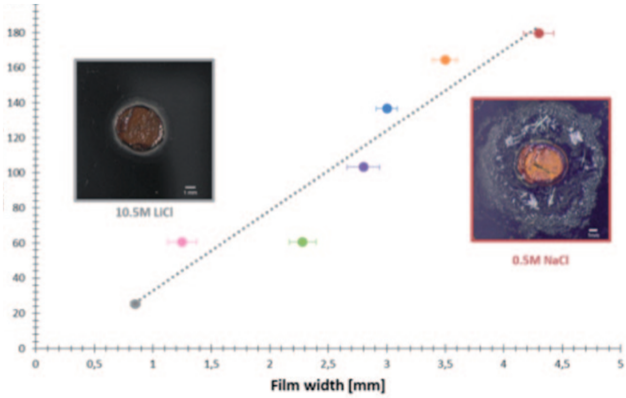


Figure 2: The corrosion rate induced by a sessile droplet from aqueous electrolyte solution deposited on an iron substrate depends to the width of the peripheral film. The measured film width is obtained after 1 day of experiment. Microscopy images of the dried system after on eday experiment from aqueous sessile droplet of 10.5M LiCl and 0.5M NaCl.

Focussing more on the corrosion influence of a sessile droplet[2], we established the presence of corrosion products and some pits demonstrate that pitting corrosion takes place if the salt concentration reches a threshold value, experimentally determined by an optical set-up. Finally, investigation of salt containing chaotropic or cosmotropic species show extremely different corrosion rates, as shown on figure 5 below.

---

[1] Soulié, V.; Lequien, F.; Ferreira-Gomès, F.; Moine, G., Féron, D.; Prené, Ph.; Moehwald, H.; Zemb, Th. And Riegler, H.; , «**Salt-Induced Iron Corrosion under Evaporating Sessile Droplets of Aqueous Sodium Chloride Solutions**. (2017) MATERIALS AND CORROSION (2017) Volume: 68 Issue: 9 Pages: 927-934

[2] Lequien, F.; Soulie, V.; Moine, G.; Lequien A. ; Feron D ;Prené Ph. ; Moehwald Ph. ; Riegler H. & Zemb, T.
Corrosion influence on the evaporation of sessile droplet ; COLLOIDS AND SURFACES A vol :546 pp 59-66

RECYCLING TASK 5

IMPREGNATION OF WOOD CELL WALL BY SALTS: SWELLING, DE-SWELLING AS CONSIDERED USING CHEMICAL BINDINGS, COLLOIDAL FORCES AND MECHANICS

A. Barbetta (MPIKG/ICSM), L. Bertinetti and P. Fratzl (MPIKG-Potsdam), T. Zemb

«Wood material» is a complex, highly anisotropic and hierarchically organized nanocomposite: when immersed in a electrolyte solution of electrolytes, we consider the work of osmotic pressure balancing the three terms of the master equation. The first step in experiments is to characterize volume differences due to solvent exchange of wood cell wall material at all length scales (*see figure 1*)[1].

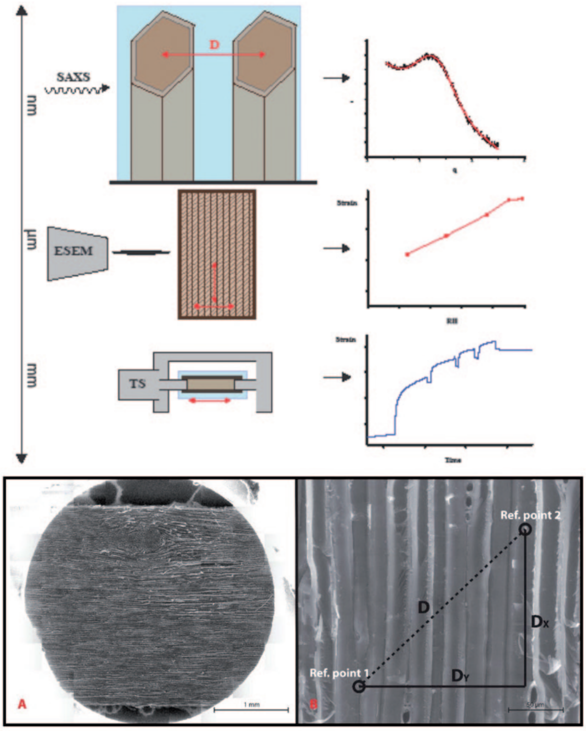


Figure 1: swelling of wood in osmotic equilibrium with atmosphere of a solution of electrolytes is investigated by Small angle X-ray micro-diffraction at the nanometre scale (top), via environmental scanning electron microscopy (middle) at the micron scale as shown below so lateral and longitudinal swelling can be obtained independently and finally at macroscopic scale using a tensile stage (bottom).

Typical strains observed are shown in the figure 2 below: An experimental result for Sodium iodide (left) is compared to expectation using the Equation of state. Extra swelling when salt is penetrating the wood cell wall. The chaotropic anion or the complexed cation is expelled from the gel, with a binding constant of the order of 2kT, i.e; approx. 5 kJ/mole). As can be seen, swelling observed can be distinguished easily from situations with double or half of the binding constant of the ion with the cellulose crystal[2].

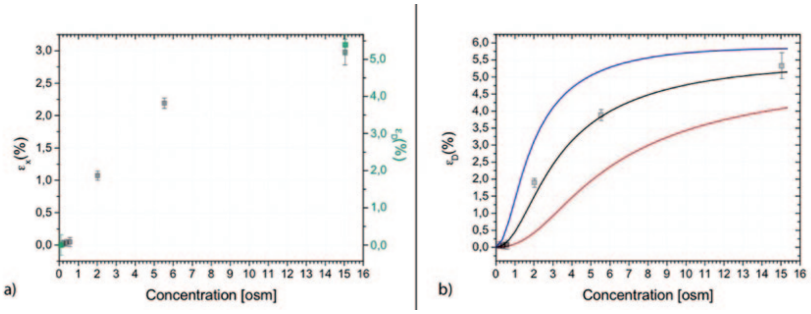


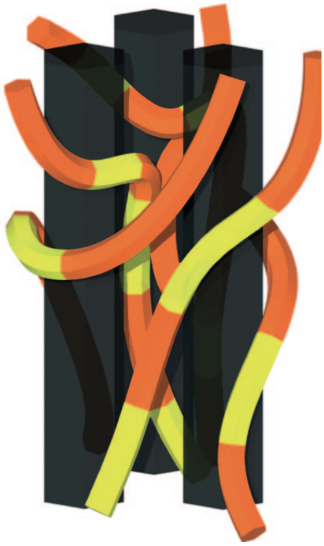
Figure 2: experimentally observed volumic strain in percent of total volume of wood cell wall obtained with a typical antagonistic salt (right) , and compared with there values of the chemical binding constant of the ion charging the cellulose microcrystals (left).

[1] Barbetta, A.; Bertinetti, L.; Moehwald, H.; Lautru, j.; Podor, R. and Zemb, Th.: **Nano-, Meso- and macro-swelling characterization of impregnated compression wood cell walls.** , (2018) WOOD SCIENCE AND TECHNOLOGY vol 52 pp:421-443

[2] Barbetta, M.; Zemb, T. and Fratzl, P., **«Impregnation and Swelling of Wood with Salts: Ion Specific Kinetics and Thermodynamics Effects.»** (2016) Adv. Mater. Interfaces page 1600437

HYDRATION FORCE IN WOOD AS A MULTI-SCALE MATERIAL: MODELLING OF WOOD FIBRES SWELLING/ DESWELLING BY ATMOSPHERIC HUMIDITY

L. Bertinetti, A. Barbetta, P. Fratzl, Th. Zemb
Collaboration ICSM with Biomaterials Dept MPIKG-Potsdam



Plants use the orientation of cellulose microfibrils to create cell walls with anisotropic properties related to specific functions. A well-known example is wood, that consists of parallel, hollow, cylindrical cells. The so-called "wood material" is a complex, highly anisotropic and hierarchically organized nanocomposite. It is characterized by hydrated stiff crystalline cellulose nanofibres parallel to each others (black on drawing) embedded in a matrix of a much softer, less anisotropic, gel of hemicelluloses, lignin (orange/ yellow hydrocarbons) and water. This matrix is hygroscopic and swells with increasing relative humidity providing a source of internal stress while the cellulose fibrils passively reorient following the stress applied to them. We use a unified approach of the equation of state of colloidal composite under hydration and dessication cycles, in the form of the master equation combining mechanical, colloidal and chemical free energy change during hydration form a reservoir of osmotic pressure Π:

$$\mathrm{d}G_m(D)+\mathrm{d}G_c(D)+\mathrm{d}G_e(D)=v_m\Pi(RH)\mathrm{d}N$$

The resulting general equation of sate relies on only one single parameter: only one single free parameter: the binding "contact point" free energy of hemicelluloses, seen as chemical "snapping" on crystals[1]. The results of the model, compared with experimental sorption data and with small angle X-rays scattering data, seem to capture the main features of the wood swelling by water with and without treatment for preservation done by chemical reactions of impregnation.

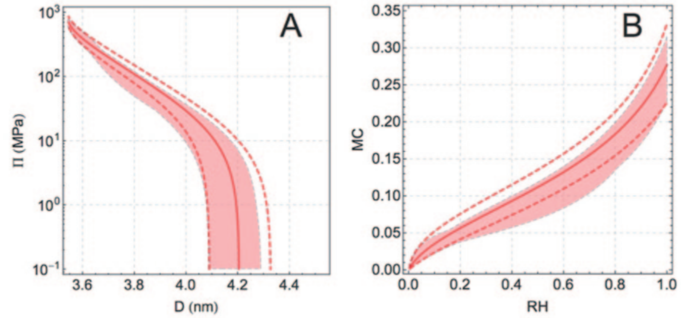


Figure 2: The EOS of wood cell wall (A) in the physical chemistry form of osmotic pressure versus spacing between cellulose crystals and (B) in the form used in material science and chemical engineering: Moisture content versus relative humidity. Dashed lines represent variations associated to uncertaineties in measured values entering the model and shaded areas concern domain of variation observed for this variable material of biological origin.

We have used the same methodology by adding the different interactions as derivatives of the free energy to derive inversely form the deswelling and further re-swelling during the impregnation of salts the energy of adsorption of the choatropic ion responsible for swelling after impregnation: we found a typical value of 8kJ/mol for the case of sodium iodide[2].

[1] L. Bertinetti, L.; Zemb, T.; Fratzl, P. , «**Chemical, colloidal and mechanical contributions to the state of water in the wood cell wall.**» IOP New Journal of physics) 2016. 18, 083048

[2] Barbetta, A., Bertinetti, L., & Zemb, T. (2017). **Composition dependent Equation of State of Cellulose Based Plant Tissues in the presence of Electrolytes**. Colloids and Surfaces A:, vol : 532, 314-322.

LABORATOIRE INTERNATIONAL ASSOCIE
L.I.A. CNRS-MPG-UNIVERSITY OF REGENSBURG «NISI» 2018-2021

From January 1, 2018, the collaboration between Marcoule/Montpellier, Potsddam associated with -Regensburg has evolved to the French-German Labotaoire international associé "NISI":

P.I., Olivier Diat (ICSM), co-P.I., Emanuel Schneck (MPI Potsdam) & Dominik Horinek (Univ. Regensburg)

- *Participant (ICSM): Thomas Zemb, Stéphane Pellet-Rostaing Pierre Bauduin, Luc Girard, Damien Bourgeois, Daniel Meyer, Jean-Francois Dufrêche, Sandrine Dourdain, Bertrand Siboulet, Magli Duvail, Tania Merhi (PhD), Jing Wang (PhD) and Max Hohenschutz (PhD)*
- *Participant (MPI): Peter Fratzl and Ernesto Scoppola (Post-Doc)*
- *Participant (Univ. Regensburg): Werner Kunz and Didier Touraud*

This program is built around nano-ions in interaction with soft interfaces. We were working for some years on the understanding of ionic or polar species transfers between two immiscible fluid phases, an aqueous phase and an organic phase. From these studies we have been able to show in some cases a complex equilibrium between the adsorption of nanometric ionic clusters and the release of adsorbed water molecules at the interface. It is known for a long time that ions according to their sizes, charge densities and polarizabilities have specific effects on the activity of water and other species in aqueous solution and that these effects can have important consequences on apolar molecules solubilisation in aqueous phase, on the self-aggregation of surface-active molecules, on the stabilization and on the interaction between soft interfaces (mono- or bi-layers).

In this MPG/CNRS cooperation action, we will focus on the polar/apolar interface and the interactions between these interfaces, these effects are often averaged in the form of a short-range repulsive hydration force with a characteristic length of a few angstroms. However, when these ions are of the order of a nanometre, these effects may appear more complex because they are exalted by an increase of the polarizability effects and sometimes by the presence of additional hydrogen bound interaction between the counter-ion themselves. These are specific to these ionic clusters or nano-ions.

This program is built around nano-ions in interaction with soft interfaces. We were working for some years on the understanding of ionic or polar species transfers between two immiscible fluid phases, an aqueous phase and an organic phase. From these studies we have been able to show in some cases a complex equilibrium between the adsorption of nanometric ionic clusters and the release of adsorbed water molecules at the interface. It is known for a long time that ions according to their sizes, charge densities and polarizabilities have specific effects on the activity of water and other species in aqueous solution and that these effects can have important consequences on apolar molecules solubilisation in aqueous phase, on the self-aggregation of surface-active molecules, on the stabilization and on the interaction between soft interfaces (mono- or bi-layers).

In this MPG/CNRS cooperation action, we will focus on the polar/apolar interface and the interactions between these interfaces, these effects are often averaged in the form of a short-range repulsive hydration force with a characteristic length of a few angstroms. However, when these ions are of the order of a nanometre, these effects may appear more complex because they are exalted by an increase of the polarizability effects and sometimes by the presence of additional hydrogen bound interaction between the counter-ion themselves. These are specific to these ionic clusters or nano-ions.

TASK 1)
HEAVY IONS AT LIQUID-LIQUID INTERFACE

(work started with E. Scoppola/ MPI Potsdam)

We have recently developed an experimental approach combining X-ray AND neutron reflectivity measurements to determine the distribution profile of ions and organic species around water/oil interfaces in order to characterize ions transfer processes for solvent extraction applications. We will use a single radiation such as X-ray and combine reflectivity with fluorescence measurements.

It is efficient when the interfacial structure is well defined but much more critical when the interface is fuzzy and that is our case for solvent extraction applications. The development of simultaneous g-fluo and neutron reflectivity experiments in time of light mode at Laue Langevin Institute is another possibility that we have chosen , neutron radiation being very sensitive to determine the distribution of organic species such as ions extractants molecules in fluid phases. This program requires first the development is focusing on a specific analytic tools to determine from these reflectivity measurements the distribution profile of several species around the interface and allow to determine the surface potential of ions, a crucial knowledge information that has be taken into account to characterize the efficiency of ions transfer and that also can be simulated via molecular dynamics approach. The development in parallel of other methods such as surface tension technique and surface wave characterisation coupled to optical interferometry is also foreseen in this project.

This task may appear to not be specifically dedicated to nanoions at soft interfaces. However, we have shown that extractant molecules and ions pairs in interactions with these ligand's molecules form some polarized aggregates at the interface and create some interphases with nanometric extensions in the normal direction.

Scientists involved: J. Wang, E. Scoppola, E. Schneck, L. Girard, M. Odorico, JF. Dufreche, S. Dourdain, T. Zemb and O. Diat

TASK 2)

INTERACTION BETWEEN NANOIONS AND MODEL 2D SELF-ASSEMBLIES

Preliminary researches were carried out in our group to study the impact of nano-ion adsorption onto 2D self-assembled structures made from phospholipidic and other integrated molecules and first results showed some antagonist effects: When nanoions adsorb onto a surface then lateral interaction act on the bilayer's flexibility and fluctuations with either a reinforcement of the bilayer stabilization and liquid crystal 3D structure in case of mesophases or with defects formation and the destructuration of the self-assembly structures The objective is to make a link between experiments results and simulations using ucrreznt models derived from the approach developed by Schwierz and Horinek. We will focus mainly on dicarbollide anions and their interactions with biological functions and support with some cancer therapy applications.

Scientists involved: T. Merhi, P. Bauduin, O. Diat, E. Schneck, D. Horinek, B; Siboulet, JF Dufreche

TASK 3)

INTERACTION BETWEEN NANO-IONS AND OLIGOMER OR POLYMER

Polyoxometalates (POMs) are anionic metal-oxygen clusters consisting of oxo-linked MOx polyhedra of early transition metals in their highest oxidation state. Their electronic versatility and the blend of p-bock elements, transitions metals and differently bound oxygen atoms (terminal and bridging) induce special properties resulting in a broad field for applications such as catalysis, material science, biology and medicine. For most of these applications the understanding of the interactions between inorganic POM clusters and organic entities is essential and much effort has been made to the design and building of POM-organic hybrid assemblies. The design of POM-organic composite materials is based on two approaches: an electrostatic coupling between an anionic POM with an organic cation and a covalent coupling with the POMs chemically grafted to organic moieties. We developed a third one based on the super-chaotropic property of such ionic clusters that allows to self-organize POM in 3D structures without any specific solvent, only water. This approach is rather pertinent for the preparation of catalytic supports and this is the objective the common PhD project that we have with this team of Regensburg University. This approach may be further extended to chemical systems of biological in which electron exchange and redox process are necessary.

Scientists involved: A. Pfitzner, T. Buchecker, D. Horinek, JF. Dufreche, P. Bauduin, O. Diat

TO DEVELOP AN EFFECTIVE EXTRACTION AND SEPARATION TECHNOLOGY TO SELECTIVELY EXTRACT RARE EARTH ELEMENTS

ERBIUM (ER), TERBIUM (TB), EUROPIUM (EU), PRASEODYMIUM (PR) NEODYMIUM (ND) AND DYSPROSIUM (DY) FROM WEEE (WASTE ELECTRICAL AND ELECTRONIC EQUIPMENTS) – N° IFC/7130-WEEE (MAY 2018 – MAY 2021)

Partners:
ICSM-UMR 5257 (Marcoule, France); Academic
Terra Nova Development (Isbergues, France); Industrial
CSIR-National Metallurgical Laboratory (Jamshedpur, India); Academic
Tata Consultancy Services Limited (Pune, India); Industrial

Rare earth are ubiquitous, have applications in primarily in clean energy, automobiles and digital technologies. Although public attention has shifted elsewhere, ensuring a secure future supply of rare earths remains an urgent policy challenge for governments and industry. Rare earth markets are small: the total market value for separated REEs was between $3 billion and $5 billion in 2013, and annual world production would fit into one large bulk carrier. Nonetheless, REE's importance for advanced materials across a range of high-tech industries – and especially their key role in boosting energy and resource efficiency – makes them too crucial to ignore. Under a business-as-usual scenario, rare earths supply will remain precarious; and a repeat of the 2010/11 supply crisis remains a distinct possibility in the medium term. Excessive price volatility and uncertainty over future availability could slow the diffusion of best available technologies, e.g., for offshore wind turbines, fluorescent light bulbs in homes, offices and stores; in the hard drives of laptops; and in mobile phones, electric vehicles, washing machines, airplanes, batteries, and many other everyday products. As the world moves towards a cleaner, greener future, the uses for these metals are likely to increase rapidly. Overall world total reserves are 130 thousand metric tonnes and China dominates overall rare earth production. It is estimated that the demand will grow by 50 % in coming 10 years. Some of the rare earth element are at the verge of criticality and are at supply risk. Thus recycling of rare earth becomes a necessity.

The current project proposal is focused on the development of suitable process scheme for the utilization of waste for the recovery of valuable rare earth metal ions. "Selective Leaching" has been targeted in the current proposal, so that rare earth ions (Nd, Dy, Pr) or (Er, Tb, Eu, Y) present in the magnet or lamps respectively comes in the aqueous solution. For the individual separation of rare earth ions from aqueous solution, suitable solvent-extractant combination has to be designed with the help of molecular modeling techniques. To compare the performance of developed combination of extractant, separation studies will also be carried out by using commercially available extractants. Therefore, the idea of the project is to give complete "Extraction" and "Separation" scheme for the recovery of rare earths from scrap magnets and fluorescent lamps, so that it can be tried on the larger scale:

a. Development of process parameters for selective leaching of rare earths metals from WEEE (Waste Electrical and Electronic Equipments - Nd-FeB magnet and fluorescent lamps).
b. Design of suitable solvent-extractant combination (e.g. task specific ionic liquids) using molecular modeling techniques.
c. Synthesis and characterization of recommended solvent-extractant combination or task specific ionic liquids for separating rare earth ions (Nd, Pr, Dy) or (Y, Eu, Tb, Er).
d. Optimization of process parameters for the separation of rare earth ions (Nd, Pr, Dy) or (Eu, Tb, Er) by solvent extraction using commercially available extractants.
e. Conduct large scale trial of the complete process developed for scrap magnets and fluorescent lamps.

ANR ICSM
2015 - 2018

FANTA-SIC PROJET ANR-12-JS08-0010

(NOVEMBRE 2012 – DÉCEMBRE 2015): UTILISATION DE SEMI-FLUOROALCANES AMPHIPHILES POUR LE SOFT-TEMPLATING EN MILIEU NON ACQUEUX, VERS LA SYNTHÈSE DE SIC À POROSITÉ CONTRÔLÉE

ICSM-UMR 5257: jeune chercheur

Dr Julien Cambedouzou

This project is dedicated to fundamental research on structural organisation mechanisms in totally anoxic and aprotic media. Through the establishment of the ternary phase diagram involving silicon-alkanes, perfluoroalkanes (PFA) and semi-fluorinated alkanes (SFA), we intend to propose a new soft-templating approach to synthesize Silicon Carbide (SiC). This approach would allow us to control the porosity of the SiC at the mesoscopic scale, and opens a perspective for elaborating monoliths.

To date, it is indeed very difficult to achieve monoliths of pure SiC (without oxide) combining exceptional mechanical and thermodynamical properties with a high specific surface area, a property of major interest for catalysis supports. Thanks to the recent progresses i) in the synthesis of organosilane molecules of controlled Si:C (1:1) stoichiometry, ii) in the control of their polymerization and iii) in the physical chemistry of fluorinated amphiphilic molecules, it becomes possible to envision an original synthesis route towards SiC, using amphiphilic molecules of SFA in presence of PFA molecules. The molecular organisation of SiC molecules can be controlled at the mesoscopic scale by tuning the proportion of fluorinated species and the temperature. In such mesophases, precursor molecules are pre-organized around a soft template made of SFA and PFA molecules. The in situ polymerization of the SiC precursor molecules allows their organization to be conserved once the fluorinated template is washed out. A subsequent thermal treatment under controlled atmosphere therefore results in a SiC ceramic of controlled mesoporosity.

This project associates fundamental studies (understanding the organisation of fluorinated amphiphilic molecules at the molecular scale in totally anhydrous and anoxic media) and a strong applied stake: the production of SiC with moulded shape and controlled porosity. The bottom-up approach presented in this project starts from the synthesis of organosilicon precursor molecules and amphiphilic molecules and stretches to the production of the SiC ceramic. A special emphasis will be put on the determination of ternary phase diagrams of {organo-silicon molecules / PFA / SFA} systems using X-ray scattering techniques

In evolution with regards to the activities of the Institut de Chimie Séparative de Marcoule, this transversal project gathers specialists of organometallic chemistry, of complex fluid physical-chemistry and of material science. In this sense, it perfectly fits the federative objectives pursued in the partner institute.

ILLA PROJET ANR-12-BS08-0021

(MARS 2012 - MARS 2016) : INTERFACES LIQUIDE-LIQUIDE ACTIVES

Dr Olivier Diat

Partenaires :
CEA DRT (Coordinateur)
IRCE Lyon – UMR 5256
ICSM-UMR5257
CTI (industriel)
Renault (industriel
ICGM – UMR 5253
LC2P2 – UMR 5265

Le projet ILLA rassemble trois équipes étudiant par des approches complémentaires des interfaces liquide/liquide mises en jeu lors de la séparation d'ions métalliques par extraction liquid-liquide (transfert sélectif de l'eau vers «l'huile», effectué par des molécules extractantes hydrophobes). Ce processus est à la base de la séparation d'ions métalliques «précieux», parfois polluants, d'intérêts industriels, sociétaux et écologiques majeurs. En combinant des expériences spécifiques de surface et la simulation moléculaire, on étudie les caractéristiques des interfaces LL (taille, polarité, intermiscibilité, dynamique) ainsi que la concentration et l'orientation d'espèces «adsorbées» (extractants, complexes, …), en suivant quatre tâches bien définies. En se focalisant sur le cas des ions lanthanides Ln3+ extraits par des diamides hydrophobes ou des ligands azotés, nous nous proposons ainsi de décrire au niveau moléculaire les différentes étapes-clé de l'extraction à l'interface ainsi que la nature et la solvatation des espèces extraites dans «l'huile».

ILLA est un projet fondamental mettant en œuvre, pour la première fois, optique non linéaire couplée à des mesures de tension de surface, synthèse de molécules extractantes chromophores comme sonde de l'interface, et simulations de dynamique moléculaire. Au-delà des interfaces planes ou courbes «au repos» (par ex. avec des sels de lanthanide seuls, ou les extractants seuls), on étudiera les interfaces «en activité», c.à.d. leur évolution temporelle lors de complexation et de transfert d'ions, permettant de suivre la cinétique des processus élémentaires à l'interface. Les études expérimentales et les simulations sont loin d'être routinières, mais faisables. Les résultats permettront de mieux comprendre ce qui se passe à l'interface, et ainsi d'améliorer la cinétique et la performance de systèmes existants, voire d'en développer de nouveaux. Les développements méthodologiques (e.g. prédiction et interprétation du signal SHG, dispositifs expérimentaux) devront aussi permettre d'étudier d'autres interfaces, comme en catalyse biphasique.

GTM PROJET ANR-13-TDMO-0006

(NOVEMBRE 2013 - OCTOBRE 2016) : THERMAL ENGINE EXHAUST MANAGMENT

Dr Daniel Meyer

Partenaires :
ICSM-UMR 5257 (Coordinateur)
CEA/DEN/DRCP-LILA)
Institut Lumière Matière UMR 5579, Villeurbanne
Modélisation et Simulations Moléculaires UMR 7177, Strasbourg

In the actual context, European emission standards become particularly severe for motor vehicle air pollution problems (EURO 5 & 6). But emission standards become more and more strict. The evolution from Euro 5 to Euro 6 (2014) aims to reduce NOx by 56% (65% efficiency), while Euro 7 will target an efficiency of 80%. The actual limitation in efficiency of car exhaust treatment comes from the thermal activation at low temperature. The GTM (Thermal Management thanks to materials) project aims to maximize the time slot catalytic activity of the post-treatment systems used in automotive vehicles. Today, an increase in pollutant emission at low temperature is observed, due to new combustion processes developed to reduce fuel consumption (lean-burn technologies) and therefore also CO2 emissions. We observe a temperature reduction in modern exhaust line, and this phenomenon has direct consequences on post-treatment systems, unable to operate knowing that they are not in their optimal temperature range. With GTM materials, the temperature ignition will be lowered from 10 to 40%. Direct pollutants include carbon monoxide (CO), hydrocarbons (HC=propene...) and nitrous oxides (NOx or NO+ N2O +NO2), whereas ozone belongs to the family of indirect pollutants produced in-situ by contact between ambient oxygen, NOx and HC. The most toxic pollutant at the moment is NOx. To reduce the production of NOx, a first approach consists of maximizing the combustion efficiency. Motor management allowed making significant gains in CO2, while reducing the exhaust gas temperatures. GTM project proposes a passive solution to develop a thermal buffer reservoir (based on SiC) coupled with precious metals coating directly on honeycombs ceramics. The GTM consortium is composed of complementary teams. It includes Renault, specialized in defining and qualifying exhaust systems, CTI, wash-coater and supplier of ceramic honeycombs and four research institutions, which are complementary in the value chain : CEA (nanomaterials and process), C2P2 (catalysis synthesis), l'ICSM / ISCM (barrier coatings and thermal reservoir) and l'IRCELYON (efficiency characterisation versus CO, HC and NOx abatement). Experimental and theoretical approaches (thermal simulations) will be implemented so as to be complementary during the whole project. Pre-dimensioning of SiC quantities and the head loss induced will be analysed in relation to the obtained thermal gain. Successive generations should allow improving the striking and the efficiency at high temperatures (hot-start materials), the head loss and the aging properties. The purpose is to reduce the NOx contents by 80% using the deNOX technologya t a temperature as low as 200°C.

VECT'OLEO PROJET ANR-14-LAB4-0005

(SEPTEMBRE 2014 - SEPTEMBRE 2017) : «LABORATOIRE DE STRUCTURATION DES CORPS GRAS NATURELS POUR LA VECTORISATION DE COMPOSÉS BIOACTIFS VÉGÉTAUX EN NUTRITION TOPIQUE ET ORALE» WITH OLEOS SA

Dr Olivier Diat

Partenaires :
ICSM-UMR 5257 (coordinateur)
OLEOS, Lunel(industriel)

L'extraction par un corps gras naturel, une huile, un beurre ou une cire végétale, de principes actifs contenus dans des végétaux est à la base du concept technologique développé et breveté par OLEOS qui propose ainsi une nouvelle génération d'actifs cosmétiques éco-conçus: les Oléoactifs®. La présentation huileuse d'un extrait végétal permet d'offrir une forme originale à la fois stabilisée et vectorisée de différentes molécules mêmes fragiles et oxydables, par exemple des flavonoïdes ou autres antioxydants phénoliques, qui s'organisent dans la phase huileuse continue au cours de l'extraction et sont ainsi protégées en formulation. Le principe repose sur la théorie du « paradoxe polaire des antioxydants »: Il y a un intérêt à ajouter dans une huile végétale des antioxydants polaires pouvant s'organiser et agir en synergie avec les antioxydants apolaires. Ce concept valorise aussi la synergie biologique in vivo en particulier dans la peau, entre les propriétés des acides gras et des micronutriments de l'huile et celles des différents bioactifs extraits. Mais cette technologie reste à ce jour limitée par deux verrous majeurs:
1/ la concentration en composés polaires lipo-extractibles par une huile est limitée,
2/ l'organisation moléculaire et colloïdale des différents composés extraits par une huile n'est pas connue et de ce fait les résultats de l'oléo-extraction restent empiriques et difficilement pilotables au niveau industriel.

Or, l'oléo-extraction ou l'obtention d'huiles végétales structurées est aujourd'hui un enjeu industriel prometteur pour obtenir des éco-ingrédients verts, sans chimie ni synthèse, plus bio-disponibles et plus facilement formulables que des extraits hydro-alcooliques classiques.

L'ICSM est un laboratoire expert de l'étude des organisations supramoléculaires et des processus dynamiques de molécules amphiphiles et d'ions aux interfaces dans le cadre de l'extraction liquide/liquide. Ce laboratoire a une connaissance scientifique et mécanistique poussée et assez unique des huiles structurées et de la complexation d'ions et d'autres molécules polaires en vue de leur séparation en système huile. Il dispose d'un équipement performant pour conduire des études physico-chimiques, thermodynamiques, microscopiques et structurales sur ces milieux. L'expertise de l'ICSM est donc tout à fait complémentaire de celle d'OLEOS sur les lipides et l'oléo-extraction. Le LABCOM VECT'OLEO permettra de mettre au point des systèmes ternaires [huile végétale + complexant naturel + composé bioactif] offrant des performances accrues en terme de concentration et de stabilité par une meilleure maitrise de l'organisation mésoscopic en système continue huile. Ce LABCOM permettra d'établir de façon durable un échange de connaissances, de créativité et d'outils analytiques permettant de piloter la création d'Oléoactifs® innovants et plus performants qui seront mis sur les marchés alimentaires et cosmétiques par OLEOS.

Au-delà des pistes d'innovation produits et procédés que VECT'OLEO apportera directement à OLEOS pour son développement concurrentiel, ce laboratoire commun contribuera à la compréhension nécessaire à l'optimisation des voies et procédés d'extraction par des solvants huileux apolaires, à la modélisation des transferts transcutanés d'espèces polaires et apolaires via des huiles structurées, à l'étude de l'impact des processus d'oxydation sur les phénomènes de stabilité de la vectorisation huileuse au sein d'une structure cellulaire (fortement dépendant de la structuration et de la dynamique des espèces chimiques aux échelles moléculaires et supramoléculaires).

Le LABCOM VECT'OLEO propose une recherche et un développement axés « 100% naturel » couplés à une gestion des ressources renouvelables (huiles végétales, plantes) et limitées en terme de demande énergétique (utilisation des ressources végétales locales) pour les axes santé et bien-être, avec des applications en dermo-cosmétique et en nutrition.

SILEXE PROJET ANR-13-CDII-0010

(JUIN 2014 – DÉCEMBRE 2017): STRATEGIC METAL RECYCLING IN IONIC LIQUIDS BY EXTRACTION AND ELECTRODEPOSITION PROCESS

Dr Stéphane Pellet-Rostaing

Partenaires :
ICSM-UMR 5257 (Coordinateur)
LCME (EA 1651, Chambery)
IJL (UMR 7198, Metz)
TND (Industriel, Isebergue)

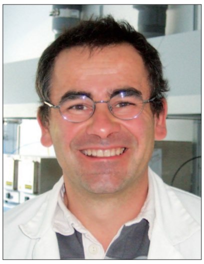
The SILEXE project brings the expertise of three academic laboratories and one industrial partner internationally recognized in the field of ion separation (ICSM-UMR 5257), ionic liquids (LCME-EA 1651), electrochemistry (IJL-UMR 7198) and metal recycling from e-cards (TerraNova). SILEXE will investigate Room Temperature Ionic Liquids (RTILs) as unusual media for strategic metal recycling, especially indium, tantalum and gold, through the use of a selective extraction (or back-extraction)/ electrodeposition process starting from lipophilic or hydrophilic ligands and Task Specific Ionic Liquids (TSILs) as extractants. A successful recycling of the assessed critical metals is very important regarding increase of resource efficiency, avoidance of possible scarcities and reduction of the overall environmental impacts linked with the life cycles of the strategic metals. Furthermore the positive contribution of the recycling sector to employment and to adding value should be taken into account. Excepted from rare earths contained in the low-energy lamps for which an industrial process has recently emerged (Solvay process), until today for some metals like tantalum in dissipative applications (cell phones), lithium (batteries), gallium, indium and germanium (up-to-date just very small and dissipative amounts in post-consumer materials), there are no running recycling technologies at commercial scales and only first steps in small (pilot) plants are initiated. However, the supply of strategic metals has a clear impact on industrial defense and security of countries that would lack them. In this context, we propose to develop an efficient process for the extraction and purification of the strategic metal In, Ta and Au. RTILs containing chelating ligands or TSILs having strong affinity with the targeted metal will be used as extracting media. The pure metal will be recovered using selective electrodeposition process. Several studies on metal separation by liquid/liquid extraction techniques involving chelating agents in Ioni Liquids, or in Task Specific Ionic Liquids are already described in the literature. It appeared thus interesting to extend the study of metal recovering by extraction and electrodeposition in ionic liquids with potentially more selective synthesized ligands and/or new task specific ionic liquids binding chelating sites. Because they play a crucial role in the ligand-metal binding, the experimental conditions of temperature, acidity, concentrations in solution combined with the ionic liquid properties, especially the nature of the anionic species (hard/soft, BF4-, NTf2-, …) will be as many of parameters which will have to be considered in order to optimise the liquid/liquid separation. Extraction from aqueous phase to hydrophobic ionic liquid containing the ligand (or a mixture of ligands for a potential synergistic effect) or the TSILs or extraction from aqueous phase directly performed in TSILs will particularly be considered. Another strategy will be envisaged, based on a preliminary extraction step from aqueous phase in conventional alcane type solvent followed by a de-extraction process from the organic phase containing the metal-ligand complex to a hydrophilic ionic liquid or task specific ionic liquid. Based on the preliminary results obtained in SILEXE, modulated techniques (selective extraction/electrodeposition and/or de-extraction/electrodeposition ligand/ TSIL, lipophilic/hydrophilic ionic liquid, initial aqueous phase containing the targeted metal, ionic strength…), could be extend to the purification of other strategic metals (Ga, Nb…).

CARAPASS PROJET ANR-16-CE08-0026

(NOVEMBRE 2016 – OCTOBRE 2020) : CARBIDE & CARBONITRIDE NANOCOMPOSITE BASED PHOTOTHERMAL SOLAR ABSORBERS

Partenaires :
IEM Montpellier, UMR5635 (coordinateur)
IRCER Limoges, PROMES Odeillo, CRM2 Nancy, ICSM Marcoule

A common industrial challenge to improve the efficiency of the solar-to-electricity conversion for concentrating solar power (CSP) is to operate at high temperatures (900-1000°C). Research and development efforts on over recent years have therefore focused on the materials that compose the solar absorber which plays the key role in the overall CSP system performance. Silicon carbide (SiC) exhibits a chemical inertness, a high temperature oxidation resistance and a robustness compatible with the operating conditions of further CSP systems. However, despite a good sunlight absorption, SiC has a high thermal emittance, leading to a poor optical selectivity. Promising properties for absorber materials can be found in transition metal carbides and nitrides of column IV according to their refractivity, their inherent spectral selectivity and a lower thermal emittance compared to SiC. However, their major limitation is their tendency to be oxidized in the targeted temperature range. By entering the scope of the Challenge 3 ―Stimuler le renouveau industrielǁ (theme ―Matériaux et procédésǁ and more particularly the priority 14), the CARAPASS project proposes to prepare nanocomposites of the type MX/SiC (M = Ti, Zr, Hf; X = C_xN_{1-x}, $0 \leq x \leq 1$) by combining SiC and transition metal carbide and/or nitride in the same materials with the goal to combine optical selectivity, thermomechanical properties, chemical inertness and oxidation resistance to fit the requirements of the next generation of high temperature absorber materials. These materials are prepared as dense monoliths to maintain their mechanical strength and robustness at high temperature. The four year CARAPASS collaborative research project brings together specialists in materials synthesis, materials characterization, and computational approaches. It is built from five French research institutes, IEM, ICSM, SPCTS, PROMES and CRM2, with complementary expertises in chemistry, in processing, in characterization of materials - especially for CSP - and in modeling which have already collaborated in the past. To reach our objectives, the project is based on the promising results obtained by IEM and ICSM with TiC/SiC nanocomposites. CARAPASS is subdivided into five interconnected scientific tasks. The first task is focused on the preparation of nanocomposite powders using two chemical routes already investigated by IEM and ICSM. The second task consists in preparing dense materials following three strategies based on pressing, casting and Spark Plasma Sintering processes to be characterized in tasks 3 and 4. Physical and chemical characterization of nanocomposites is the topic of the task 3. In addition to standard material science techniques available in each institute, the thermostructural, mechanical and thermal properties of the nanocomposite monoliths will be evaluated before and after thermal aging. The task 4 studies the optical characterization of the nanocomposites to demonstrate the selective behavior of nanocomposites The optical properties will also be measured after accelerated aging. A theoretical work will be done in task 5 to provide for each selected chemical composition the IR spectra and the visible-UV optical spectra using density functional theory and the GW approximation. The present project is built to elaborate materials that are expected to lead to benefits for the advancement of science, industry and society and should allow France to be in place on this growing thematic at international scale.



ICSM : Dr Xavier Deschanels

TURBO PROJET ANR-16-CE34-0003

(OCTOBRE 2016 – NOVEMBRE 2018) : TOXICITY OF URANIUM: MULTI-LEVEL APPROACH OF BIOMINERALIZATION PROCESS IN BONE

Partenaires :
Université Nice Sophia Antipolis - CEA TIRO-BIAM (coordinateur)
Université Nice Sophia Antipolis - Institut de Chimie de Nice
CEA/INAC/SCIB Laboratoire Chimie Inorganique et Biologique
ICSM-LHYS

Uranium chemical toxicity is a subject of concern for the general population as various anthropic activities have led to a substantial increase of the uranium background concentration in the environment. If the actual trend is to reduce nuclear energy in Western Europe, other countries like Russia, China or India have been substantially investing in the development of new nuclear power-plants. Thus the use of uranium will certainly remain a concern for the future generations, worldwide. Most experimental studies related to the health effects of uranium were dedicated to its radiotoxicity and its acute chemical toxicity (nephrotoxicity). Some animal studies and few epidemiological studies also considered chronical exposure, but the data are still too sparse to derive a toxicological threshold associated with long-term effects. Moreover, although the skeleton is well known to be the main site of uranium long-term accumulation, the chemical effects of uranium on bone health remain an open question. Bone is a complex organ composed of an organo-mineral matrix, undergoing constant remodeling thanks to a tightly regulated cellular system. Therefore the question of how uranium interacts with the physiological environment and accumulates in bone matrix can only be answered using a multi-level and multidisciplinary approach, which relies on both molecular and cellular understanding. Recently, we (the consortium of this project) demonstrated that uranium is transported in the blood as complexes with proteins involved in bone metabolism. In addition, we showed that this actinide element affects the main functions of bone cells in vitro, i.e. construction and resorption. The present project represents the first comprehensive mechanistic investigation of uranium interaction with the bone matrix. We propose to study the exchange mechanisms between uranium and bone in vitro and ex vivo, at three different levels: the molecular level, with synthetic biomimetic bone matrices and peptides modeling relevant biological binding sites in proteins; the biochemical level, with bone matrix proteins and circulating proteins; and the cellular level, involving osteoblast/osteocyte and osteoclast functions. This innovative global approach using a multi-level strategy will lead to a better understanding of the mechanisms involved in bio-mineralization of uranium and will help to design and assess new detoxification (also called decorporation) agents for this metal. Moreover, the interdisciplinary procedures developed in this study are of general interest and will bring added value regarding other toxic metals which also accumulate in bone.

ICSM : Dr Damien Bourgeois

CADET PROJET ANR-ANDRA-RTSCNADAAI600I4
(MARCH 2016 – SEPTEMBER 2019): CAVITATION-ASSISTED DECONTAMINATION

Partenaires :
ICSM UMR 5257
Institute Jean Le Rond d'Alembert (D'ALEMBERT) UMR 7190 (Coordinator)

The decommissioning of nuclear facilities has become a topic of great interest because of the large number of facilities which were built many years ago and which will have to be retired from service in the near future. As a result of this activity, a wide range of solid and liquid wastes arise. Aqueous solutions of complexing organic acids (EDTA, oxalic acid, citric acid, ascorbic acid) are frequently applied to enhance radionuclide removal from the contaminated surfaces. The removal of radionuclides from this secondary waste requires appropriate process to destroy the complexing organic matter. This project addresses the problem of minimization of organic contaminants in secondary liquid radioactive waste formed during the decontamination of nuclear devices. The minimization of the generation and spread of radioactivity, and the minimization of the volume of radioactive wastes to levels «as low as reasonably achievable» (ALARA) has both safety and economic significance. The feasibility of scaling-up to industrialization should also be considered taking into account that the decontamination technique should not be labor-intensive, difficult to handle, or difficult to automate.

CADET project based on cavitation techniques meets these requirements. Indeed, cavitation-based treatment does not require large amounts of side reagents due to in situ generation of strong oxidizers enable organics mineralization. Cavitation processing can be easily automated thus providing maximal level of safety for personal. In this fundamental collaborative project, the aim is to provide the evidence for the activity of coupled cavitations (acoustic and shock induced (spalling)) for organic acids oxidation in waste water produced during decontamination of nuclear facilities and to generate better understanding on developing fields in sonochemical degradation technology. All possible effects brought about by the addition of catalysts with ultrasonic irradiation or shock induced cavitation to remove organic compounds formed complexes with radionuclides from wastewater streams will be studied.

Thus, three main objectives were identified and will be developed in 4 tasks. The first objective is to provide a new cavitation-based process for wasted-water treatment generated during decontamination of nuclear facilities. For this, 2 types of cavitation generation, spalling and ultrasound, based on D'ALEMBERT and ICSM background will be used respectively. The second objective is to confront the two approaches in order to optimize the process also in coupling the cavitation with heterogeneous catalysts. The third objective is to optimize the catalysts according to specific conditions of processing, such as the presence of local shock waves and shearing forces as well as significant concentration of organic acids with a strong complexing ability.

ICSM : Dr Serguei Nikitenko

DYNAMISTE PROJET ANR-15-CE07-0013

(OCTOBRE 2015 – MARS 2020) : **DYNAMICS OF ALUMINO-SILICATES FLUIDS**

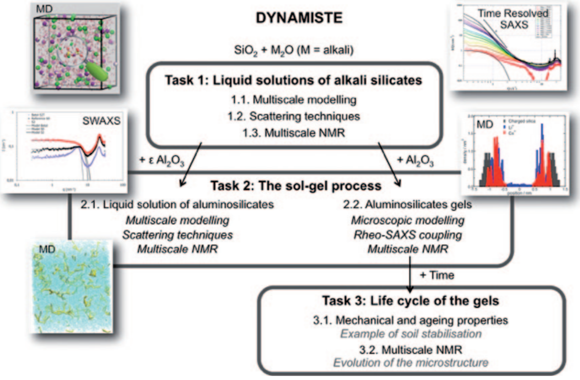
Dr Magali Duvail

Partenaires:
ICSM-UMR 5257 (coordinator)
CEA Marcoule (DEN/DE2D)
Laboratoire Charles Coulomb – UMR 5221 (Université de Montpellier)
Wöllner GmbH & Co.KG (Industrial, Ludwigshafen, Germany)

DYNAMISTE aims at developing experimental and theoretical tools in order to optimize industrial processes in which alkali solutions of aluminosilicates are involved in an attempt of developing sustainable and clean industry. This project gathers three academic laboratories recognized for their expertise in the physical chemistry of condensed matter, the Institut de Chimie Séparative de Marcoule with competency in "green chemistry" science, a CEA department for the waste retreatment and conditioning and specialist for the characterization and formulation of cement-based materials, and a CNRS team at the Laboratoire Charles Coulomb expert in multi-scale NMR technics, in collaboration with the German industrial partner Wöllner GmbH & Co.KG, who is one of the leaders in production of alkali silicate solutions.

Thanks to their environmental acceptability and their adaptability over a wide range of applications, alkali solutions of aluminosilicates are increasingly used. During the last 10 years, they have increased their important role as inorganic and water based binders, notably for the production of mineral based, ecological materials for the building and construction industry. Alkali-silicate solutions became more and more important for the alkali activation in geopolymer application, which is considered as green chemistry. Sodium aluminosilicate gel are also used for so-called "ground stabilization" and as "sealing layers" in order to avoid the inflow of groundwater in construction pits or the reinforcement of sandy ground. Although such solutions are increasingly used in the industry, there remain outstanding questions regarding their stabilities, and more precisely concerning the gelation process that is driven by the composition of the solution. It is therefore crucial to provide realistic description of such fluids, which remains quite not well known, and has to be confirmed experimentally and theoretically.

This project relies on a synergic approach coupling both experiments and modeling. In order to access all the spatio-temporal phenomena of such systems, the experimental part consists in studies based on (i) rheology techniques coupled with scattering techniques: Dynamic light scattering (DLS), small and wide angle x-ray and (or) neutron scattering and diffraction (SWAXS, SANS and XRD), and on (ii) multi-scale NMR approaches (from Å to few tens μm). In the meantime, the theoretical part is based on multi-scale methods coupling molecular dynamics and coarse-grained simulations, allowing for accessing the structural and dynamical properties of these fluids at both the molecular and supramolecular scales.



Organization of DYNAMISTE.

These experimental and theoretical developments applied in the context of the soil stabilization will be transferable and adaptable to further important industrial application systems, such as dispersion of clays, geopolymer binders, ecological mineral paints and concrete acceleration.

X-MAS2 PROJET ANR-17-CE06-0004

(DECEMBER 2017-NOVEMBER 2020): XENOTIME: A MATERIAL FOR ACTINIDES SPECIFIC STORAGE

Dr Adel Mesbah

Partenaire: ICSM, UMR 5257 (LIME/LNER)

For safer and clean nuclear energy, X-MAS² project intends to develop promising phosphate matrices dedicated to the long term storage of high level nuclear wastes. This project will consider the xenotime phase having a general formula of $LnPO_4$ (Ln = Tb–Lu) and crystallizes in the zircon structure type. In the case if the trivalent actinides or their lanthanide surrogates the incorporation goes through the formation of solid solutions of $Ln_{1-x}An_xPO_4$. Whereas with tetravalent actinides (Th, U), two different mechanisms will be explored leading to the formation of $Ca_xAn_xLn_{1-2x}PO_4$ et $An_xLn_{1-x}(SiO_4)_x(PO_4)_{1-x}$ compounds. For the first time such materials will be synthesized by wet chemistry methods allowing the formation of pure and homogeneous phases and will be thoroughly characterized. Afterward, their thermal behavior, sintering ability and also their chemical durability will be evaluated in order to propose efficient matrices for the conditioning of high level nuclear wastes.

FOAMEX PROJET ANR-17-CE08-0016

(FÉVRIER 2018 – FÉVRIER 2022) : MOUSSES DE LIXIVIATION POUR L'EXTRACTION DE MÉTAUX DES DÉCHETS ÉLECTRONIQUES

Partenaires :
ESPCI (Coordinateur)
ICSM-UMR 5257
BRGM (Industriel)
EXTRACTHIVE (start-up industriel)

The recovery of metals from WEEE, Waste from Electrical and Electronic Equipment, is becoming a major challenge to preserve natural metal resources while treating a large amount of waste. Available recycling processes present several drawbacks : pyrometallurgy, based on a smelting process, is highly energy consuming, generates large amounts of off-gases and there are only a few installations in EU requiring non ecological transportation of wastes. Hydrometallurgy, which consists in leaching the metal wastes to extract metal ions in solution, is more suitable for small and local installations, but it generates very large volumes of effluents which need to be treated. The goal of this project is to use foams as a leaching medium to extract and concentrate metal ions from shredded PCBs (Printed circuit boards), the most valuable WEEE. Foams contain 90% of air and 10% of liquids, therefore this idea would help decreasing the amount of effluents. Moreover we expect to improve the efficiency of standard leaching methods due to a better dispersion of waste particle in the foam channels. We expect that our project, by reducing the amount of effluents generated during leaching, will contribute to solving some of the issues of current hydrometallurgy methods and which prevent their industrial development at very large scale. This project will be an opportunity for the start up Extracthive to develop an expertise on foam processes for recycling metals from WEEE, which then may be applied to other types of waste such as batteries and therefore to reach new clients.

ICSM : Dr Olivier Diat

MULTISEPAR PROJET ANR-15-CE07-0013-01

(FEB. 2019 – AUG. 2022): «MODELISATION MULTI-ÉCHELLE DES PHASES ORGANIQUES POUR L'EXTRACTION LIQUID-LIQUIDE »

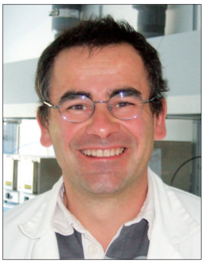
Pr Jean-Francois Dufrêche

Partenaires :
ICSM-UMR 5257 (coordinator)
CEA Marcoule (DEN/DMRC)
Laboratoire Phenix Sorbonne Université (Paris)

The ANR MULTISEPAR project aims to model rare earth (lanthanide) separation processes used in hydrometallurgy and for recycling. More specifically, it will focus on the solvent phase of liquid-liquid extraction processes, the modelling of which being currently at a very early stage. The multi-scale approach will be based on three complementary levels of description. First, at the atomic level, molecular dynamics simulations will calculate the structure and speciation in these solvent phases. The molecular interaction potential that we will use here has recently been validated from ab initio simulations by comparison with spectroscopy experiments. An umbrella sampling methodology will calculate the forces between solutes. The purpose of this step will be both the determination of the physico-chemical ingredients required for solvent phase modelling and also the calculation of the mesoscopic properties used by the other more macroscopic description scales. In another level of descriptions, mesoscopic Brownian simulations will be performed to calculate the effects at greater distance. Based on molecular simulation data (effective interaction potential and mobilities), either Brownian dynamics simulations or Multiparticle Collision dynamics simulations will be used to access the largest scales. The solutes activity coefficients and the stability of the solvent phase can thus be calculated. At the dynamic level, solute transport (diffusion and electrical conductivity) as well as viscosity will also be studied because they drive many industrial processes. As both experiments and molecular simulations show that in some cases solutes decompose poorly into independent particles but rather form a continuous network of hydrophilic parts in the solvent phase, we will also propose a second mesoscopic model to describe these solvent phases, this time based on a microemulsion model. Using a Gaussian random field methodology, we will propose a code representing the Gibbs energy of the solvent phase, which will make it possible to predict both the structure and the extraction properties. The fundamental quantities of this level of description will be here the properties of curvature (spontaneous curvature and rigidity) due to the extractants which will be deduced from the molecular simulations. The study of extraction as a function of the concentrations in the aqueous phase and of the extractant concentration will validate this methodology. We believe that this calculation will be a success if this microemulsion model can represent extraction equilibria with a much smaller set of parameters than traditional models based on multiple chemical equilibria between species. Thus, this project on lanthanide extraction could lead to a model that will be implemented in chemical engineering codes describing this process. We hope that through this multiscale project and the extensive use of numerical computing resources a new image of extraction mechanism will emerge from molecular modelling and that it will be able to bridge the gap to the macroscopic descriptions of this method of separation chemistry.

AUTOMACT PROJET ANR-18-CE05-XX

(OCT. 2018-OCT. 2022): "SOLID FIXATION AND AUTO-CONDITIONING OF ACTINIDE ELEMENTS COMING FROM CONTAMINATED LIQUID OUTFLOWS"



Dr Xavier Deschanels

Partenaires :
ICSM, UMR 5257 (coordinateur)
CIMAP GANIL Caen, IRAMIS Saclay, ICG Montpellier

The objective of this basic research project is to develop a new strategy for the treatment of radioactive effluents based on the use of a porous functionalized support. This support would allow at the same time the separation of the RadioNucleide (RN) using a selective organic function, and their encapsulation after collapse of the porosity by a «soft» way (sol-gel, heating under stress, irradiation effect). This new concept would result in obtaining a primary wasteform matrix. Mesoporous silicas will be used as model support materials, because the nanometric size of their pores allows easy closure. Furthermore, the silica has a chemical composition close to high-level nuclear waste packaging materials (glass). This new so-called separation / conditioning strategy would constitute a significant simplification of the number of step, compared to «traditional» processes for the treatment of radioactive effluents. Such traditionnal processes usually require a concentration step of radioactivity (evaporation, precipitation, etc.), followed by of a embedding step. It could be adapted to any type of liquid effluents, aqueous or organic, containing radionuclides emitter alpha, beta, gamma. This process could be interesting for the treatment of effluents produced in nuclear installations (STEL ...), but also for the treatment of effluents from dismantling sites because of its compactness. In this project we will focus our study on the treatment of effluents containing actinides, which have a significant radiotoxicity linked to the alpha decays induced . This mode of disintegration could be beneficial for the collapse of the mesoporous structure , leading directly to a «primary wasteform matrix». The closure of the porosity under self-irradiation will therefore be particularly studied, with the realization of materials doped with short-life actinides (244Cm, 238Pu). Another innovative aspect of the AUTOMACT project will be the search and grafting of selective actinide ligands. For that, tributyl phosphate, which is used in the Purex process for the separation of uranium and plutonium, is a potential candidate. The purpose of this project is therefore to propose a new all-in-one RN separation / conditioning route using specific materials allowing both decontamination operations and their simple evolution towards a primary containment matrix.

DECIMAL PROJET INVESTISSEMENT D'AVENIR ANDRA
(OCT 2017- SEPT 2021): "PHENOMENOLOGICAL DESCRIPTION OF THE CORROSION AND ITS IMPACT ON THE DURABILITY OF ENCAPSULATED MAGNESIUM WASTES IN HYDRAULIC BINDERS "

Dr Diane Rebiscoul

Partenaires:
CEA/DEN (coordinateur)
INSA Rennes
IRCP-ENSCP
ORANO
ICSM

The DECIMAL project (call for projects ANDRA « Optimization of radioactive dismantling waste's management ») takes place in the context of the nuclear waste treatment. This fundamental research project, involves four research groups (CEA, ICSM, INSA and IRCP), an industrial partner (ORANO) and also the CEA as nuclear waste producer.

The reprocessing of spent nuclear fuels from French UNGG (Uranium Natural Graphite Gas) nuclear reactors has generated cladding wastes mainly made of magnesium alloys. The CEA strategy is to encapsulate these intermediate-level long-lived wastes into a geopolymer matrix. Thus, the durability of the geopolymer/ magnesium alloy with respect to the storage requirements supplied by ANDRA has to be studied.
Indeed, the reactivity of the magnesium wastes with water in repository implies that the metal can corrode resulting in a dihydrogen gas release that is detrimental to the safe storage of conditioned waste packages. This reactivity may also be affected by the irradiation due to the radioactivity of the spent fuel cladding.

Regarding this context, the objective of this project is to develop a methodology to characterize the impact of the reactivity of encapsulated magnesium alloy in a geopolymer matrix, on its durability, and to understand the processes occurring during the evolution of the metal/matrix interface during aging with or without irradiation. The DECIMAL project proposes a dual approach to study the reactivity of the MgZr alloy: the electrochemical analysis of the kinetics of corrosion of the MgZr alloy encapsulated in geopolymers in the presence or absence of passivating agent and the characterization of the metal/matrix interface (Ph.D Rémi Boubon at LNER). The impact of the reactivity of Mg on the matrix will be considered as chemo-hydro-mechanical properties. This methodology will allow the determination of the corrosion processes occurring between the metal and the matrix, their evolution with time and under irradiation.

LABEX CHEMISYST

POLE
chimie
Balard

LABEX CHEMISYST

Scientific interest in complex systems is continuously growing because of their tremendous spectacular developments at the boundaries of sciences. Examples include cognitive models of thinking, human genome, ecosystems, metabolism, systems chemistry, nanochemistry, material science, etc. From research into complex networks emerge powerful advances in many scientific disciplines: biology, mathematics, engineering, physics, economics, computing science and recently also in chemistry and material science. Within this context, multivalent interactions, representing multiple copies of a specific recognition element and exhibiting a large range of reversible connectivies, can generate adaptive networks of increased dimensional behaviors. This gives the opportunity to extend and to engineer multivalent interactions in order to control the organization of complex matter across extended scale. It generates systems which may possess novel properties not present at molecular level. This opens wide perspectives and one can foresee a fundamental transition from supramolecular design toward constitutional selection approaches, which might give great potential in various applications, as demonstrated through **CheMISyst**.

CheMISyst associates 6 research units spread on three sites around an interdisciplinary project devoted to molecular and interfacial chemistry with a focus on the non-covalent long range forces driving self-assembly. Thus, **CheMISyst** is dedicated to the study and development of chemical systems, from thermodynamic and structural viewpoints, with strong input from modern analytical chemistry and with a focus on long-range non-covalent self-organization of fluids and solids at nanometer to micrometer scales. The objective is to achieve "systems" capable of selectively recognizing, encapsulating, transporting or transforming ions and molecules in various media. This includes interfacial chemistry, which deals with the study of the properties of ions and molecules confined at the surface of a solid or at the interface of two fluids. The project aims at promoting the abovementioned fields of expertise of the Balard Institutes (ICGM, IBMM, IEM, ICSM) to the international forefront. Accordingly, the contour of scientists was extended to include a team of "soft matter" physicists, of the Laboratory Charles Coulomb (UM) and the Centre of Materials of l'Ecole des Mines, in accordance with the regional dimension of the project.

The main topics underlying all the studies are:
I) the identification of the forces at the origin of the molecular and supramolecular properties;
II) the understanding of self-assembly and its consequences on the macroscopic properties of molecular systems and materials; iii) the development of predictive models.

It is organized around 4 clusters:

CLUSTER 1:
Molecular and interfacial systems for task specific materials
CLUSTER 2:
Chemical systems of self-assembled biomolecules
CLUSTER 3:
Chemical systems for separation and recycling
CLUSTER 4:
Cooperation, synergism and diversity in intermolecular interactions

1) MOLECULAR AND INTERFACIAL SYSTEMS FOR TASK SPECIFIC MATERIALS

This cluster includes materials preparation and processing, analysis, characterisation of task-specific properties such as ion and electron transfer, magnetic exchange, energy conversion and storage processes, and investigation of the interfaces developed within the materials and with their environment, using both experimental and modelling approaches. It builds upon the internationally recognised strengths of Balard chemists in the development of multifunctional materials with designed texture, morphology and properties. Moreover it is based on theoretical methods for a greater fundamental understanding of the factors driving spatial/temporal self-assembly and self-evolving behaviour under the influence of external stimuli. For example, it is devoted to the development of materials as surface-modified nanoparticles, fibres, membranes or monoliths as single components or nanocomposites with hierarchical or monodisperse porosity for hydrogen permselectivity, lithium ion battery electrodes, photocatalytic clean-up of water, photonics, light harvesting and nanoelectronics.

2) CHEMICAL SYSTEMS OF SELF-ASSEMBLED BIOMOLECULES

This second cluster aims at developing intelligent compounds, drugs and biomaterials based on the elaboration of relevant molecular systems. The understanding of the molecular and structural bases of biological processes allows conception of bio-inspired synthetic molecules and functional assemblies as active as natural systems (genetic, proteic, lipidic, saccharidic systems) and endowed with new features. Gathering the skills and expertise of biologists, analysts, physicists, and synthetic chemists of CheMISyst, this cluster has stimulated the participation of CheMISyst scientists in national calls for proposals and initiated international collaborations.

3) CHEMICAL SYSTEMS FOR SEPARATION AND RECYCLING

The scientific topics developed within this cluster concern the elementary processes involved in the dissolution (ores and solid wastes), the separation processes and the recycling/storage of targets from complex media (acidic, salted with organics…) and this considering different scales of observation (from the molecular level toward colloidal, mesoscopic and macroscopic scale). As defined, the objectives are to enable, perform and use the separation phenomena using particularly the conceptual and practical possibilities of nano-chemistry, defined from systems for which long-range interactions and surface energy dominate the behaviour. Specifically, the cluster 3 will be focussed on chemistry and physical chemistry of extracting systems and processes for recycling metals of interest (strategic metals, heavy metals, radionuclides, organic pollutants…) from manufacturing waste, such as technological devices, in the end of first life or contaminated solutions. Thus, this cluster aims at developing, understanding and optimizing the selective ion separation processes by developing and synthesizing specific original extracting agents ant materials and by studying the mechanisms associated that govern the selectivity, including cooperative supramolecular phenomena. More particularly, it includes solvent extraction in ionic liquids or supercritical fluids, membrane filtration, and adsorption on specific hybrid materials, with a special focus on analysis and characterization of the extraction mechanisms, using both experimental and modelling approaches. Finally, it also targets specific materials for decontamination which find applications in water treatment or decorporation.

4) COOPERATION, SYNERGISM AND DIVERSITY IN INTERMOLECULAR INTERACTIONS

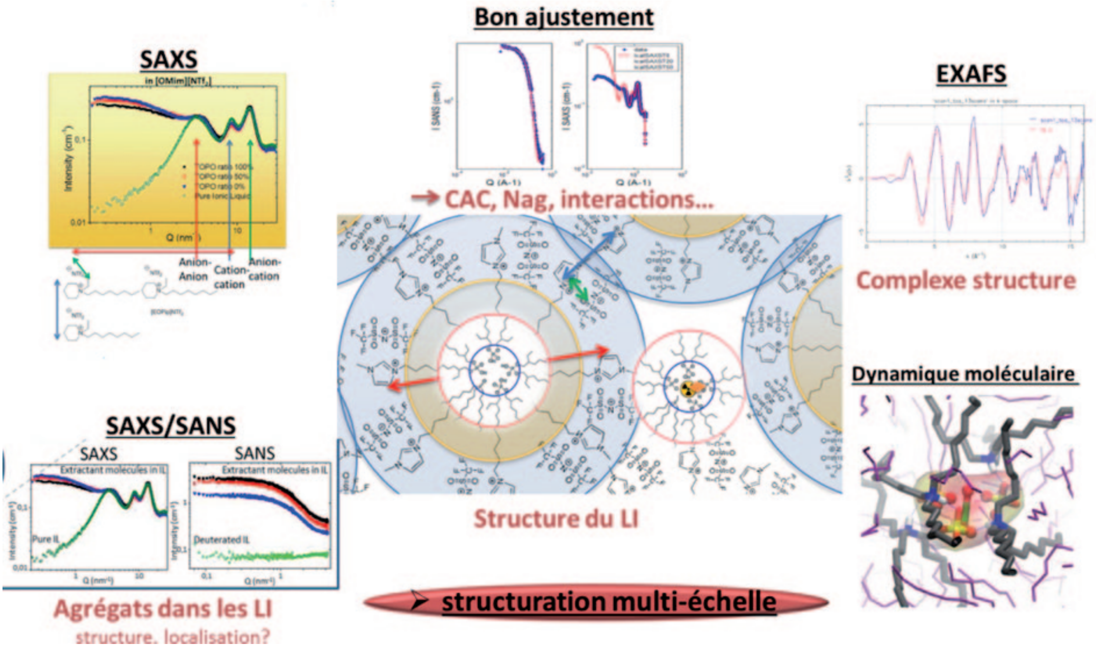
This cluster has a common central theme based on long-range interactions and their frequency dependence, with the aim to identify experimentally the forces at the origin of the behaviour of molecular and interfacial systems, to model them by developing predictive models and use this knowledge to develop new materials and processes based on colloidal and interfacial chemistry. Characterisation of structure, dynamics, reaction kinetics, and thermodynamic properties of such systems requires deployment of a broad range of experimental and theoretical methods. From the fundamental viewpoint, this cluster encompasses study of the interplay between solvation and association, and hydrophobic and electrostatic interactions, to understand the self-organisation of molecular systems and its consequences on the macroscopic properties of the material. Several totally new emerging high risk / high reward projects are working together in synergy, spanning use of double hydrophilic self-assembled amphiphiles as templates for sol-gel chemistry, controlled ion-specific separation using multi-scale porous ionosilica or grafted nanoparticles of ionic crystals.

EXTRACTION MECHANISMS IN IONIC LIQUID MEDIUM FOR THE EXTRACTION OF METALS OF INTEREST
« MERLIN »

	NOM	**Prénom**	**Institut**
Responsable	*DOURDAIN*	*Sandrine*	*ICSM*
Co-responsable 1	*ARRACHART*	*Guilhem*	*ICSM*
Co-responsable 2	*CAMBEDOUZOU*	*Julian*	*IEMM*
Post-Doctorant	*AUGUSTO LOPEZ*	*Cesar*	*ICSM*

Date de démarrage du projet	*1er mai 2018*
Date de fin de projet	*1er décembre 2019*

As part of an approach applied to the recycling of metals of interest, this fundamental study aims at better understanding the extraction performances in ionic liquid media. The objective of this post doctorate is to study and compare the effect of different ionic liquids on the supramolecular aggregation of extraction phases and to put them in relation with their extraction properties. This study will focus on extracting systems already well known and characterized in our laboratory for conventional diluents in the context of the extraction of metals of interest as rare earths. The effect of these new diluents on the extraction performances will be characterized by ICP measurement, X-ray fluorescence, NMR, acid and Karl Fisher titration. These will then be connected to the aggregation properties of extracting molecules determined by scattering measurements of X-ray and neutron at small angles, and by physico-chemical measurements such as surface tensiometry.

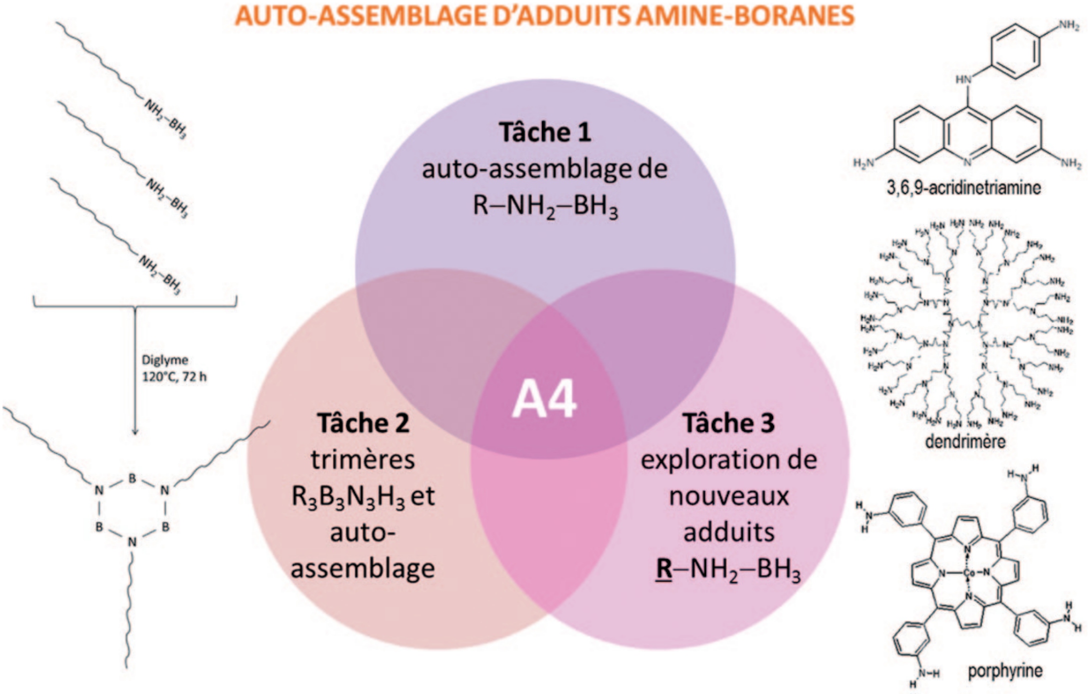


SELF-ASSEMBLY OF AMMONIUM BORANE HYBRID ALKANES IN ORGANIC SOLVENTS
« A4 »

	NOM	**Prénom**	**Institut**
Responsable	*DEMIRCI*	*Umit*	*IEMM*
Co-responsable 1	*ALAUZUN*	*Johan*	*ICGM*
Co-responsable 2	*DOURDAIN*	*Sandrine*	*ICSM*
Post-Doctorant	*Antigoni*	*Theodoratu*	

Date de démarrage du projet	*1er mars 2018*
Date de fin de projet	*1er octobre 2019*

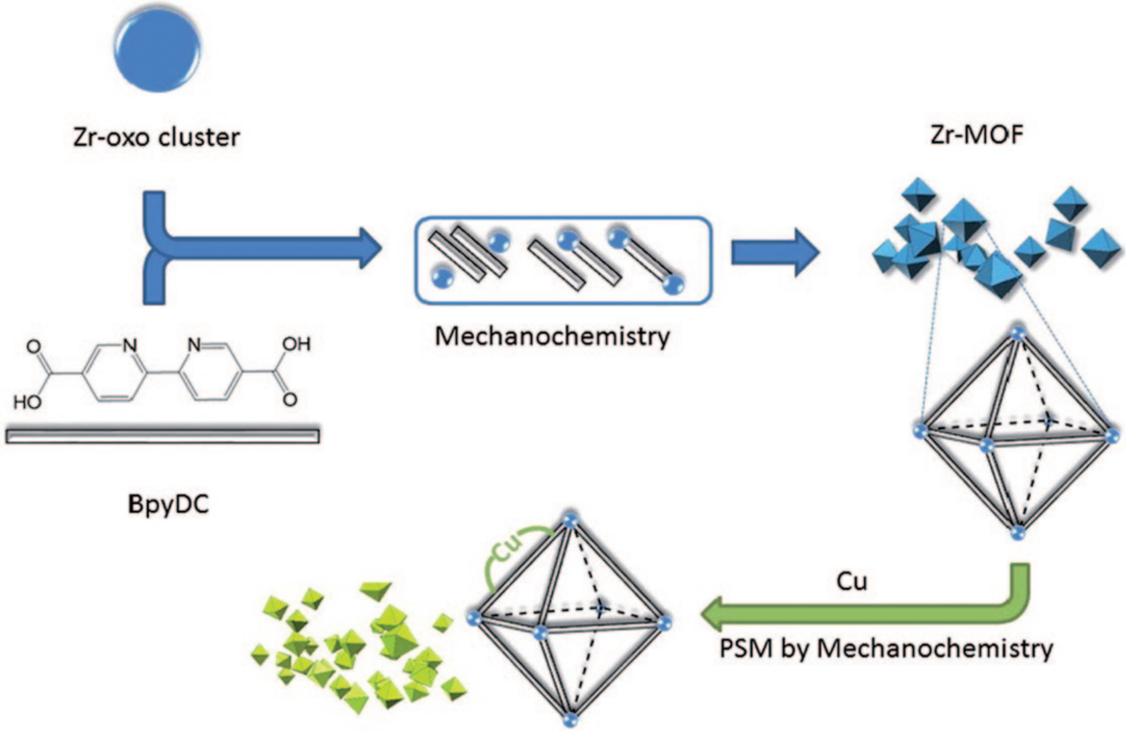
The A4 project aims at developing molecules having $-NH_2-BH_3$ groups (with protic hydrogens together with hydridic hydrogens, *i.e.* $H^{\delta}+$ versus $H^{\delta}-$) within the context of the supramolecular chemistry. Our idea is to study the interactions $H^{\delta}+\cdots H^{\delta}-$ between the different hydrogens that can exist in the amine-borane adducts. Indeed, such interactions could lead to self-assembling/-organization of systems in solution. Our idea is also to better understand the dynamics behind the assembled/organized systems, and then to elaborate new materials. The consortium involves 3 partners, IEMM, ICGM and ICSM, with complementary expertise in chemistry of amine-/hydrazine-boranes, organic synthesis, and characterization of self-assembling.



SYNTHESIS AND POST-SYNTHETIC MODIFICATION OF UIO-67 TYPE METAL-ORGANIC FRAMEWORKS BY MECHANOCHEMISTRY

	NOM	**Prénom**	**Institut**
Responsable	CARBONI	Michaël	ICSM
Co-responsable 1	LAMATY	Frédéric	IBMM
Co-responsable 2	BANTREIL	Xavier	IBMM
PhD	BLANC	Anatole	

We report the synthesis of zirconium metal-organic frameworks by a mechanochemical route. The frameworks are obtained by the coordination of a zirconium cluster with the biphenyldicarboxylic acid linker to obtain UiO-67 or with the isostructural 2,2′-bipyridine-5,5′-dicarboxylic acid to access to a functional MOF (UiO-67-bpy). In a second mechanochemical reaction, it has been possible to coordinate by post-synthetic modification a copper salt on each bipyridine site (UiO-67-bpy-Cu). Both materials exhibit crystallinity and porosity (up to 750 m2/g) showing the possibility to get access to elaborated materials in a cleaner way than the classical solvothermal route in DMF.



Scientific production:
« Synthesis and post-synthetic modification of UiO-67 type metal-organic frameworks by mechanochemistry »
H. Ali-Moussa, R. Navarro Amador, J. Martinez, F. Lamaty, M. Carboni, X. Bantreil
Materials Letters, 197, 171-174 (2017)

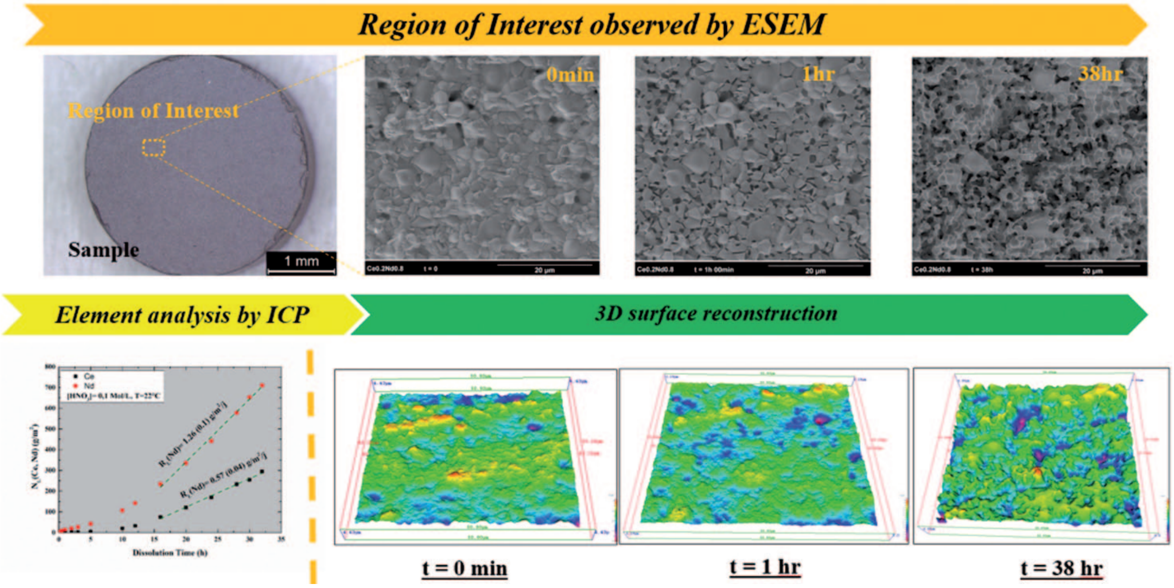
CHARACTERIZATION OF EVOLVING SOLID/LIQUID INTERFACES DURING DISSOLUTION BY 3D ANALYSIS AT THE MICROSCOPIC SCALE BY SEM

DISSO3D

	NOM	**Prénom**	**Institut**
Responsable	*PODOR*	*Renaud*	*ICSM*
Co-responsable 1	*DACHEUX*	*Nicolas*	*ICSM*
Co-responsable 2	*SZENKNECT*	*Stéphanie*	*ICSM*
Post-Doctorant	*BEN KACEM*	*Ilyes*	*ICSM*

Date de démarrage du projet	*08 janvier 2018*
Date de fin de projet	*07 juillet 2019*

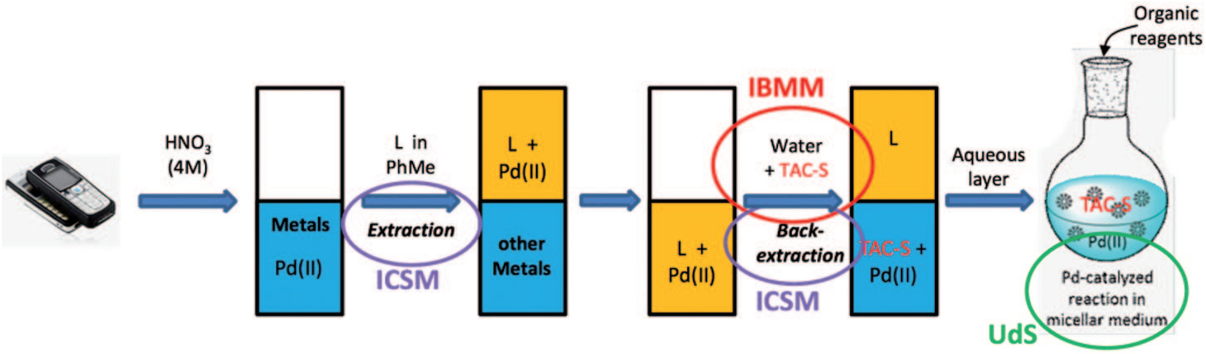
This proposal aims to develop a new methodology for the characterization of solid-liquid interfaces during the dissolution process, mainly focused on the 3D reconstruction of surfaces on the basis of tilted SEM image series. The 3D images will be recorded regularly during the sample dissolution in order to determine accurately the local quantities of dissolved matter. The studied materials will be model compounds that are of interest in several application fields: catalysis, solid oxide fuel cells, surrogates for the nuclear fuel. They will be chosen in the CeO_2-Nd_2O_3 binary system. This system allows preparing materials with variable crystal structures and microstructures, depending of the sample composition in order to adapt the dissolution kinetics to the sample observation techniques. In parallel with the methodological developments, numerical modelling based on image processing will be developed to link the local dissolved volumes (mainly related with the preferential dissolution) with the dissolution rates measured at the macroscopic scale.



CONCEPTION ET ÉTUDE PHYSICO-CHIMIQUE D'AMPHIPHILES AUTO-ASSEMBLÉES POUR L'EXTRACTION DE MÉTAUX ET LA CATALYSE EN MILIEU AQUEUX : DE LA VALORAISATION DES DÉCHETS ÉKECTRONIQUES À LA CHIMIE VERTE (ACRONYME : AMPHOREX)

Responsable	***Institut/Equipe***	***Autres participants permanents de l'équipe participant***
Damien BOURGEOIS *damien.bourgeois@cea.fr*	*ICSM/Laboratoire des Systèmes Hybrides pour la Séparation*	
Co-responsable		
Christine PEPIN *christine.pepin@univ-avignon.fr*	*IBMM/Chimie Bioorganique et Systèmes Amphiphiles*	Françoise BONNETE *francoise.bonnete@univ-avignon.fr*

Ce projet vise à étudier et développer un principe novateur pour la valorisation de métaux issus du recyclage, en particulier du Pd, consistant en l'utilisation directe d'une phase organique issue d'une extraction liquide-liquide pour effectuer des réactions organo-catalysées en phase micellaire aqueuse. Le passage du Pd de la phase organique à la phase aqueuse est assuré par des tensio-actifs (TA) développés par l'équipe CBSA de l'IBMM[1] (C. Pépin & F. Bonneté), et dont la structure vise à être optimisée afin de répondre aux contraintes liées à la récupération par voie hydrométallurgique du Pd issu de déchets électroniques,[2] assurée par l'équipe LHYS de l'ICSM (D. Bourgeois). Suite à une preuve de concept récemment acquise en partenariat entre ces deux équipes du Labex CheMISyst et une équipe de Strasbourg (UdS, F. Bihel), il s'agit ici d'établir de façon rationnelle une relation entre la structure des TA, modulable à façon, les propriétés physico-chimiques des assemblages résultant de leur auto-association, et leur aptitude à contre-extraire puis stabiliser le Pd en phase aqueuse. Les connaissances fondamentales ainsi acquises permettront alors une valorisation efficace de ces systèmes.



---

[1] K. Astafyeva et al., J. Mater. Chem. B, 2015, 3, 2892. 2 R. Poirot et al., Solvent Ext. Ion Exch. 2014, 529.

SYNTHESIS OF ZEOLITE MONOLITHS WITH HIERARCHICAL POROSITY FOR PROCESS INTENSIFICATION IN NUCLEAR WASTEWATER TREATMENT IN CONTINUOUS FLOW

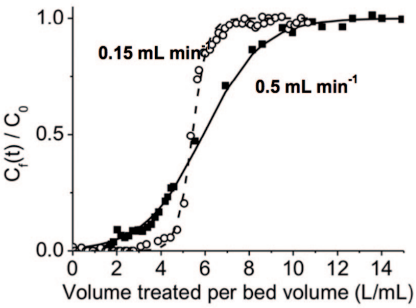
	NOM	**PRENOM**	**MAIL**	**INSTITUT**	**EQUIPE - nom abrégé**
Responsable	GALARNEAU	ANNE	anne.galarneau@enscm.fr	ICGM	MACS
Co-responsable 1	GRANDJEAN	AGNES	agnes.grandjean@cea.fr	CEA	DTCD/SPDE
(Post) Doctorant	SAÏD	BILEL	bilel.said@enscm.fr	ICGM	MACS

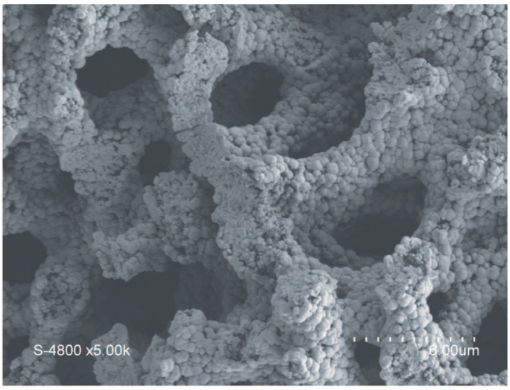
Date de démarrage du projet	Octobre 2012
Date de fin du projet	Octobre 2015

The aim of the project is to understand and control ions transport phenomena in inorganic systems with different hierarchical porosities (micro-, meso- and macroporosity) to develop the best microreactors to capture efficiently radioactive ions as Sr and Cs in continuous flow in complex seawater as Fukushima case. For safety reasons, zeolite monoliths with hierarchical porosity will be developed as an alternative to ion-exchange resins to avoid organic degradation under irradiation and to propose direct storage materials without any powder to handle. First, silica monoliths with meso- and macroporosity will be synthesized by sol-gel process combined with phase separation (spinodal decomposition) between an inorganic/polymer phase and water. Then the silica skeleton of the monolith will be transformed into high ion-exchange capacity zeolites (LTA, FAU-X) by different pseudomorphic transformations. The cladding of the monoliths by several technics will be attempted.

The project is a solution to answer to the driving question of Chemisyst concerning "Environment urgency and eco-technolgies". The project aims towards the development of self-organized and nanostructured materials by design and soft-templating to enhance ion transfer pathways to improve and address safe trapping of pollutants as radioactive ions in non conventional media as complex sea water. The control of the shape of the materials as monotliths directly provides a new separation technology in nuclear industry in continuous flow processes, avoids manipulation, of toxic substances and allows a direct storage.

A first macro-/microporous LTA monolith exhibiting micronic cristals in the skeleton has been synthesized and promising results for the capture of Sr in seawater were obtained[1]. Four times more volume of contaminated water can be treated with 1 g of material in the monolith technology in comparison to batch. In the Labex project, we have improved and developed this new technology for faster separation by enhancing the accessibility of the ions to the ion-exchange sites of the zeolite by synthesizing nanocristals in the skeleton of the monolith (SEM pictures) leading to mesopores formation. New zeolites monoliths with larger micropores as FAU- X have been also synthesized and are promising to develop radioactive Cs removal monolith technology.





---

[1] A. Sachse, A. Merceille, Y. Barré, A. Grandjean, F. Fajula, A. Galarneau, Micropor. Mesopor. Mater., 2012, 164, 251

COMPARATIVE SCREENING OF EXTRACTION-RECOVERY OF MICROALGAE BIOMASS

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
Responsable	ARRACHART	Guilhem	guilhem.arrachart@cea.fr	ICSM	LTSM
Co-responsable	LE MOIGNE	Nicolas	nicolas.le-moigne@mines-ales.fr	EMA	C2MA
Stagiaires	ROUSSEY	Sophie	Stage IUT – avril/juin 2013	ICSM	
	SYLVAIN	Olivier	Stage ENSCM – mars / sept. 2013	EMA	
	DEVILLE	Caroline	Stage IUT – avril / juin 2014	ICSM	
	DALLE	Klervi	Stage Master 2 – mars / sept. 2014	EMA	

Date de démarrage du projet	Mars 2013
Date de fin du projet	Mars 2016

Microalgae are recognised as an important renewable source of lipids, proteins and polymers which make them promising sources of food, energy, chemicals and materials.

Each of the currently available methods of extraction depends on a specific pattern phase diagram and a particular combination of cohesive energy and affinity of the extractant phase.

A clear challenge must be that the extraction process can tolerate the presence of water associated with the biomass. The purpose of this project is to make a screening of extraction process obtained by presently known methods of extraction and identify the key parameters (water content, solvent strength, pretreatment, cell- disruption) that should governed the extraction efficiency of lipids or polymers of microalgae biomass.

• *Scientific driving question, in the context of system chemistry :*

Can we get new insight in extraction methods that does not require complex and degrading pretreatment of the algal biomass ?

Can we add value of the algal biomass as a new source of materials ?

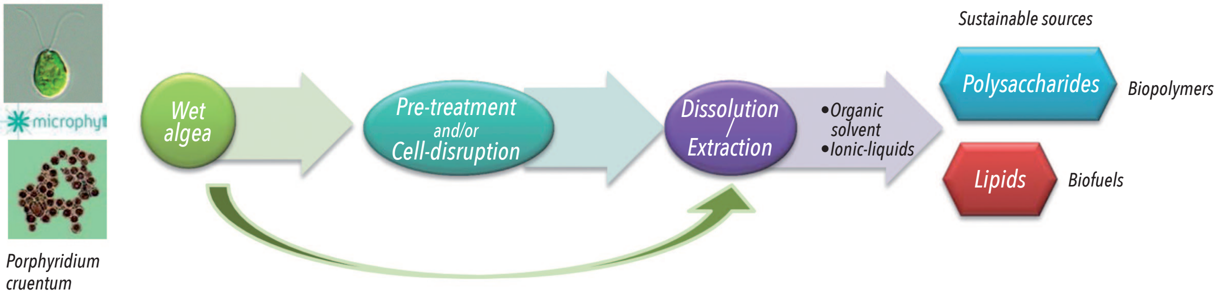
The aim of this study was to develop a method of lipids and / or polymers (mainly polysaccharides but also glycoproteins…) extraction from harvested algal biomass that does not require complex and degrading pretreatment.

The effects of solvent types, pretreatment (lyophilization, centrifugation) and cell-disruption (sonication, autoclaving process) on microalgae biomass extraction have been examined.

Compared to traditional chemical methods involving solvent addition usually organic and toxic chemicals such as hexane, ionic-liquids are tunable solvents that represent an interesting alternative for solvent extraction process (in terms of sustainable development and efficiency).

The rheological behaviour of the resulting polymer solutions show that high molecular weight molecules can be extracted, which is promising for a further implementation in material forming (film, spinning, foams).

Extraction process from dry or wet microalgae biomass



TRANSFER OF IONS AND COLLOIDS THROUGH LIQUID-LIQUID INTERFACE ASSISTED BY ULTRA-SOUND

	NOM	**PRENOM**	**MAIL**	**INSTITUT**	**EQUIPE - nom abrégé**
Responsable	DIAT	Olivier	olivier.diat@cea.fr	ICSM	Ions aux Interfaces Actives
Co-responsable 1	STOCCO	Antonio	antonio.stocco@univ-montp2.fr	L2C	Matière molle
Co-responsable 2	IN	Martin	martin.in@univ-montp2.fr	L2C	Matière molle
Co-responsable 3	MOEHWALD	Helmuth	helmuth.moehwald@mpikg.mpg.de	MPIKG	Interfaces
Post-doctorante	BOUBEKRI	Rym	rym.boubekri@univ-montp2.fr	L2C/ICSM	Matière molle Ions aux Interfaces Actives

Date de démarrage du projet	Octobre 2013
Date de fin du projet	Mars 2015

This project gathers three complementary teams to study transfer process at liquid/liquid interfaces. Ion and colloid extraction from water to an non-aqueous phase under the effect of ultrasounds (US) is the main target of the Project. Here, we focus on sound wave frequencies in the MHz region, where absorption of ultrasonic energy is associated to dehydration/hydration mechanism of ionic species. Thus, we aim at investigating the chemical and physical effects on the transfer kinetics. By coupling specific surface experiments we have first investigated the effects of US on the fluid surface roughness and deformation. Then we have studied the adsorption of ions submitted to high frequency ultrasounds at the water interface. A major aim is to obtain insights into interfacial events involved in the transfer of ions and colloids (nanoparticles) from an aqueous to an non aqueous media upon ultrasonic waves.

• Scientific driving question, in the context of system chemistry :

Can we induce the ions transfer via their dehydration?

Can ellipsometry and surface tension measurements be used to probe the adsorption of ions at the interface?

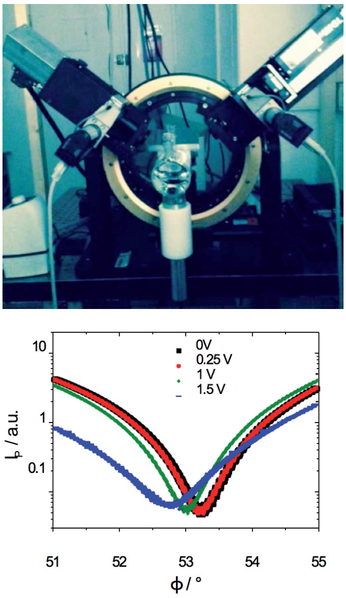


Fig. 1: Ellipsometry set up with a newly designed US cell (top). Reflectivity measurements at the water/air interfaces (down) at different US intensities (in volt). The shift in the minimum Intensity I_P has been attributed to a macroscopic interface deformation induced by US. For low US intensity (0.25 V) the surface roughness is in the nanometric range.

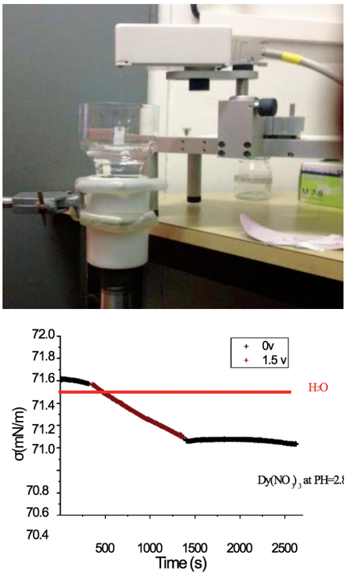


Fig. 2: Surface tension set up with an US cell (top). Surface tension evolution in time of water and dysprosium nitrate aqueous solution (down). A clear change is observed for the salt solution under 1.5 V of 10 MHz US (wine curve).

ON-EX : ION EXCHANGE REACTIONS WITH IONOSILICAS

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
Responsable	PRELOT	Bénédicte	Benedicte.prelot@um2.fr	ICGM	AIME
Co-responsable 1	HESEMANN	Peter	Peter.hesemann@univ-montp2.fr	ICGM	CMOS
Co-responsable 2	PELLET-ROSTAING	Stéphane	Stephane.pellet-rostaing@cea.fr	ICSM	
Doctorant	THACH	Ut-Dong	Ut-dong.thach@etud.univ-montp2.fr	ICGM	CMOS-AIME

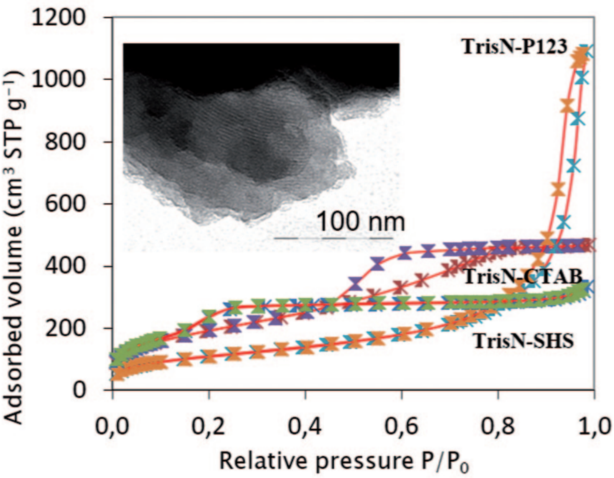
Date de démarrage du projet	Octobre 2013
Date de fin du projet	Septembre 2016

The aim of this project is to develop new and specific anions exchangers based on ionosilicas. A series of materials displaying high surface area and well-ordered pore architecture will be synthesized by template directed hydrolysis polycondensation reactions starting from various ionic precursors. This will give access to original solids, with tuneable interfacial properties, such as hydrophilic/hydrophobic contributions. Sorption capacities and related thermodynamic data will be compiled in order to evidence anionic sorption/exchange mechanisms. The ultimate objective is to develop a separation / regeneration process, based on shaped materials with potential Hoffmeister selectivity and high radiolytic stability.

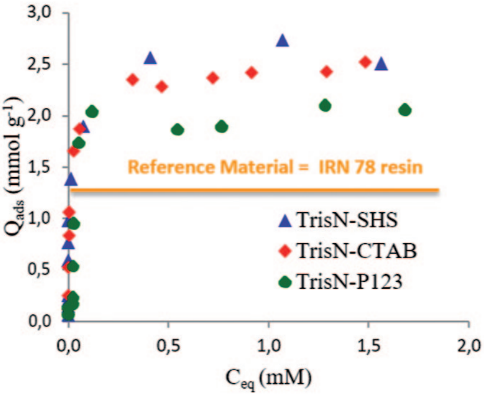
- ***Scientific driving question, in the context of system chemistry :***

Elaboration of ionosilica with high exchange capacity, tuneable structure and defined physicochemical properties. Determination of hydrophilicity/hydrophobicity, acido-basicity of the ionosilicas using molecular probes. Thermodynamics of the anions exchange/sorption process.

Separation & regeneration cycles of anion exchangers.



N_2 adsorption isotherm and TEM images



CrO_4^{2-} adsorption capacity

PICKERING EMULSIONS STABILIZED BY COORDINATION POLYMERS NANOPARTICLES

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
Responsable	CAUSSE	Jérémy	jeremy.causse@cea.fr	ICSM	LNER
Co-responsable 1	GUARI	Yannick	yannick.guari@univ-montp2.fr	ICGM	CMOS
Co-responsable 2	LARIONOVA	Joulia	joulia.larionova@univ-mont2.fr	ICGM	CMOS
Co-responsable 3	LONG	Jérôme	jerome.long@univ-montp2.fr	ICGM	CMOS
Stagiaire de niveau M2		En cours de recrutement			

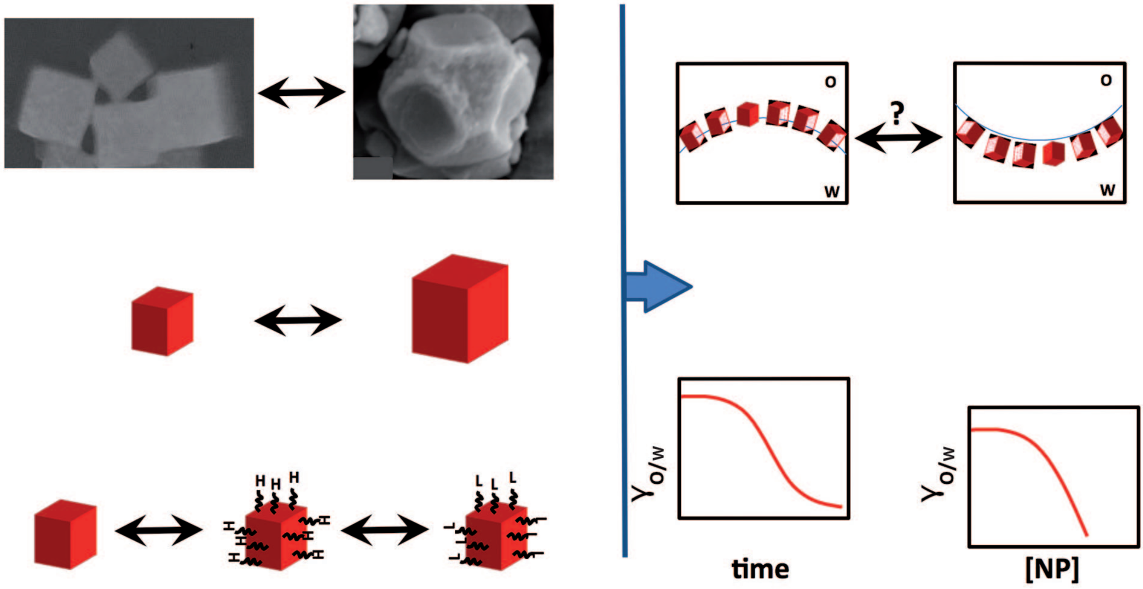
Date de démarrage du projet	Février 2015
Date de fin du projet	Août 2016

The goal of this project is to study the stabilization of oil/water interface with coordination polymers nanoparticles (NPs). The main idea is to prepare emulsions stabilized with solid particles, also known as Pickering emulsions, and to use it as monolithic materials precursor. In this case, the nanoparticles function is both to stabilize emulsion and to functionalize the final material.

The chosen coordination polymers come from metal haxacyanoferrate family compounds also known as Prussian Blue Analogs (PBA). The first part of this project concerns the synthesis of such NPs with various sizes, shape and hydrophilic lipophilic balance (HLB). Then, the studies will be focused on the assessment of the interfacial activity of theses NPs and more paticularly the influence of each parameter.

- ***Scientific driving question, in the context of system chemistry :***

How do NPs changes (size, shape, HLB) influence stabilization of a typical oil/water interface?



CANAUX À EAU SYNTHÉTIQUES POLARISÉS EN SYSTÈMES LIPIDIQUES : VERS UNE DIODE À EAU- diEAUde

	NOM	PRENOM	MAIL	INSTITUT	EQUIPE - nom abrégé
Responsable	BARBOIU	Mihail	mihail-dumitru.barboiu@univ-montp2.fr	IEM	NSA
Co-responsable 1	BONNETE	Françoise	francoise.bonnete@univ-avignon.fr	IBMM	
Co-responsable 1	ZEMB	Thomas	thomas.zemb@icsm.fr	ICSM	
Doctorant	KOCSIS	Isvan			

Date de démarrage du projet	Octobre 2014
Date de fin du projet	Octobre 2017

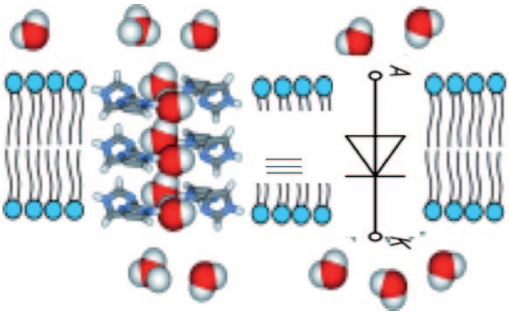
La pression osmotique peut être assimilée à une différence de potentiel chimique. Alors que des transistors et des diodes servent l'électronique, peut-on imaginer des systèmes analogues afin de contrôler technologiquement, cette force à la fois immuable et omniprésente dans le vivant ? La conception de canaux synthétiques mimant le fonctionnement des protéines-canal naturelles sera entreprise dans ce projet par une nouvelle approche multidisciplinaire incluant l'expertise chimique et la maîtrise de l'organisation supramoléculaire de ces canaux artificiels ainsi que la capacité à cristalliser ces systèmes dans leur état fonctionnel au sein de la membrane. Une des clés du projet sera de former des canaux permettant d'orienter le passage de l'eau (grâce à son dipôle) si possible de façon variable et commutable et ainsi créer par analogie une « diode à eau ». Des molécules bolaformes développées par l'IEM connues pour leur capacité à s'auto-organiser et à transporter spécifiquement des molécules d'eau ou des ions seront insérés dans des membranes dont les lipides et les tensioactifs constitutifs développés par l'IBMM seront choisis afin d'une part de favoriser leur activité de canal synthétique et d'autre part leur cristallisation.

• *Scientific driving question, in the context of system chemistry :*

Une bibliothèque de composés bolaformes étant à disposition, il s'agit maintenant d'appréhender les structures formées, en déterminant le diagramme de phases liquide-cristallines de nos systèmes « amphiphile-eau » à la façon de Luzzatti et al. ; les canaux cristallisés sont appelés «punctuated planes» (illustration Dubois et al.). Il resterait alors à maîtriser la mesure des potentiels chimiques de l'eau : ceci peut être fait par cristallisation en phase cubique comme décrit par Landau et Pebay-Peyroula.

L'expérience accumulée dans ce domaine peut donc aider à mieux comprendre et résoudre les aspects qualitatifs de l'intégration des canaux artificiels mis au point à l'IEM. Alors que la cristallisation en phase méso des protéines membranaires est souvent perçue comme un art difficile, la cristallisation de telles structures en systèmes membranaires peut être conduite de manière rationnelle à l'aide d'outils amphiphiles adaptés. Elle devra être effectuée selon les règles de l'art actuellement utilisées avec de plus en plus de succès pour cristalliser les protéines membranaires en systèmes membranaires. Elle nécessite l'utilisation de lipides et de tensioactifs capables d'assurer une intégration de ces systèmes canal dans les membranes et de faciliter leur interaction et leur cristallisation dans la membrane. L'IBMM possède cette expertise à travers son expérience de la synthèse d'outils amphiphiles pour la manipulation et la cristallisation de protéines membranaires.

En rassemblant des chercheurs de trois instituts du Labex, IBMM, ICSM et IEM capables ensembles a) de fabriquer des canaux mimant l'activité des protéines de type porine, b) de concevoir, fabriquer et manipuler des matrices membranaires capables d'accueillir ces canaux artificiels et de les cristalliser, c) de rationaliser le processus d'auto- assemblage de ces canaux artificiels et d) d'évaluer la pression osmotique et l'activité de l'eau, nous pensons que les ingrédients seront réunis pour effectuer des avancées significatives dans un domaine crucial de la recherche fondamentale sur les canaux artificiels pouvant conduire rapidement à des technologies appliquées dans le domaine des membranes d'ultrafiltration et de séparation des ions.



LabEx CheMISyst

5th Practical Summer School

July 5th, 6th and 7th, 2016

"SIMPLE BUT PRACTICAL MODELLING OF EXPERIMENTS FOR MOLECULAR SYSTEM DRIVEN BY WEAK LONG-RANGE INTERACTIONS"

PRACTICAL SESSIONS ON COMPUTERS

PRACTICAL 1
Calculation of effective surface charges and ion adsorption isotherms in pores for solids including non-electrostatic terms

PRACTICAL 2
Simulation of scattering experiments with defined shapes and long-range interactions. Colloids, nanoparticles, polymers, gels, concentrated solutions. Structure factors and osmotic compressibility

PRACTICAL 3
Brownian modelling of experimental systems. Application to porous media

Tuesday, July 5th, 2016

9h30 - 10h00 Welcome to the school

10h00 - 11h30 Flash presentation of each participant *(5 min / 2-3 slides per participant)*

11h30 - 12h15 What can be learned from comparing experimental results by comparison with parameter-poor generic models:
- predicting surface "charge"
- calculating the scattering pattern for a given hypothetic stabilisation via weak long-range interactions
- making minimal models of molecular dynamics for objects diffusing near a pore

Thomas ZEMB, ICSM

12h15 – 13h15 Lunch buffet, ICSM

13h15 - 18h15 **PRACTICAL 1**
Calculation of effective surface charges and ion adsorption isotherms in pores for solids including non-electrostatic terms
Teachers: Julien CAMBEDOUZOU, ICSM & Diane REBISCOUL, ICSM

18H30 - 19H15 Invited lecture
"Temporal Evolution of Self-Assembled Systems - Some Principles and Ways of Studying Their Structural Changes by SAS"
Pr. Michael. GRADZIELSKI, TU Berlin

19h30 – 21h00 Dinner buffet, ICSM

Program – Practical Summer School 2016 – LabEx CheMISyst - Version 30.06.2016

Wednesday, July 6th, 2016

8H45 - 13H00	**PRACTICAL 2** Simulation of scattering experiments with defined shapes and long-range interactions. Colloids, nanoparticles, polymers, gels, concentrated solutions. Structure factors and osmotic compressibility ***Teachers: Sylvain PREVOST & Olivier DIAT, ICSM***
13h00 - 14h00	*Lunch buffet, ICSM*
14h15 - 18H15	**PRACTICAL 3** Brownian modelling of experimental systems. Application to porous media ***Teachers: Jean-Francois DUFRÊCHE, ICSM & Bertrand SIBOULET, ICSM***
18h30 - 19h15	Invited lecture *"Calculations of Dispersion Energies Using Density Functional Theory Methods"* ***Pr. Young Kee KANG, Chungbuk National University*** *- Invited professor 2016 by LabEx CheMISyst*
20H00 - 22h00	*Dinner buffet, restaurant "Lauret's"*

Thursday, July 7th, 2016

9h00 - 13h00	Reports in common obtained by the 12 different groups (two students working together). ***Discussion leader: André AYRAL, IEM & Thomas ZEMB, ICSM***
9h00 - 10h00	Practicals n° 1 (3-4 groups)
10h00 - 11h00	Practicals n° 2 (3-4 groups)
11h00 - 11h15	*Coffee break*
11h15 - 12h15	Practicals n° 3 (3-4 groups)
12h15 - 13h00	Evaluation of session, participation certificates given individually to participants & group photo
13h00 - 14h00	*Final buffet, ICSM*

14h00 - End of school

Agenda of the 4th edition of the LabEx CheMISyst Scientific Days 2016

	Wednesday 23/11	Thursday 24/11	Friday 25/11
Morning 8h30 - 13h	▪ Opening of the event ▪ Lecture - Prof. Bao-Lian SU's about « Energy » ▪ Presentations of LabEx projects	▪ Lecture – Prof. Pierre VOGEL about « Santé » ▪ Presentations of LabEx projects	▪ Lecture about « Dual use research » ▪ Presentations of LabEx projects
	Lunch 13h – 14h30	**Lunch** 13h – 14h00	**Lunch** 13h – 14h00
Afternoon 14h/14h30 – 18h	▪ Lecture – Prof. Julien Leclaire about « Green Chemistry » ▪ Presentations of LabEx projects	▪ 14h – 16h : Workshops : Clusters 1 & 3 en // ▪ 16h – 18 h : Worshops : Clusters 2 & 4 en //	▪ Presentation of the workshops' conclusions ▪ 15h30 : Lecture - Luca Bertinetti
	Cocktail reception 18h – 20h		

TEACHING

TEACHING ACTIVITIES LINKED TO ICSM

In cooperation with ENSCM and Ecole doctorale ED 459
And
Institut National des Sciences et Techniques Nucléaires - INSTN – antenne de Marcoule

ICSM develops teaching activities in five directions:

1 The master "Chimie Séparative, Matériaux et Procédés", created in 2005 by INSTN/Marcoule and University of Montpellier.
Two years of teaching (M1/M2) associating separation chemistry, radiochemistry, material chemistry and chemical processes engineering with application to the front-end and the back-end of the nuclear fuel cycle (extraction, separation and purification, elaboration, sintering, dissolution, radioactive waste management, decommissioning and so on). The practical is divided in four semesters including main courses, practices, bibliographic studies and two training periods of 4 months (1st year) and 6 months (2nd year). Since 2008, a large part of the teachings is shared with the 3rd year option of ENSCM dedicated the radiochemistry and environment. 10-15 students plus a similar number of students follow the training every year from ENSCM. Teaching was progressively diffused in English (written and/or oral). Teaching is aimed at the diffusion of critical knowledge on chemistry, radiochemistry, interfaces chemistry, conception and synthesis of new materials for nuclear purpose and processes linked to nuclear and alternative energy production.

2 The active participation of several ICSM members in four main courses of the Institut Franco-Chinois à l'Energie Nucléaire
(IFCEN at the Sun Yat Sen University, Zhuhai, China), a Sino-French engineer school in which ENSCM is one of the five main partners. Several courses including nuclear fuels, analytical strategy of actinides and chemistry related to the front-end and back-end of the nuclear fuel cycle are (will be) given in the 2015-2020 period.

3 The Annual practical separation chemistry summer-school:
Full five day sessions, including 2 days of practical and a session devoted to understanding experimental results on the light of the concepts developed in the lecture part. Sometimes, it can be coupled to another summer-school like this year. This summer school, initially created in 2007 by INSTN for the whole research at CEA-Marcoule, has been specialized for ICSM from 2009. Since 2012, the teachers and students are coming from the Six UMR associated in Chemisyst project (detailed programs are found in the Annex: 7eme Ecole pratique d'été Labex CheMISyst 2018 on "natural chemical systems in presence of electrolytes: the case of wood" & summer school on "Thermodynamics and energetics of soft-matter systems").

4 The "Thursday Lectures on separation chemistry", as M3/D1 program was aimed for masters and PhD students (credits given by ED459),
one lesson more on the experimental side and one more theoretical side which were delivered in the ICSM building every Thursday (during months of winter-time). These have been replaced by SPOC on "Science and technology for recycling industrial wastes and formulating stable concentrated solutions" since beginning of 2018 (see flyer of announcement in the annex).

5 The European school of SURFACES AND NUCLEAR SCIENCES
was organized by ICSM for its third edition (2012, 2015 and 2018) around the scope of Surfaces and Nuclear. It brought together in a friendly atmosphere more than 21 participants and 18 speakers from different research centers such as the CEA (Saclay, Marcoule, Cadarache), IPN Orsay, ICSM, and ANDRA belonging to the community of researchers and doctoral students studying physicochemical modifications occurring on solid or liquid surfaces, for problems related or not to nuclear energy (see annex).

MASTER CSMP – 1ST YEAR (MAIN COURSES)

Basis in chemical processes
Nuclear fuel cycle: from ore to reprocessing
IR and Raman spectroscopies
Liquid and solid NMR
Preparation and properties of colloids
Structure determination in solids
Preparation of inorganic materials
Basis in solution Chemistry
Solution chemistry applied to actinides
Basis in radioactivity
Chimiometry
Radiation-matter interactions – Radioprotection
High-temperature chemistry
Radwaste matrices
Coordination chemistry for f elements
Radiochemistry and chemistry at the trace level
Bibliographic training

MASTER CSMP – 2ND YEAR (MAIN COURSES)

Weak interactions and partitioning chemistry
Analytical chemistry for actinides
Processes for waste treatment and conditioning
Processes for partitioning with membranes
Front-end of nuclear fuel cycle: extraction and separation chemistry
Dissolution and radiation damages in ceramics
Modeling for separation and confinement
Safety and Radioprotection
Nuclear fuels: synthesis and refabrication
Liquid-liquid extraction: thermodynamics, kinetics and processes
Long-term behavior: glasses
Molecular and supramolecular chemistry of f and d elements
Bibliographic training).

EUROPEAN SCHOOL OF SURFACES AND NUCLEAR SCIENCES

MARCOULE INSTITUTE FOR SEPARATION CHEMISTRY
14 -18 MAY 2018 PORQUEROLLES, FRANCE

La EUROPEAN SCHOOL OF SURFACES AND NUCLEAR SCIENCES qui correspond à la troisième édition des écoles thématiques Surfaces et Nucléaire I et II (2012 et 2015) a permis de réunir dans une ambiance conviviale plus de 21 participants et 18 intervenants provenant de différents centres de recherche comme le CEA (centres de Saclay, Marcoule, Cadarache), de l'IPN Orsay, de l'ICSM, et de l'ANDRA appartenant à la communauté des chercheurs et des doctorants étudiant les modifications physico-chimiques survenant sur des surfaces solides ou liquides, pour des problématiques liées ou non au nucléaire.

L'objectif scientifique de l'école était de mettre en relation les participants avec des spécialistes des techniques et de doter les participants des bases théoriques leur permettant de concevoir de nouvelles expériences en lien avec leurs besoins. Ces bases ont été illustrées de quelques exemples d'applications dans le domaine du nucléaire. Les participants ont pu aussi obtenir une liste des différentes installations et techniques de caractérisation de surface disponibles en environnement nucléarisé en France et en Europe.

De plus, les participants ont pu se faire connaître via des « présentations flash » et exprimer leurs besoins en termes de caractérisations. Ceci a permis d'ouvrir un espace de discussion avec les spécialistes présents et d'initier des collaborations entre équipes.

A noter la programmation du prochain rendez-vous en 2021 :
EUROPEAN SCHOOL OF SURFACES AND NUCLEAR SCIENCES II.

Organisatrices ICSM: Stéphanie Szenknect - LIME, Sandrine Dourdain - LTSM, Diane Rébiscoul –LNER

ECOLE THÉMATIQUE RÉFLECTIVITÉ DES RAYONS X ET DES NEUTRONS

10 – 12 OCTOBRE 2018

La 2ème édition de cette école organisée à l'ICSM avait pour objectif de former des étudiants aux principes théoriques de la réflectivité, à son utilisation, aux traitements des données ainsi qu'à leur exploitation au travers de cours et de travaux pratiques. Plusieurs cas d'études ont été présentés afin de montrer aux participants toutes les potentialités de cette méthode d'analyse de surface. Cette école a réuni 23 participants dont des doctorants et des jeunes chercheurs travaillant dans le domaine des surfaces et des couches minces et souhaitant utiliser la réflectivité.

Cette édition a été un réel succès comme en témoigne un article rédigé par 3 participants du CNRS et publié sur le site de **l'Association Française de Cristallographie** :

https://www.afc.asso.fr/l-association/afc-news/1400-des-photons-et-des-neutrons-en-incidence-rasante-a-marcoule

Ecole Organisée par l'Institut Européen des Membranes (IEM; CNRS / UM / ENSCM) et l'Institut de Chimie Séparative de Marcoule (ICSM; CEA / CNRS / UM / ENSCM) avec le soutien de la formation permanente du CNRS :

DOURDAIN Sandrine (CEA-ICSM)
REBISCOUL Diane (CEA-ICSM)
VAN DER LEE Arie (CNRS-IEM)

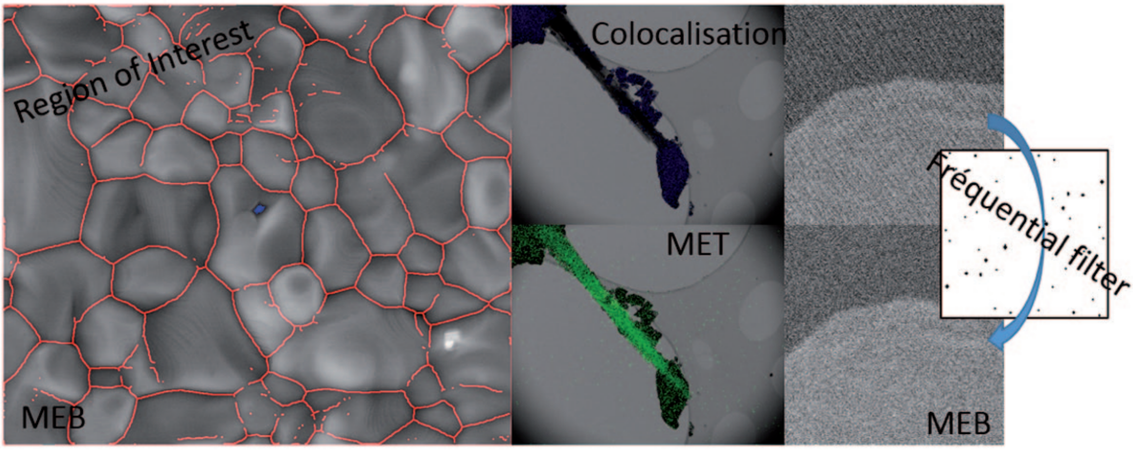
Invités:
Samuel TARDIF (esrf)
Thomas Zemb (ICSM)

TRAINING:
IMAGE ANALYSIS FOR ELECTRON MICROSCOPY

	NOM	***Prénom***	***Institut***
Responsable	*LE GOFF*	*Xavier*	*ICSM*
Co-responsable	*BRAU*	*Henri-Pierre*	*ICSM*

Training	***2016 (2) 2017 (1) 2018 (2)***

With the advent of the digital era, nowadays images are multidimensional numerical data that can be processed and analyzed quantitatively to extract more information. ImageJ/Fiji open source software (imagej.net/) is a powerful tool available to process and analyze digital images. Moreover, it also allows the automation of image analysis with custom macros and plugins. With this training, we intend to give a general introduction to ImageJ/Fiji, show how to use it to extract quantitative data and how to write simple macros. This training is focused on the analysis of microscopy images but is targeted to all people engaged in research, that wants to start using ImageJ/Fiji for image analysis in general.



Pre-registration is necessary because of the limited number of places in the school.
A short description of research activity and a CV should be sent to softmatter2018@ill.fr
The organising committee will examine your application and inform you in June 2018.

Pre-registration deadline : 20 May 2018
Notification of acceptance : 3 June 2018
Registration deadline : 17 June 2018

Registration fee (including VAT):

- 200€ including lecture material, lunches, social dinner and accommodation (2 nights)
- 150€ including lecture material, lunches and social dinner

Organisers
Leonardo Chiappisi
Thomas Zemb

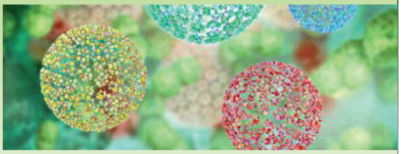
Workshop assistants
Alison Mader
Pauline Charriaux

Email address : softmatter2018@ill.fr

Web site :
https://workshops.ill.fr/e/softmatter2018

Thermodynamics and energetics of soft matter systems

Institut Laue-Langevin, Grenoble, France
from 24 to 26 July 2018



Soft matter pervades into daily life under several forms: biological matter, foams, food products, ink, tires, and many others. In contrast to their very different appearance, all these systems are governed by the same, fundamental physical laws. Aim of the school is providing an overview of the forces governing the behavior of soft matter systems and introducing the most relevant techniques to probe such interactions. The school proposes frontal lectures for doctoral students working in the field of soft matter given by recognized experts from all over Europe. Poster sessions will be opened for discussion on research topic and experimental results between students and invited lecturers.

PÔLE chimie Balard
LabEx CheMISyst

NEUTRONS FOR SOCIETY

PSCM
PARTNERSHIP FOR SOFT CONDENSED MATTER

SETARAM Instrumentation
KEP Technologies

Tue – 24.7	
9:00 - 9:45	Welcome and Registration *Hall ILL4*
10:00 - 11:30	ESRF Guided Tour *Visitor Center*
12:00 - 13:00	Lunch *ESRF/ILL Canteen*
13:30 - 13:45	School Opening *Chadwick Amphitheatre*
14:00 - 15:30	Lecture 1: **Introduction to colloid and interface Science** *Emanuel Schneck* Introduction to colloid and interface science & its applications. Basic concepts. Van der Waals interactions, the electric double layer, and DLVO theory. Further interaction mechanisms (steric, depletion).
15:30 - 16:00	Coffee Break
16:00- 17:30	Lecture 2: **Fundamentals of self-assembly processes** *Christoph Schalley* Basic Principles in Supra- molecular Chemistry. Non- Covalent Interactions and Host- Guest Complexes. Free energy landscape, polydispersity, cooperativity.
17:30	Poster Session & Discussion with Wine and Cheese *Hall ILL4*

Wen - 25.7	
9:00 - 10:30	Lecture 3: **Methods in Calorimetry and Volumetry** *Giuseppe Lazzara* Free energy and its derivatives: the partial molar quantities. Relevance in colloidal systems and methods to access them. Enthalpy changes in supramolecular aggregates: van't Hoff vs direct methods. Introduction and experimental tips in calorimetry and volumetry. Isothenral titration calorimetry: equilibrium and kinetics. Prediction abilities and case studies.
10:30 - 10:45	Coffee Break
10:45 - 12:15	Lecture 4: **Introduction to colloid and interface Science** *Roland Winter* Methods to probe the energetics, structure and conformational dynamics of biomolecular systems - Introduction to cell membranes, model biomembranes, lipid phase transitions. Proteins and their stability, free energy landscape, folding kinetics, interactions. Methods to probe the thermodynamics, conformation, dynamics and interactions of biomolecules.
12:15 - 14:00	Lunch *ESRF/ILL Canteen*
14:00 - 16:00	ILL/PSCM Guided Tour
16:00 - 17:30	Poster Session & Discussion
17:30 - 20:00	Free Afternoon
20:00	Social Dinner

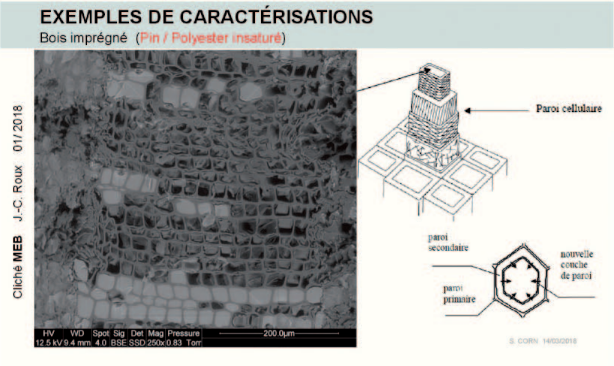
Thu - 26.7	
9:00 - 10:30	Lecture 5: **Physics of macromolecular systems** *Julian Oberdisse* Conformation of polymer chains, chain statistics, polymer solutions and blends, thermodynamics, phase separation, mechanical properties.
10:30 - 10:45	Coffee Break
10:45 - 12:15	Lecture 6: **Thermodynamics of interfaces** *Antonio Stocco* Thermodynamics of interfaces and adsorption, surface tension, contact angle, wetting. Interaction between surfaces and stabilisation mechanisms (foams, emulsions).
12:15 - 14:00	Lunch *ESRF/ILL Canteen*
14:00 - 15:30	Lecture 7: **Solvation and Solubilization** *Dominik Horinek* Ideal and real mixtures and solutions. Molecules and macromolecules in solution. Free energy of solvation, chemical potentials, activity coefficients: experimental and theoretical approaches. A microscopic view from homogeneous to structured solutions: osmolytes, hydrotropes, surfactants. Concepts from Kirkwood-Buff theory. Solubilization in micro-structured solvents.
16:00	School Closing

$7^{\text{ème}}$ Ecole Pratique d'Eté LabEx CheMISyst 2018

Comportement d'un système chimique naturel et fonctionnel en présence d'électrolytes : cas du bois

Le LabEx CheMISyst organise depuis sept ans, son école d'été ouverte à tous les doctorants, post-doctorants et chercheurs de la communauté du Pôle chimie Balard et du LabEx CheMISyst.

Cette année, l'école d'été organisée du 28 au 31 aout 2018 à Alès, regroupe une partie théorique et une partie pratique sur le thème « Comportement d'un système chimique naturel et fonctionnel en présence d'électrolytes : cas du bois ».



Sur le même format que la précédente édition qui fut un réel succès (pédagogie inversée), les participants de l'école prépareront avant et pendant l'école, un exposé de 25 min, par binôme, sur un cours de leur choix parmi ceux proposés. Cette pédagogie active, impliquant les apprenants dans des activités participatives et coopératives, privilégie les échanges avec les conférenciers et les interactions des étudiants entre eux.

L'objectif de ces cours est d'illustrer concrètement l'application des interactions non covalentes et des systèmes chimiques à travers des exemples d'applications issus des travaux de recherche des participants, tout en s'appuyant sur les concepts généraux développés lors de l'école d'été 2017*. Afin d'aider les étudiants dans la préparation de cet exercice original et formateur, des temps seront consacrés à la finalisation des cours, en présence des encadrants.

**Retrouvez les présentations des cours inversés de l'édition 2017 réalisées par les étudiants, sur le site du [Pôle chimie Balard](#) (mot de passe d'accès aux fichiers : LC2017).*

Date

Du lundi 28 au vendredi 31 août 2018

Présence obligatoire la semaine

Lieu

Ecole des Mines d'Alès, Alès (Gard 30)

Comité scientifique et pédagogique

Thomas ZEMB
Martin IN
Gwenn LE-SAOUT
Nicolas LEMOIGNE
Claire LONGUET
José-Marie LOPEZ-CUESTA
Nicolas LOUVAIN
Aurélie TAGUET

Organisation

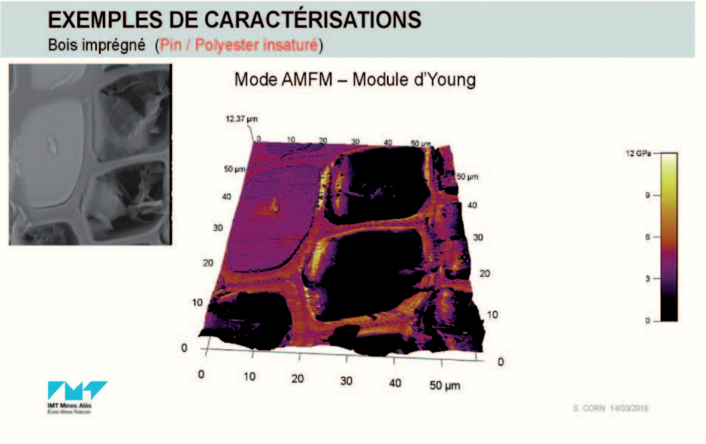
Pauline CHARRIAUX
Chargée de Projets
LabEx CheMISyst
labex@polechimie-balard.fr

Document mis à jour le 18/05/2018

7ème Ecole Pratique d'Eté LabEx CheMISyst 2018

Durant ces cinq jours, les participants effectueront eux-mêmes des expériences lors de travaux pratiques qui donneront ensuite lieu à des communications orales et des discussions concernant les résultats obtenus par chacun. Ces travaux pratiques seront réalisés dans les locaux de l'Ecole des Mines d'Alès.

Enfin, trois conférenciers viendront présenter leurs travaux lors de cette 7ème édition de l'école du LabEx CheMISyst.



EXEMPLES DE CARACTÉRISATIONS

Bois imprégné (Pin / Polyester insaturé)

Mode AMFM – Module d'Young

S. CORN 14/03/2018

Liste des cours en pédagogie inversée :

(Format : 25 min + 10 min questions / discussions)

1. Pickering emulsions
2. Self-assembly in ionic liquids
3. Kinetics of exchange between phases
4. DLA and RLA
5. How biology makes general interactions specific
6. Screened electrostatic interactions in aqueous extracting systems
7. Characterising, morphology and disorder
8. Rehydration and adhesion
9. Interactions and structuration in mixed solvents

La participation à l'école est gratuite mais obligatoire et valide un crédit à l'ED SCB.

Inscriptions obligatoires en ligne sur le site du Pôle chimie Balard avant le 14 juin 2018

Nombre de places disponibles :

20

Public :

Doctorants, post-doctorants et responsables de projets LabEx CheMISyst*

Doctorants inscrits à l'ED SCB

Ensemble de la communauté Balard et du LabEx CheMISyst (chercheurs, enseignants-chercheurs ...)

Document mis à jour le 18/05/2018

SPECIALIZED PRIVATE ON-LINE COURSE (SPOC)

SPOC ON RECYCLING CHEMISTRY: FROM THEORY TO PRACTICE SCIENCE AND TECHNOLOGY FOR RECYCLING INDUSTRIAL WASTES AND FORMULATING STABLE CONCENTRATED SOLUTIONS

PROGRAM OF THE SPOC

PREREQUISITE CONCEPTS

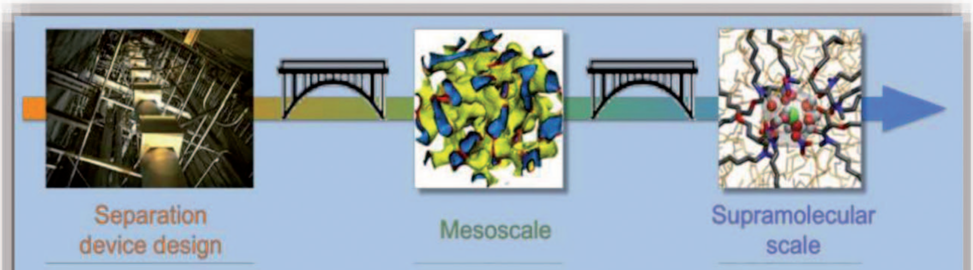
Solvents and solubilisation
Hydrotropes and surfactant-free microemulsions Deep eutectic solvents
Chemical potential: a general view at equilibrium The Gibbs triangle and its usage
Osmosis and electrolyte solutions Specific ion effects in solution Specific ion effects at interfaces
Dynamics in electrolytes solution: a panorama

SCIENTIFIC BASIS

Establishing binary phase diagram
Pseudo-phases versus microphases Reading binary phase diagrams Solubilisation in two phases systems Establishing ternary phase diagrams Ternary phase diagrams
Contacting two liquids for extraction
Basis of liquid-liquid extraction: chemistry and molecular forces

IMPLEMENTATION IN EFFICIENT SEPARATION PROCESSES

Basic concepts of liquid formulation Liquid–liquid extraction at mesoscale Macroscopic modelling: fluxes and mass balance Typical devices used in liquid-liquid extraction
Addressing apparatus design: scale-up and scale-down Cloud point extraction in practice
Ionic liquids
Ternary phase diagrams and safety of extraction Separation by transport properties (flotation) Precipitation in emulsion in liquid-liquid columns



RECYCLING CHEMISTRY: FROM THEORY TO PRACTICE

Mixing and separating for recycling and reformulation of metals as well as electrolytes contained in extremis « wastes » requires to master dissolution, formulation of complex fluid, selective extraction and finally re-mixing in order to obtain recycled product with new economic value. These lectures focus on the scientific basis of recycling and delivery, illustrated by knowledge-based examples of optimized technology involved in effective separation of species between phases.

Science and technology for recycling industrial wastes and formulating stable concentrated solutions

Registrations open January 22nd , 2018 via FUN

Courses and on-line quizz start February 26th, 2018

Sophie Charton

CEA Marcoule

Jean François Dufrêche

University of Montpellier

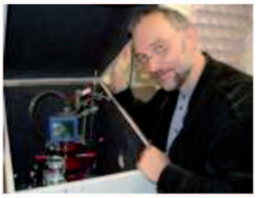
Werner KUNZ

University of Regensburg

Thomas ZEMB

University of Montpellier

INSTN



A certificate of participation will be delivered after successfull completion of quizz generated for each chapter by FUN (France Université Numérique).

SCIENTIFIC PRICE: EUROPEAN GOLD MEDAL

Overbeek lecture delivered by Thomas Zemb, founding Director of ICSM, at the University of Madrid , September 8th, 2017 :

« ...how investigations of "strange" colloidal behaviour investigated by innovative experimental methods and new theoretical approaches at meso-scale can be the source the source of intensified and greener separation processes »

Chair : Pr Debora Berti, President of the European Colloid and Interface Society - Madrid , 2017

In 2005 ECIS created the Overbeek Gold Medal to acknowledge excellent careers in, and inspiring contributions to, the field of colloid and interface science. The prize is awarded annually at the general meeting of ECIS first week of September. The Overbeek Medal is supported by the Overbeek Foundation, which gratefully acknowledges donations made by individuals, institutions and companies.

The Overbeek Gold Medal honours leadership and scientific excellence in the field of colloid and interface science over an entire career. Hence the Overbeek Gold Medal recognizes extended periods of scientific excellence that have had an outstanding impact on this field.

Source : *http://www.ecis-web.eu/overbeek.htm*

Thomas Zemb received the Thomas Graham medal from the Deutsche Kolloid Gesellechaft at the University of Paderborn in September 2013 and gave a lecture on: Recycling metals by controlled transfer of ionic species between complex fluids: en route to «ienaics»[1]*.*

---

[1] Zemb, T.; Bauer, C.; Bauduin, P.; Belloni, L.; Dejugnat, C.; Diat, O.; Dubois, V.; Dufreche, J. F.; Dourdain, S.; Duvail, M., et al., «Recycling metals by controlled transfer of ionic species between complex fluids: en route to «ienaics».» Colloid Polym Sci 2015, 293 (1), 1-22.

OUTLOOK

Thomas. Zemb, Stéphane Pellet-Rostaing et Dominique Alpe-Conchy

The current report summarizes the successes obtained in the last four years, three hundred publications and a number of external citations per year of ICSM of the order of 2000 (as per web of science), just above the MIT Chemical engineering and behind the Universty of Leuwen (Pr K. Binnemans) or the case of recylcing, in nanoscience for energy, ICSM is in the top five in world class congresses such as ECIS and IACIS and associated journals. The focus of the scientific and technical efforts, initialy defined by several reports of the Academy of Science in the early 2000, has been defined in the period 2015-2020, which has to be updated within the new goals assigned to CEA in 2018 for the next contract 2020-2024 associating the CEA, CNRS, University of Montpellier and ENSCM.

One of the reasons of success is that a significant in the three hundred primary scientific papers in "A" ranked journals, thirty patents and about ten reviews have been obtained by the participation and co-authorship of colleagues from R/D departements in charge of applications. These departments act from the demand of the industrial partners AREVA/ORANO, but also on a more prospective research at TRL 1-4 when engineers in R/D departments are associated in common programs with scientist and University teachers of ICSM. Moreover, nearly a third of the impact of papers are made in collaboration with international co-signature. Last but not least, more than half of the papers are co-signed by complementary teams within the Institute: to our best knowledge, this is a unique case of pluridisciplinary science. As a unique case in France since world war two, three international Humboldt prices have been attributed to works in separation physical chemistry that were developed in Marcoule: Helmuth Möhwald in 2008, Thomas Zemb in 2010 and Werner Kunz in 2014.

During the last period of four years, integration of goals, usage of skills developed in the environmental characterisation methods as well as in the meso-scale theory were more and more considered. Moreover, the distinction made since the creation of the ICSM between "understanding", i.e. demonstrating predictive power of models build on first principles and "optimizing", i.e. demonstrating the feasibility of new chemical systems in selective extraction, sometimes implemented in breakthrough technological processes (thus including the principles of "green chemistry and green engineering"), this through cooperation with our colleagues of CEA/DEN and/or other academic and industrial partners appeared more and more fuzzy. As a consequence, a cluster of competence and cooperation centred on **"Innovation in Extraction and Recycling"** naturally emerged.

As stated above, properly optimize, one first needs to understand and predict. Thus, this large number of innovations also illustrated by the exceptional number of patents (21 between 2015 and 2018) could not grow at cutting-edge world-class level (as shown by citations in international literature) without the closer contacts between observation and theory. In practice, the emerging was possible because of the tools used in the statistical mechanics of interfaces, for example via Gaussian random wavelets. Systematically free energy of transfer was considered in this emerging specific "ienaics" approach with some similarity with neutronics, electrochemistry and nanoscience. This cluster of **"Methodologies and theory in separation chemistry"** grows continuously due to a large number of experimental protocols, such as the measure and calculation of "lost" extracting molecules not active in separation, or new separation methods without classical extractant/surfactant. No less importantly, the recent advances in the field of soft X-ray microscopy and electron microscopies which allow the direct observation of supramolecular aggregates in solution with a very high resolution or the coupling specific stages or cells (controlled relative humidity or high temperature) with modern electron microscopes allowing the precise characterization of physico-chemical properties such as self-healing, sintering, dissolution, chemical reactivity through in situ experiments…

No separation process can be made without knowledge of the "durability of materials", i.e. materials that should withstands to extreme constraints and long usage, not only in the life-cycle of the nuclear fuel, but also in this of all materials necessary in the technologies for alternative energies. Life-cycle of all the implemented technology must be investigated and mastered as proposed in the cluster **"Optimisation of materials life-cycle for energy"**. Solid/solid and solid/liquid interfaces are considered here since the physical and chemical properties of these materials (durability, robustness, extraction, confinement…) depend on their synthesis, i.e. from the nature of the precursors (colloid, solution, emulsion…) to the final material (sintered, porous, powder, thin film).

To facilitate the understanding of the underlying profound unity, the pages describing each research projects have been regrouped in this booklet in those three clusters.

ICSM has to propose an updated version of scientific goals at the end of the current period in December 2020. The question stands: what is next behind the corner? A plan will be proposed by the direction of ICSM to the scientific council of December 5th, 2018 and this booklet is aimed in the present version to identify strengths and weaknesses of ICSM in order to participate in the effort via its 2020-2024 contractual goals of research in energy, via all facets of recycling.

Stéphane Pellet-Rostaing

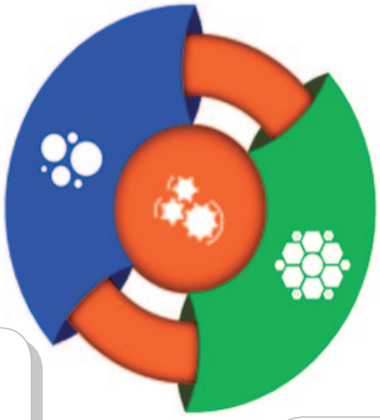
T Zemb

Thomas Zemb

THE CONNECTED CLUSTERS OF INNOVATION AT ICSM

METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

Via the refinement of experimental tools (microscopies, radiation scattering, spectroscopies) and multi-scale predictive modelling (supramolecular, mesoscopic and colloidal).



INNOVATION IN EXTRACTION AND RECYCLING

Via the knowledge of the supra-molecular, weak and long-range interactions, for a technological break-through in eco-friendly separation chemistry.

LIFE-CYCLE OPTIMIZATION OF MATERIALS FOR ENERGY

Via the understanding of the chemical and physico-chemical mechanisms linked to the evolution of liquid-solid and solid-solid interfaces in materials for energy production (nuclear and alternative).

Multi-scale theories and microscopic observations are methodologies for consolidating innovative separation and recycling progresses as well as material life-time for carbon - free energies based on green chemistry principles.

PUBLICATIONS

2019

INNOVATIONS POUR L'EXTRACTION ET LE RECYCLAGE

1. D. Gomes Rodrigues, S. Monge, S. Pellet-Rostaing, N. Dacheux, D. Bouyer, C. Faur -**Sorption properties of carbamoylmethylphosphonated-based polymer combining both sorption and thermosensitive properties: new valuable hydrosoluble materials for rare earth elements sorption-** Chemical Engineering Journal 2019, 335, 871-880.

OPTIMISATION DU CYCLE DE VIE DES MATÉRIAUX POUR L'ENERGIE

2. A. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S. I. Nikitenko, S. Abate, S. Perathoner, P. Lacroix-Desmazes -**Unconventional Pathways for Designing Silica-Supported Pt and Pd Catalysts With Hierarchical Porosity**- chap 18, In: Studies in Surface Science and Catalysis, Vol. 178Elsevier B. V. Eds 2019.

3. L. Parizot, T. Chave, M.-E. Galvez, H. Dutilleul, P. Da Costa, S. I. Nikitenko -**Sonocatalytic Oxidation of EDTA in Aqueous Solutions Over Noble Metal-Free Co_3O_4/TiO_2 Catalyst**- Appl. Cat. B: Environ. 2019, 241, 10-17.

4. Smith, A. L., Kauric, G., Van Eijck, L., Goubitz, K., Clavier, N., Wallez, G., Konings, R. J. M.: -**Structural and thermodynamic study of Cs3Na(MoO4)2: Margin to the safe operation of Sodium cooled Fast Reactors**-, Journal of Solid State Chemistry 2019, 269, 1-8.

2018

INNOVATIONS POUR L'EXTRACTION ET LE RECYCLAGE

5. E. Billy, M. Joulié, R. Loucounet, A. Boulineau, E. De Vito, D. Meyer - **«Dissolution Mechanisms of LiNi1/3Mn1/3Co1/3O2 Positive Electrode Material from Lithium-Ion Batteries in Acid Solution»** - ACS Appl. Mater. Interfaces (2018) 10 (19), 16424–16435.

6. G. Smolyakov, S. Parrès-Maynadié, D. Bourgeois, B. Dautriche, J. Pouessel, J.M. Grassot, D. Mabire, D. Meyer, S. Pellet-Rostaing, O. Diat - **«Efficient liquid-liquid extraction of NaCl governed by simultaneous cation and anion coordination»** - Desalination (2018) 432, 40-45.

7. B. Braibant, D. Bourgeois, D. Meyer - **«Three-liquid-phase extraction in metal recovery from complex mixtures»** - Separation and Purification Technology (2018) 195, 367.

8. R. Navarro Amador, L. Cirre M. Carboni, D. Meyer - **«BTEX removal from aqueous solution with hydrophobic Zr metal organic frameworks»** - Journal of Environmental Management(2018) 214, 17-22.

9. C. Arrambide, S. Marie, G. Arrachart, S. Pellet-Rostaing -**Selective extraction and separation of germanium by catechol based resins**- Separation and Purification Technology 2018, 193, 214-219.

10. R. Turgis, G. Arrachart, S. Michel, S. Legeai, M. Lejeune, M. Draye, S. Pellet-Rostaing -**Ketone functionalized task specific ionic liquids for selective tantalum extraction**- Separation and Purification Technology 2018, 196, 174-182.

11. G. Smolyakov, S. Parres-Maynadie, D. Bourgeois, B. Dautriche, J. Pouessel, J.-M. Grassot, D. Mabire, D. Meyer, S. Pellet-Rostaing, O. Diat -**Efficient liquid-liquid extraction of NaCl governed by simultaneous cation and anion coordination**- Desalination 2018, 432, 40-45.

12. M. Toure, G. Arrachart, J. Duhamet, S.Pellet-Rostaing -**Tantalum and Niobium selective extraction by alkyl-acetophenone**- Metals 2018, 8, 654.

13. R. Besnard, R. Winkler, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing -**Ion extraction applications of bilayer-structured hybrid silicas**- Materials Chemistry Frontiers 2018, 2, 1031-1039.

14. E. Dalodière, M. Virot, T. Dumas, D. Guillaumont, M.-C. Illy, C. Berthon, L. Guerin, A. Rossberg, L. Venault, P. Moisy, S. I. Nikitenko -**Structural and magnetic susceptibility characterization of Pu(V) aqua ion using sonochemistry as a facile synthesis method**- Inorg. Chem. Front. 2018, 5, 100-111.

15. R. Ji, M. Virot, R. Pflieger, R. Podor, X. Le Goff, S. I. Nikitenko -**Controlled «golf ball shape» structuring of Mg surface under acoustic cavitation**- Ultrason. Sonochem. 2018, 40, 30-40.

16. S. I. Nikitenko, T. Chave, X. Le Goff -**Insights into the Photothermal Hydrogen Production from Glycerol Aqueous Solutions over Noble Metal-Free Ti@TiO2 Core-Shell Nanoparticles**- Part. Part. Syst. Char. 2018, 10, 1800265.

17. Li, W. S. J.; Gasc, F.; Pinot, J.; Causse, J.; Poirot, H.; Pinaud, J.; Bouilhac, C.; Simonaire, H.; Barth, D.; Lacroix-Desmazes, P. -**Extraction of palladium from alumina-supported catalyst in supercritical CO2 using functional fluorinated polymers**- The Journal of Supercritical Fluids 2018, 138, 207-214.

18. Micheau C., Diat O., Bauduin P. -**Ion foam flotation of neodymium: From speciation to extraction**- Journal of Molecular Liquids 2018, 253, 217-227.

19. Ut Dong Thach, B. Prelot, S. Pellet-Rostaing, J. Zajac, P. Hesemann -**Surface Properties and Chemical Constitution as Crucial Parameters for the Sorption Properties of Ionosilicas: The Case of Chromate Adsorption**- ACS Applied Nano Materials 2018, sous presse

20. M. Wehbie, X. Le Goff, G. Arrachart, Y. Karamé, S. Pellet-Rostaing -**N-Alkyl-Calix[4]azacrowns for the selective extraction of uranium**- Dalton Transaction 2018, sous presse

21. Fadel O., Gomes Rodrigues D., Girard L., Bauduin P., Rossignol-Castera A., L'Hermite A., Gaillard J.-C., Diat O. -**Separation and identification of polar polyphenols in oily formulation using high-performance thin-layer chromatography and mass spectroscopy techniques.**- Oilseeds and fats, Crops and Lipids 2018, accepted.

OPTIMISATION DU CYCLE DE VIE DES MATÉRIAUX POUR L'ENERGIE

22. G. Genesio, J. Maynadie, M. Carboni, D. Meyer - **«Recent status on MOF Thin Films on Transparent Conductive Oxides substrates (ITO or FTO)»** - New J. Chem. (2018) 42, 2351-2363.

23. A. F. Sierra-Salazar, A. Ayral, T. Chave, S. I. Nikitenko, P. J. Kooyman, F. D. Tichelaar, S. Abate, S. Perathoner, P. Lacroix-Desmazes -**Engineering of silica-supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel process ? II. Catalytic performance**- Micropor. Mesopor. Mat. 2018, 256, 227-234.

24. A. F. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S. I. Nikitenko, S. Perathoner, P. Lacroix-Desmazes -**Hierarchical Porosity Tailoring of Sol-Gel Derived Pt/SiO2 Catalysts**- Top. Catal. 61 (2018) 1424-1436.

25. A. F. Sierra-Salazar, J. W. Li, M. Bathfield, A. Ayral, S. Abate, T. Chave, S. I. Nikitenko, V. Hulea, S. Perathoner P. Lacroix-Desmazes -**Hierarchically Porous Pd/SiO2 Catalyst by Combination of Miniemulsion Polymerization and Sol-gel Method for the Direct Synthesis of H2O2**- Top. Catal. 2018, 306, 16-22.

26. Seydoux-Guillaume, A. M.; Deschanels, X.; Baumier, C.; Neumeier, S.; Weber, W. J.; Peuget, S. -**Why natural monazite never becomes amorphous: Experimental evidence for alpha self-healing**- American Mineralogist 2018, 103 (5), 824-827.

27. Gonçalves, M. C.; Pereira, R. F. P.; Ferreira, P.; Carbó-Argibay, E.; Catita, J.; Toquer, G.; Nunes, S. C.; Bermudez, V. d. Z. -**Structuring of di-alkyl-urethanesils**- J Sol-Gel Sci Technol 2018.

28. Birault, A.; Molina, E.; Carcel, C.; Bartlett, J.; Marcotte, N.; Toquer, G.; Lacroix-Desmazes, P.; Gerardin, C.; Wong Chi Man, M. -**Synthesis of lamellar mesostructured phenylene-bridged periodic mesoporous organosilicas (PMO) templated by polyion complex (PIC) micelles**- J Sol-Gel Sci Technol 2018.

29. Trillaud, V., Maynadie, J., Manaud, J., Hidalgo, J., Meyer, D., Podor, R., Dacheux, N., Clavier, N.: -**Synthesis of size-controlled UO_2 microspheres from the hydrothermal conversion of U(IV) aspartate**- Crystengcomm 2018.

30. Mesbah, A., Prakash, J., Beard, J. C., Malliakas, C. D., Ibers, J. A.: -**Synthesis, crystal structure, and optical properties of $K(Th_{0.75}Sr_{0.25})_2Se_6$**-, Inorganic Chemistry 2018, 57, 7877-7880.

31. Mesbah, A., Prakash, J., Beard, J., Malliakas, C. D., Lebegue, S., Ibers, J. A.: -**Syntheses, Modulated Crystal Structures of $Ba_{6-2x}U_2+xAg_4Se_{12}$ (x = 0 and 0.5), and Crystal Structure and Spectroscopy of $Sr_4Th_{2.78}Cu_4S_{12}$**-, Journal of Solid State Chemistry 2018, 268, 30-35.

32. Mesbah, A., Prakash, J., Beard, J., Lebègue, S., Ibers, J. A.: -**Synthesis and crystal structure of $Cs_2U_2(P_2Se_9)(Se_2)_2$**-, Zeitschrift Fur Anorganische Und Allgemeine Chemie 2018.

33. Laniesse, P., Cau-Dit-Coumes, C., Poulesquen, A., Bourchy, A., Mesbah, A., Le Saout, G., Gaveau, P.: -**Setting and hardening process of a wollastonite-based brushite cement**-, Cement and Concrete Research 2018, 106, 65-76.

34. Gausse, C., Szenknect, S., Mesbah, A., Clavier, N., Neumeier, S., Dacheux, N.: -**Dissolution kinetics of monazite LnPO4 (Ln = La to Gd): A multiparametric study**-, Applied Geochemistry 2018, 93, 81-93.

35. Estevenon, P., Welcomme, E., Szenknect, S., Mesbah, A., Moisy, P., Poinssot, C., Dacheux, N.: -**Impact of carbonate ions on the synthesis of $ThSiO_4$ under hydrothermal conditions**-, Inorganic Chemistry 2018, 57, 12398-12408.

36. Estevenon, P., Welcomme, E., Szenknect, S., Mesbah, A., Moisy, P., Poinssot, C., Dacheux, N.: -**Multiparametric study of the synthesis of $ThSiO_4$ under hydrothermal conditions in acidic media**-, Inorganic Chemistry 2018, 57, 9393-9402.

37. Dalger, T., Szenknect, S., Tocino, F., Claparede, L., Mesbah, A., Moisy, P., Dacheux, N.: -**Kinetics of dissolution of $Th_{0.25}U_{0.75}O_2$ sintered pellets in various acidic conditions**-, Journal of Nuclear Materials 2018, 510, 109-122.

38. Clavier, N., Mesbah, A., Szenknect, S., Dacheux, N.: -**Monazite, rhabdophane, churchite and xenotime: vibrational spectroscopy of Gadolinium phosphate polymorphs**-, Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy 2018, 205, 85-94.

39. Champenois, J. B., Mesbah, A., Danoux-Papin, A., Cau-Dit-Coumes, C., Dacheux, N.: -**$LiAl_2(OH)_6OH.2H_2O$ solubility product and corresponding hydrogen production under γ-irradiation**-, Journal of Nuclear Materials 2018, 508, 92-99.

40. Cau-Dit-Coumes, C., Farcy, O., Antonucci, P., Champenois, J. B., Lambertin, D., Mesbah, A.: -**Design of self-dessicating binders using calcium sulfoaluminate cement : influence of the cement composition and sulfate source**-, Advances in Cement Research 2018.

41. Arinicheva, Y., Gausse, C., Neumeier, S., Brandt, F., Rozov, K., Szenknect, S., Dacheux, N., Bosbach, D., Deissmann, G.: -**Influence of temperature on the dissolution kinetics of synthetic $LaPO_4$** – monazite in acidic media between 50 and 130°C-, Journal of Nuclear Materials 2018, 509, 488-495.

42. Arinicheva, Y., Clavier, N., Neumeier, S., Podor, R., Bukaemskiy, A., Klinkenberg, M., Roth, G., Dacheux, N., Bosbach, D.: -**Effect of powder morphology on sintering kinetics, microstructure and mechanical properties of monazite ceramics-**, Journal of the European Ceramic Society 2018, 38, 227-234.

43. Alexandre, J. C., Dacheux, N., Aupiais, J.: -**Determination of the stability constants of Pu(VI) carbonate complexes by capillary electrophoresis coupled with inductively coupled plasma mass spectrometer**-, Radiochimica Acta 2018, 106, 801-807.

44. Perez T., Latu-Romain L., Podor R., Lautru J., Parsa Y., Mathieu S., Vilasi M., Wouters Y. - **In-situ oxide growth characterization of Mn-containing Ni-25Cr (wt.%) model alloys at 1050°C** - Oxidation of Metals 2018, 89(5), 781-795.

45. Jacquet P., Podor R., Ravaux J., Lautru J., Teisseire J., Gozhyk I., Jupille J., Lazzari R. - **On the influence of oxygen on solid-state dewetting of polycristalline silver thin films** - Acta Materialia 2018, 143, 281-290.

46. Lequien F. , Soulié V., Moine G., Lequien A., Feron D., Prené P. , Moehwald H., Riegler H. -**Corrosion influence on the evaporation of a sessile droplet**- COLLOIDS AND SURFACES A-PHYSICOCHEMICAL AND ENGINEERING ASPECTS 2018 Vol 66 pp. 59-66

MÉTHODOLOGIES ET THÉORIES POUR LA CHIMIE SÉPARATIVE

47. Špadina M., Bohinc K. Zemb. Th. Dufrêche J.-F. - **Multicomponent Model for the Prediction of Nuclear Waste/Rare-Earth Extraction Processes** – Langmuir 2018, 34, 10434-10447.

48. Karmakar A., Duvail M., Bley M., Zemb T., Dufrêche J.-F. – **Combined Supramolecular and Mesoscale Modelling of Liquid–Liquid Extraction of Rare Earth Salts** – Colloids and Surfaces A: Physicochemical and Engineering Aspects 2018, 555, 713-727.

49. Bley M., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Activity Coefficients of Aqueous Sodium, Calcium, and Europium Nitrate Solutions from Osmotic Equilibrium MD Simulations** – Journal of Physical Chemistry B 2018, 122 (31), 7726-7736.

50. Villard A., Toquer G., Siboulet B., Trens Ph., Grandjean A., Dufrêche J.-F. – **Sorption pH Dependance of Strontium/Calcium by Sodium Nonatitanate** – Chemosphere 2018, 202, 33-39.

51. Sivakumarasamy R., Hartkamp R., Siboulet B., Dufrêche J.-F., Nishiguchi K., Fujiwara A., Clément N. – **Selective Layer-Free Blood Serum Ionogram Based on Ion-Specific Interactions with a Nanotransistor** – Nature Materials 2018, 17, 464-470.

52. Bley M., Duvail M., Guilbaud Ph., Penisson Ch., Theisen J., Gabriel J.-Ch., Dufrêche J.-F. – **Molecular Simulation of Binary Phase Diagrams From the Osmotic Equilibrium Method: Vapour Pressure and Activity in Water–Ethanol Mixtures** – Molecular Physics 2018, 116 (15-16), 2009-2021.

53. Špadina M., Gourdin-Bertin S., Drazic G., Selmani A., Dufrêche J.-F., Bohinc K. – **Charge Properties of TiO2 Nanotubes in NaNO3 Aqueous Solution** – ACS Applied Materials & Interfaces 2018, 10 (15), 13130-13142.

54. Buchecker T., Schmid P., Renaudineau S., Diat O., Proust A., Pfitzner A., Bauduin P. -**Polyoxometalates in the Hofmeister series**- Chemical Communications 2018, 54, 1833-1836.

55. Krickl S., Touraud D., Bauduin P., Zinn T., Kunz W. -**Enzyme activity of horseradish peroxidase in surfactant-free microemulsions**- Journal of Colloid and Interface Science 2018, 516, 466-475.

56. Malinenko A., Jonchere A., Girard L., Parres-Maynadie S., Diat O., Bauduin P. -**Are Keggin's POMs Charged Nanocolloids or Multicharged Anions?**- Langmuir 2018, 34, 2026-2038.

57. Zaulet A., Teixidor F., Bauduin P., Diat O., Hirva P., Ofori A., Vinas C. -**Deciphering the role of the cation in anionic cobaltabisdicarbollide clusters**- Journal of Organometallic Chemistry 2018, 865, 214-225.

58. D. Bengio, E. Mendes, S. Pellet-Rostaing, P. Moisy -**Electrochemical behavior of platinium and gold electrodes in the aprotic ionic liquid N,N-trimethylbutylammonium-bis(trifluoromethylsulfonyl)imide**- Journal of Electroanalytical Chemistry 2018, 823, 445-454.

59. R. Ji, R. Pflieger, M. Virot, S.I. Nikitenko -**Multibubble Sonochemistry and Sonoluminescence at 100 kHz: The Missing Link between Low- and High-Frequency Ultrasound**- J. Phys. Chem. B 2018, 122, 6989-6994.

60. T. Belmonte, H. Kabbara, C. Noel, R. Pflieger -**Analysis of Zn I emission lines observed during a spark discharge in liquid nitrogen for zinc nanosheet synthesis**- Plasma Sour. Sci. Technol. 2018, 27, 074004.

61. R. Pflieger, L. Gravier, G. Guillot, M. Ashokkumar, S.I. Nikitenko -**Inverse effects of the gas feed positioning on sonochemistry and sonoluminescence**- Ultrason. Sonochem. B 2018, 46, 10-17.

62. Pereira, R. F. P.; Nunes, S. C.; Toquer, G.; Cardoso, M. A.; Valente, A. J. M.; Ferro, M. C.; Silva, M. M.; Carlos, L. D.; Ferreira, R. A. S.; Bermudez, V. D. -**Novel Highly Luminescent Amine-Functionalized Bridged Silsesquioxanes**- Frontiers in Chemistry 2018, 5 (131), 1-15.

63. Ronzani, A. L., Pointurier, F., Rittner, M., Borovinskaya, O., Tanner, M., Hubert, A., Humbert, A. C., Aupiais, J., Dacheux, N.: -**Capabilities of laser ablation - ICP-TOF-MS coupling for isotopic analysis of individual micrometric particles**-, Journal of Analytical Atomic Spectrometry 2018.

64. Niania M., Podor R., Britton T. B., Li C., Cooper S., Svetkov N., Skinner S., Kilner J. - **In-situ study of strontium segregation in LSCF in ambient atmospheres using HT-ESEM** - Journal of Materials Chemistry A 2018, 6, 14120-14135.

65. Barbetta A., Bertinetti L., Lautru J., Podor R., Zemb T. - **Nano-, Meso- and Macro-swelling characterization of impregnated compression wood cell walls** - Wood Science and Technology 2018, 52(2), 421-443.

66. Fournier J., Régnier E., Faure F., Le Goff X., Brau H.-P., Brackx E., Pinet O. - **Application of the JMAK model for crystal dissolution kinetics in a borosilicate melt** - Journal of Non-Crystalline Solids 2018, 489, 77-83.

67. Fournier J., Régnier E., Faure F., Le Goff X., Brau H.-P., Brackx E., Pinet O. - **Modeling of dissolution kinetics of rare earth crystals in a borosilicate glass melt** - Journal of Non-Crystalline Solids 2018, 481, 248-253.

68. Mougnaud S., Tribet M., Renault J.-P., Gin S., Peuget S., Podor R., Jégou C. - **Long-term glass leaching: irradiation as a way to refine mechanisms** – Journal of Nuclear Materials 2018, 510, 168-177.

69. Corti M., Raudino A., Cantu L., Theisen J. Pleines M. and Zemb T. -**Nanometric Surface Oscillation Spectroscopy of Water-Poor Microemulsions**- Langmuir 2018 34 pp 8154-8162.

70. Pleines M, Duhamet J. and Zemb T. -**Understanding and Predicting of the Clouding Phenomenon by Spontaneous and Effective Packing concepts**- J. of Surfactant and detergents 2018 in press

2017

INNOVATIONS POUR L'EXTRACTION ET LE RECYCLAGE

71. M. Cognet, T. Gutel, D. Peralta, J. Maynadie, M. Carboni, D. Meyer - **«Iron(II)-Benzene Phosphonate Coordination Polymers as an Efficient Active Material for Negative Electrode of Lithium-Ion Batteries»** - Journal of The Electrochemical Society (2017) 164, 12, A2552-A2554.

72. M. Joulie, E. Billy, R. Laucoumet, D. Meyer - **«Current collectors as reducing agent to dissolve active materials of positive electrodes from Li-ion battery wastes «** - Hydrometallurgy (2017) 169, 426-432.

73. M.-C. Dul, B. Braibant, S. Dourdain, S. Pellet-Rostaing, D. Bourgeois, D. Meyer - **«Perfluoroalkyl- vs alkyl substituted malonamides Supramolecular effects and consequences for extraction of metals «** - Journal of Fluorine Chemistry (2017) 200, 59-65.

74. B. Braibant, X. Le Goff, D. Bourgeois, D. Meyer - **«Impact of the Long-Range Electronic Effect of a Fluorous Ponytail on Metal Coordination during Solvent Extraction»** - Chem Phys Chem (2017) 18, 24, 3583.

75. R. Navarro Amador, M. Carboni, D. Meyer - **« Sorption and photodegradation under visible light irradiation of an organic pollutant by a heterogeneous UiO-67-Ru-Ti MOF obtained by Post-Synthetic Exchange «** - RSC Advances (2017) 7, 29, 195-200.

76. Fadel O., Girard L., Gomes Rodrigues D., Bauduin P., Le Goff X., Rossignol-Castera A., L'Hermitte A., Diat O. -**Micellization in vegetable oils: A structural characterisation**- Colloids and Surfaces B-Biointerfaces 2017, 154, 279-286.

77. C. R. Canovas, R. Perez-Lopez, F. Macias, S. Chapron, J. M. Nieto, S. Pellet-Rostaing -**Exploration of fertilizer industry wastes as potential source of critical raw materials**- Journal of Cleaner Technology 2017, 143, 497-505.

78. A. Leydier, G. Arrachart, R. Turgis, G. Bernier, C. Marie, M. Miguirditchian, S. Pellet-Rostaing -**Recovery of uranium (VI) from concentrated phosphoric acid using bifunctional reagents**- Hydrometallurgy 2017, 171, 262-266

79. M. Wehbie, G. Arrachart, C. Arrambide Cruz, I. Karamé, L. Ghannam, S. Pellet-Rostaing -**Organization of diglycolamides on resorcinarene cavitand and its effect on the selective extraction and separation of HREEs**- Separation and Purification Technology 2017, 187, 311-318.

80. J. Rey, S. Atak, S. Dourdain, G. Arrachart, S. Pellet-Rostaing -**Synergistic Extraction of Rare Earth Elements from Phosphoric Acid Medium using a Mixture of Surfactant AOT and DEHCNPB**- Solvent Extraction and Ion Exchange 2017, 35, 321-331.

81. M. Wehbie, G. Arrachart, I. Karamé, L. Ghannam, S. Pellet-Rostaing -**An ionic liquid-based extraction system using diglycolamide functionalized macrocyclic platforms for the extraction and recovery of lanthanides-** Dalton Transaction 2017, 46, 16505-16515.

82. Draouil, H.; Alvarez, L.; Causse, J.; Flaud, V.; Zaibi, M. A.; Bantignies, J. L.; Oueslati, M.; Cambedouzou, J. -**Copper hexacyanoferrate functionalized singlewalled carbon nanotubes for selective cesium extraction**- New Journal of Chemistry 2017, 41 (15), 7705-7713.

83. Jehannin M., Charton S., Corso B., Moehwald H., Riegler H. and Zemb T. -**Structured solvent effects on precipitation** - COLLOID AND POLYMER SCIENCE 2017, Vol: 295 pp : 1817-1826

84. Duhamet J., Moehwald H., Pleines M. and Zemb T. -**Self-Regulated Ion Permeation through Extraction Membranes**- Langmuir 2017, Vol : 33 pp : 9873-9879

85. Breil C., Vian MA, Zemb T, Kunz W. and Chemat F. ; **«Bligh and Dyer» and Folch Methods for Solid-Liquid-Liquid Extraction of Lipids from Microorganisms. Comprehension of Solvatation Mechanisms and towards Substitution with Alternative Solvents** INTERNATIONAL JOURNAL OF MOLECULAR SCIENCES 2017, vol 18, Article Number: 708 DOI: 10.3390/ijms18040708

OPTIMISATION DU CYCLE DE VIE DES MATÉRIAUX POUR L'ENERGIE

86. N. Clavier, J. Maynadié, A. Mesbah, J. Hidalgo, R. Lauwerier, G.I. Nkou Bouala, S. Parrès-Maynadié, D. Meyer, N. Dacheux, R. Podor - **«Thorium aspartate tetrahydrate precursor to ThO_2: Comparison of hydrothermal and thermal conversions»** - J. Nucl. Mater. (2017) 487, 331-342.

87. H. Ali-Moussa, R. Navarro Amador, J. Martinez, F. Lamaty, M. Carboni, X. Bantreil - **« Synthesis and post-synthetic modification of UiO-67 type metal-organic frameworks by mechanochemistry «** - Materials Letters (2017) 197, 171-174.

88. X. Wang, V. Goudy, G. Genesio, J. Maynadie, D. Meyer, M. Fontecave - **« Ruthenium–cobalt dinuclear complexes as photocatalysts for CO_2 reduction «** - Chemical Communications (2017) 53, 5040-5043.

89. Y. Lou, S. Dourdain, Y. Serruys, D. Siméone, N. Mollard, X. Deschanels -**Structure evolution of mesoporous silica under heavy ion irradiations of intermediate energies**- J. Meso. Microporous materials 2017, 251, 146-154.

90. R. Besnard, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing -**Tuning the Morphology of Functionalized Silica using Amphiphilic Organosilanes**- Journal of Sol-Gel Science and Technology 2017, 82, 452-467.

91. T. Chave, X. Le Goff, A. Scheinost, S. I. Nikitenko -Insights into the Structure and Thermal Stability of Uranyl Aluminate Nanoparticles- New J. Chem. 2017, 41, 1160-1167.
E. Dalodière, M. Virot, V. Morosini, T. Chave, T. Dumas, C. Hennig, T. Wiss, O. Dieste Blanco, D. K. Shuh, T. Tyliszczak, L. Venault, P. Moisy, S. I. Nikitenko -**Insights into the Sonochemical Synthesis and Properties of Salt-Free Intrinsic Plutonium Colloids**- Sci. Reports 2017, 7, 43514-43524.

92. E. Dalodière, M. Virot, V. Morosini, T. Chave, T. Dumas, C. Hennig, T. Wiss, O. Dieste Blanco, D. K. Shuh, T. Tyliszczak, L. Venault, P. Moisy, S. I. Nikitenko -**Insights into the Sonochemical Synthesis and Properties of Salt-Free Intrinsic Plutonium Colloids**- Sci. Reports 2017, 7, 43514-43524.

93. Shehayeb, S.; Deschanels, X.; Karamé, I.; Ghannam, L.; Toquer, G. -**Spectrally selective coatings obtained from electrophoretic deposition of CuO nanoparticles**- Surface and Coatings Technology 2017, 322, 38-45.

94. Rebiscoul, D.; Cambedouzou, J.; Brossel, M.; Baum, M.; Szenknect, S. -**Evolution of silica walls of nanopores filled with water and ions**- In 15th Water-Rock Interaction International Symposium, Wri-15, Marques, J. M.; Chambel, A., Eds. 2017; Vol. 17, pp 88-91.

95. Ortiz, D. G.; Pochat-Bohatier, C.; Cambedouzou, J.; Balme, S.; Bechelany, M.; Miele, P. -**Inverse Pickering Emulsion Stabilized by Exfoliated Hexagonal-Boron Nitride (h-BN)**- Langmuir 2017, 33 (46), 13394-13400.

96. Nunes, S. C.; Toquer, G.; Cardoso, M. A.; Mayoral, A.; Ferreira, R. A. S.; Carlos, L. D.; Ferreira, P.; Almeida, P.; Cattoën, X.; Wong Chi Man, M.; de Zea Bermudez, V. -**Structuring of Alkyl-Triazole Bridged Silsesquioxanes**- ChemistrySelect 2017, 2 (1), 432-442.

97. Mayer, M.; Dedovets, D.; Guari, Y.; Larionova, J.; Long, J.; Causse, J. -**Synthesis of Poly(diallyldimethylammonium) capped copper hexacyanoferrates (CuHCF) nanoparticles: an efficient stabiliser for Pickering emulsions**- Journal of Colloid and Interface Science 2017, 364-372.

98. Mansas, C.; Delaye, J. M.; Charpentier, T.; Bruguier, F.; Bouty, O.; Penelon, B.; Arena, H.; Rebiscoul, D. -**Drivers of Water Transport in Glass: Chemical or Topological Effect of the Glass Network?**- Journal of Physical Chemistry C 2017, 121 (30), 16201-16215.

99. Leblanc, M.; Causse, J.; Lu, Z.; Rébiscoul, D. -**Stable uranium sols as precursors for the elaboration of nanostructured nc-UO_2 materials**- Colloids and Surfaces A: Physicochemical and Engineering Aspects 2017, 522, 18-27.

100. Belarbi, H.; Boudjema, L.; Shepherd, C.; Ramsahye, N.; Toquer, G.; Chang, J.-S.; Trens, P. -**Adsorption and separation of hydrocarbons by the metal organic framework MIL-101(Cr)**- Colloids and Surfaces A: Physicochemical and Engineering Aspects 2017, 520, 46-52.

101. Arena, H.; Godon, N.; Rebiscoul, D.; Frugier, R.; Podor, R.; Garces, E.; Cabie, M.; Mestre, J. P. -**Impact of iron and magnesium on glass alteration: Characterization of the secondary phases and determination of their solubility constants**- Applied Geochemistry 2017, 82, 119-133.

102. Szenknect, S., Dacheux, N., Ewing, R. C., Navrotsky, A.: -**Reply to comment by Konings and Plyasunov on «First experimental determination of the solubility constant of coffinite»**-, Geochimica Et Cosmochimica Acta 2017, 212, 374-376.

103. Smith, A. L., Kauric, G., van Eijck, L., Goubitz, K., Wallez, G., Griveau, J. C., Colineau, E., Clavier, N., Konings, R. J. M.: -**Structural and thermodynamic study of dicesium molybdate $Cs_2Mo_2O_7$: Implications for fast neutron reactors**-, Journal of Solid State Chemistry 2017, 253, 89-102.

104. Qin, D. W., Mesbah, A., Gausse, C., Szenknect, S., Dacheux, N., Clavier, N.: -**Incorporation of thorium in the rhabdophane structure: Synthesis and characterization of $Pr_{1-2x}Ca_xTh_xPO_4 \cdot nH_2O$ solid solutions**-, Journal of Nuclear Materials 2017, 492, 88-96.

105. Qin, D., Gausse, C., Szenknect, S., Mesbah, A., Clavier, N., Dacheux, N.: -**Solubility product of the thorium phosphate hydrogen-phosphate hydrate ($Th_2(PO_4)_2(HPO_4) \cdot H_2O$, TPHPH)**-, Journal of Chemical Thermodynamics 2017, 114, 151-164.

106. Mesbah, A., Prakash, J., Malliakas, C. D., Lebegue, S., Badawi, M., Ibers, J. A.: -**Syntheses, crystal structures, and optical properties of $CsBa_5Ti_2Se_9Cl$ and $CsBa_2Cl_5$**-, Journal of Solid State Chemistry 2017, 253, 258-262.

107. Mesbah, A., Francois, M.: -**Polymorphism and polytypism in zinc aliphatic carboxylate: The complex case of $Zn(C_{11}H_{21}O_2)_2$**, Materials Letters 2017, 197, 228-232.

108. Mesbah, A., Clavier, N., Elkaim, E., Szenknect, S., Dacheux, N.: -**In pursuit of the rhabdophane crystal structure: from the hydrated monoclinic $LnPO_4 \cdot 0.667H_2O$ to the hexagonal $LnPO_4$ (Ln = Nd, Sm, Gd, Eu and Dy)**-, Journal of Solid State Chemistry 2017, 249, 221-227.

109. Cordara, T., Szenknect, S., Claparede, L., Podor, R., Mesbah, A., Lavalette, C., Dacheux, N.: -**Kinetics of dissolution of UO_2 in nitric acid solutions: A multiparametric study of the non-catalysed reaction**-, Journal of Nuclear Materials 2017, 496, 251-264.

110. Clavier, N., Maynadie, J., Mesbah, A., Hidalgo, J., Lauwerier, R., Nkou Bouala, G. I., Parres-Maynadie, S., Meyer, D., Dacheux, N., Podor, R.: -**Thorium aspartate tetrahydrate precursor to ThO_2: Comparison of hydrothermal and thermal conversions**, Journal of Nuclear Materials 2017, 487, 331-342.

111. Clavier, N., Cherkaski, Y., Martinez, J., Costis, S., Cordara, T., Audubert, F., Brissonneau, L., Dacheux, N.: -**Synthesis and Direct Sintering of Nanosized $(MIV,MIII)O_{2-x}$ Hydrated Oxides as Electrolyte Ceramics**-, Chemphyschem 2017, 18, 2666-2674.

112. Claparede, L., Guigue, M., Jouan, G., Nadah, N., Dacheux, N., Moisy, P.: -**Long-term behavior of refractory thorium-plutonium dioxide solid solutions**-, Journal of Nuclear Materials 2017, 483, 158-166.

113. Cherkaski, Y., Clavier, N., Brissonneau, L., Podor, R., Dacheux, N.: -**Densification behavior and microstructure evolution of yttrium-doped ThO_2 ceramics**-, Journal of the European Ceramic Society 2017, 37, 3381-3391.

114. Gasparrini C., Podor R., Pettina M., Horlait D., Chater R., Vandeperre L., Lee W.E. - Maltese cross formation and oxidation of zirconium carbide - Oxidation of Metals 2017, 88, 509-519.

115. Barbetta A., Bertinetti L. and Zemb, T. -**Composition dependent Equation of State of cellulose based plant tissues in the presence of electrolytes**- COLLOIDS AND SURFACES A 2017, 532, 314-322.

116. Soulie V., Lequien F., Ferreira-Gomes F., Moine G., Féron D., Prené P. , Moehwald H., Zemb t. and Riegler H. -**Salt-induced iron corrosion under evaporating sessile droplets of aqueous sodium chloride solutions**- MATERIALS AND CORROSION 2017, 68 927-934.

117. Barbetta A., Fratzl P., Zemb t. and Bertinetti L. -**Impregnation and Swelling of Wood with Salts: Ion Specific Kinetics and Thermodynamics Effects**- ADVANCED MATERIALS INTERFACES 2017, 4 Number : SI -1600437

MÉTHODOLOGIES ET THÉORIES POUR LA CHIMIE SÉPARATIVE

118. Rey J., Bley M., Dufrêche J.-F., Gourdin S., Pellet-Rostaing S, Zemb Th., Dourdain S. – **Thermodynamic Description of Synergy in Solvent Extraction: II Thermodynamic Balance of Driving Forces Implied in Synergistic Extraction** – Langmuir 2017, 33 (46), 13168-13179.

119. Bley M., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Simulating Osmotic Equilibria: A New Tool to Calculate Activity Coefficients in Concentrated Aqueous Salt Solutions** – Journal of Physical Chemistry B 2017, 121 (41), 9647-9658.

120. Duvail M., van Damme S., Guilbaud Ph., Chen Y. S., Zemb Th., Dufrêche J.-F. – **The Role of Curvature Effects in Liquid–Liquid Extraction: Assessing Organic Phase Mesoscopic Properties From MD Simulations** – Soft Matter 2017, 13, 5518-5526.

121. Allaire G., Bernard O., Dufrêche J.-F., Mikelic A. – **Ion Transport through Deformable Porous Media: Derivation of the Macroscopic Equations Using Upscaling** – Computational & Applied Mathematics 2017, 36, 1431-1462.

122. Pham T. T., Jonchère A., Dufrêche J.-F., Brevet P.-F., Diat O. – **Analysis of the Second Harmonic Generation Signal From a Liquid/Air and Liquid/Liquid Interface** – The Journal of Chemical Physics 2017, 146, 144701.

123. Siboulet B., Hocine S., Hartkamp R., Dufrêche J.-F. – **Scrutinizing Electro-Osmosis and Surface Conductivity with Molecular Dynamics** – Journal of Physical Chemistry C 2017, 121 (12), 6756-6769.

124. Chen Y. S., Duvail M., Guilbaud Ph., Dufrêche J.-F. – **Stability of Reverse Micelles in Rare-Earth Separation: a Chemical Model Based on a Molecular Approach** – Physical Chemistry Chemical Physics 2017, 19, 7094-7100.

125. Lahrouch F., Chamayou A.-C., Creff G., Duvail M., Hennig Ch., Lozano-Rodriguez M. J., Den Auwer Ch. , Di Giorgio Ch. – **A Combined Spectroscopic/Molecular Dynamic Study for Investigating a Methyl Carboxylated PEI as a Potential Uranium Decorporation Agent** – Inorganic Chemistry 2017, 56 (3), 1300-1308.

126. S. Ameziane-Le Hir, D. Bourgeois, C. Basset, A. Hagège, C. Vidaud - «Reactivity of U-**associated osteopontin with lactoferrin: a one-to-many complex «** – Metallomics 2017, 9, 865-875.

127. T. Lopian, S. Schoettl, S. Prevost, S. Pellet-Rostaing, D. Horinek, W. Kunz, T. Zemb -**Morphologies Observed in Ultraflexible Microemulsions with and without the Presence of a Strong Acid**- ACS Central Science 2017, 2, 467-475.
128. Buchecker T., Krickl S., Meyer A., Grillo I., Bauduin P., Konig B., Pfitzner A., Kunz W. -**Mesoscale structuring of binary liquids and its impact on chemical reactivity probed by photocatalysis**- Abstracts of Papers of the American Chemical Society 2017, 254.

129. Buchecker T., Krickl S., Winkler R., Grillo I., Bauduin P., Touraud D., Pfitzner A., Kunz W. -**The impact of the structuring of hydrotropes in water on the mesoscale solubilisation of a third hydrophobic component**- Physical Chemistry Chemical Physics 2017, 19, 1806-1816.

130. Buchecker T., Le Goff X., Naskar B., Pfitzner A., Diat O., Bauduin P. -**Polyoxometalate/Polyethylene Glycol Interactions in Water: From Nanoassemblies in Water to Crystal Formation by Electrostatic Screening**- Chemistry-a European Journal 2017, 23, 8434-8442.

131. Diat O., Pham T., Dufreche J. F., Girard L., Brevet P. F., Jonchere A., Scoppola E. -**Solvent extraction: Structure of the liquid/liquid interface containing a diamide ligand**- Abstracts of Papers of the American Chemical Society 2017, 254.

132. Guilbaud P., Berthon L., Louisfrema W., Diat O., Zorz N. -**Determination of the Structures of Uranyl-Tri-n-butyl-Phosphate Aggregates by Coupling Experimental Results with Molecular Dynamic Simulations**- Chemistry-a European Journal 2017, 23, 16660-16670.

133. Krickl S., Buchecker T., Meyer A. U., Grillo I., Touraud D., Bauduin P., Konig B., Pfitzner A., Kunz W. -**A systematic study of the influence of mesoscale structuring on the kinetics of a chemical reaction**- Physical Chemistry Chemical Physics 2017, 19, 23773-23780.

134. Ledercq L., Bauduin P., Nardello-Rataj V. -**Supramolecular «Big Bang» in a Single-Ionic Surfactant/ Water System Driven by Electrostatic Repulsion: From Vesicles to Micelles**- Langmuir 2017, 33, 3395-3403.

135. Rodrigues D. G., Fadel O., Bauduin P., Girard L., Guilbaud P., L'Hermitte A., Rossignol-Castera A., Diat O. -**Self-assembly of a bio-based extractant in methyl esters: combination of small angle X-ray scattering experiments and molecular dynamics simulations**- Green Chemistry 2017, 19, 4680-4689.

136. R. Pflieger, T. Ouerhani, T. Belmonte, S. I. Nikitenko -**Use of NH ($A^3\Pi$–$X^3\Sigma$-) sonoluminescence for diagnostics of nonequilibrium plasma produced by multibubble cavitation**- Phys. Chem. Chem. Phys. 2017, 19, 26272-26279.

137. S. I. Nikitenko, R. Pflieger -**Toward a New Paradigm for Sonochemistry: Short Review on Nonequilibrium Plasma Observations by Means of MBSL Spectroscopy in Aqueous Solutions**- S Ultrason. Sonochem. 2017, 35, 623-630.

138. Baum, M.; Rebiscoul, D.; Tardif, S.; Tas, N.; Mercury, L.; Rieutord, F. -**X-Ray Reflectivity analysis of SiO2 nanochannels filled with water and ions: a new method for the determination of the spatial distribution of ions inside confined media**- In 15th Water-Rock Interaction International Symposium, Wri-15, Marques, J. M.; Chambel, A., Eds. 2017; Vol. 17, pp 682-685.

139. Szenknect, S., Finkeldei, S., Brandt, F., Ravaux, J., Odorico, M., Podor, R., Lautru, J., Dacheux, N., Bosbach, D.: -**Monitoring the microstructural evolution of $Nd_2Zr_2O_7$ pyrochlore during dissolution at 90°C in 4 M HCl: Implications regarding the evaluation of the chemical durability**-, Journal of Nuclear Materials 2017, 496, 97-108.

140. Nkou Bouala, G. I., Clavier, N., Lechelle, J., Monnier, J., Ricolleau, C., Dacheux, N., Podor, R.: -**High-temperature electron microscopy study of ThO2 microspheres sintering**-, Journal of the European Ceramic Society 2017, 37, 727-738.

141. Clavier, N., Nkou Bouala, G. I., Lechelle, J., Martinez, J., Dacheux, N., Podor, R.: -**Novel approaches for the in situ study of the sintering of nuclear oxide fuel materials and their surrogates**-, Radiochimica Acta 2017, 105, 879-892.

142. Pisani C., Gaillard J.-C., Odorico M., Nyalosaso J. L., Charnay C., Guari Y., Chopineau J., Devoiselle J.-M., Armengaud J., Prat O. - **The timeline of corona formation around silica nanocarriers highlights the role of the protein interactome** - Nanoscale 2017, 9(5), 1840-1851.

143. Godon C., Teulon J.-M., Odorico M., Basset C., Meillan M., Vellutini L., Chen S. W., Pellequer J.-L. - **Conditions to minimize soft single biomolecule deformation when imaging with atomic force microscopy** - Journal of Structural Biology 2017, 197(3), 322-329.

144. Gasparrini C., Podor R., Horlait D., Rushton M. J. D., Fiquet O., Lee W. E. - **Oxidation of UC: an in situ high temperature environmental scanning electron microscopy study** - Journal of Nuclear Materials (2017) 494, 127-137.

145. Schillers H., Rianna C., Schäpe J., Luque T., Doschke H., Wälte M., Uriarte J. J., Campillo N., Michanetzis G. P. A., Bobrowska J., Dumitru A., Herruzo E. T., Bovio S., Parot P., Galluzzi M., Podestà A., Puricelli L., Scheuring S., Missirlis Y., Garcia R., Odorico M., Teulon J.-M., Lafont F., Lekka M., Rico F., Rigato A., Pellequer J.-L., Oberleithner H., Navajas D., Radmacher M. - **Standardized Nanomechanical Atomic Force Microscopy Procedure (SNAP) for Measuring Soft and Biological Samples** - Scientific Reports 2017, 7(5117).

146. Jehannin M., Charton S., Corso B., Mohwald H., Riegler H., Zemb T. - **Structured solvent effects on precipitation. Microscopically organized cerium oxalate particles** - Colloid and Polymer Science 2017, 295(10), 1817-1826.

147. Prevost S., Gradzielski M. and Zemb T.; **Self-assembly, phase behaviour and structural behaviour as observed by scattering for classical and non-classical microemulsions** - Advances in Colloid and Interface Science 2017, vol 247 pp : 374-396.

2016

INNOVATIONS POUR L'EXTRACTION ET LE RECYCLAGE

148. E. Perez, M.-L. André, R. Navarro Amador, F. Hyvrard, J. Borrini, M. Carboni, D. Meyer - **«Recovery of metals from simulant spent lithium-ion battery as organophosphonate coordination polymers in aqueous media. «** - Journal of Hazardous Material 2016),337, 617-621.

149. E. Perez, R. Navarro Amador, M. Carboni, D. Meyer - **« In-Situ Precipitation of Metal-Organic Frameworks from a simulant battery waste solution»** - Materials Letters 2016, 167, 188-191.

150. R. Poirot, X. Le Goff, O. Diat, D. Bourgeois, D. Meyer - **« Metal Recognition Driven by Weak Interactions: a Case Study in Solvent Extraction »** - ChemPhysChem 2016, 17, 14, 2112.

151. V. Goudy, J. Maynadié, X. Le Goff, D. Meyer, M. Fontecave - **« Synthesis, electrochemical and spectroscopic properties of ruthenium(II) complexes containing 2,6-di(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)aryl ligands»** - New J. Chem. 2016, 40, 1704-1714.

152. M. Miguirditchian, G. Bernier, V. Pacary, C. Balaguer, C. Sorel, M. Bertrand, B. Camès, A. Leydier, R. Turgis, G. Arrachart, S. Pellet-Rostaing, H. Mokhtari -**Development of a new solvent extraction process based on the DEHCNPB extractant for the selective recovery of uranium from phosphoric acid**- Solvent Extraction and Ion Exchange 2016, 34, 274-289.

153. R. Turgis, G. Arrachart, D. Virieux, M. Draye, S. Legeai, S. Pellet-Rostaing -**Performances and mechanistic investigations of triphosphine trioxide / ionic liquid system for rare earth extraction**- Dalton Trans. 2016, 45, 1259 - 1268.

154. M. Wehbie, G. Arrachart, I. Karamé, L. Ghannam, S. Pellet-Rostaing -**Triazole Diglycolamide Cavitand for lanthanide extraction**- Separation and Purification Technology 2016, 169, 17-24.
155. M. Wehbie, G. Arrachart, I. Karamé, L. Ghannam, S. Pellet-Rostaing -**Diglycolamide-functionalized resorcinarene for rare earths extraction**- New J. Chem 2016, 40, 9344-9351.

156. R. Turgis, A. Leydier, G. Arrachart, F. Burdet, S. Dourdain, G. Bernier, M. Miguirditchian, S. Pellet-Rostaing -**Carbamoylalkylphosphonates type ligand for uranium extraction from phosphates ores**- Procedia Engineering, 2016, 138, 258-266.

157. S. Chapron, C. Marie, V. Pacary, G. Arrachart, M. Miguirditchian, S. Pellet-Rostaing -**Separation of Americium by liquid-liquid extraction using diglycolamides water-soluble complexing agents**- Procedia Chemistry 2016, 21, 133-139.

158. M. Virot, T. Chave, V. Morosini, R. Pflieger, S. I. Nikitenko, L. Venault, P. Moisy -**Sonochemistry of Actinides**- Actinide Research Quarterly LANL Report 2016, 67-72.

159. X. Beaudoux, M. Virot, T. Chave, G. Durand, G. Leturcq, S. I. Nikitenko -**Vitamin C boosts ceria-based catalysts recycling**- Green Chem. 2016, 18, 3656-3668.

160. X. Beaudoux, M. Virot, T. Chave, G. Leturcq, G. Jouan, L. Venault, P. Moisy, S. I. Nikitenko -**Ultrasound-assisted reductive dissolution of CeO_2 and PuO_2 in the presence of Ti particles**- Dalton. Trans. 2016, 45 8802-8815.

161. E. Dalodière, M. Virot, P. Moisy, S. I. Nikitenko -**Effect of ultrasonic frequency on H2O2 sonochemical formation rate in aqueous nitric acid solutions in the presence of oxygen**- Ultrason. Sonochem. 2016, 29, 198-204.

162. S. I. Nikitenko, R. Pflieger, T. Chave, M. Virot -**Activation de molecules, de particules et de surfaces par cavitation acoustique**- L'actualité Chimique 2016, 410, 23-26.

163. V. Morosini, T. Chave, M. Virot, P. Moisy, S. I. Nikitenko -**Sonochemical Water Splitting in the Presence of Powdered Metal Oxides**- Ultrason. Sonochem. 2016, 29, 512-516.

164. Sommer-Marquez, A.; Mansas, C.; Talha, N.; Rey, C.; Causse, J. -**Reinforced silica monoliths functionalised with metal hexacyanoferrates for cesium decontamination: a combination of a one-pot procedure and skeleton calcination**- Rsc Advances 2016, 6 (77), 73475-73484.

165. Luca, V.; Tejada, J. J.; Vega, D.; Arrachart, G.; Rey, C. -**Zirconium(IV)–Benzene Phosphonate Coordination Polymers: Lanthanide and Actinide Extraction and Thermal Properties**- Inorganic Chemistry 2016, 55 (16), 7928-7943.

166. Grandjean, A.; Delchet, C.; Causse, J.; Barré, Y.; Guari, Y.; Larionova, J. -**Effect of the chemical nature of different transition metal ferrocyanides to entrap Cs**- J Radioanal Nucl Chem 2016, 307 (1), 427-436.

OPTIMISATION DU CYCLE DE VIE DES MATÉRIAUX POUR L'ENERGIE

167. S. M. Butorin, K. O. Kvashnina, J. R. Vegelius, D. Meyer, D. K. Shuh - **« High-resolution X-ray absorption spectroscopy as a probe of crystal-field and covalency effects in actinide compounds «** - Proceedings of the National Academy of Sciences (2016) 113, 29, 8093-8097.

168. R. Navarro Amador, M. Carboni, D. Meyer - **« Photosensitive Titanium and Zirconium Metal Organic Frameworks: Current research and future possibilities»** - Materials Letters (2016) 166, 327-338.

169. K. Ruffray, M. Autillo, X. Le Goff, J. Maynadié, D. Meyer - **«Influence of the solvent, structure and substituents of ruthenium(II) polypyridyl complexes on their electrochemical and photo-physical properties»** - Inorganica Chimica Acta (2016) 440, 26 – 37.

170. Nardin T., Gouze B., Cambedouzou J., Diat O. -**Soft templated mesoporous SiC from polycarbosilane grafted onto triblock copolymers**- Materials Letters 2016, 185, 424-427.
171. R. Besnard, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing -**Tuning Nanostructure of Highly Functionalized Silica Using Amphiphilic Organosilanes: curvature agent effect**- Langmuir 2016, 32, 4624-4634.

172. A. F. Sierra Salazar, T. Chave, A. Ayral, S. I. Nikitenko, V. Hulea, P. J. Kooyman, F. D. Tichelaar, S. Perathoner, P. Lacroix-Desmazes -**Engineering of silica supported platinum catalysts with hierarchical porosity combining latex synthesis, sonochemistry and sol-gel process, I. Material preparation**- Micropor. Mesopor. Mat. 2016, 234, 207-214.

173. Gossard, A.; Toquer, G.; Causse, J.; Grandjean, A. -**Monolithic zirconia foams synthesis from emulsion stabilized by colloidal clusters**- Chemical Engineering Journal 2016, 285, 528-535.

174. Gossard, A.; Grasland, F.; Le Goff, X.; Grandjean, A.; Toquer, G. -**Control of the nanocrystalline zirconia structure through a colloidal sol-gel process**- Solid State Sciences 2016, 55, 21-28.

175. Gasc, F.; Corso, B.; Causse, J.; Lacroix-Desmazes, P. -**Study of self-association of gradient copolymers in supercritical CO_2 thanks to synchrotron and in-house small-angle X-rays scattering measurements**- The Journal of Supercritical Fluids 2016, 114, 26-31.

176. Dedovets, D.; Bauduin, P.; Causse, J.; Girard, L.; Diat, O. -**Switchable self-assembly of Prussian blue analogs nano-tiles triggered by salt stimulus**- Physical Chemistry Chemical Physics 2016, 18, 3188-3196.

177. Aréna, H.; Godon, N.; Rébiscoul, D.; Podor, R.; Garcès, E.; Cabie, M.; Mestre, J. P. -**Impact of Zn, Mg, Ni and Co elements on glass alteration: Additive effects**- Journal of Nuclear Materials 2016, 470, 55-67.

178. Szenknect, S., Mesbah, A., Cordara, T., Clavier, N., Brau, H. P., Le Goff, X., Poinssot, C., Ewing, R. C., Dacheux, N.: -**First experimental determination of the solubility constant of coffinite**- Geochimica Et Cosmochimica Acta 2016, 181, 36-53.

179. Sene, S., Pizzoccaro, M. A., Vezzani, J., Reinholdt, M., Gaveau, P., Berthomieu, D., Begu, S., Gervais, C., Bonhomme, C., Renaudin, G., Mesbah, A., van der Lee, A., Smith, M. E., Laurencin, D.: -**Coordination Networks Based on Boronate and Benzoxaborolate Ligands**- Crystals 2016, 6.

180. Prakash, J., Mesbah, A., Beard, J. C., Malliakas, C. D., Ibers, J. A.: -**Syntheses, crystal structures, and resistivities of the two new ternary uranium selenides, Er_3USe_8 and Yb_3USe_8**- Journal of Solid State Chemistry 2016, 233, 90-94.

181. Prakash, J., Mesbah, A., Beard, J., Rocca, D., Lebegue, S., Malliakas, C. D., Ibers, J. A.: -**Two new ternary chalcogenides Ba_2ZnQ_3 (Q = Se, Te) with chains of ZnQ_4 tetrahedra: syntheses, crystal structure, and optical and electronic properties**- Zeitschrift Fur Naturforschung Section B-a Journal of Chemical Sciences 2016, 71, 425-429.

182. Neumeier, S., Arinicheva, Y., Clavier, N., Podor, R., Bukaemskiy, A., Modolo, G., Dacheux, N., Bosbach, D.: -**The effect of the synthesis route of monazite precursors on the microstructure of sintered pellets**- Progress in Nuclear Energy 2016, 92, 298-305.

183. Mohun, R., Desgranges, L., Lechelle, J., Simon, P., Guimbretiere, G., Canizares, A., Duval, F., Jegou, C., Magnin, M., Clavier, N., Dacheux, N., Valot, C., Vauchy, R.: -**Charged defects during alpha-irradiation of actinide oxides as revealed by Raman and luminescence spectroscopy**- Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms 2016, 374, 67-70.

184. Mesbah, A., Prakash, J., Rocca, D., Lebegue, S., Beard, J. C., Lewis, B. A., Ibers, J. A.: -**Syntheses, crystal structure, and electronic properties of the five $ABaMQ_4$ compounds $RbBaPS_4$, $CsBaPS_4$, $CsBaVS_4$, $RbBaVSe_4$, and $CsBaVSe_4$**- Journal of Solid State Chemistry 2016, 233, 217-220.

185. Mesbah, A., Prakash, J., Ibers, J. A.: -**Overview of the crystal chemistry of the actinide chalcogenides: incorporation of the alkaline-earth elements**-, Dalton Transactions 2016, 45, 16067-16080.

186. Mesbah, A., Clavier, N., Qin, D. W., Szenknect, S., Gausse, C., Dacheux, N.: -**Synthesis and characterization of $Ln_{1-2x}Ca_xTh_xPO_4 \cdot nH_2O$ rhabdophane-type precursors to monazite**- Abstracts of Papers of the American Chemical Society 2016, 252.

187. Mesbah, A., Clavier, N., Lozano-Rodriguez, M. J., Szenknect, S., Dacheux, N.: -**Incorporation of Thorium in the Zircon Structure Type through the $Th_{1-x}Er_x(SiO_4)_{1-x}(PO_4)x$ Thorite-Xenotime Solid Solution**- Inorganic Chemistry 2016, 55, 11273-11282.

188. Mesbah, A., Clavier, N., Gausse, C., Qin, D. W., Szenknect, S., Lozano-Rodriguez, J., Dacheux, N.: -**Thorium incorporation in phosphates matrices: the case of the rhabdophane and xenotime**-Abstracts of Papers of the American Chemical Society 2016, 252.

189. Lahalle, H., Cau-Dit-Coumes, C., Mesbah, A., Lambertin, D., Cannes, C., Delpech, S., Gauffinet, S.: -**Investigation of magnesium phosphate cement hydration in diluted suspension and its retardation by boric acid**- Cement and Concrete Research 2016, 87, 77-86.

190. Guo, X. F., Szenknect, S., Mesbah, A., Clavier, N., Poinssot, C., Wu, D., Xu, H. W., Dacheux, N., Ewing, R. C., Navrotsky, A.: -**Energetics of a Uranothorite ($Th_{1-x}U_xSiO_4$) Solid Solution**-, Chemistry of Materials 2016, 28, 7117-7124.

191. Gausse, C., Szenknect, S., Qin, D. W., Mesbah, A., Clavier, N., Neumeier, S., Bosbach, D., Dacheux, N.: -**Determination of the Solubility of Rhabdophanes $LnPO_4$·center dot $0.667H_2O$ (Ln = La to Dy)**- European Journal of Inorganic Chemistry 2016, 4615-4630.

192. Gabard, M., Cherkaski, Y., Clavier, N., Brissonneau, L., Steil, M. C., Fouletier, J., Mesbah, A., Dacheux, N.: -**Preparation, characterization and sintering of yttrium-doped ThO_2 for oxygen sensors applications**- Journal of Alloys and Compounds 2016, 689, 374-382.

193. Tamain C., Arab-Chapelet B., Rivenet M., Le Goff X.F., Loubert G., Grandjean S., Abraham F. - **What about americium oxalate in the $M_2(C_2O_4)_3(H_2O)_6{\cdot}nH_2O$ (M=Ln, An) series? Synthesis, crystal structure, spectroscopic characterizations and comparison** - Inorganic Chemistry 2016, 55(1), 51-61.

194. Castanié S., Carlier T., Méar F. O., Saitzek S., Blach J.-F., Podor R., Montagne L. - **Self-healing glassy thin coating for high temperature application** - Applied Materials & Interfaces 2016, 8(2), 4208-4215.

195. Fournier M., Ull A., Nicoleau E., Inagaki Y., Odorico M., Frugier P., Gin S. - **Glass dissolution rate measurement and calculation revisited** - Journal of Nuclear Materials 2016, 476, 140-154.

196. Barbetta A.; Zemb T. and P. Fratzl, -**Impregnation and Swelling of Wood with Salts: Ion Specific Kinetics and Thermodynamics Effects**- Adv. Mater. Interfaces 2016, 1600437 (DOI: 10.1002/admi.201600437).

197. Bertinetti L.; Zemb T.; Fratzl P. -**Chemical, colloidal and mechanical contributions to the state of water in the wood cell wall**- IOP New Journal of physics 2016. 18, n° 083048.

MÉTHODOLOGIES ET THÉORIES POUR LA CHIMIE SÉPARATIVE

198. Rey J., Dourdain S., Dufrêche J.-F., Berthon L., Muller J. M., Pellet-Rostaing S., Zemb Th. – **Thermodynamic Description of Synergy in Solvent Extraction: I. Enthalpy of Mixing at the Origin of Synergistic Aggregation** – Langmuir 2016, 32 (49), 13095-13105.

199. Bley M., Siboulet B., Karmakar A., Zemb Th., Dufrêche J.-F. – **A Predictive Model of Reverse Micelles Solubilizing Water for Solvent Extraction** – Journal of Colloid and Interface Science 2016, 479, 106-114.

200. Scoppola E., Watkins E. B., Campbell R. A., Konovalov O., Girard L., Dufrêche J.-F., Ferru G., Fragneto G., Diat O. – **Solvent Extraction: Structure of the Liquid-Liquid Interface Containing a Diamide Ligand** – Angewandte Chemie International Edition 2016, 55 (32), 9326-9330.

201. Moeyaert P., Dumas Th., Guillaumont D., Kvashnina K., Sorel Ch., Miguirditchian M., Moisy Ph., Dufrêche J.-F. – **Modeling and Speciation Study of Uranium(VI) and Technetium(VII) Coextraction with DEHiBA** – Inorganic Chemistry 2016, 55 (13), 6511-6519.

202. Hocine S., Hartkamp R., Siboulet B., Duvail M., Coasne B., Turq P., Dufrêche J.-F. – **How Ion Condensation Occurs at a Charged Surface: a Molecular Dynamics Investigation of the Stern Layer for Water-silica Interfaces** – Journal of Physical Chemistry C 2016, 120 (2), 963-973.

203. Bacle P., Dufrêche J.-F., Rotenberg B., Bourg I. C., Marry V. – **Modeling the Transport of Water and Ionic Tracers in a Micrometric Clay Sample** – Applied Clay Science 2016, 123, 18-28.

204. Boubekri R., Gross M., In M., Diat O., Nobili M., Mohwald H., Stocco A. -**MHz Ultrasound Induced Roughness of Fluid Interfaces**- Langmuir 2016, 32, 10177-10183.

205. Prevost S., Lopian T., Pleines M., Diat O., Zemb T. -**Small-angle scattering and morphologies of ultra-flexible microemulsions**- Journal of Applied Crystallography 2016, 49, 2063-2072.

206. Scoppola E., Watkins E. B., Campbell R. A., Konovalov O., Girard L., Dufreche J. F., Ferru G., Fragneto G., Diat O. -**Solvent Extraction: Structure of the Liquid-Liquid Interface Containing a Diamide Ligand**-Angewandte Chemie-International Edition 2016, 55, 9326-9330.

207. Zemb T. N., Klossek M., Lopian T., Marcus J., Schoettl S., Horinek D., Prevost S. F., Touraud D., Diat O., Marcelja S., Kunz W. -**How to explain microemulsions formed by solvent mixtures without conventional surfactants**- Proceedings of the National Academy of Sciences of the United States of America 2016, 113, 4260-4265.

208. O. Pecheur, S. Dourdain,D. Guillaumont, J. Rey, P. Guilbaud, L. Berthon, M.-C. Charbonnel, S. Pellet-Rostaing, F. Testard -**Synergism in HDEHP/TOPO liquid-liquid extraction system: an intrinsic ligands property?**- Journal of Physical Chemistry B 2016, 120 (10), 2814–2823.

209. O. Pecheur, D. Guillaumont, S. Dourdain, L. Berthon, R. Turgis, C. Fillaux, G. Arrachart and F. Testard -**Uranium Extraction by a Bifunctional AmidoPhosphonic Acid: Coordination Structure and Aggregation**- Solvent Extraction and Ion Exchange 2016, 34, 260 – 273.

210. P. J. Bruggeman, M. J. Kushner, B. R. Locke, J. G. E. Gardeniers, W. G. Graham, D. B. Graves, R. C. H. M. Hofman-Caris, D. Maric, J. P. Reid, E. Ceriani, D. Fernandez Rivas, J. E. Foster, S. C. Garrick, Y. Gorbanev, S. Hamaguchi, F. Iza, H. Jablonowski, E. Klimova, J. Kolb, F. Krcma, P. Lukes, Z. Machala, I. Marinov, D. Mariotti, S. Mededovic Thagard, D. Minakata, E. Neyts, J. Pawlat, Z. L. Petrovic, R. Pflieger, S. Reuter, D. C. Schram, S. Schröter, M. Shiraiwa, B. Tarabová, P. A. Tsai, J. R. R. Verlet, T. von Woedtke, K. R. Wilson, K. Yasui, G. Zvereva -**Plasma-Liquid Interactions: A Review and Roadmap**- Plasma Sources Sci. Technol. 2016, 25, 053002 (59pp).

211. Prakash, J., Tarasenko, M. S., Mesbah, A., Lebegue, S., Malliakas, C. D., Ibers, J. A.: -**Synthesis, Crystal Structure, Theoretical, and Resistivity Study of BaUSe3**- Inorganic Chemistry 2016, 55, 7734-7738.

212. Nkou Bouala, G. I., Clavier, N., Martin, S., Lechelle, J., Favrichon, J., Brau, H. P., Dacheux, N., Podor, R.: -**From in Situ HT-ESEM Observations to Simulation: How Does Polycrystallinity Affects the Sintering of CeO2 Microspheres?**- Journal of Physical Chemistry C 2016, 120, 386-395.

213. Kroeker, S., Schuller, S., Wren, J. E. C., Greer, B. J., Mesbah, A.: -**Cs-133 and Na-23 MAS NMR Spectroscopy of Molybdate Crystallization in Model Nuclear Glasses**- Journal of the American Ceramic Society 2016, 99, 1557-1564.

214. Clavier, N., Cretaz, F., Szenknect, S., Mesbah, A., Poinssot, C., Descostes, M., Dacheux, N.: -**Vibrational spectroscopy of synthetic analogues of ankoleite, chernikovite and intermediate solid solution**- Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy 2016, 156, 143-150.

215. Castanié S., Méar F., Podor R., Suhonen H., Montagne L. - **2D and 3D observation and mechanism of self-healing in glass-boron composites** - Journal of the American Ceramic Society 2016, 99(3), 849-855.

216. Mehedi H., Ravaux J., Yazda K., Michel T., Tahir S., Odorico M., Podor R., Jourdain V. - **Increased chemical reactivity of single-walled carbon nanotubes on oxide substrates: In situ imaging and effect of electron and laser irradiations** - Nano Research 2016, 9, 517-529.

217. Jacquet P., Podor R., Ravaux J., Teisseire J., Gozhyk I., Jupille J., Lazzari R. - **Grain growth : key in understanding silver solid-state dewetting** - Scripta Materialia 2016, 115, 128-132.

218. Pedraza F., Podor R. - **Influence of annealing conditions on the formation of hollow Al2O3 microspheres studied by in situ ESEM** - Materials Characterization 2016, 113, 198-206.

219. Mir A. H., Boizot B., Charpentier T., Gennisson M., Odorico M., Podor R., Jegou C., Bouffard S., Peuget S. - **Surface and bulk electron irradiation effects in simple and complex glasses** - Journal of Chemical Physics 2016, 453, 141-149.

220. Mehedi H-A., Ravaux J., Tahir S., Podor R., Jourdain V. - **In situ study of single-walled carbon nanotube growth in an environmental scanning electron microscope** - Nanotechnology 2016, 27, 505701.

221. Zemb T., Kunz W. -**Weak aggregation: State of the art, expectations and open questions**- Curr Opin Colloid In 2016, 22, 113-119.

222. Zemb T., Holmberg K., Kunz W. - **Weak Self Assembly**- Curr Opin Colloid In 2016, 22, A1-A3.

223. Kunz W., Holmberg K., Zemb T. -**Hydrotropes**.- Curr Opin Colloid In 2016, 22, 99-107.

2015

INNOVATIONS POUR L'EXTRACTION ET LE RECYCLAGE

224. J. Borrini, A. Favre-Reguillon, M. Lemaire, S. Gracia, G. Arrachart, G. Bernier, S. Pellet-Rostaing -**Water soluble PDCA derivatives for selective Ln(III)/An(III) and Am(III)/Cm(III) separation-** Solvent Extraction and Ion Exchange 2015, 33, 224-235.

225. S. Chapron, C. Marie, G. Arrachart, M. Miguirditchian, and S. Pellet-Rostaing -**New Insight into the Americium/Curium Separation by Solvent Extraction Using Diglycolamides**- Solvent Extraction and Ion Exchange 2015, 33, 236-248.

226. Rahal, R., Annani, F., Pellet-Rostaing, S., Arrachart, G. -**Surface modification of titanium oxide nanoparticles with chelating molecules: New recognition devices for controlling the selectivity towards lanthanides ionic separation**- Daniele, S. Separation and Purification Technology 2015, 147, 220 – 226.

227. Fischer V., Marcus J., Touraud D., Diat O., Kunz W. -**Toward surfactant-free and water-free microemulsions**- Journal of Colloid and Interface Science 2015, 453, 186-193.

228. Marcus J., Touraud D., Prevost S., Diat O., Zemb T., Kunz W. -**Influence of additives on the structure of surfactant-free microemulsions**- Physical Chemistry Chemical Physics 2015, 17, 32528-32538.

229. Micheau C., Schneider A., Girard L., Bauduin P. -**Evaluation of ion separation coefficients by foam flotation using a carboxylate surfactant**- Colloids and Surfaces a-Physicochemical and Engineering Aspects 2015, 470, 52-59.

230. Hong B., Leclercq L., Collinet-Fressancourt M., Lai J., Bauduin P., Aubry J.-M., Nardello-Rataj V. -**Synergy between bis(dimethyldioctylammonium) molybdate and tetraethylene glycol monooctyl ether: A winning combination for interfacial catalysis in thermo-controlled and switchable microemulsions**- Journal of Molecular Catalysis a-Chemical 2015, 397, 142-149.

231. G. Arrachart, A. Keenaan, S. Gracia, R. turgis, V. Dubois, S. Pellet-Rostaing -**Design and evaluation of superchelating resins through EDTA and DTPA modified ligands**- Solvent Extraction and Ion Exchange 2015, 50, 1882-1889.

232. D. Gomes-Rodriguez, N. Dacheux, S. Pellet-Rostaing, C. Faur, D. Bouyer, S. Monge -**The first report on phosphonate-based homopolymers combining both chelating and thermosensitive properties of gadolinium: synthesis and evaluation**- Polymer chemistry 2015, 6, 5264-5272.

233. S. Gracia, G. Arrachart, C. Marie, S. Chapron, M. Miguirditchian, S. Pellet-Rostaing -**Separation of Am (III) by solvent extraction using water-soluble H4tpaen derivatives**- Tetrahedron 2015, 71, 5321-5336.

234. M. Virot, L. Venault, P. Moisy, S. I. Nikitenko -S**onochemical redox reactions of Pu(III) and Pu(IV) in aqueous nitric solutions**- Dalton Trans. 2015, 44, 2567-2574.

235. R. Pflieger, J. Lee, S. I. Nikitenko, M. Ashokkumar -**Influence of He and Ar Flow Rates and NaCl Concentration on the Size Distribution of Bubbles Generated by Power Ultrasound**- J. Phys. Chem. B 2015, 119, 12682-12688.

236. R. Pflieger, T. Chave, M. Virot, S. I. Nikitenko -**La Sonochimie, une Chimie sans Réactifs**-Actualité Chimique N397-398 2015, 135-136.

237. X. Beaudoux, M. Virot, T. Chave, G. Leturcq, N. Clavier, N. Dacheux, S. I. Nikitenko -**Catalytic Dissolution of Ceria-Lanthanide Mixed Oxides Provides Environmentally Friendly Partitioning of Lanthanides and Platinum**- Hydrometallurgy 2015, 151, 107-115.

238. Lavaud, C.; Goettmann, F.; Grandjean, A.; Causse, J. -**Simultaneous lanthanides and surfactants micelles removal from aqueous outflows by complexation and sol-gel chemistry**- Separation and Purification Technology 2015, 145, 17-23.

239. Fustier M., Le Goff X.F., Lutz M., Slootweg J.-C., Mézailles N. - **Scandium carbene complexes: Synthesis of mixed alkyl, amido, and phosphido derivatives** - Organometallics 2015, 34(1), 63-72. Optimisation du Cycle de vie des Matériaux pour l'Energie

240. T. Nardin, J. Cambedouzou, J. Ravaux, C. Rey, D. Meyer and O. Diat - **«Elaborating ordered silicon carbide nanorods by preceramic polymer nanocasting»** - RSC Advances 2015, 3 (6), 86156.

241. T. Nardin, B. Gouze, J. Cambedouzou, P. Bauduin, MWC. Man, X. Deschanels, D. Bourgeois, D. Meyer and O. Diat - **«Elaboration of porous silicon carbide by soft templating molecular precursors with semi-fluorinated alkanes»** - Journal Of Materials Chemistry A 2015, 3 (6), 3082 – 3090.

242. G. Chatelain, D. Bourgeois, J. Ravaux, O. Averseng, C. Vidaux and D. Meyer - **«Incorporation of uranium into a biomimetic apatite: physicochemical and biological aspects»** - Journal Of Biological Inorganic Chemistry 2015, 20 (6), 497 – 507.

243. Mouri A., Diat O., El Ghzaoui A., Ly I., Dorandeu C., Maurel J. C., Devoisselle J.-M., Legrand P. -**Development of pharmaceutical clear gel based on Peceol®, lecithin, ethanol and water: Physicochemical characterization and stability study**- Journal of Colloid and Interface Science 2015, 457, 152-161.

244. R. Besnard, G. Arrachart, J. Cambedouzou and S. Pellet-Rostaing -**Structural study of hybrid silica bilayers from "bolaamphiphile" organosilane precursors: catalytic and thermal effects-** RSC Advance 2015, 5, 57521-57531.

245. M. Coulibaly, G. Arrachart, A. Mesbah and X. Deschanels -**From colloidal precursors to metal carbides nanocomposites MC (M=Ti, Zr, Hf and Si): synthesis, characterization and optical spectral selectivity studies**- Solar Energy Materials & Solar Cells 2015, 143 473 – 479.

246. Y. Lou, G. Toquer, S. Dourdain, C. Rey, C. Grygiel, D. Simeone and X. Deschanels -**Structure evolution of mesoporous silica SBA-15 and MCM-41 under swift heavy ion irradiation**- Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2015, 365-A, 336 – 341.

247. R. Besnard, G. Arrachart, J. Cambedouzou, S. Pellet-Rostaing -**Organosilica-Metallic Sandwiches Materials as Precursors for Palladium and Platinum Nanoparticle Synthesis**- RSC Advances 2015, 5, 77619-77628.

248. S. I. Nikitenko, T. Chave, C. Cau, H.-P. Brau, V. Flaud -**Photothermal Hydrogen Production Using Noble-Metal-Free Ti@TiO2 Core-Shell Nanoparticles under Visible-NIR Light Irradiation**- ACS Catal. 2015, 5, 4790-4795.

249. Rebiscoul, D.; Tormos, V.; Godon, N.; Mestre, J. P.; Cabie, M.; Amiard, G.; Foy, E.; Frugier, P.; Gin, S. -**Reactive transport processes occurring during nuclear glass alteration in presence of magnetite**- Applied Geochemistry 2015, 58, 26-37.

250. Rebiscoul, D.; Cambedouzou, J.; Briman, I. M.; Cabie, M.; Brau, H. P.; Diat, O. -**Water Dynamics in Nanoporous Alteration Layer Coming from Glass Alteration: An Experimental Approach**- Journal of Physical Chemistry C 2015, 119 (28), 15982-15993.

251. Parruzot, B.; Jollivet, P.; Rébiscoul, D.; Gin, S. -**Long-term alteration of basaltic glass: Mechanisms and rates**- Geochimica et Cosmochimica Acta 2015, 154, 28-48.

252. Ward, M. D., Oh, G. N., Mesbah, A., Lee, M., Choi, E. S., Ibers, J. A.: -**Syntheses and characterization of the cubic uranium chalcogenides $Rh_2U_6S_{15}$, $Cs_2Ti_2U_6Se_{15}$, $Cs_2Cr_2U_6Se_{15}$, and $Cs_2Ti_2U_6Te_{15}$**- Journal of Solid State Chemistry 2015, 228, 14-19.

253. Sene, S., Begu, S., Gervais, C., Renaudin, G., Mesbah, A., Smith, M. E., Mutin, P. H., van der Lee, A., Nedelec, J. M., Bonhomme, C., Laurencin, D.: -**Intercalation of Benzoxaborolate Anions in Layered Double Hydroxides: Toward Hybrid Formulations for Benzoxaborole Drugs**- Chemistry of Materials 2015, 27, 1242-1254.

254. Renaudin, G., Mesbah, A., Dilnesa, B. Z., Francois, M., Lothenbach, B.: -**Crystal chemistry of iron containing cementitious AFm layered hydrates**- Current Inorganic Chemistry 2015, 5, 184-193.

255. Prakash, J., Mesbah, A., Ward, M. D., Lebegue, S., Malliakas, C. D., Lee, M., Choi, E. S., Ibers, J. A.: -**Synthesis, Crystal Structure, Resistivity, Magnetic, and Theoretical Study of $ScUS_3$**- Inorganic Chemistry 2015, 54, 1684-1689.

256. Prakash, J., Mesbah, A., Lebegue, S., Malliakas, C. D., Ibers, J. A.: -**Synthesis, crystal structure, resistivity, and electronic structure of the U(V) quaternary polyselenide $Ba_8PdU_2Se_{12}(Se_2)_2$**- Journal of Solid State Chemistry 2015, 230, 70-74.

257. Prakash, J., Mesbah, A., Beard, J. C., Ibers, J. A.: -**Syntheses and Crystal Structures of $BaAgTbS_3$, $BaCuGdTe_3$, $BaCuTbTe_3$, $BaAgTbTe_3$, and $CsAgUTe_3$**- Zeitschrift Fur Anorganische Und Allgemeine Chemie 2015, 641, 1253-1257.

258. Prakash, J., Mesbah, A., Beard, J., Lebegue, S., Malliakas, C. D., Ibers, J. A.: -**Three New Quaternary Actinide Chalcogenides Ba_3TiUTe_7, Ba_3CrUTe_7, and $Ba_3CrThTe_7$: Syntheses, Crystal Structures, Transport Properties, and Theoretical Studies**- Inorganic Chemistry 2015, 54, 3688-3694.

259. Prakash, J., Mesbah, A., Beard, J., Lebegue, S., Malliakas, C. D., Ibers, J. A.: -**Synthesis, crystal structure, optical, and electronic study of the new ternary thorium selenide $Ba_3ThSe_3(Se_2)_2$**- Journal of Solid State Chemistry 2015, 231, 163-168.

260. Nicoleau, E., Schuller, S., Angeli, F., Charpentier, T., Jollivet, P., Le Gac, A., Fournier, M., Mesbah, A., Vasconcelos, F.: -**Phase separation and crystallization effects on the structure and durability of molybdenum borosilicate glass**- Journal of Non-Crystalline Solids 2015, 427, 120-133.

261. Nabhan, D., Kapusta, B., Billaud, P., Colas, K., Hamon, D., Dacheux, N.: -**Effects of pH, surface finish and thermal treatment on the corrosion of AlFeNi aluminum alloy. Characterization of oxide layers**-, Journal of Nuclear Materials (2015), 457, 196-204.

262. Mesbah, A., Szenknect, S., Clavier, N., Lozano-Rodriguez, J., Poinssot, C., Den Auwer, C., Ewing, R. C., Dacheux, N.: -**Coffinite, $USiO_4$, Is Abundant in Nature: So Why Is It So Difficult To Synthesize?**- Inorganic Chemistry 2015, 54, 6687-6696.

263. Mesbah, A., Stojko, W., Lebegue, S., Malliakas, C. D., Frazer, L., Ibers, J. A.: -**The U^{5+} compound $Ba_9Ag_{10}U_4S_{24}$: Synthesis, structure, and electronic properties**- Journal of Solid State Chemistry 2015, 221, 398-404.

264. Mesbah, A., Prakash, J., Lebegue, S., Stojko, W., Ibers, J. A.: -**Syntheses, crystal structures, and electronic properties of $Ba_8Si_2US_{14}$ and $Ba_8SiFeUS_{14}$**- Solid State Sciences 2015, 48, 120-124.

265. Mesbah, A., Prakash, J., Beard, J. C., Pozzi, E. A., Tarasenko, M. S., Lebegue, S., Malliakas, C. D., Van Duyne, R. P., Ibers, J. A.: -**Positional Flexibility: Syntheses and Characterization of Six Uranium Chalcogenides Related to the 2H Hexagonal Perovskite Family**- Inorganic Chemistry 2015, 54, 2851-2857.

266. Mesbah, A., Prakash, J., Beard, J. C., Lebegue, S., Malliakas, C. D., Ibers, J. A.: -**Syntheses, Crystal Structures, Optical and Theoretical Studies of the Actinide Thiophosphates $SrU(PS_4)_2$, $BaU(PS_4)_2$, and $SrTh(PS_4)_2$**- Inorganic Chemistry 2015, 54, 2970-2975.

267. Mesbah, A., Prakash, J., Beard, J. C., Lebegue, S., Malliakas, C. D., Ibers, J. A.: -**Four New Actinide Chalcogenides $Ba_2Cu_4USe_6$, $Ba_2Cu_2ThSe_5$, $Ba_2Cu_2USe_5$, and $Sr_2Cu_2US_5$: Crystal Structures and Physical Properties**- Inorganic Chemistry 2015, 54, 9138-9145.

268. Martinez, J., Clavier, N., Mesbah, A., Audubert, F., Le Goff, X. F., Vigier, N., Dacheux, N.: -**An original precipitation route toward the preparation and the sintering of highly reactive uranium cerium dioxide powders**- Journal of Nuclear Materials 2015, 462, 173-181.

269. Martinez, J., Clavier, N., Ducasse, T., Mesbah, A., Audubert, F., Corso, B., Vigier, N., Dacheux, N.: -**From uranium(IV) oxalate to sintered UO_2: Consequences of the powders' thermal history on the microstructure**- Journal of the European Ceramic Society 2015, 35, 4535-4546.

270. Guo, X. F., Szenknect, S., Mesbah, A., Labs, S., Clavier, N., Poinssot, C., Ushakov, S. V., Curtius, H., Bosbach, D., Ewing, R. C., Burns, P. C., Dacheux, N., Navrotsky, A.: -**Thermodynamics of formation of coffinite, USiO4**- Proceedings of the National Academy of Sciences of the United States of America 2015, 112, 6551-6555.

271. Falaise, C., Assen, A., Mihalcea, I., Volkringer, C., Mesbah, A., Dacheux, N., Loiseau, T.: -**Coordination polymers of uranium(IV) terephthalates**- Dalton Transactions 2015, 44, 2639-2649.

272. Curti, E., Puranen, A., Grolimund, D., Jadernas, D., Sheptyakov, D., Mesbah, A.: -**Characterization of selenium in UO2 spent nuclear fuel by micro X-ray absorption spectroscopy and its thermodynamic stability**-, Environmental Science-Processes & Impacts (2015), 17, 1760-1768.

273. Claparede, L., Tocino, F., Szenknect, S., Mesbah, A., Clavier, N., Moisy, P., Dacheux, N.: -**Dissolution of $Th_{1-x}U_xO_2$: Effects of chemical composition and microstructure**- Journal of Nuclear Materials 2015, 457, 304-316.

274. Lepoitevin M., Coulon P.E., Bechelany M., Cambedouzou J., Janot J.M., Balme S. - **Influence of nanopore surface charge and magnesium ion on polyadenosine translocation** - Nanotechnology 2015, 26(14), 144001.

275. Carlier T., Méar F. O., Saitzek S., Blach J.-F., Podor R., Montagne L. - **Matériaux vitreux auto-cicatrisants pour application à haute température, élaborés sous forme de couches minces** - Matériaux & Techniques 2015, 103, 406-411.

276. Dine S., Aïd S., Ouaras K., Malard V., Odorico M., Herlin-Boime N., Habert A., Gerbil-Margueron A., Grisolia C., Chêne J., Pieters G., Rousseau B., Vrel D. - **Synthesis of tungsten nanopowders: Comparison of milling, SHS, MASHS and milling-induced chemical processes** - Advanced Powder Technology 2015, 26(5), 1300-1305.

277. Pisani C., Gaillard J.-C., Nouvel V., Odorico M., Armengaud J., Prat O. - **High-throughput, quantitative assessment of the effects of low-dose silica nanoparticles on lung cells: grasping complex toxicity with a great depth of field** - BMC Genomics 2015, 16(315).

MÉTHODOLOGIES ET THÉORIES POUR LA CHIMIE SÉPARATIVE

278. Zemb Th., Bauer C., Bauduin P., Belloni L., Déjugnat Ch., Diat O., Dubois V., Dufrêche J.-F., Dourdain S., Duvail M., Larpent C., Testard F., Pellet-Rostaing S. – **Recycling Metals by Controlled Transfer of Ionic Species: En Route to Ienaics** – Colloid and Polymer Science 2015 293 (1), 1-22.

279. Nguyen T.-N., Duvail M., Villard A., Molina J. J., Guibaud Ph., Dufrêche J.-F. – **Multi-Scale Modelling of Uranyl Chloride Solutions** – Journal of Chemical Physics 2015, 142 (2), 024501.

280. Dufrêche J.-F., Zemb Th. – **Effect of Long-Range Interactions on Ion Equilibria in Liquid-Liquid Extraction** – Chemical Physics Letters 2015, 662, 45-49.

281. Duvail M., Villard A., Nguyen T.-N., Dufrêche J.-F. – **Thermodynamics of Associated Electrolytes in Water: Molecular Dynamics Simulations of Sulfate Solutions** – Journal of Physical Chemistry B 2015, 119 (34), 11184-11195.

282. Villard A., Siboulet B., Toquer G., Merceille A., Grandjean A., Dufrêche J.-F. – **Stronium Selectivity in Sodium Nonatitanate $Na_4Ti_9O_{20}\cdot xH_2O$** – Journal of Hazardous Materials 2015, 283, 432-438.

283. Hartkamp R., Siboulet B., Dufrêche J.-F., Coasne B. – **Ion-Specific Adsorption and Electroosmosis in Charged Amorphous Porous Silica** – Physical Chemistry Chemical Physics 2015, 17, 24683-24695.

284. Moeyaert P., Abiad L., Sorel Ch., Dufrêche J.-F., Ruas A., Moisy Ph. – **Density and Activity of Pertechnetic Acid Aqueous Solutions at T=298.15 K** – Journal of Chemical Thermodynamics 2015, 91, 94-100.

285. Moeyaert P., Abiad L., Sorel Ch., Dufrêche J.-F., Ruas A., Moisy Ph. – **Density and Activity of Perrhenic Acid Aqueous solutions at T = 298.15 K** – Journal of Chemical Thermodynamics 2015, 85, 61-67.

286. D. Bourgeois, B. Burt-Pichat, X. Le Goff, J. Garrevoet, P. Tack, G. Falkenberg, L. Van Hoorebeke, L. Vincze, MA Denecke, D. Meyer, C. Vidaud and G. Boivin - **«Micro-distribution of uranium in bone after contamination: new insight into its mechanism of accumulation into bone tissue»** - Analytical And Bioanalytical Chemistry 2015, 407 (22), 6619 – 6625.

287. TN. Suong Huynh, D. Bourgeois, C. Basset, C. Vidaud and A. Hagege - **«Assessment of CE-ICP/MS hyphenation for the study of uranyl/protein interactions: CE and CEC»** - Electrophoresis 2015, 36 (11-12), 1374 – 1382.

288. Gassin P.-M., Girard L., Martin-Gassin G., Brusselle D., Jonchere A., Diat O., Vinas C., Teixidor F., Bauduin P. -**Surface Activity and Molecular Organization of Metallacarboranes at the Air-Water Interface Revealed by Nonlinear Optics**- Langmuir 2015, 31, 2297-2303.

289. Khoshsima A., Dehghani M., Touraud D., Marcus J., Diat O., Kunz W. -**Nanostructures in clear and homogeneous mixtures of rapeseed oil and ethanol in the presence of green additives**- Colloid and Polymer Science 2015, 293, 3225-3235.

290. Li Y., Fabiano-Tixier A. S., Ruiz K., Castera A. R., Bauduin P., Diat O., Chemat F. -**Comprehension of direct extraction of hydrophilic antioxidants using vegetable oils by polar paradox theory and small angle X-ray scattering analysis**- Food Chemistry 2015, 173, 873-880.

291. Naskar B., Diat O., Nardello-Rataj V., Bauduin P. -**Nanometer-Size Polyoxometalate Anions Adsorb Strongly on Neutral Soft Surfaces**- Journal of Physical Chemistry C 2015, 119, 20985-20992.

292. Scoppola E., Watkins E., Li Destri G., Porcar L., Campbell R. A., Konovalov O., Fragneto G., Diat O. -**Structure of a liquid/liquid interface during solvent extraction combining X-ray and neutron reflectivity measurements**- Physical Chemistry Chemical Physics 2015, 17, 15093-15097.

293. J. Rey, S. Dourdain, L. Berthon, J. Jestin, S. Pellet-Rostaing, T. Zemb -**Synergy in Extraction System Chemistry: Combining Configurational Entropy, Film Bending, and Perturbation of Complexation** - Langmuir 2015, 31(25), 7006-15.

294. T. Sukhbaatar, S. Dourdain, R. Turgis, J. Rey, G. Arrachart, S. Pellet-Rostaing -**Ionic liquid as diluent in solvent extraction: first evidence of supramolecular aggregation**- Chemical Communication 2015, 51, 15960-15963.

295. T. Ouerhani, R. Pflieger, W. Ben Messaoud, S. I. Nikitenko -**Spectroscopy of Sonoluminescence and Sonochemistry in Water Saturated with N2/Ar Mixtures**- J Phys Chem B 2015, 119, 15885-15891.

296. R. Pflieger, T. Chave, G. Vite, L. Jouve, S. I. Nikitenko -**Effect of Operational Conditions on Sonoluminescence and Kinetics of H_2O_2 Formation During the Sonolysis of Water in the Presence of Ar/O2 Gas Mixture**- Ultrason. Sonochem. 26 (2015) 169-175.

297. R. Pflieger, A.A. Ndiaye, T. Chave, S. I. Nikitenko -**Influence of Ultrasonic Frequency on Swan Band Sonoluminescence and Sonochemical Activity in Aqueous tert-Butyl Alcohol Solutions**- J. Phys. Chem. B 2015, 119, 284-290.

298. Nkou Bouala, G. I., Clavier, N., Lechelle, J., Mesbah, A., Dacheux, N., Podor, R.: -**In situ HT-ESEM study of crystallites growth within CeO_2 microspheres**- Ceramics International 2015, 41, 14703-14711.

299. Pfeifer G., Ribagnac P., Le Goff X. F., Wiecko J., Mézailles N., Müller C. - **Reactivity of aromatic phosphorus heterocycles: Differences between non-functionalized and pyridyl-substituted 2,4,6-triarylphosphinines** - European Journal of Inorganic Chemistry 2015, 2, 240-249.

300. Podor R., Pailhon D., Ravaux J., Brau H.P. - **Development of an integrated thermocouple for the accurate sample temperature measurement during high temperature Environmental Scanning Electron Microscope (HT-ESEM) experiments** - Microscopy and Microanalysis 2015, 21(2), 307-312.

301. Brackx E., Pages S., Dugne O., Podor R. - **Recent analytical developments for powder characterization** - European Physical Journal Special Topics 2015, 224, 1787-1804.

302. Huguet-Garcia J., Jankowiak A., Miro S., Gosset D., Podor R., Meslin E., Serruys Y., Costantini J.-M. - **In-situ ESEM and TEM observations of the thermal annealing effects on ion-amorphized 6H-SiC and nanophased SiC fibers** - Physica Status Solidi B 2015, 1, 149-152.

303. Alvarez L., Fall F., Belhboub A., Le Parc R., Almadori Y., Arenal R., Aznar R., Dieudonne P., Hermet P., Rahmani A., Jousselme B., Campidelli S., Cambedouzou J., Saito T., Bantignies J.-L. - **1D molecular crystal of phthalocyanine confined into single-walled carbon nanotubes** – Journal of Physical Chemistry C 2015, 119(9), 5202-5210.

304. Benito Q., Le Goff X.F., Nocton G., Fargues A., Garcia A., Berhault A., Kahlal S.,. Saillard J.-Y, Martineau C., Trebosc J., Gacoin T., Boilot J.-P., Perruchas S. - **Geometry flexibility of copper iodide clusters: Variability in luminescence thermochromism** - Inorganic Chemistry 2015, 54(9), 4483-4494.

305. Huguet-Garcia J., Jankowiak A., Miro S., Podor R., Meslin E., Thome L., Serruys Y., Costantini J.-M. - **Characterization of the ion-amorphization process and thermal annealing effects on third generation SiC fibers and 6H-SiC** - EPJ Nuclear Science Technology ,2015, 1(8).

306. Kelly R.P., Bell T.D. M., Cox R.P., Daniels D.P., Deacon G.B., Jaroschik F., Junk P.C., Le Goff X.F., Lemercier G., Martinez A., Wang J., Werner D. - **Divalent tetra- and pentaphenylcyclopentadienyl europium and samarium sandwich and half-sandwich complexes: synthesis, characterization and remarkable luminescence** - Organometallics 2015, 34(23), 5624-5636.

307. Niania M., Podor R., Skinner S. J., Kilner J. A. - **In-Situ Surface Analysis of SOFC Cathode Degradation Using High Temperature Environmental Scanning Electron Microscopy** - ECS Transactions 2015, 68(1), 665-670.

308. Schottl, S.; Touraud, D.; Kunz, W.; Zemb, T.; Horinek, D., -**Consistent definitions of «the interface» in surfactant-free micellar aggregates**- Colloid Surface A 2015, 480, 222-227.

309. Boskovic, P.; Sokol, V.; Zemb, T.; Touraud, D.; Kunz, W., -**Weak Micelle-Like Aggregation in Ternary Liquid Mixtures as Revealed by Conductivity, Surface Tension, and Light Scattering**- J Phys Chem B 2015, 119 (30), 9933-9939.

310. Zemb, T.; Kralchevsky, P. A., -**Depletion forces in single phase and multi-phase complex fluids**- Curr Opin Colloid In 2015, 20 (1), 1-2.

311. Jehannin M., Charton S., Karpitschka S., Zemb T., Moehwald H. and Riegler H. ; **Periodic Precipitation Patterns during Coalescence of Reacting Sessile Droplets** ; Langmuir 2015 vol 31 pp : 11484-11490.

312. Chiappisi, L.; Yalcinkaya, H.; Gopalakrishnan, V. K.; Gradzielski, M.; Zemb, T., -**Catanionic surfactant systems-thermodynamic and structural conditions revisited**- Colloid Polym Sci 2015, 293 (11), 3131-3143

313. Arnould, A.; Perez, A. A.; Gaillard, C.; Douliez, J. P.; Cousin, F.; Santiago, L. G.; Zemb, T.; Anton, M.; Fameau, A. L., -**Self-assembly of myristic acid in the presence of choline hydroxide: Effect of molar ratio and temperature**- J Colloid Interf Sci 2015, 445, 285-293.

LIST OF PATENTS

Brevets 2018

- Podor R., Szenknect S., Brau H.-P., Ravaux J., Salacroup J., Gonnet G., Cabane J., Candelas A., « Housing for a sample for use in electron microscopy », fin 2018
- Pellet-Rostaing S., Arrachart G., Turgis R., Marry F., Draye M., Lejeune M., Legeai S., Michel S., Thomas C., « Liquides ioniques pour le recyclage de l'or et du palladium par procédé d'extraction/électrodéposition », fin 2018
- Meyer, D., Carboni, M., Bourgeois, D., Sini K., « Procédé d'extraction de composés organiques fluorés à partir d'un milieu aqueux les contenant », FR 1850511, dépôt le 23/01/2018

Brevets 2017

- Leydier A., Arrachart G., Pellet-Rostaing, S., Turgis R., Chapron S., « Utilisation de composés bifonctionnels, à fonctions acide phosphonique/phosphonate et amine, pour extraire l'uranium (VI) de solutions aqueuses d'acide nitrique », FR 1759993, dépôt 23/10/2017
- Mansas C., Causse J., Deschanels X., Grandjean A., « Nanoparticules à structure cœur en analogue de bleu de Prusse-coquille, leur procédé de préparation, matériaux les comprenant, et procédé d'extraction de cations métalliques », FR 17 50568, dépôt le 24/01/2017
- Meyer, D., Bourgeois, D., « Procédé amélioré de récupération du palladium des autres éléments métalliques présents dans une phase aqueuse nitrique utilisant comme extractants des malonamides », FR 17 58240, dépôt le 07/09/2017
- Meyer, D., Bourgeois, D., Braibant, B., « Procédé de séparation du palladium des autres éléments métalliques présents dans une phase aqueuse nitrique utilisant comme extractants des malonamides particuliers », FR 17 58241, dépôt le 07/09/2017
- Dacheux N., Pellet-Rostaing S., Gomes Rodrigues D., Monge-Darcos S., Faur C., Bouyer D., « Method for separating uranium and/or thorium », 17185115.7 – 1362, dépôt le 07.08.2017
- Theisen J., Christophe P, Zemb T., Gabriel J-C, Mizaikoff B., Wilk A., Kokoric V., "Apparatus for the measurement of chemical activity coefficients of gas phase species in thermodynamic equilibrium with liquid phase", EP17 198247.3 dépôt le 25/10/2017

Brevets 2016

- Bourgeois D., Meyer D., Bihel F., Contino-Pepin C., Schmitt M., Wagner P., Desgranges S., « Utilisation de surfactants pour la dés-extraction de palladium contenu dans des phases organiques », EP 16180529
- Pellet-Rostaing S., Arrachart G., Turgis R., Tourré M., Duhamet J., « Extraction sélective des terres rares de solutions aqueuses acides par un monoamide », FR 16/61294, dépôt 21/11/16
- Szenknect, S., Ziouane, Y., Maihatchi-Ahamed, A., Dacheux, N., Descostes, M., Mesbah, A., « Procédé d'immobilisation de l'uranium dans les eaux naturelles par précipitation d'un phosphate d'uranyle », FR 16/58525, dépôt 13/09/2016
- Rey, J., Pellet-Rostaing, S., Dourdain, S., Atak, S., Arrachart, G., « Nouvel extractant, utile pour extraire des terres rares d'une solution aqueuse d'acide phosphorique, et ses applications », FR 16/58626, dépôt 15/09/2016

Brevets 2015

- Bauduin, P., Diat, O., Dedovets, D., « Procédé de séparation sélectif d'un cation métallique à partir d'un milieu liquide aqueux », FR 15/56604, dépôt 10/07/2015
- Sommer Marquez, A., Causse, J., Grandjean, A., Deschanels, X., « Matériaux monolithiques inorganiques alvéolaires échangeurs cationiques, procédé de préparation et procédé de séparation les mettant en œuvre » FR 15/55535, dépôt 17/06/2015

- Arrachart, G., Leydier, A., Dubois, V., Turgis, R., Pellet-Rostaing, S., « Composés à fonctions oxyde de phosphine et amine, utiles comme ligands de l'uranium(VI), et leurs utilisations, notamment pour extraire l'uranium(VI) de solutions aqueuses d'acide sulfurique », FR 15/52886, dépôt 03/04/2015
- Arrachart, G., Turgis, R., Bernier, G., Leydier, A., Pellet-Rostaing, S., Miguirditchian, M., Burdet, F., « Nouveaux composés bifonctionnels, utiles comme ligands de l'uranium (VI), et leurs utilisations, notamment pour extraire l'uranium (VI) de solutions aqueuses d'acide phosphorique », FR 15/52888, dépôt 03/04/2015
- Dubois, V., Mary, F., Arrachart, G., Leydier, A., Pellet-Rostaing, S., « Utilisation de nouveaux composés pour l'extraction sélective de terres rares de solutions aqueuses comprenant de l'acide phosphorique et procédé d'extraction associé », FR 15/54119, dépôt 07/05/2015
- Szenknect, S., Brau, H.-P., Salacroup, J., Podor, R., Ravaux, J., « Cellule de suivi de réaction solide/liquide ou solide/gaz pour microscope électronique à balayage », FR 15/59465, dépôt 05/10/2015, abandon 09/2016
- Meyer, D., Joulie, M., Billy, E., Laucournet, R., « Procédé de dissolution d'un oxyde métallique en présence d'un métal réducteur », FR 15/52546, dépôt 26/03/2015
- Turgis, R., Arrachart, R., Pellet-Rostaing, S., Draye, M., Legeai, S., Virieux, D., Thomas, C., « Procédés d'extraction et de récupération du tantale présent dans une phase aqueuse acide au moyen d'un liquide ionique, et utilisation d'un tel liquide ionique pour extraire le tantale d'une phase aqueuse acide », FR 15/57636, dépôt 10/08/2015

LISTE DES MEMBRES DU CONSEIL SCIENTIFIQUE DE L'ICSM 2018

NOM PRÉNOM	NOMMÉ EN	ADRESSE	TEL	FAX	MAIL
Haut-commissaire a l'Energie Atomique		F-91191 GIF SUR YVETTE			
BOULLIS Bernard Directeur de Programme	2007	DEN/DISN/Direction du Cycle et des Déchets Bât 121 - PC n° 8 - CEA Saclay F-91191 GIF SUR YVETTE	01 69 08 64 55	01 69 08 32 32	*bernard.boullis@cea.fr*
CASTAING Jean-Christophe Project Coordinator - Solvay	2016	Solvay Recherche et Innovation, Centre de Paris 52, rue de la Haie Coq F-93320 AUBERVILLIERS Cedex	01 49 37 60 23 06 79 67 50 86		*jean-christophe.castaing@solvay.com*
CHAUDRET Bruno Directeur de Recherches CNRS	2012	Laboratoire de Physique et Chimie des Nano-Objets – UMR 5215 Institut National des Sciences Appliquées 135 avenue de Rangueil F-31077 TOULOUSE CEDEX 4	05 61 33 31 81	05 61 55 30 03	*bruno.chaudret@insa-toulouse.fr*
CRAVOTTO Giancarlo Professeur à l'Université de Turin	2018	Università degli Studi di Torino Dipartimento di Scienza e Tecnologia del Farmaco Via Verdi, 8 - 10124 TORINO	+39 (0)116707183	+39(0)112367684	*giancarlo.cravotto@unito.it*
DAILLANT Jean Directeur général de SOLEIL	2012	Synchroton SOLEIL – L'Orme des Merisiers Saint Aubin – BP 48 F-91192 GIF SUR YVETTE Cedex	01 69 35 90 11	01 69 35 94 59	*jean.daillant@synchroton-soleil.fr*
DAVIAUD François Directeur du Service de Physique de l'Etat Condensé	2016	Service de Physique de l'Etat Condensé Bâtiment 772, point courrier 135 CEA Saclay F-91191 GIF SUR YVETTE CEDEX	01 69 08 72 40	0 1 69 08 87 86	*francois.daviaud@cea.fr*
DENECKE Melissa Scientific Director Dalton Nuclear Institute	2012	Dalton Nuclear Institute | The University of Manchester | Pariser Building | Floor G | Sackville Street | Manchester |M13 9PL GB-MANCHESTER	+44 (0)1613064302	+44 (0)1612754506	*melissa.denecke@manchester.ac.uk*
DONARD Olivier Directeur de Recherche CNRS Représentant section 13 Directeur de l'Equipex MARSS	2016	Center of Mass Spectrometry for Reactivity and Speciation Sciences IPREM CNRS UMR 5254 Université de Pau et des Pays de l'Adour Hélioparc - F-64053 PAU	05 59 40 77 51 06 78 78 92 80		*olivier.donard@univ-pau.fr*
DUMY Pascal Président du Comité de pilotage du pôle Balard	2014	ENSCM 240 avenue du Professeur Emile Jeanbrau 34296 MONTPELLIER cédex 5	04 67 14 72 70	04 67 14 72 71	*direction.enscm@enscm.fr*
PRADIER Claire-Marie Directrice Adjointe Scientifique INC	2016	CNRS – Institut de Chimie 3 rue Michel-Ange F-75794 PARIS CEDEX 16	01 44 96 40 97		*claire-marie.pradier@cnrs-dir.fr*
SCHMITT Véronique Directeur de Recherche Représentant section 11	2012	UPR8641 - Centre de Recherche Paul Pascal 115 Avenue du Dr Schweitzer F-33600 PESSAC	05 56 84 56 67	05.56.84.56.00	*schmitt@crpp-bordeaux.cnrs.fr*
SENENTZ Gérald Directeur R&D	2014	AREVA Tour AREVA – BAL 2619 C-1 - 1 place Jean Millier 92084 PARIS La Défense Cedex	01 34 96 07 95 06 84 77 75 36		*gerald.senentz@areva.com*

MEMBRES D'HONNEUR

NOM PRÉNOM	NOMMÉ EN	ADRESSE	TEL	FAX	MAIL
CABUIL Valérie Professeur Rectrice de l'Académie d'Amiens	2016	Rectorat de l'Académie d'Amiens 20 Bd d'Alsace-Lorraine 80063 Amiens Cedex 9	03 22 82 69 52		*valerie.cabuil@ac-amiens.fr*
CHAMBAUD Gilberte Professeur émérite	2012	Université Paris-Est Marne-la-Vallée Laboratoire de Modélisation et Simulation Multi Echelle Boulevard Descartes – Cité Descartes F-77454-CHAMPS SUR MARNE MARNE LA VALLEE	01 60 95 73 03	01 60 95 73 20	*gilberte.chambaud@univ-mlv.fr*
LEROY Maurice Professeur Vice-président de la CNE	2011	Commission Nationale d'Evaluation (CNE) 244 boulevard Saint-Germain 75007 PARIS	06 84 52 64 03	01 44 49 80 93	*mjf.leroy@gmail.com*
MARTIN-DEIDIER Loick Conseiller Scientifique	2011	CEA Direction de l'Energie Nucléaire CEA/SACLAY F-91191 GIF SUR YVETTE CEDEX	01 69 08 64 53 (secrétariat) 06 80 57 16 08	01 69 08 61 95	*loick.martin-deidier@cea.fr*

De haut en bas et de gauche à droite :

Bonnet C.
Denecke M.
Schmitt V.
Pradier C-M.
Senentz G.
Castaing J-C.
Daviaud F.
Cravotto G.
Martin-Deidier L.
Boullis B.
Daillant J.
Donard O.

PLAN D'ACCÈS ICSM

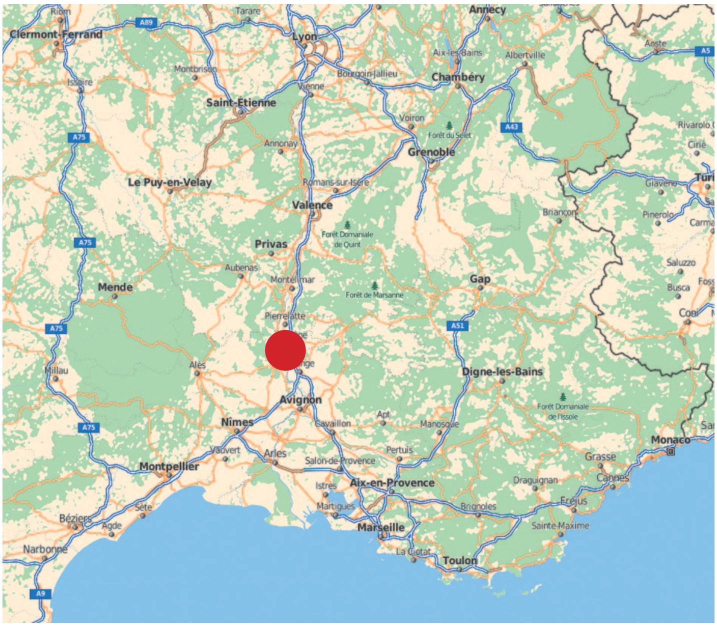
Institut de Chimie Séparative de Marcoule (ICSM)
UMR 5257, BP 17171, 30207 Bagnols-sur-Cèze cedex
Tél. +33 (0)4 66 79 66 28 - Fax +33 (0)4 66 79 76 11
www.icsm.fr

- **Depuis Montpellier,** rejoindre l'A9 en direction de Nîmes/Lyon. Prendre la sortie 22 et continuer sur la N580 direction Bagnols-sur-Cèze. Après la traversée de L'Ardoise, prendre la direction de Marcoule sur la D138a.

- **Depuis Marseille,** rejoindre l'A7, direction Lyon, sortie 21, Orange-centre. Continuer direction Caderousse (D17) puis direction Marcoule (D131a).

- **Depuis Lyon,** rejoindre l'A7 direction Marseille et sortie 21 Orange-centre. Continuer direction Caderousse (D17) puis direction Marcoule (D131a).

- **Depuis la gare TGV Avignon,** rejoindre la N100 en direction de Remoulins/Nîmes, puis prendre à droitela N580 en direction de Bagnols-sur-Cèze jusqu'à la traversée de L'Ardoise et prendre la direction de Marcoule sur la D138a.



Bollène

Sortie 19
Alès / Bollène
Pont-St-Esprit
Pierrelatte
C.N. Tricastin
Vaison-La-Romaine

Bagnols-sur-Cèze

Sortie 21
Orange-centre
Caderousse
Valréas/Nyons

Orange

Sortie 22
Roquemaure
Bagnols-sur-Cèze
Villeneuve-les-A.
Avignon/Marcoule
Z.I. L'Ardoise

Roquemaure

Entrée CEA-Marcoule

Parking Visiatome

INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCOULE

ICSM - Centre de Marcoule
BP 17171 - 30207 BAGNOLS-SUR-CEZE DECEX
Tél. +33 (0)4 66 79 66 28
Fax +33 (0)4 66 79 76 11
www.icsm.fr

POLE
chimie
Balard