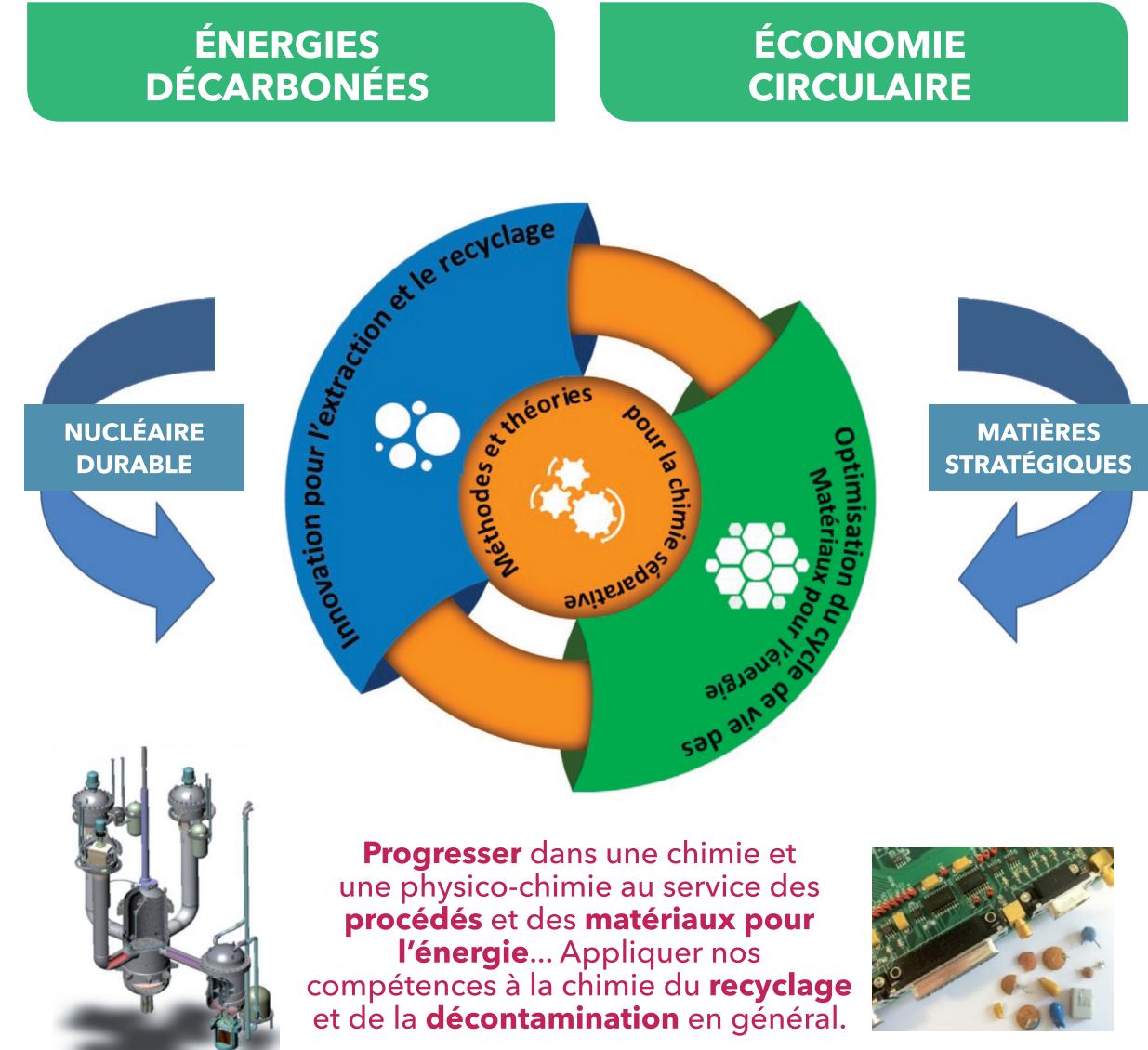




**INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCouLE**

CHIMIE ET PHYSICO-CHIMIE DU RECYCLAGE



Progresser dans une chimie et une physico-chimie au service des **procédés** et des **matériaux pour l'énergie**... Appliquer nos compétences à la chimie du **recyclage** et de la **décontamination** en général.

Pour une recherche intégrée aux ambitions du CEA, du Pôle Chimie université de Montpellier



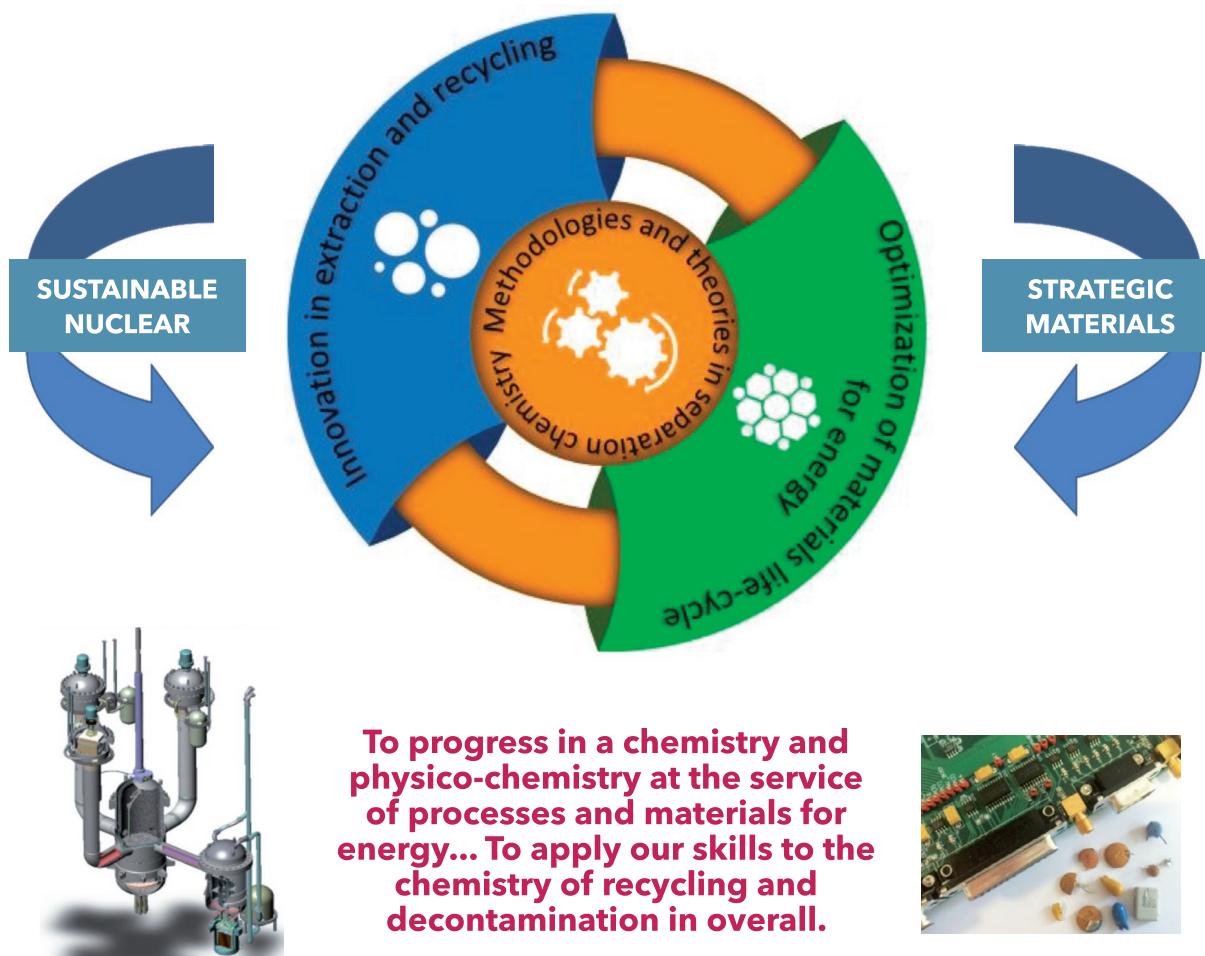
CHEMISTRY AND PHYSICAL CHEMISTRY OF RECYCLING



INSTITUT DE
CHIMIE
SÉPARATIVE DE
MARCOULE

DECARBONATED
ENERGY

CIRCULAR
ECONOMY



To progress in a chemistry and physico-chemistry at the service of processes and materials for energy... To apply our skills to the chemistry of recycling and decontamination in overall.

For an integrated research to the CEA, the Montpellier University Chemistry cluster ambitions.

RAPPORT SCIENTIFIQUE 2019 - 2022 SCIENTIFIC REPORT



Personnel de l'ICSM
ICSM staff



PRÉFACE

II

L'unité mixte de recherche «Institut de chimie de séparation de Marcoule» a été créée conjointement par le CEA, le CNRS, l'Université de Montpellier et l'Ecole Nationale Supérieure de Chimie de Montpellier en mars 2007. Le bâtiment a été inauguré en juin 2009 avec en janvier 2010, l'autorisation de démarrer des expériences incluant quelques grammes d'uranium appauvri et de thorium naturel. Depuis, au rythme des appels à projets nationaux et internationaux, l'ICSM vise à développer une recherche fondamentale avec comme objectif principal de «proposer des choix» pour le développement de procédés de chimie de séparation dans les domaines des énergies décarbonées. L'intégration des enjeux d'une énergie nucléaire durable et les défis d'une économie circulaire dans son ensemble sont de réelles opportunités d'innovation et permettent d'afficher l'ICSM avec une reconnaissance unique en France et une visibilité internationale.

Les huit équipes de recherche travaillent donc toujours dans le sens des questions scientifiques ouvertes telles que définies et publiées par l'académie française (missions scientifiques contractuelles). La chimie de séparation, une branche de la chimie physique, est un domaine clé de la «chimie verte», et est fortement liée aux nanosciences, aux colloïdes et aux interfaces puisque toutes les séparations proviennent d'un transfert de phase: liquide-liquide, liquide-solide ou même liquide-air. La chimie de séparation est à la base des technologies du recyclage, tandis que le recyclage est à la base de l'économie circulaire et que l'économie circulaire est la seule stratégie durable dans un monde aux ressources limitées. Tous les scientifiques, ingénieurs, techniciens et étudiants ont pour objectif commun d'acquérir les connaissances nécessaires à l'amélioration des méthodes dans ce domaine.

Stéphane Pellet-Rostaing

Olivier Diat

UK

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 structure was officially opened in June 2009, and studies with a few grams of naturally occurring thorium and depleted uranium were allowed to begin in January 2010. Since ICSM seeks to develop fundamental research with the rhythm of national and international calls, with as main goal to «propose new options» for the development of separation chemical processes in the decarbonated energies domains. The integration of a sustainable nuclear energy issues and the challenges of a circular economy in its overall are real opportunities for innovation and with unique recognition in France and international visibility.

The eight 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 interfaces since all separations are sourced in phase transfer: liquid-liquid, liquid-solid or even liquid-air. Separation chemistry is the basis of recycling technologies, 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

Olivier Diat

FOREWORD

In December 2022, the ICSM will have a staff of about one hundred, including 44 permanent staff (21 CEA, 14 CNRS, 9 UM / ENSCM) and 43 non-permanent staff, with 24 PhD students (24), 10 post-doctoral/ATER/CDD students (10), apprentices (7) and administrative staff (2) (27 CEA, 9 CNRS and 7 UM/ENSCM). In addition, more than 25 undergraduate and graduate students join the eight teams for a few months each year, including about ten students in the master's degree programme in chemistry in Montpellier entitled "Separation Chemistry, materials and processes".

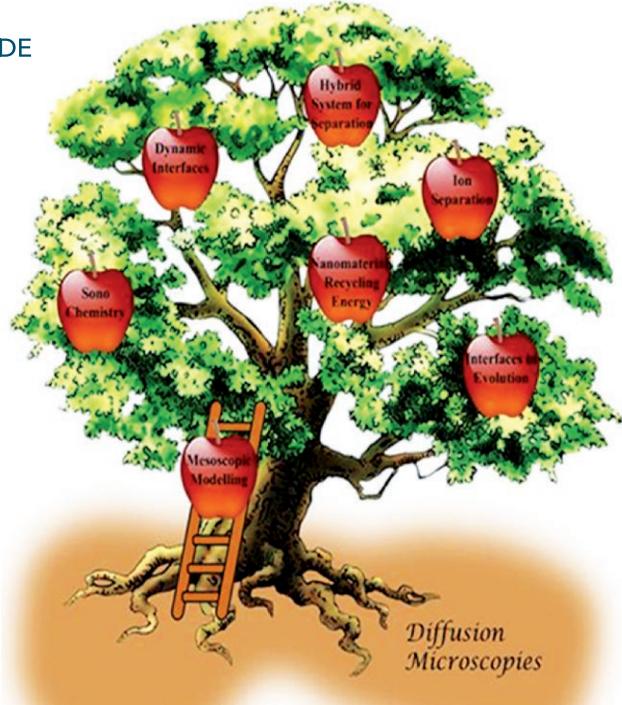
Since the first edition in 2006 in Montpellier, practical schools in separation chemistry and instrumentation are (co)organised by ICSM, often during the summer period. Since 2012, we can mention the practical summer school organised jointly with associated teams within the «CheMISyst» laboratory of excellence and on a common theme of chemistry using the so-called long-range interactions beyond the nearest neighbour bond. There are also several thematic schools on «X-ray and neutron reflectivity», on «Surfaces and nuclear» and on "small angle radiation scattering".

This report issued every 2 years gives here an overview of the ongoing projects (ANR and European projects) and the work published over 4 sliding years and this since January 2019. Our studies are partly grouped under three axes, which constitute the pillars of our research and training activity and are defined by **Innovation in extraction and recycling**, **Optimization of materials life-cycle for energy**, **Methodologies and theory of separation chemistry**.

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



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II

La production d'énergie à partir de combustibles fossiles dont l'impact négatif sur le climat et l'environnement est aujourd'hui inacceptable. Elle est accompagnée de nouvelles exigences en matière de sécurité des installations et de gestion de leurs déchets, mais également de la nécessité d'un recyclage, considéré jusqu'à présent comme exceptionnel, mais qui doit devenir la règle universelle et économiquement acceptable. Elle confronte les scientifiques à une demande sociétale forte pour des solutions maîtrisées en matière de technologies pour les énergies décarbonées, inscrite dans les lois françaises sur la transition énergétique du 13 juillet 2005 et 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 œuvre dans des dispositifs optimisés.

Au-delà du domaine nucléaire et dans un monde fini en ressources naturelles, fermer les cycles relève d'une démarche de tri sélectif maîtrisé, qu'il s'agisse de séparation ionique, moléculaire ou colloïdale. Recycler les matières dites « stratégiques » comme les terres rares, les platinoïdes et autres métaux précieux 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 créée en 2007 est aujourd'hui constituée de huit équipes travaillant en synergie :

- Systèmes hybrides pour la séparation (Damien BOURGEOIS)
- 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 (Xavier Le GOFF)
- Modélisation et chimie théorique (Jean-François DUFRÈCHE).

En réponse à une demande sociétale sans cesse en évolution face aux défis énergétiques et environnementaux actuels et futurs, les recherches menées à l'ICSM participent à déconstruire

l'image polluante et dangereuse de la chimie dans le domaine de l'extraction et de la purification de matières valorisables. L'ICSM se doit d'anticiper et de proposer des solutions aux verrous scientifiques permettant une diminution drastique des pollutions et de l'empreinte environnementale des procédés de la chimie séparative. La diminution du coût énergétique des procédés mis en œuvre, une meilleure gestion de l'eau, la limitation de la quantité et du volume de déchets, l'utilisation de matières premières renouvelables y sont des challenges majeurs. L'ICSM travaille à la découverte de méthodes de synthèses originales et plus efficaces, à la mise en œuvre de méthodes d'activations comme les techniques ultrasonores et micro-ondes, à l'optimisation et à l'intensification de procédés, au développement de théories et de méthodes d'analyse toujours plus performantes, à des techniques de traitement des matières et effluents de plus en plus efficientes. Cet effort doit s'intensifier et se rationaliser, en particulier vers le développement des interfaces, source d'innovation majeure résultant du croisement de compétences. Au cours de la dernière période de quatre ans, l'intégration des objectifs, l'utilisation des compétences développées dans les méthodes de caractérisation de l'environnement ainsi que dans la théorie de la méso-échelle ont été de plus en plus considérées. De plus, la distinction faite depuis la création de l'ICSM entre « comprendre », c'est-à-dire démontrer la puissance prédictive de modèles basés sur des principes premiers et « optimiser », c'est-à-dire démontrer la faisabilité de nouveaux systèmes chimiques dans l'extraction sélective, incluant ainsi les principes « de chimie et d'ingénierie verte » s'est avérée être pertinente.

En conséquence, trois axes de réflexion et de coopération en équipes ont naturellement émergé dont le premier centré sur « *l'innovation dans l'extraction et le recyclage* ».

Comme indiqué ci-dessus, optimiser nécessite de mieux comprendre et prévoir en associant développement expérimental et théorie. L'innovation à l'ICSM, illustrée par le nombre exceptionnel de brevets déposés (plus d'une vingtaine entre 2019 et 2022), ne pourrait pas se développer à un niveau de pointe de classe mondiale (comme le montrent les citations dans la littérature internationale) sans les corrélations fortes entre observation et théorie. En pratique, l'émergence a été possible grâce aux outils utilisés dans la physique statistique des interfaces, par exemple via les ondelettes aléatoires gaussiennes. L'énergie de transfert systématiquement libre a été prise en compte dans cette approche émergente spécifique sous le terme de la « ienaics » avec une certaine similitude avec la neutronique, l'électrochimie et la nanoscience.

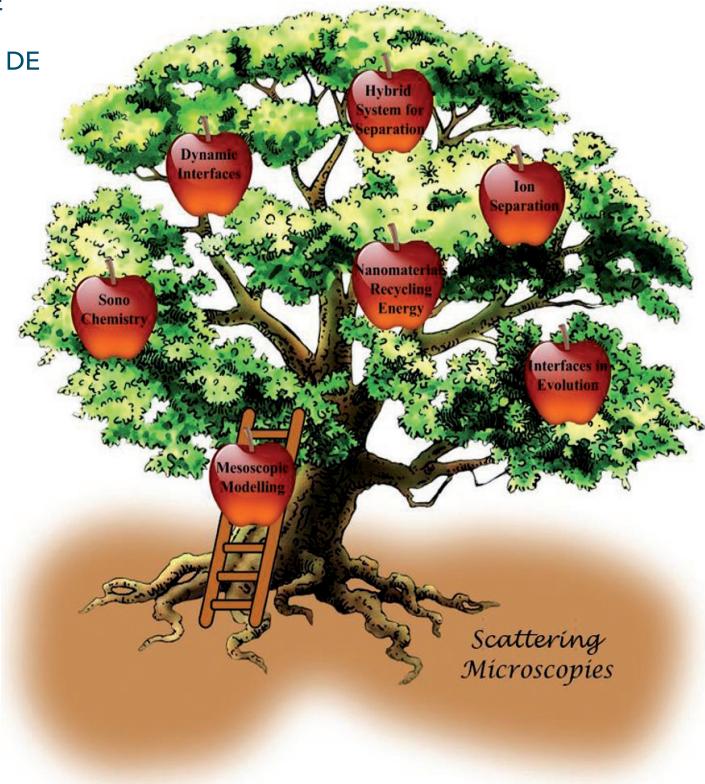
Ainsi, le second axe rassemblant des compétences autour de « *Méthodologies et théorie de la chimie de séparation* » ne cesse de s'étoffer grâce à un grand nombre de protocoles expérimentaux, tels que la mesure et le calcul des molécules d'extraction « perdues » non actives dans la séparation, ou de nouvelles méthodes de séparation sans agent d'extraction/tensioactif classique. Non moins importantes sont les avancées récentes dans les domaines de la microscopie électronique de surface couplée à des analyse d'image et des cellules spécifiques (humidité relative contrôlée ou température élevée) avec des permettant la caractérisation précise de propriétés physico-chimiques telles que l'auto-guérison, le frittage, la dissolution, la réactivité chimique par des expériences in situ.

Aucun processus de séparation ne peut être réalisé sans la connaissance de la « durabilité des matériaux », c'est-à-dire des matériaux qui doivent résister à des contraintes extrêmes et à une longue utilisation, non seulement dans le cycle de vie du combustible nucléaire, mais aussi dans celui de tous les matériaux nécessaires aux technologies des énergies alternatives. Le cycle de vie de toutes les technologies mises en œuvre doit être étudié et maîtrisé comme proposé dans l'axe « *Optimisation du cycle de vie des matériaux pour l'énergie* ». Les interfaces solides/solides, solides/liquides et solides/gaz sont ici considérées puisque les propriétés physiques et chimiques de ces matériaux (durabilité, robustesse, capacité de confinement et de rétention...) dépendent de leur synthèse, c'est-à-dire de la nature des précurseurs (colloïde, solution, émulsion...) au matériau final (fritté, poreux, poudre, film mince).

Un certain nombre de projet de recherche étudiés au cours de ces quatre dernières années ont donc été regroupées par axe afin de faciliter l'ordre de leur lecture.

Séparative

L'Institut de Chimie séparative de Marcoule, créé en 2007, est actuellement dirigé par Stéphane Pellet-Rostaing et ce 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 de l'université de Montpellier** 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 2022 une cinquantaine de permanents dont environ 40 chercheurs, ingénieurs et techniciens, environ 10 administratifs, technicien et ingénieurs d'exploitation et autant de non-permanents thésards et post-doctorants. Les propositions de stages au niveau master, post-doc et thèses sont accessibles sur le site www.icsm.fr.



It is currently undesirable to produce energy using fossil fuels because of their detrimental effects on the ecology and climate. It comes with additional criteria for the security of the facilities and the management of their wastes, as well as the necessity for recycling, which was previously thought to be an exception but now must be the standard and an economically viable practice. It presents scientists with a significant social demand for managed solutions in carbon-free energy technology, as reflected in French laws on energy transition from July 13, 2005, and August 18, 2015. Future «sustainable nuclear power,» which completes the fuel cycle, will rely on ostensibly «breakthrough» developments in separation chemistry, involving complex fluids in optimized devices.

Beyond the nuclear sector and in a world with limited natural resources, closure cycles are a part of a regulated extraction/separation/purification process with its two linked side-processes, dissolution and reformation of materials. As long as primary and secondary resources are involved, ionic, molecular, or colloidal dissolution and separation have to be understood and modeled predictively in order to allow growth of the recycling industry, as the core of the circular economy. One of the initial challenges in this separation chemistry, which belongs to the nanosciences, is recycling so-called «strategic» materials like rare earths, PGMs, or some metalloids like germanium or antimony.

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** (Damien BOURGEOIS)
- **Ions at active interfaces** (Olivier DIAT)
- **on 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** (Xavier Le GOFF)
- **Modeling and theoretical chemistry** (Pr. Jean-François DUFRÈCHE).

The research done at ICSM contributes to dismantling the polluting and dangerous picture of chemistry in the field of extraction and purification of recoverable materials in response to an

ever-changing societal demand in a clean energy as well as environmental issues. ICSM must anticipate and propose solutions to the scientific challenges that will allow a drastic reduction in pollution and the environmental footprint of separation chemistry processes. Reducing the energy cost of the processes used, a better water management, limiting the quantity and volume of waste and using renewable raw materials are major challenges for the institute. ICSM is working on the discovery of original and more efficient synthesis methods, the implementation of activation methods such as ultrasonic and microwave techniques, the optimisation and intensification of processes, the development of ever more efficient analysis theories and methods, and increasingly efficient techniques for treating materials and effluents. This effort must be intensified and rationalised, in particular towards the development of interfaces with other expertises, a major source of innovation resulting from the crossing of skills. During the last four-year period, the integration of objectives, the use of skills developed in environmental characterisation methods and in mesoscale theory have been increasingly considered. Furthermore, the distinction made since the creation of the ICSM between «understanding», i.e. demonstrating the predictive power of models based on first principles, and «optimising», i.e. demonstrating the feasibility of new chemical systems in selective extraction, thus including the principles of «green chemistry and engineering», has proven to be relevant.

As a consequence, a first cluster of competence and cooperation centered on "[Innovation in Extraction and Recycling](#)" naturally emerged. As stated above, one first needs to understand and predict. This means that without closer connections between observation and theory, the large number of innovations that are also demonstrated by the exceptional number of patents (more than 20 between 2019 and 2022) could not develop at a cutting-edge world-class level (as shown by citations in international literature). In practice, this 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 developing a specific "ienails" approach with some similarity with neutronics, electrochemistry and nanoscience. Due to a large number of experimental protocols, such as the measurement and calculation of «lost» extraction molecules that are not active in the separation or new separation techniques without a conventional extraction agent/surfactant, the second axis gathering competences around «[Methodologies and theory of separation chemistry](#)» continues to expand. Recent developments in the fields of surface electron microscopy coupled to image analysis and the development of specific experimental cells (with a controlled relative humidity or achieving elevated temperature) have made it possible to precisely characterize physico-chemical properties such as self-healing, sintering, dissolution, and chemical reactivity through *in situ* experiments.

Without understanding of «durability of materials,» or materials that should endure tremendous constraints and long usage, no separation process can be constructed. This applies to all materials required in alternative energy technologies as well as those used in the life cycle of nuclear fuel. Every technology that has been put into use needs to have its life cycle studied and mastered, as suggested in the cluster «[Optimization of materials life-cycle for energy](#)». Since the physical and chemical characteristics of these materials (durability, robustness, ability to confine and filter, etc.) depend on their synthesis, i.e., from the nature of the precursors (colloid, solution, emulsion, etc.) to the final material, solid/solid, solid/liquid and solid/gas interfaces (sintered, porous, powder, thin film) are taken into consideration in this cluster activities.

A number of the research projects investigated over the past four years have therefore been gathered by axis in order to make easier their reading.

The Institute for Separation Chemistry of Marcoule has been created in 2007 and is nowadays managed by Stéphane Pellet-Rostaing since 2013. Located 110 km NE of Montpellier and 25 km north of Avignon, ICSM is a component of the "Pôle de Chimie" of Montpellier University and one of the partners of the Excellence laboratory "Chemisyst" 2012-2022, devoted to the Long Range chemical interactions (LRI) in "molecular and interfacial systems chemistry". Having effectively started its research activities in January 2010, the Institute was sized to hold in 2022 about fifty permanent staff including about 40 researchers, engineers and technicians, about 10 administrative, technical, operational and safety engineers and as many non-permanent PhDs and post-docs.

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



ICSM - PERMANENTS 2019 - 2022

Equipe DIR

Directeur PELLET-ROSTAING Stéphane
 Directeur Adjoint DIAT Olivier 01/19
 Adj. Directeur ASOU-POTHET Marielle 11/22 ->
 Adj. Directeur ALPE-CONCHY Dominique -> 09/22
 Assistante HAON Véronique 12/20 ->
 Gestionnaire VIDAL Alice
 Gestionnaire MENASRIA Aurélie

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 ISI
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 Exploitation
 Exploitation
 DIAS Mathilde
 MARCHAL Nicolas
 VARON Renaud -> 12/21
 PESCE Claude 01/20 ->
 LAROZAS Daniel 03/21 ->

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Chef d'équipe BOURGEOIS Damien 01/22 ->
 CR MEYER Daniel 01/22 ->
 Chercheur CARBONI Michaël
 MDC MAYNADIE Jérôme

Equipe 2 - L2IA

Chef d'équipe DIAT Olivier
 Chercheur BAUDUIN Pierre
 MDC GIRARD Luc
 IE JONCHERE Alban
 IE PASQUIER Coralie 01/21 ->

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 IE GIUSTI Fabrice 07/18 ->

Equipe 5 - LNER

Chef d'équipe DESCHANELS Xavier
 Chercheur CAUSSE Jérémy
 IE REY Cyrielle
 MDC TOQUER Guillaume

Equipe 6 - LIME

Chef d'équipe DACHEUX Nicolas
 MDC CLAPAREDE Laurent
 CR CLAVIER Nicolas
 CR MESBAH Adel -> 03/21
 Chercheur SZENKNECT Stéphanie

Equipe 7

Equipe 8 – L2ME

Chef d'équipe LE GOFF Xavier
 Ingénieur BRAU Henri-Pierre
 Chercheur REBISCOUL Diane
 IE LAUTRU Joseph
 IR PODOR Renaud
 IE MAYNADIE Sandra
 Ingénieur ODORICO Michaël
 IE QUINTARD Guillaume 09/21

Equipe 9

Equipe 10 - LMCT

Chef d'équipe DUFRECHE Jean-François
 Chercheur DUVAIL Magali
 Chercheur SIBOULET Bertrand

CEA
 CNRS
 UM ENSCM
 Autres
 Partis



ICSM - NON PERMANENTS 2019 - 2022

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 SCHAPPLER Mireille 02/11/2020-01/05/2021
 PLESSE Nathalie 15/11/2021-31/12/2022

APPRENTI
 BADAROUX Rémy 01/09/2022 – 31/08/2023

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 MORTADA Bouchra 19/07/2021-18/07/2023
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 BASTIEN JALLY 08/09/2022-07/09/2023

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 RIMSANT Damien 10/2016-10/2019
 CHEVALIER Aline 16/10/2017-15/01/2021
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 LORIGNON Fabrice 31/10/2018-30/12/2021
 MAKOMBE Elizabeth 04/11/2019-03/02/2023
 MARTIN ROMO Y MORALES Mickael 02/11/2020-01/11/2023
 RIANT Tennessee 02/11/2020-01/11/2023
 MONEUSE Raphaël 01/12/2020-30/09/2023

POST-DOCTORANT ou CHERCHEUR
 WANG Jingxian 17/10/2017-30/06/2019

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CDD ITA
 SUKHBAAATAR Tamir 25/11/2019-24/07/2020
 LE Anh-Hoang 09/09/2019-09/03/2020
 LELONG Evan 18/10/2021-17/10/2022
 SROUR Hassan 01/10/2021-30/09/2022
 NDEBULIA WATCHOU Frantz 17/05/2021-16/11/2021

POST-DOCTORANT ou CHERCHEUR
 MOSSAND Guillaume 30/07/2017-03/06/2019
 HERNAN Castro 01/04/2019-30/04/2019
 LOPEZ USMA Cesar Augusto 01/05/2018-31/10/2019
 ARRAMBIDE CRUZ Carlos 01/07/2020-30/09/2021

DOCTORANT

ARTESE Alexandre 02/11/2016-01/11/2019
 WINKLER Robert 02/11/2016-01/11/2019
BEKKAR Fatima 05/12/2018-31/03/2020
 FELINES Nicolas 16/10/2017-15/01/2021
 LU Zijun Quentin 07/11/2017-06/01/2021
 BEN-GHOZI BOUVRANDE Justine 23/10/2018-22/10/2022
OYE AUKE Ruth 01/10/2018-30/12/2021
 XING Chen Océane 08/10/2018-07/10/2022
BELFQUEH Sahar 10/12/2018-09/03/2022
 EL MAANGAR Asmae 14/11/2018-31/01/2022
 GINOT Loriane 02/11/2021-01/11/2024
 STEMLINGER Simon 04/11/2019-03/11/2022
COUTURIER Julien 01/01/2021-31/12/2023
EL KHOUERY Claudine 01/10/2020-01/10/2023
 GUERINONI Elise 21/10/2020-20/10/2023
 LE MIRE David 02/11/2020-01/11/2023

EQUIPE 4 LSFC

CDD ITA
SLEIMAN Noura 15/07/2019-14/07/2020

CDD CHERCHEUR
MICHEAU Cyril 11/03/2019-17/01/2020

DOCTORANT
BONATO Laura 16/10/2017-15/10/2020
EL HAKIM Sara 22/11/2018-21/11/2021
COT-AURIOL Manon 21/10/2019-20/02/2023
HERR Sophie 04/11/2019-03/02/2023
MARGATE Julien 05/10/2021-04/10/2024

EQUIPE 6 LIME

APPRENTI
BALME Kévin 01/09/2021-31/08/2022
ZANNOUH Wassima 01/09/2021-23/08/2022
TRONYO Marie 01/09/2022-31/08/2023
SCHUPPE Laura 01/09/2022-23/08/2023

POST-DOCTORANT ou CHERCHEUR
ALBY Délphia 19/03/2018-31/08/2019
RAFIUDDIN Mohamed Ruwaid 18/06/2018-18/11/2020

DOCTORANT
ESTEVENON Paul 10/2016-10/2019
DESFougères Lénaïc 10/2016-10/2019
TRILLAUD Victor 14/10/2016-13/10/2019
QIN Danwen David 01/09/2016-31/08/2020
DALGER Thomas 14/10/2016-13/10/2019
MANAUD Jérémie 02/10/2017-30/11/2020
BERTOLOTTO Solène 10/2017-10/2020
MASSONNET Malvina 15/10/2018-14/10/2021
KACZMAREK Thibault 15/10/2018-14/10/2021
ASPLANATO Pierre 10/2019-10/2022
MONTAIGNE Théo 21/10/2019-20/10/2022
ROCHE Alison 01/10/2020-30/09/2023
BARRAL Thomas 19/10/2020-18/10/2023
BENARIB Sofian 21/10/2020-18/10/2023
HISAINY Mohammad 04/10/2021-03/10/2024
HOURS Charles 12/2019-12/2022
GILLET Célia 15/10/2018 – 14/10/2021
CAPRANI Raphaël 02/10/2020-01/10/2023
DESAGUILIER Marie-Margaux 02/10/2020-01/10/2023

CDD ITA
ZUNINO Morgan 18/06/2018-17/12/2020
DI MASCIO Lara 14/09/2020-13/09/2022
ANZALONE Eddie 14/09/2020-30/01/2022
IMBERT Paul-Henri 14/09/2020-13/12/2022
COLOMBEAU-BEDOS Thomas 10/01/2022-09/01/2023

EQUIPE 5 LNER

APPRENTI

COSTE Anna 01/09/2019-01/09/2020
BRISCESE Lucas 01/09/2019-01/09/2020
RAFFO Freddy 01/09/2022-31/08/2022

CDD CHERCHEUR

SINGARAVELU Chandra Mohan 17/12/2018-05/12/2021
MANSAS Clémentine 04/01/21-03/01/23
LIN Jun 19/04/2022-18/10/2022

DOCTORANT

MONNIER Julien 14/10/2016-13/10/2019

LEBLANC Martin 01/10/2016-01/10/2019

BOUALI Sofiane 01/10/2016-01/10/2019

RUSSO Baptiste 09/10/2017-11/12/2020

BOUBON Rémi 01/10/2017-30/12/2020

LU Zjie Martin 01/10/2017-30/09/2021

LIN Jun 15/10/2018-15/01/2022

TRATNJEK Toni 21/10/2019-20/10/2022

DIDIER Florian 01/10/2019-30/09/2022

HAUTECOUVERTURE Anna 19/10/2020-18/10/2023

ROCH Rayan 02/11/2021-01/11/2024

DE LAHARPE Pierre 02/11/2022-01/11/2025

POST-DOCTORANT ou CHERCHEUR

ARENA Hélène – 21/11/2016-20/01/2019

RUSSO Baptiste – 14/12/2020-13/06/2022

KHODER Hassan 02/11/2020-01/11/2021

EQUIPE 8 L2ME

POST-DOCTORANT ou CHERCHEUR

BEN KACEM Ilyes 08/01/2018-07/07/2019

PINAUD Laetitia 04/01/2021-03/07/2022

TARON Mélanie 20/06/2022-19/06/2024

PEIRERA MACHADO Norma 02/05/2022-01/05/2023

DOCTORANT

MENDONCA Jérôme 02/09/2019-31/08/2022

CDD ITA

ARENA Hélène 28/01/2019-27/07/2019

APPRENTI

HASSAK Siham 1/10/2020-30/09/22

EQUIPE 10 LMCT

DOCTORANT

COSTE Amaury 01/10/2016-30/09/2019

SPADINA Mario 01/02/2016-31/01/2019

COQUIL Mathilde 10/2017-01/2021

VATIN Marin 15/10/2018-14/10/2021

HILAIRE Lolita 15/10/2018-14/10/2021

WANG Kunuy 01/10/2019-30/09/2022

JAMI Ludovic 01/10/2019-30/09/2022

COLLE Thomas 02/11/2020-01/11/2023

POST-DOCTORANT ou CHERCHEUR

FOUCAUD Yann 09/12/2019-08/12/2020

LE CROM Sébastien 01/02/2021-31/07/2022

ŽIBERNA Lara 03/10/2022-02/10/2025

GUILLAM Erwann 17/10/2022-16/10/2025



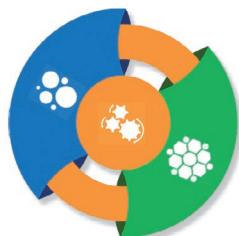
ORGANISATION DE CE RAPPORT SCIENTIFIQUE À 4 ANS (2019-2022)



Chacune des huit équipes de recherche rassemble des chercheurs et des ingénieurs sur des compétences spécifiques et qui peuvent sembler très différentes et éloignées à la base. Cependant un grand nombre de résultats sont obtenus au travers de travaux communs leur permettant de publier dans des revues très variées et à participer à un ensemble très éclectiques de conférences internationales.

Au travers de trois axes principaux, les actions de recherche avec des objectifs ciblés que se donnent les chimistes, physico-chimistes créatifs et le personnel en appui à cette recherche sont rassemblées dans ce rapport sous forme de fiches distribuées dans les 3 axes définis dans l'introduction (pages 10-11). Ces axes guident le choix des priorités soutenues financièrement tout en conservant une grande autonomie de réflexion sur des sujets connexes qui pourraient bénéficier de ces recherches.

Axes :



INNOVATION DANS L'EXTRACTION ET LE RECYCLAGE

OPTIMISATION DU CYCLE DE VIE DES MATERIAUX POUR L'ENERGIE

METHODOLOGIES ET THEORIES DE LA CHIMIE DE SEPARATION

Les objectifs ciblés restent :

- Comprendre les mécanismes chimiques qui sous-tendent les processus de séparation chimique et développer des modèles prédictifs
- Optimiser les méthodes de séparation connues, afin d'imaginer, de proposer et de tester des méthodes de séparation optimisées ou innovantes.
- Anticiper le cycle de vie des matériaux utilisés dans le cadre de la production d'énergie nucléaire et alternative
- Développer la «chimie verte» sous toutes ses facettes, y compris la sonochimie.
- Développer des théories et des méthodes de caractérisation et de modélisation.

Les objectifs de recherche s'étendent de la science directement liée à l'énergie nucléaire au recyclage non nucléaire et à la chimie des matériaux, avec une grande partie de la recherche ayant un intérêt «double».

Ensuite, les principaux projets européens/internationaux ainsi que les projets nationaux à travers l'ANR et les projets régionaux à travers le Labex CheMISyst et enfin des processus de valorisation ou pré-maturisation sont listés et résumés. Le personnel de l'ICSM est également impliqué dans de nombreuses activités d'enseignement. À la fin de ce rapport sont répertoriées les références bibliographiques des recherches et brevet de l'ICSM couvrant la période 2017-2020.

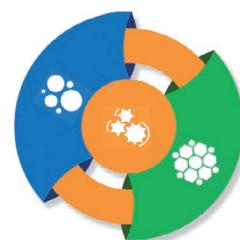
ORGANIZATION OF THE FOUR-YEAR (2019-2022) ICSM SCIENTIFIC REPORT



Each of the eight active research groups gathers researchers and engineers with specific skills that may seem very different. However, a large number of results are obtained through joined studies allowing them to publish in a wide variety of journals and to participate in a very eclectic set of international conferences.

Through three main axes, the research actions with targeted objectives, that creative chemists, physico-chemists and all staff in support to this research, are gathered in this report in the form of sheets distributed in the 3 axis as defined in the introduction (pages 12-13 pommier). These axes guide the choice of priorities for financial support while maintaining a large autonomy of reflection on related topics that could benefit from this research.

Axis:



INNOVATION IN EXTRACTION AND RECYCLING

OPTIMIZING OF MATERIALS LIFE-CYCLE FOR ENERGY

METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

Focused objectives are still:

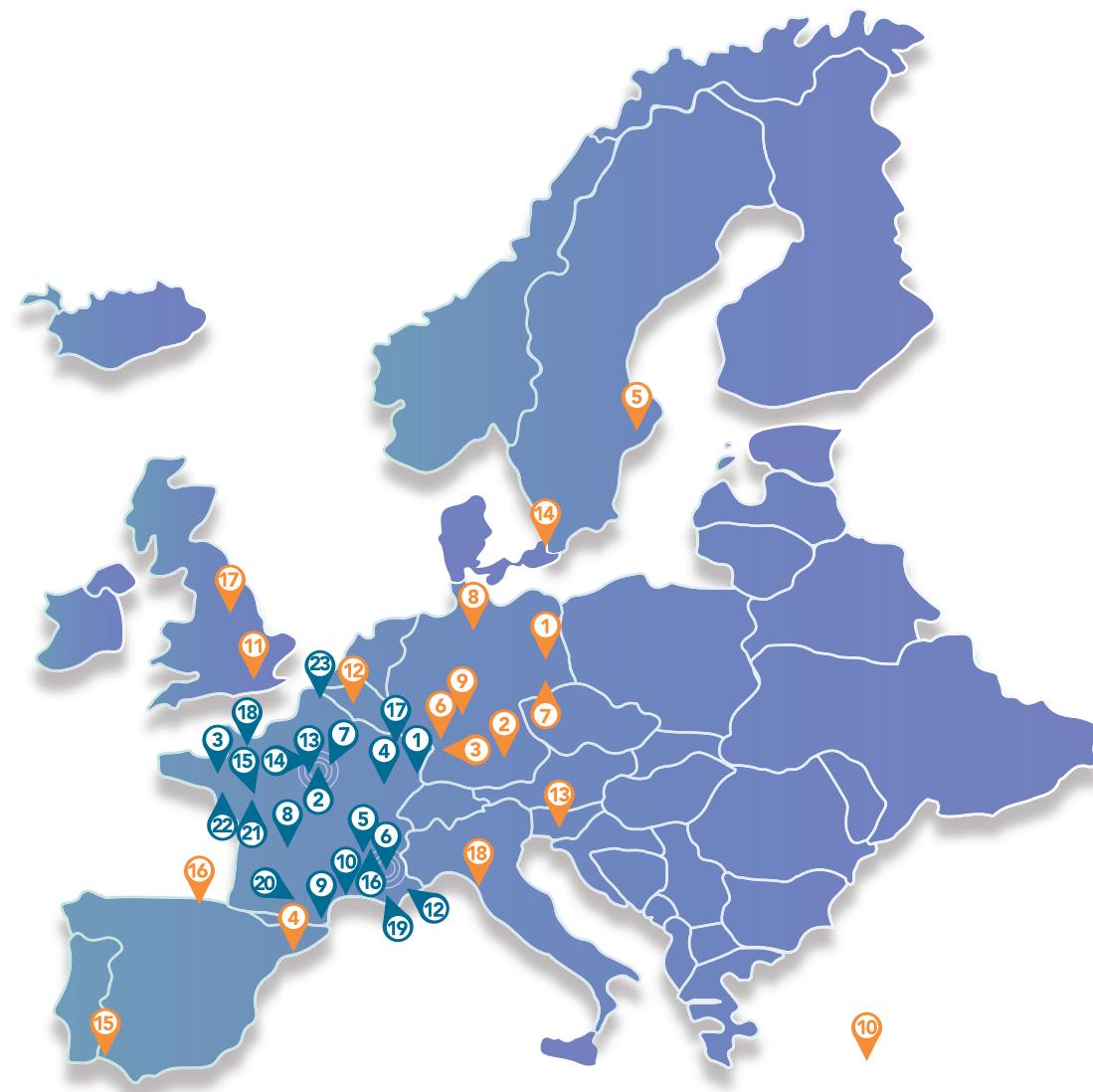
- Understand chemical mechanisms underlying processes of chemical separation and develop predictive models
- Optimize known methods for separation, in order to imagine, propose and test optimized or innovative separation methods.
- Anticipate the life-cycle of materials used in the context of nuclear and alternative energy productions
- Develop "Green Chemistry" in all its facets, including sonochemistry.
- Develop Theories and Methods for characterisation and modelling.

Research objectives range from science directly related to nuclear energy to non-nuclear recycling and materials chemistry, with much of the research having a «dual» interest.

Then, the main European/international projects as well as national projects through ANR and regional projects through CheMISyst Labex and finally valorisation or pre-maturation processes are listed and summarized. ICSM staff is also involved in many teaching activities. At the end of this report are listed the bibliographical references of ICSM's research and patents covering the 2017-2020 period.

COLLABORATIONS ACTIVES EN COURS (DEPUIS 2019) AVEC DES PARTENAIRES EUROPÉENS

ACTIVE COLLABORATIONS WITH EUROPEAN PARTNERS



EN FRANCE

① STRASBOURG	⑨ PERPIGNAN	⑯ METZ	⑯ BERLIN	⑩ CYPRUS
② PARIS	⑩ MONTPELLIER	⑰ CAEN	② REGENSBURG	⑪ LONDON
③ RENNES	⑪ NIMES	⑲ AIX EN PROVENCE	③ KONSTANZ	⑫ LEUVEN
④ NANCY	⑫ NICE	⑳ TOULOUSE	④ BARCELONE	⑬ LJUBLJANA
⑤ LYON	⑬ SACLAY	㉑ POITIERS	⑤ STOCKHOLM	⑭ LUND
⑥ GRENOBLE	⑭ VERSAILLES	㉒ NANTES	⑥ KARLSRUHE	⑮ HUELVA
⑦ AUBERVILLIERS	⑮ TOURS	㉓ LILLE	⑦ DRESDEN	⑯ BILBAO
⑧ MOGES	⑯ CHAMBERY		⑧ BREMEN	⑰ SHEFFIELD
			⑨ DARMSTADT	⑱ PISA

EN EUROPE (HORS FRANCE) :

① STRASBOURG	⑨ PERPIGNAN	⑯ METZ	⑯ BERLIN	⑩ CYPRUS
② PARIS	⑩ MONTPELLIER	⑰ CAEN	② REGENSBURG	⑪ LONDON
③ RENNES	⑪ NIMES	⑲ AIX EN PROVENCE	③ KONSTANZ	⑫ LEUVEN
④ NANCY	⑫ NICE	⑳ TOULOUSE	④ BARCELONE	⑬ LJUBLJANA
⑤ LYON	⑬ SACLAY	㉑ POITIERS	⑤ STOCKHOLM	⑭ LUND
⑥ GRENOBLE	⑭ VERSAILLES	㉒ NANTES	⑥ KARLSRUHE	⑮ HUELVA
⑦ AUBERVILLIERS	⑮ TOURS	㉓ LILLE	⑦ DRESDEN	⑯ BILBAO
⑧ MOGES	⑯ CHAMBERY		⑧ BREMEN	⑰ SHEFFIELD
			⑨ DARMSTADT	⑱ PISA



LES MISSIONS SCIENTIFIQUES CONTRACTUELLES DE L'ICSM

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 4^{ème} 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 économies 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'ex-

traction/séparation considérés biphasiques (liquide/liquide, solide/liquide) ou monphasiques (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'électro-nucléaire, 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 (sono-chimie) 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 sono-chimie 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 du catalyseur.

A proximité de surfaces solides macroscopiques, les bulles de cavitation sont susceptibles d'implorer 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 EVO-LUTION (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 correspondent 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 aux-

quals 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 électro-niques 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.

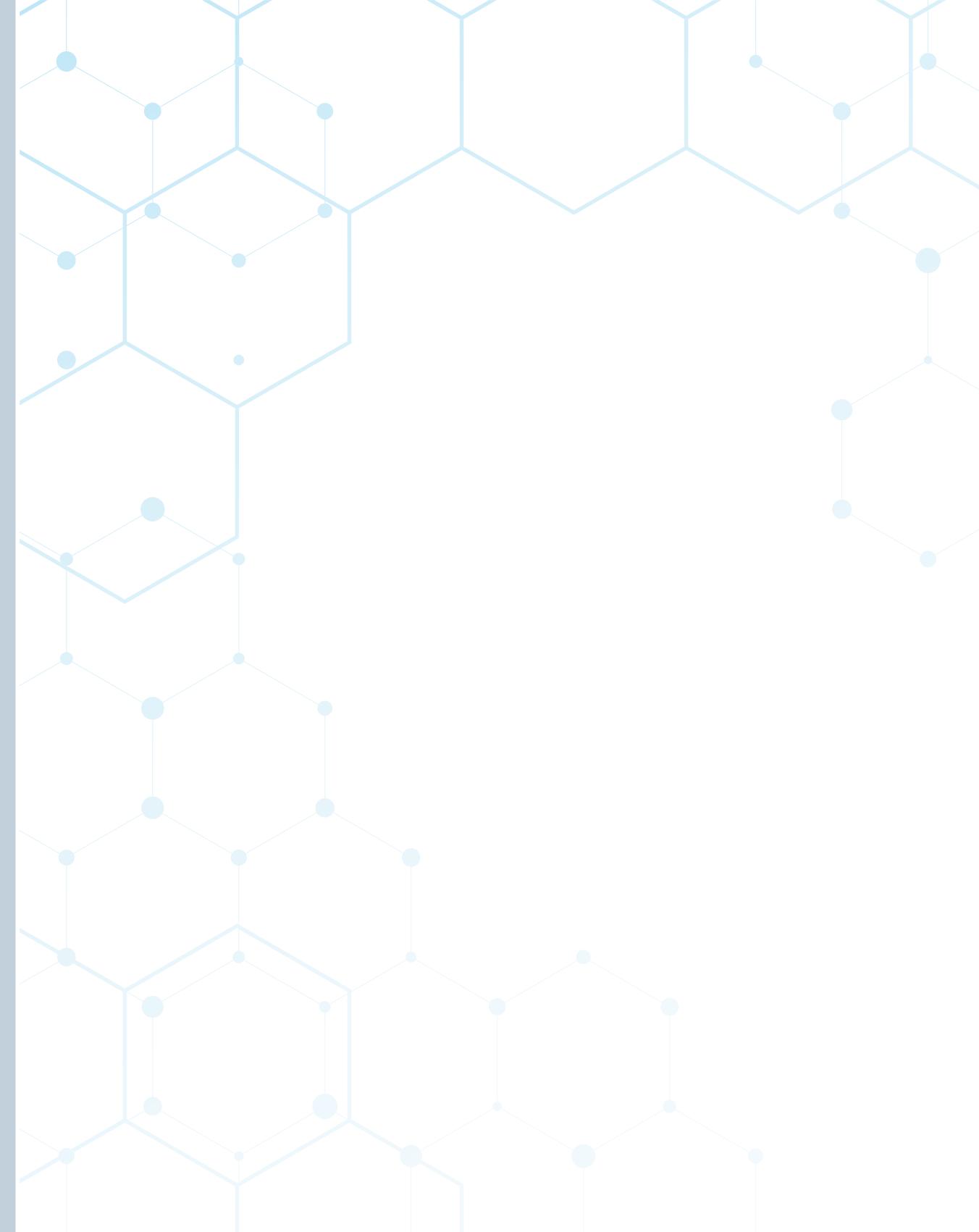
THÉMATIQUE 8 MODÉLISATION MÉSOSCOPIQUE ET CHIMIE THÉORIQUE (LMCT)

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.



PERSONNEL D'APPUI À LA RECHERCHE ET ÉQUIPEMENTS SCIENTIFIQUES

L'organisation de l'ICSM s'articule donc autour d'une stratégie de recherche structurée en 8 équipes mais aussi d'une équipe de direction avec son administrateur gestionnaire et chef d'installation (CEA/DEN) qui dirige les équipes de gestion et d'appui technique de l'unité (exploitation et sécurité) et son secrétariat, d'une équipe de gestion administrative et financière chargées de l'exécution budgétaire, des opérations de gestion du personnel et de la formation, des achats, des missions et du support de communication de l'unité sur les 4 tutelles. Enfin une équipe d'installation en charge de fonctions multiples (correspondants déchets et effluents, transport, sources radioactives et matières nucléaires, avec l'appui des labos, correspondants des nombreux contrats du centre de Marcoule comme la maintenance, ventilation, protection physique, nettoyage, petits travaux, CEP,...) (cf. organigramme personnels permanents) complète la partie direction.

Les activités du personnel administratif correspondent à environ 8 ETPT toute tutelle confondue (pour 32 ETPT Recherche, 4 ETPT Enseignement) afin de recevoir et gérer dans les meilleures conditions environ 10 post-doctorants/CDD, 20 doctorants, une trentaine de stagiaires/apprentis (Master, IUT, BTS) par an. Ces activités couplées à celle de la recherche et de l'enseignement permettent de garantir 1) de la qualité scientifique de la recherche et du respect de l'intégrité scientifique, 2) de la sécurité à tous les niveaux de par le statut de l'unité en tant qu'ICPE chimie déclarée (l'unité possède des matières nucléaires en quantité réduite, 1 kg d'uranium naturel ou appauvri et de thorium) ainsi que des risques chimiques avec, en priorité, les substances CMR. Les formations obligatoires sont assurées pour accéder aux laboratoires et permettre un travail de recherche en toute sécurité en s'engageant de manière responsable et considérant un développement durable, associant maintien de la

paix, croissance économique, protection de l'environnement et développement social, dont l'objectif est de satisfaire les besoins actuels de la société et de préparer l'avenir en anticipant les besoins des générations futures.

La gestion des ressources financières (prestations, contrats européens, nationaux PIA et autres financements publics, des collectivités territoriales, contrats de recherches industriels ou des SATT et autres prestations de type expertises, conseils, services) doit être parfaitement maîtrisée afin de mener à bien l'activité de l'ICSM.

Les spécialités de l'ICSM nécessitent l'utilisation d'équipements spécifiques (voir figure) adaptés aux domaines d'expertise en synthèse organique et matériaux de purification associés (Chromatographie automatisée, HPLC semi-préparative), synthèse et caractérisation de matériaux inorganiques et hybrides organiques/inorganiques (fours, ATD/ATG, analyses élémentaires, analyseur de surface, dilatométrie) ainsi que d'équipements expérimentaux originaux (réacteurs multifréquences pour la sonochimie, cellules de filtration membranaire, colonnes de flottation, cuve de Langmuir) et d'analyses classiques (UV-Vis, FTIR, chromatographie ionique, GC-MS) ou spécifique (tensiométrie à goutte, DLS, détection acoustique). Les équipements mi-lourds utilisés dans le cadre des missions scientifiques de l'ICSM sont en partie affectés dans les laboratoires de l'Institut, notamment les équipements d'analyses (Diffusion/Diffraction de rayons X, Microscopie Electronique à Balayage Environnemental, RMN 400 MHz liquide et solide, ICP-OES, ICP-MS, spectroscopie Raman, banc d'optique non-linéaire) qui sont pour la plupart mutualisés au sein de la Plate-forme Commune d'Analyses et de Caractérisation (PAC) du pôle de Chimie MUSE. Ils sont en cours de jouvence pour maintenir une excellence dans les recherches de l'institut comme

le MEB et bientôt le banc de diffusion X aux petits angles et la RMN. Pour les caractérisations par diffusion de neutrons et de rayons X haute résolution, les équipes effectuent leurs analyses sur les grands instruments de l'Institut Laue-Langevin (ILL) ou au Laboratoire Léon Brillouin (LLB, fermé depuis 2020). De même, pour celles par rayons X avec du temps

de faisceau synchrotron demandé sur les lignes de SOLEIL ou à l'ESRF ou encore au centre HZ à Berlin ou DESY à Hambourg. Dans le cadre des études menées sur la caractérisation de matériaux sous irradiation ioniques, les expérimentations s'effectuent sur JANNUS (Saclay) et au GANIL (Caen).



1 / HYBRID SYSTEMS FOR THE SEPARATION

Au 1^{er} décembre 2022 l'équipe est composée de 4 permanents :

- 1 Chercheur (DR) CNRS, responsable d'équipe (Dr. Damien Bourgeois)
- 1 Ingénieur-chercheur CEA/DRF (Dr. Michaël Carboni)
- 1 Enseignant-chercheur (MCF) UM (Dr. Jérôme Maynadié)
- 1 Ingénieur-chercheur CEA/DES (Dr. Daniel Meyer)

Et sur la période 2019-2022 de non-permanents :

Post-doctorants :

- Jingxian Wang (ANR TURBO, 2017-19): Solid-liquid exchange between uranium and a synthetic apatite: towards uranium decorporation from bone matrix.
Boushra Mortada (contrat CEA/PTC, 2021-22): 2D-deposition of MOF on glass.

Ingénieurs d'étude ou de recherche en CDD :

- Sébastien Cher (contrat Arcelor Mittal, 2019-20) : Synthèse et étude de nano-matériaux.
Nathalie Scalisi (contrat Région-Sovamep, 2019-20) : Amélioration des procédés de récupération de l'or.
Anthony Brunet-Manquat (ANR CAREME, 2022-23) : Préparation de catalyseurs issus du recyclage.
Valentin Pierre (Projet Plan de relance/Sovamep, 2022-24) : Développement de procédés de récupération de métaux précieux.

Doctorants :

- Valentin Lacanau (thèse Labex, 2015-2019) : Conception et étude physico-chimique d'amphiphiles auto-assemblés pour l'extraction de métaux et la catalyse en milieu aqueux.
Damien Rinsant (thèse CEA/DES coll. DMRC, 2016-19) : Elaboration de matériaux hybrides fonctionnalisés de type MOF pour l'extraction sélective de l'uranium.
Marine Cognet (thèse UM, 2016-19) : Elaboration de matériaux hybrides pour le stockage de l'énergie et le recyclage de batteries Li-ion.
Ali Moussaoui (thèse CEA/DEN, 2018-21) : Séparation Liquide/Liquide pilotée par la cinétique.
Fabrice Lorignon (thèse Région / CEA Valo, 2018-21) : Mise en forme de MOFs sous forme monolithique.
Aline Chevalier (thèse CEA/DEN, coll. Univ. Strasbourg, 2017-21) : Extraction liquide-liquide et séparation de métaux à l'aide de bibliothèques dynamiques covalentes.
Elisa Ré (thèse CEA/DEN, 2017-21) : Conception et élaboration de matériaux hybrides à base d'uranium et de thorium.
Julie Durain (thèse CEA/DEN, 2017-2021) : Voies alternatives courtes au multi-recyclage du plutonium : études de systèmes triphasiques et applications pour la séparation des actinides.
Elisabeth Makombé (thèse CEA/DES, 2019-23) : Reformulation solvant et recyclage d'actinides.
Michael Martin-Romo y Morales (thèse Région / Saint Gobain (CNRS), 2020-23) : Valorisation directe de métaux précieux issus du recyclage sous forme de dispositifs pour dépollution.
Tennesse Riant (thèse CEA/DRF, 2020-23) : Comportement de composés lamellaires à pas contrôlé d'oxydes de métaux de transition comme matériaux d'électrodes de batteries.
Raphaël Moneuse (thèse UM, 2020-23) : Séparation des métaux par dynamique adaptative.

Apprentis :

- Eléonore Lagae Capelle (2018-21)
Sabrine Medjouel (2021-24)



The team



Understanding the behaviour of metals in complex organic phases is central to the development of efficient recycling and waste management processes. The approaches generally developed in hydrometallurgy are mostly aimed at mastering single steps, based on either liquid or solid unit operations. The team proposes to integrate all of these developments into global extraction-separation-isolation-purification chains, under the concept of circular separative chemistry of metals. This simplification of the processes aims at 1) a better management of the mixtures, 2) a better flexibility in front of a raw material of variable composition, and 3) a decrease in the number of steps, generally synonymous with a control of the generated effluents. Moreover, the concept of recycling is not restricted to the isolation of a purified metal, and the team takes into account the final material: the developed processes best integrate the recovery of the target metal in the form of a finished product, for a similar or different application.

Laboratory studies focus on describing and understanding the properties of metal-based molecular and supramolecular systems (d and f). The central question lies on the determination of the role of interactions between a metal center and its near and distant environment in a process of matter organization. This organization is then used to form either complex organic phases specific to a metal, or specific assemblies such as coordination polymes. In this context, the team does not seek to develop new tools (new molecules, new solids, new synthesis methodologies), while possessing a perfect mastery of existing tools, including mechanistic aspects at the molecular level. The systems thus studied aim at the development of innovative separation processes, di- or tri-phasic, targeting various metals of interest with various physico-chemical properties (valence, charge density, etc.) such as transition metals (Pd, Au, Ni, Co, Mn, Ru, Al, Sc), lanthanides or actinides (U, Th and Pu).

At the fundamental level, the focus is set on problems related to adaptive separation, aiming at a controlled management of processes that can handle an incoming flow of variable composition. In the subsequent use of fluorinated compounds, our understanding of the relative importance of strong and weak interactions in the extraction and separation of metals allowed us to propose an original approach based on spontaneous segregation of organic phases. Using a conventional organic phase based on tributyl phosphate (TBP), a first biphasic system is obtained after extraction of U and Th at high temperature (70°C). The two phases are separated, then the organic phase

loaded with U and Th is cooled below a critical temperature (about 50°C) where it separates into a heavy organic phase and a light organic phase. Two flows are thus obtained: the first contains almost all the Th in the presence of a part of the U, in a controlled ratio, the second contains the surplus of U. The U/Th ratio in the heavy phase is controlled by the final temperature of the system (PhD thesis J. Durain). At the same time, the development of adaptive systems was envisaged through an approach based on the implementation of dynamic covalent libraries: Unlike the conventional method where a single molecule is designed to extract metal cations under specific conditions, dynamic covalent chemistry makes it possible to induce the generation of extractant species according to the composition of the medium. In collaboration with the LCS (ISIS), the LHyS team applied this approach to the extraction of copper nitrate (II) by an organic phase based on a dynamic library of acylhydrazone-like constituents that self-build and distribute within the biphasic system. The addition of copper(II) cations to this library triggers a modification of its composition and the regulation of extractant molecules caused by the coordination with metal cations (PhD thesis A. Chevalier, then PhD thesis R. Moneuse).

The molecular systems studied are then used for the development of short circuits, in the different areas of the life cycle of metals treated at ICSM: Regarding the nuclear fuel cycle, the studies carried out aim at the simplification of a closed cycle driven by safety, through a controlled management of mixtures of actinides. The control of the separation is ensured by a judicious choice of the molecular topology of the extractants used, mainly malonamides, which allows to play on the kinetic (PhD thesis S.A. Moussaoui) and thermodynamic (PhD thesis E. Makombé) aspects of the separation. The approach also integrates the final matter aspect by the direct and controlled preparation of actinide materials, pure or in mixture, and organized on the nanoscale. As nanoscale organized hybrid materials can exhibit unusual properties compared to conventional inorganic materials, the team developed two bottom-up approaches to target controlled preparation of such materials. First, we developed a one-step approach leading to lamellar nano-sheets using a ternary molecular system (dicarboxylic acid, oleylamine, dibenzyl oxide, PhD thesis E. Re). In these nanosheets, the interlamellar distance can be adjusted according to the length of the dicarboxylic acid used. The second approach, based on the functionalization of nanoparticles, showed that it was possible to use click chemistry as well as electrostatic interactions to build materials organized by association of nanoparticles (S. Cher contract).

In the waste and recycling industry, the approach developed aims to improve the value chain by directly preparing, without purification, compounds with high added value, taking into account economic and ecological models. Various applications are addressed through an established network of academic and industrial collaborations:

- First, in the open cycle, through the continuation of the study of the synthesis of materials for the depollution from battery waste, by direct valorization after recovery of precious metals (Pd, Au) contained in electronic or industrial waste: Based on the fundamental studies already published, the team has developed different hydrometallurgical approaches for the recovery of Pd. In collaboration with various groups, it was then possible to propose a short recycling route of the Pd by its direct valorization as a catalyst (PhD thesis V. Lacanau). This work is continuing within the framework of the CAREME project funded by the ANR (PhD thesis M. Martin Romo y Morales, contract A. Brunet-Manquat). Finally, it should be noted that all the research carried out in this field has led to a close collaboration with the company SOVAMEP to optimize the recovery of precious metals (Au and Pd, contracts N. Scalisi then V. Pierre).

- Then, in a closed cycle as part of the development of materials precursors for energy storage: Energy storage and its circular economy represent a major societal challenge for years to come. In this area, the LHyS team is very interested in the Li-ion battery cycle and in particular the active electrode cycle through an integrated approach based on various hydrometallurgical processes. This cycle includes the manufacture, dissolution and separation of species in a closed cycle mainly based on the use of hybrid materials such as MOF (Metal-Organic Frameworks, M. Cognet and T. Riant PhD theses). All these actions include fundamental and applied studies and involve several national and international external groups (SCARCE project, E. Lagae-Capelle contract).

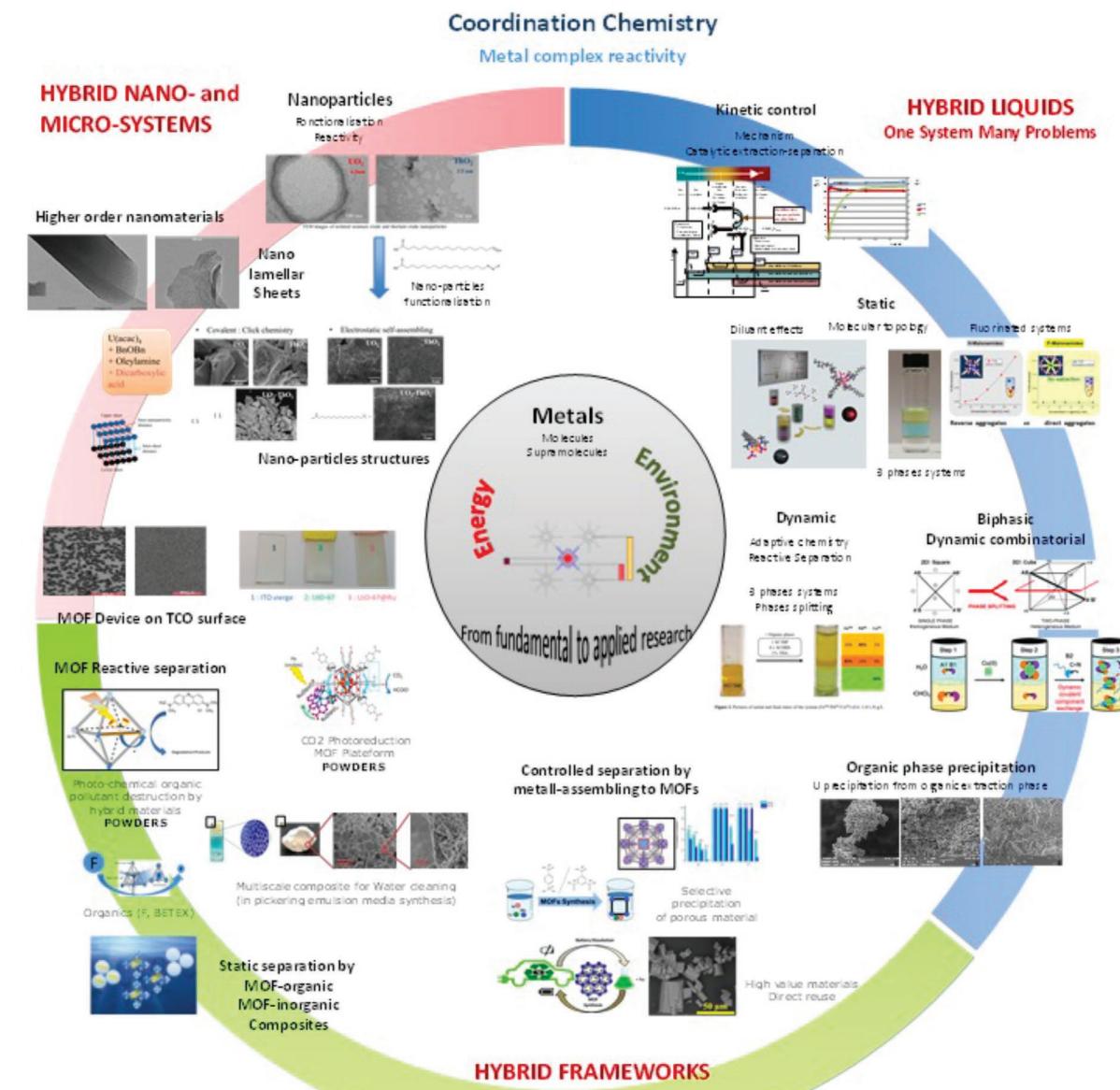
Finally, in a more general way, in order to respond to the lack of possibilities of shaping porous materials with a wide applicability, we developed, in collaboration with a team of the CEA Marcoule (LPSD), a hierarchically porous material preparation approach based on the stabilization of Pickering emulsions using MOF (PhD thesis F. Lorignon). Other means of shaping MOF-based materials are being studied in the laboratory, such as 3D printing (S. Medjouel contract) or thin-film deposition (post-doctoral B. Mortada).



La compréhension du comportement des métaux dans des phases organiques complexes est au cœur du développement de procédés efficaces de recyclage et de gestion des déchets. Les approches généralement développées en hydrométaux visent la plupart du temps à la maîtrise d'étapes unitaires, par voie liquide ou solide. L'équipe propose d'intégrer l'ensemble de ces développements dans des enchainements globaux extraction-séparation-fin matière, sous le concept de la chimie séparative circulaire des métaux. Cette simplification des procédés vise à 1) une meilleure gestion des mélanges, 2) une meilleure flexibilité face à une matière première de composition variable, et 3) une diminution du nombre d'étapes, généralement synonyme d'une maîtrise des effluents générés. En outre, la notion de recyclage n'est pas restreinte à l'isolement d'un métal purifié, et l'équipe prend en compte la fin matière : les procédés développés intègrent au mieux la valorisation du métal ciblé sous forme de produit fini, pour une application similaire ou différente.

Les études menées au laboratoire sont centrées sur la description et la compréhension des propriétés de systèmes moléculaires et supramoléculaires à base de métaux (d et f). Il s'agit de déterminer le rôle des interactions entre un centre métallique et son environnement proche et lointain dans un processus d'organisation de la matière, puis de mettre à profit cette organisation pour former soit des phases organiques complexes spécifiques à un métal, soit des assemblages spécifiques type polymère de coordination. Dans ce cadre, l'équipe ne cherche pas à développer de nouveaux outils (nouvelles molécules, nouveaux solides, nouvelles méthodologies de synthèse), tout en possédant une maîtrise parfaite des outils existants, incluant les aspects mécanistiques au niveau moléculaire. Les systèmes étudiés visent ensuite au développement de procédés de séparation innovants, di- ou triphasiques, ciblant divers métaux d'intérêt de propriétés physico-chimiques (valence, densité de charge...) variées comme les métaux de transition (Pd, Au, Ni, Co, Mn, Ru, Al, Sc), les lanthanides ou les actinides (U, Th et Pu).

Au niveau fondamental, l'accent est mis sur des problématiques de séparation adaptative, visant à un pilotage contrôlé de procédés pouvant traiter un flux entrant de composition variable. Dans la suite de l'utilisation de composés fluorés, notre compréhension de l'importance relative des interactions fortes et faibles dans l'extraction et la séparation des métaux nous a permis de proposer une approche originale basée sur la démixtion spontanée de phases organiques.



En utilisant une phase organique classique basée sur du phosphate de tributyle (TBP), un premier système biphasique est obtenu après extraction de U et Th à haute température (T1, 70°C). Les deux phases sont séparées, puis la phase organique chargée en U et Th est refroidie en dessous d'une température critique (environ 50°C) où elle se sépare en une phase organique lourde et une phase organique légère. Deux flux sont ainsi obtenus : le premier contient presque tout le Th en présence d'une partie de l'U, dans un rapport contrôlé, le second contient le surplus d'U. Le rapport U/Th en phase lourde est contrôlé par la température finale du système (thèse J. Durain). Le développement de systèmes adaptatifs a en parallèle été envisagé par une approche basée sur la mise en œuvre de bibliothèques covalentes dynamiques : Contrairement à la méthode classique où une seule molécule est conçue pour extraire des cations métalliques dans des conditions spécifiques, la chimie covalente dynamique permet d'induire la génération des espèces extractantes en fonction de la composition du milieu. En collaboration avec le LCS (ISIS), l'équipe LHyS a appliquée cette approche à l'extraction du nitrate de cuivre (II) par une phase organique basée sur une bibliothèque dynamique de constituants type acylhydrazone qui s'auto-construisent et se distribuent au sein du système biphasique. L'ajout de cations cuivre(II) à cette bibliothèque déclenche une modification de sa composition et la régulation des molécules de ligand entraînée par la coordination aux cations métalliques (thèse A. Chevalier, puis thèse R. Moneuse).

Les systèmes moléculaires étudiés sont ensuite utilisés pour la mise au point de circuits courts, dans les différents domaines du cycle de vie des métaux traités à l'ICSM : Au niveau du cycle du combustible nucléaire, les études effectuées visent à la simplification d'un cycle fermé piloté par la sûreté, grâce à une gestion contrôlée de mélanges d'actinides. Le pilotage de la séparation est assuré par un choix judicieux de la topologie moléculaire des extractants utilisés, principalement des malonamides, qui permet de jouer sur les aspects cinétique (thèse S.A. Moussaoui) et thermodynamique (thèse E. Makombé) de la séparation. L'approche intègre aussi l'aspect fin matière par la préparation directe et contrôlée de matériaux d'actinides, purs ou en mélange, organisés à l'échelle nanométrique. Comme les matériaux hybrides organisés à l'échelle nanométrique peuvent afficher des propriétés inhabituelles par rapport aux matériaux inorganiques classiques, l'équipe a développé deux approches bottom-up pour viser la préparation contrôlée de

ce type de matériaux. Tout d'abord, nous avons développé une approche en une seule étape menant à des nano-feuilles lamellaires par l'utilisation d'un système moléculaire ternaire (acide dicarboxylique, oléylamine, oxyde de dibenzyle, thèse E. Ré). Dans ces nano-feuilles, la distance interlamellaire peut être ajustée en fonction de la longueur de l'acide dicarboxylique employé. La seconde approche, basée sur la fonctionnalisation de nanoparticules, a montré qu'il était possible d'utiliser la chimie « click » ainsi que les interactions électrostatiques pour construire des matériaux organisés par association de nanoparticules (contrat S. Cher).

Dans l'industrie des déchets et du recyclage, l'approche développée vise à améliorer la chaîne de valeur par la préparation directe, sans purification, de composés à haute valeur ajoutée, en tenant compte des modèles économiques et écologiques. Diverses applications sont abordées, grâce à un réseau établi de collaborations académiques et industrielles :

- En premier lieu, en cycle ouvert, dans la suite de l'étude de la synthèse de matériaux pour la dépollution à partir de déchets de batterie, par la valorisation directe après récupération des métaux précieux (Pd, Au) contenus dans des déchets électroniques ou industriels : Sur la base des études fondamentales déjà publiées, l'équipe a développé différentes approches hydrométallurgiques pour la récupération du Pd. En collaboration avec différents groupes, il a ensuite été possible de proposer une voie de recyclage courte du Pd par sa valorisation directe sous forme de catalyseur (thèse V. Lacanau). Ces travaux se poursuivent dans le cadre du projet CAREME financé par l'ANR (thèse M. Martin Romo y Morales, contrat A. Brunet-Manquat). Enfin, signalons que toutes les recherches menées dans ce domaine ont conduit à une collaboration étroite avec la société SOVAMEP pour optimiser la récupération des métaux précieux (Au et Pd, contrats N. Scalisi puis V. Pierre).
- Ensuite, en cycle fermé dans le cadre du développement de précurseurs de matériaux pour le stockage de l'énergie : Le stockage d'énergie et son économie circulaire représentent un enjeu sociétal majeur pour les années à venir. Dans ce domaine, l'équipe LHyS s'intéresse vivement au cycle des batteries Li-ion et plus particulièrement à celui de l'électrode active par une approche intégrée reposant sur divers procédés hydrométallurgiques. Ce cycle comprend la fabrication, la dissolution et la séparation des espèces dans un cycle fermé principalement basé sur l'utilisation de matériaux hybrides type MOF (Metal-Orga-

nic Frameworks, thèses M. Cognet et T. Riant). Toutes ces actions comprennent des études fondamentales et appliquées et impliquent plusieurs groupes externes nationaux et internationaux (projet SCARCE, contrat E. Lagae-Capelle).

Finalement, de manière plus générale, afin de répondre au manque de possibilités de mise en forme des matériaux poreux avec une large applicabilité, nous avons développé, en collaboration avec une équipe du CEA Marcoule (LPSD), une approche de préparation de matériaux hiérarchiquement poreux basée sur la stabilisation d'émulsions de Pickering au moyen de MOF (thèse F. Lorignon). D'autres moyens de mise en forme de matériaux à base de MOF sont en cours d'étude au laboratoire, comme l'impression 3D (contrat S. Medjouel) ou le dépôt sur couches minces (post-doctorat B. Mortada).



2/ LABORATOIRE DES IONS AUX INTERFACES ACTIVES

Au 1^{er} décembre 2022 l'équipe est composée de:

1 chercheur CEA/DRF responsable d'équipe (Dr. Olivier Diat)
1 ingénieur-chercheur CEA/DRF (Dr. Pierre Bauduin)
1 enseignant-chercheur ENSCM (Pr. Luc Girard)
1 ingénieur d'étude CNRS (Alban Jonchère)
1 ingénieur d'étude CNRS (Coralie Pasquier)

Post-doctorants:

Dr. Abderazak Masmoudi (projet CEA/PTC, 2021-22) : Extraction de métaux précieux par flottation ionique

CDD:

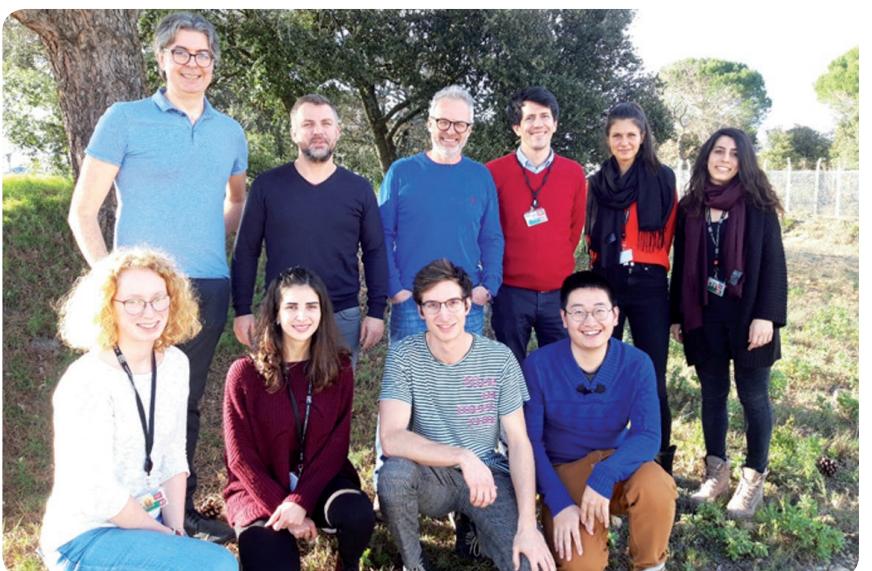
Emile Regnier (ingénieur ANR Foamex, 2019-21) : DEEE / Extraction par flottation ionique
Camille Liadouze (ingénieur ANR Foamex, 2021-22) : DEEE/ Extraction par flottation ionique

Doctorants:

Tania Merhi (thèse ENSCM, 2017-20): Nano-ions de type dicarbollide en interaction avec des surfaces modèles biologiques.
Max Hohenschutz (thèse région Occitanie/ Extrachive, 2017-20): Nano-ions en interaction avec des surfaces non-ionique.
Jing Wang (thèse CEA/DEN, 2017-20): Etude de l'interface liquide/liquide : expérience et modélisation moléculaire.
Ioanna Chazapi (thèse CEA, 2019-22): Effet de solubilisation avec des nano-ions.
Klaudia Skorzewska (thèse CEA, 2019-22): Flottation superchaotrope.
Julien Lamolinairie (co-direction thèse ILL avec Teclis Instrument, 2020-23) : Foam'up.
Philipp Schmid (co-direction thèse Univ. Regensburg, 2019-22): Nanoions and hydrotropes.
Raimoana Frogier (thèse UM, 2021-24): Nanoions en interaction avec surfaces fonctionnalisées.
Valentin Legrand (thèse UM, 2022-25): Flottation superchaotrope, extraction du tungstène

Apprentis:

Amélie Cartier (BTS, CEA 2021-23) : Physico-chimie des nano-ions en solution
Lorelei Demonet (BTS, CEA 2022-23) : Activation redox de nano-ions par stimulus optique



L'extraction liquide/liquide est un procédé de séparation contrôlé par la thermodynamique et/ou la cinétique de distribution des espèces chimiques (sels ou molécules) à séparer entre deux phases liquides non miscibles, usuellement une phase aqueuse et une phase organique. Son optimisation (rendement, coût, réduction de déchets) nécessite de comprendre les phénomènes de diffusion des espèces dans les phases liquides et aux interfaces, leurs hydratation/déhydratation (solvatation/désolvatation) aux interfaces et leur temps de résidence aux interfaces. La recherche dans ce domaine et au sein de l'équipe s'est focalisée sur :

- i) La dispersion des espèces ioniques ou non-ioniques et leurs spéciations moléculaires ou supramoléculaires dans chacune des phases en étudiant et ajustant la nature du solvant (aqueux or organique) plus ou moins complexe (des systèmes de solvants purs jusqu'à de mélanges binaires ou ternaire) et sa structuration à différentes échelles,
- ii) La structuration moléculaire et/ou supramoléculaire de ces solvants à leurs interfaces de contact qui diffèrent de celle du volume

Déclinée dans le cas des actinides et des lanthanides, une problématique d'importance pour le tri ionique associé au cycle du combustible, cette recherche cognitive s'est étendue au fil des ans à des cas de dépollution, de recyclage, d'extraction de molécules actives tout en prenant en compte l'impact environnemental qui requiert (i) la réduction des volumes de solvants ou leur régénération par des étapes simples et peu couteuses, (ii) l'optimisation physico-chimique de procédés pour les rendre plus efficaces et modulaires c'est-à-dire facilement adaptables, (iii) la formulation de solvants verts. L'utilisation de la mousse comme milieu d'extraction est un exemple de procédé permettant de réduire l'impact environnemental. Les mousses ont des atouts certains pour la chimie séparative car elles ont une structure fluide métastable avec une interface fluide/air ultradéveloppée pouvant être utilisée pour extraire et séparer des solutés. Si l'extraction des métaux sous leur forme cationique, ainsi que leur sélectivité, dans un procédé d'extraction liquide/liquide est classiquement étudié en optimisant i) la structure chimique du ligand pour jouer sur la balance complexation/solubilisation ainsi que ii) le phénomène d'émulsification associé. Des progrès sont attendus par l'étude et la compréhension des phénomènes physico-chimiques aux interface et par la maîtrise de l'hydratation des ions ou clusters ioniques (nano-ions) en phase aqueuse.

Dans ce rapport, nous avons sélectionné des exemples de nos recherches sur lesquels nous sommes porteurs ou plutôt les acteurs principaux: un premier exemple dans l'axe méthodologie et simulation concerne l'étude d'interface liquide/liquide comprenant des extractants (ligands) par une technique d'optique non linéaire et en utilisant en parallèle des outils de dynamique moléculaire afin de pouvoir appréhender l'organisation des ions et molécules extractantes autour de l'interface pendant un processus de transfert d'espèces. C'est un travail de thèse en collaboration avec le DMRC/LILA. Un deuxième exemple concerne l'étude de mousses dans l'axe 1, une structure tri-dimensionnelle et labile afin d'extraire des ions ou des particules en limitant la quantité de solvant. Enfin un développement fort au sein de l'équipe après plusieurs années d'études concerne les nano-ions qui sont de ions de taille nanométrique montrant un propriété superchaotrope quand leur densité de charge devient inférieure à 12 charges/nm³. Ces édifices moléculaires ioniques se lient avec de la matière organique en phase aqueuse et peuvent ainsi jouer de multiples rôles par exemple comme (co-)tensioactifs en s'auto-associant avec des tensioactifs, solubilisants, agents structurants à l'échelle supramoléculaires ou hydrotropes. Les nano-ions peuvent donc être vu comme de vrais couteaux « suisse » dans la physico-chimie des ions et colloïdes. La thématique « nano-ions » prend un fort essor au sein de l'équipe en restant focalisé sur les propriétés interfaciales dans le domaine de la solubilisation, extraction et séparation tout en nous permettant d'élargir nos recherches vers les domaines de la biologie et médecine.

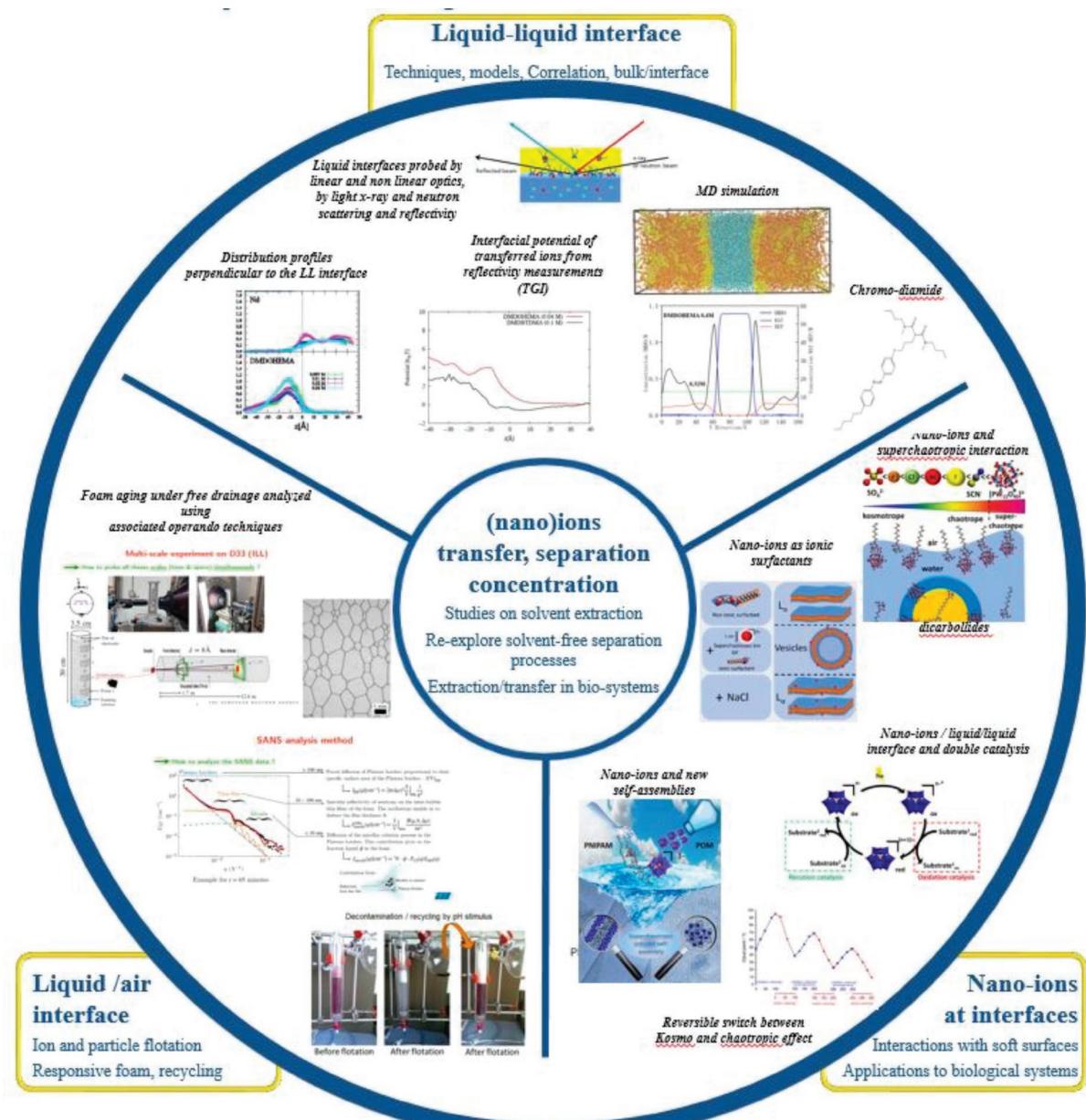


A separation method known as liquid/liquid extraction involves controlling the distribution of the molecular species to be separated between two immiscible liquid phases, typically an aqueous phase and an organic phase, using thermodynamic and kinetic principles. Understanding the diffusion phenomena of species in the bulk and at interfaces, the hydration/dehydration - solvation/de-solvation phenomena at the interfaces, and their residence time at the interfaces is required for optimizing applications (yield, cost, and waste reduction). The team's research in this area has focused on:

- i) the dispersion of ionic or non-ionic species and, consequently, their molecular or supramolecular speciation in each phase by studying and adjusting the nature of the more or less complex solvent (pure, binary, ternary).
- ii) the molecular and/or supramolecular structuring of these solvents at their interfaces, which differs from the volume

By optimizing the chemical structure of the ligand to influence the complexation/solubilization balance as well as the emulsification phenomenon, metals in their cationic form can be extracted in a liquid/liquid extraction process with a control on its selectivity. By looking at the ion transfer from the perspective of interfaces and related physico-chemical phenomena, as well as by managing the hydration of ions or ionic clusters in the aqueous phase, progress in ion extraction can be made. In the past, this cognitive research was developed for actinides and lanthanides, a significant issue related to the radioactive fuel cycle processing, and it has been later expanded to tackle decontamination.

mination of liquids, recycling of crucial metals, and extraction of bioactive compounds. A significant benefit can be produced by the formulation of green solvents, the physico-chemical optimization of processes to make them more efficient and modular, or readily adaptable, and the reduction of solvent volumes or their regeneration by straightforward and inexpensive techniques. One example of process with low environmental impact is by using foams, a fluid structure that is metastable and has a highly developed fluid/air interface, that can be used to remove solutes from fluid phases.



3/ LABORATOIRE DU TRI IONIQUE PAR LES SYSTEMES MOLECULAIRES AUTO-ASSEMBLÉS

Au 1^{er} décembre 2022 l'équipe est composée de 6 permanents:

- 1 DR CNRS responsable d'équipe (Stéphane Pellet-Rostaing),
- 1 Pr CEA/DRF (Thomas Zemb)
- 1 MDC UM - HDR (Guilhem Arrachart)
- 1 Ingénieur CEA/DRF - HDR (Sandrine Dourdain)
- 1 Technicienne CEA/DES (Béatrice Baus-Lagarde)
- 1 Ingénieur de recherche CNRS (Fabrice Giusti)

Et sur la période 2019-2022 de non-permanents:

Post-doctorants :

- Antigoni Theodoratou (UM Labex, co-direction avec ICGM, 2019-2020): Auto-Assemblage d'Adduits Amines-boranes
- Cesar Augusto Lopez Usma (UM LABEX 2018-2020) : Mécanismes d'extraction en milieux liquides ioniques.
- Guillaume Mossand (CNRS, 2019-2020) : Bis-catecholamides polymérisés pour l'extraction d'uranium de l'eau de mer.
- Carlos Arrambide Cruz (ANR DECAP 2020-21): Formulations polymériques pour la déorporation d'uranium.
- Evan Lelong (ANR RECALL, 2022-23): Matériaux chélatant pour un procédé solide/liquide d'extraction d'ion dissous en milieu acide faible.

CDDs:

- Tamir Sukhbataar (CEFIPRA franco-Indien, 2019-2020) : « Transformisme » moléculaire et procédés de recyclage de terres rares contenues dans les aimants permanents.
- Guillaume Mossand (programme AREVA/NOPRA, 2019) : Extraction de métaux compétiteurs de l'uranium en milieu sulfurique
- Anh-Hoang Le (SATT/ ANR SILEXE, 2019) : Liquides ioniques pour le recyclage de l'or contenu dans les cartes électroniques.
- Frantz Ndebulia Watchou (SATT, 2021) : résines formo-phénoliques biosourcées pour l'extraction d'uranium de l'eau de mer.
- Hassan Srour (SOLVAY, 2021) : résines formophénoliques pour l'extraction de lithium de saumures.
- Hassan Srour (projet SOLAMAT, 2021-22): valorisation d'un déchet de l'industrie des lubrifiants.
- Evan Lelong (projet CEA/TEENV, 2021-22): résines formophénoliques pour l'extraction d'uranium de saumures.

Doctorants :

- Alexandre Artese (CEA/DEN thèse phare, 2016-19) : Caractérisation de ligands bifonctionnels N,P pour la co-extraction U/Pu en milieu nitrique.
- Robert Winkler (CEA/DRF, 2016-19) : Approche « tout en un » pour la mise en œuvre de matériaux hybrides à hautes capacités extractantes.
- Nicolas Felines (CEA/DES thèse phare, 2017-20): Monoamides énantiopurs pour l'extraction de l'uranium.
- Zijun Lu (CEA/DES 2017-20): Solution of amphiphilic ion pairs in equilibrium with an aqueous phase: mechanistic study of extraction.
- Justine BenGhozi-Bouvrande (CEA/DES 2018-21): Les liquides poreux : un nouveau concept pour l'extraction liquide-liquide.
- Ruth Oye-Auke (Contrat Doctoral UM, 2018-21): Méthodologies de synthèse et étude de résines biosourcées thermodorçissables pour la récupération de métaux d'intérêt.
- Chen Xing (China Scholarship Council (CSC), 2018-22): Concentration and selective recovery of uranium using nanofiltration processes.
- Sahar Belfqueh (Région-BRGM, 2018-22): Recyclage et valorisation des terres rares contenues dans des solutions faiblement acides.
- Asmae El Maangar (CEA, 2018-22): L'extraction raisonnée de métaux stratégiques par des hydrotropes.
- Fatima Bekkar (PNE, accueil 18 mois, 2018-19): Synthèse contrôlée de résine chélatante pour le recyclage.
- Simon Stemplinger (thèse CEA, 2019-22) : Théorie de la centrifugation douce dans des fluides structurés formulés à base d'hydrotropes.
- Elise Guerinoni (CEA/DES, 2020-23): Etudes des mécanismes d'extraction de l'uranium en milieu sulfurique par des amines tertiaires à chaînes alkyles ramifiées.
- David Le Mire (CEA/DES, 2020-23): Effect of chirality on the extraction mechanisms of extractant molecules such as enantiopure monoamides for U/Pu extraction.

Claudine El Khoury (SAFAR, CNRSL/Ambassade France): Synthèse et évaluation de thiourée polymérisé pour le traitement et l'extraction de métaux par procédé solide/liquide.

Julien Couturier (co-direction thèse avec CEREGE - CNRS, 2020-23): Extraction responsable et sélective de métaux critiques à partir de sources secondaires.

Lorianne Ginot (thèse CEA focus ECC, 2021-24): Développement de liquides poreux pour l'extraction des métaux d'intérêt à partir de déchets d'aimants permanents.

Baptiste Bernicot (Thèse UM, 2022-25) : DES et NaDES hydrophobes pour l'extraction liquide/liquide

Marine Thimotée (Thèse CEA/DES, 2022-2025) : Amino- et amido-phosphonates chiraux pour l'extraction d'actinides.

Apprentis:

Raphaelle Piton (2020-22) : EDTA, DTPA et CDTA lipophiles pour l'extraction de terres rares

Marie Moneuse. (2022-23) : Synthèse et caractérisation d'extractant chiraux



L'équipe « Tri Ionique par des Systèmes Moléculaires Auto-assemblés » (LTSM) est aujourd'hui constituée de 6 permanents, Guilhem Arrachart, Maître de Conférence UM (09/2009), Sandrine Dourdain, Ingénieur CEA/DRF (07/2010), Béatrice Baus-Lagarde, Technicienne CEA/DES (04/2016), et Fabrice Giusti, Ingénieur de recherche CNRS (07/2018), Thomas Zemb, Ingénieur CEA/DRF et Professeur INSTN (01/2019) et Stéphane Pellet-Rostaing, Directeur de Recherche CNRS (01/2009). Les orientations de recherche développées au LTSM sont principalement intégrées aux axes « Innovation pour l'extraction et le recyclage », et en connexion étroite avec les axes « Méthodologies et théories en chimie séparative » et « Optimisation du cycle de vie des matériaux pour l'énergie ». L'équipe valorise la complémentarité de ses compétences en chimie de synthèse, chimie analytique et en nanosciences pour une optimisation raisonnée et maîtrisée des procédés de séparation et de recyclage. Les systèmes moléculaires synthétisés sont mis en œuvre aussi bien dans des procédés classiques (liquide/liquide, solide/liquide) ou moins conventionnels

(membranes, solvants non usuels) avec une orientation dans la compréhension des mécanismes qui gouvernent la séparation. Les publications traitant de l'extraction liquide-liquide se placent exclusivement dans le cadre de la chimie organo-métallique, de la chimie supramoléculaire ou de la physico-chimie des systèmes auto-assemblés. Le LTSM développe une vue générale « iénaïque » des énergies libres de transfert qui est une vision « nanosciences » de l'électrochimie classique, sans champ extérieur mais qui tient compte des interactions faibles au-delà du premier voisin. L'approche « iénaïque » prévoit la conception et la synthèse d'extractants spécifiques originaux (pinces moléculaires, macrocycles, résines) ainsi que l'étude des mécanismes associés gouvernant l'affinité et la sélectivité, et permet en outre de faire des prédictions quantitatives sans paramètres non mesurables. La possibilité d'exalter la complexation par l'auto-association de complexants sous forme de micelles, fibrilles ou cristaux liquides est explorée dans le but de concevoir des procédés de tri ionique en rupture. Au-delà du domaine purement nucléaire,

ces effets sélectifs sont aussi mis en œuvre dans différents procédés liés au recyclage de matières associées à la production d'énergie et plus généralement, dans les ambitions de développement durable et de transition énergétique, 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 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 programmes européens (ERC REE-Cycle, H2020 REFRAM) et internationaux comme les programmes Franco-Libanais SAFAR ou Franco-Indien CEFIPRA, les programmes de co-financement par la région, ainsi que la coordination du LABEX Chemisyst, celle du Lab'MUSE Chimie et celle du GDR SENA (Franco-Russe) sont à l'origine des projets de recherche commun avec CEA/DES, CEA/DRF, 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, ORANO, 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).



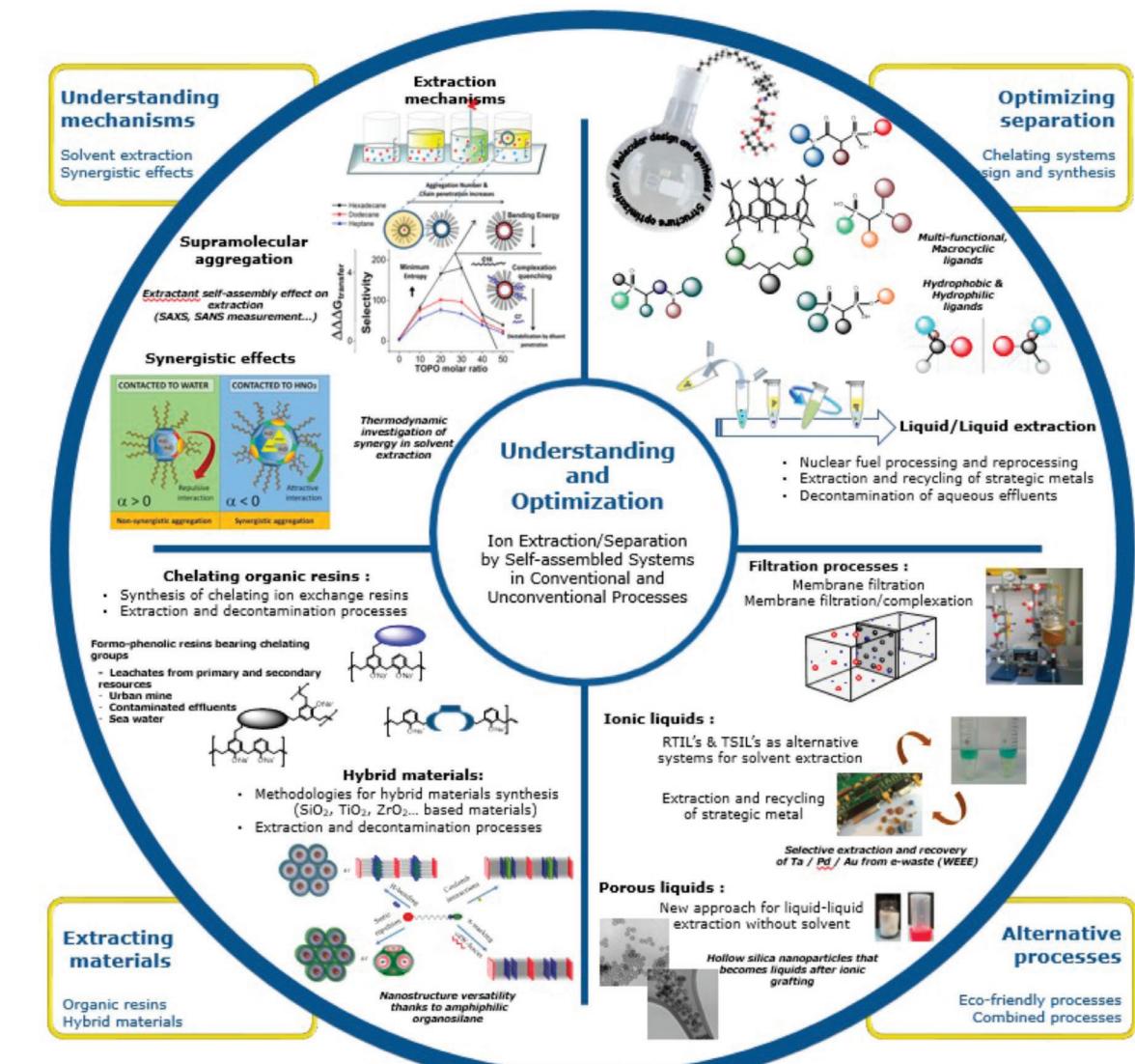
The group «Ion Separation by Self-assembled Molecular Systems» (LTSM) is today composed of 6 permanent staff, Guilhem Arrachart, Lecturer UM (09/2009), Sandrine Dourdain, Engineer CEA/DRF (07/2010), Beatrice Baus-Lagarde, Technician CEA/DEN (04/2016), Fabrice Giusti, CNRS Research Engineer (07/2018), Thomas Zemb, CEA/DRF Engineer and INSTN Professor (01/2019) and Stéphane Pellet-Rostaing, CNRS Research Director (01/2009). The main strategic lines of research developed at LTSM are mainly integrated into the axes «Innovation for extraction and recycling», and in close connection with the axes «Methodologies and theories in separation chemistry» and «Optimization of the life cycle of materials for energy».

The group values the complementary nature of its skills in synthetic chemistry, analytical chemistry and nanoscience implementing separation-recycling processes via chelating systems for the extraction and purification of metal cations. These molecular systems are implemented in both conventional (liquid/liquid, solid/liquid) and less conventional processes (membranes, non conventional solvents) with an orientation towards understanding the mechanisms governing separation. The two thousand publications per year dealing with liquid-liquid extraction are all within the framework of organometallic chemistry, supramolecular chemistry or the physical chemistry of self-assembled systems. The LTSM is developing an «ienaic» general view of free transfer energies: ienaic is a «nanosciences» view of classical electrochemistry, without an external field but which takes into account weak interactions beyond the first neighbor. The «ienaic» approach allows the design and synthesis of original specific extractants (molecular tweezers, macrocycles, resins) as well as the study of the associated mechanisms governing affinity and selectivity, which can be the subject of quantitative predictions without non-measurable parameters. This allows the synthesis and implementation of original and specific extracting agents (molecular tweezers, macrocycles, resins) as well as the study of associated mechanisms which govern affinity and selectivity, in particular by taking into account supramolecular cooperative phenomena. The opportunity of enhancing complexation by the self-association of complexing agents in the form of micelles, fibrils or liquid crystals is investigated with the aim of designing disruptive ion separation processes. Beyond the purely nuclear field, these selective effects are studied and implemented in various processes linked to the recycling of materials, associated with energy production and more generally, in the ambitions of sustainable development and energy transition, for example in decontamination or for the selective recycling of strategic metals.

The LTSM is involved in a “colloidal” approach – the triple point where physics, chemistry and technology meet- via a cognitive approach linked to the core orientations of the Alliance ANCRE and SNRI (today ‘Europe 2020 Strategy’) in the framework of renewable energy and circular economy. This covers the current and future nuclear fuel cycle (upstream and downstream) as well as 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 colla-

borations (Morphosis, ADIONICS), through ANR (CD2I), by Europe (ERA-MIN), European program (ERC REE-Round, H2020 REFRAM), the Franco-Lebanese “SAFAR” or French-Indian CEFIPRA programs, as well as the coordination of the LABEX Chemisyst and the Lab'MUSE CHIMIE and that of the GDR SENA (Franco-Russian) are at the origin of the joint research projects with CEA/DES, CEA/DRF, Montpellier University (ICGM, IEM), Savoie University (LCME), Lorraine University (IJL), Lyon University (ESRD), Lebanese University (Beirut), Regensburg University, ICPE (Moscow), Argonne (USA), CNEA (Argentina), TND, AREVA, Morphosis, Chemec Oy. Alongside the research, LTSM performs service contracts (synthesis, analysis and characterization, expertises ...) to the CEA/DES and other industrial (VEOLIA, ONET-Technology, St Gobain, Cis-Bio).



4/ LABORATOIRE DE SONOCHIMIE EN FLUIDES COMPLEXES (LSFC)

Au 1^{er} décembre 2022 l'équipe est composée de 4 permanents:

- 1 directeur de recherche CNRS responsable d'équipe (Dr. Sergueï Nikitenko)
- 1 ingénieur-chercheur DR CEA/DES (Dr. Rachel Pflieger)
- 1 chargé de recherche CR-CNRS (Dr. Tony Chave)
- 1 ingénieur-chercheur CEA/DES (Dr. Matthieu Virot)

Et sur la période 2019-2022 de non-permanents:

Postdoctorant :

Cyril Micheau (projet bottom-up CEA, 2019-20): Etude des colloïdes de plutonium.

CDD :

Noura Sleiman (IRT-M2P collaboration ICSM-UTINAM, 2019-20) : Etude de HIFU.

Doctorants :

Lauréanne Parizot (PIA ANDRA « CADET », codirection ICSM – IJLRA, 2016-19): Etude de la cavitation par impact et par ultrasons pour la dégradation des composés organiques.

Laura Bonato (thèse CEA/DEN 2017-20): Réactivité d'oxydes d'actinides nanostructurés en vue de leur dissolution sous l'effet de la cavitation acoustique.

Sara El Hakim (thèse UM 2018-21): Réactions sonocatalytiques et photocatalytiques en présence de nanocatalyseurs innovants pour l'énergie et l'environnement.

Manon Cot-Auriol (thèse CEA codir CEA/DES/DMRC, 2019-23): Etude de la réactivité de colloïdes d'actinides et de leurs mécanismes de formation.

Sophie Herr (thèse CEA/DES collaboration DMRC, 2019-23): Apport de la cavitation acoustique dans le traitement des sols contaminés au Cs ou pollués aux métaux lourds.

Julien Margate (thèse CEA/DES 2021-24): Préparation, caractérisation structurale et réactivité de peroxydes d'actinides.

Rita Salameh (thèse Région Occitanie - CEA/DES, collaboration DMRC, 2022-25): Dépollution de terres modèles par lixiviation assistée par sonification.

David-William's Nzodom Djozing (thèse UM 2022-25) : Synthèse sonohydrothermale de nanomatériaux



L'objectif principal du laboratoire de sonochemistry dans les fluides complexes (LSFC) consiste à mener des études fondamentales sur les mécanismes des réactions sonochemistry (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 sonochemistry 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 microbulles 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 1010 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 ».



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 1010 K·s⁻¹. Our recent studies revealed the formation of a non-equilibrium 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:

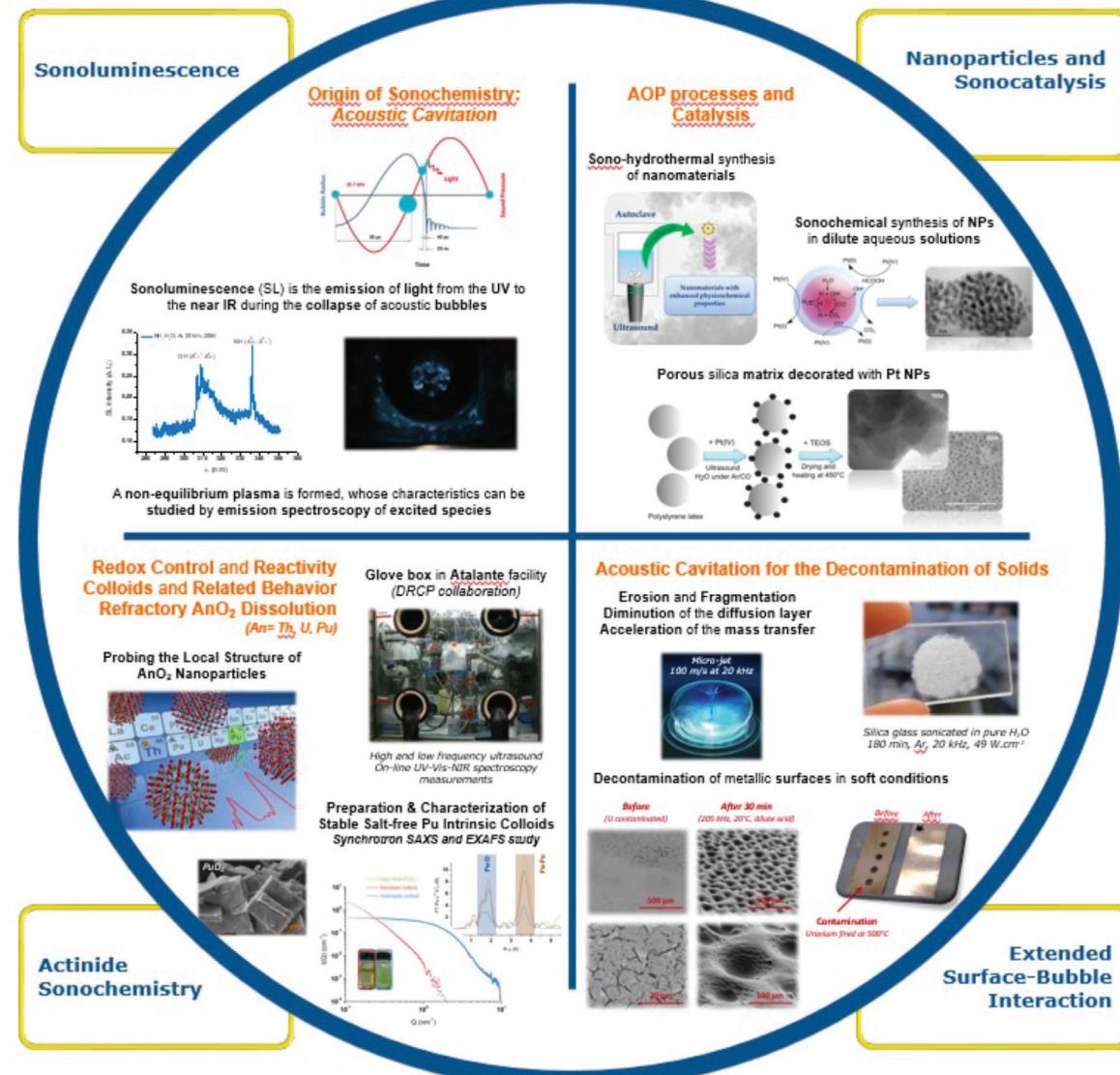
- Multibubble sonoluminescence
- Sonochemical reactivity at solid-liquid interfaces
- Sonochemical synthesis of nanomaterials and sonocatalysis
- Sonochemistry of actinides

Les thématiques du LSFC:

- Spectroscopie de sonoluminescence
- Réactivité sonochemistry à l'interface solide-liquide
- Synthèse sonochemistry de nanomatériaux et sonocatalyse
- Sonochemistry des actinides

Projets (collaborations)

- 2019-23 LINA Projet Région Occitanie
- 2020 Projet PEPS Cellule Energie CNRS (ICSM-IEM)
- 2016-19, 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 ; UTINAM, Besançon ; Institut Jean Lamour, Nancy ; Université de Melbourne, Australie)
- Dissolution sonochemistry des oxydes d'actinides (CEA/DES)
- Colloïdes de plutonium(IV) (CEA/DES ; JRC Karlsruhe Allemagne ; ESRF Grenoble ; 2015-2016 projet TALISMAN, 2018-19 projet Bottom-up SONISCOP)
- 2018-19, Synthèse sonochemistry de nanoparticules pour les applications biomédicales (TORSKAL)
- 2018-19, Dispersion ultrasonore de fibres naturelles (APM FORENSIA)
- 2022 – 2027, PEPR ECOCHEM



5/ NANOMATERIALS FOR ENERGY AND RECYCLING PROCESSES

Au 1^{er} décembre 2022 l'équipe est composée de 4 permanents:

- 1 Directeur de Recherche CEA/DES responsable d'équipe (Dr. Xavier Deschanel)
- 1 Ingénieur-chercheur CEA/DES (Dr. Jérémie Causse)
- 1 Enseignant-chercheur ENSCM (Dr. Guillaume Toquer)
- 1 Ingénieur d'étude UM (Cyrielle Rey)

Et sur la période 2019-2022 de non-permanents:

Post-doctorants :

- Singaravelu Chandra Mohan (CEA/DES, 2019, puis PTC Nanoreval, 2020-21, puis dispositif MAGELLAN 2022) : EXCIDOTS
- Hassan Khoder (Fondation maison de la chimie, 2020-22) : Etude de la dynamique de l'eau au sein de solutions aqueuses confinées dans des matériaux modèles à base de silice.
- Baptiste Russo (CNRS, 2020-22) : Projet Valorisation ABRIceaux.
- Clémentine Mansas (ANR AUTOMACT, 2021-22) : Functionalized mesoporous silicas - Application to waste conditioning.
- Jun Lin (ANR AUTOMACT, 2022) : Pu-doped mesoporous silica for the treatment of contaminated liquid effluents

Doctorants :

- Julien Monnier (CEA/DES, 2016-19): Synthèse d'oxydes d'actinides par combustion des nitrates.
- Martin Zijie Lu (CSC Chine, 2017-21): Study of colloidal sol-gel transition for the elaboration of actinides oxides materials with controlled and organized mesoporosity.
- Rémi Boubon (CEA/DES PIA ANDRA, 2017-20) : Etude de l'évolution de l'interface entre les géopolymères et l'alliage Mg-Zr.
- Baptiste Russo (Région/CEA-DES, 2017-20) : Matériaux nanocompoSites pOreux élaborés à partir de balle de riz de Camargue uTilisés comme sOrbants (RISOTO).
- Toni Tratnjek (CEA/DES, 2019-22) : Vers de nouveaux matériaux à porosité hiérarchisée pour la capture de produits de fission (Sr, Cs).
- Florian Didier (UM, 2019-22) : Dépôt électrophorétique de nanoparticules pour des absorbeurs solaires photo-thermiques.



Jun Lin (CEA/DRF, 2018-21) : Comportement des silices mésoporeuses sous irradiation par des ions de haute énergie.

Anna Hautecouverture (CEA/DES, 2020-23) : Synthèse de solution solide d'oxydes d'actinides par combustion en solution.

Ryan Roch (CEA focus DEM, 2021-24) : Développement de capteurs intégrant des carbon-dots pour la détection de rayonnement ionisant.

Pierre De Laharpe (CEA/DES, 2022-25) : Auto-réparation des gels d'altération des verres nucléaires sous irradiation

Apprentis :

Anna Coste (Licence Pro, CNRS, Coll. L2IA, 2019-20) : Synthèse et caractérisation par spectroscopie infrarouge de la silice SBA-15.

Luca Briscese (Licence Pro, CNRS, 2019-20) : Synthèse et étude de silices mésoporeuses fonctionnalisées pour la sorption et le confinement de radionucléides.

Freddy Raffo (Licence PRO, CEA, 2022-23) : Matériaux sitinakite pour la capture du strontium

CDD :

Thomas Bedos-Colombeau (PTC Mosac, 2021) : Modélisation de la stabilité d'oxydes mixtes d'actinides sous-stoechiométriques



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 2017-2020 sont résumées dans les pages suivantes et peuvent s'inscrire dans les 3 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)
- Nanostructuration et optimisation d'une propriété d'usage (Décontamination/dépollution d'effluents, sélectivité optique, révélation de radioactivité alpha/béta....)
- Comportement des nanomatériaux sous irradiation

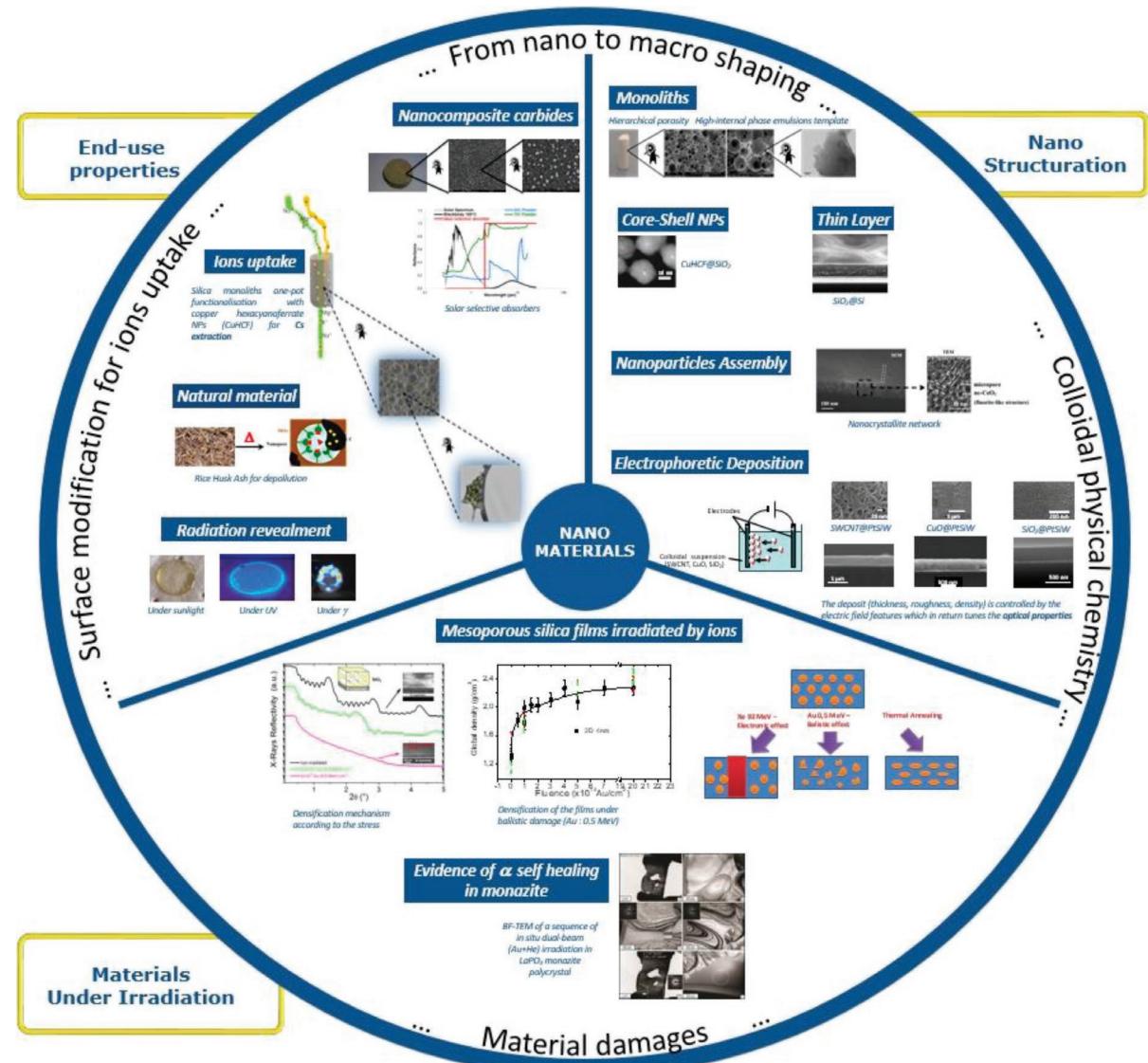
This team (LNER) presents strong scientific, technical as well as teaching skills to meet challenges arising from research on nanomaterials for low-carbon energy. The common thread of all the LNER research topics is the development of structured materials at different scales, with the aim of understanding 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 hierar-

chical 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 2017-2020 are summarised in the following pages and can be divided in 3 main themes:

- Nanostructured materials synthetic routes: From precursor (colloid, solution, emulsion...) to the final material (powder, thin film, bulk)
- Nanostructuring and optimization of an end user property (Decontamination / depollution of effluents, optical selectivity, alpha / beta radioactivity revelation, etc.)
- Radiation damage in nanomaterials



6/ EVOLVING INTERFACES IN MATERIALS

Au 1^{er} décembre 2022 l'équipe est composée de 4 permanents :

- 1 Professeur des Universités, responsable d'équipe (Pr. Nicolas Dacheux)
- 1 Directeur de Recherche CNRS (Dr. Nicolas Clavier)
- 1 Chercheur CEA (Dr. Stéphanie Szenknect)
- 1 Maître de Conférences (Dr. Laurent Claparède)

Et sur la période 2019-2022 de 23 non-permanents :

Post-Doctorants :

- Dr. Delphia Alby (CNRS ICSM/Amphos/Standford/SKB, 2018-2019) : Coffinitization of UO₂ pellets in conditions representative of geologic disposal of spent nuclear fuel.
- Dr. Ilyes Ben Kacem (Labex Chemisyst, 2018-2019) : Suivi de l'évolution d'interfaces solide-liquide en cours de dissolution par analyse 3D à l'échelle microscopique par MEB.
- Dr. Mohammed Ruwaid Rafiuddin (ANR Xmas, 2018-2020) : La xénotime pour le conditionnement et stockage des actinides.

CDD :

- Eddie Anzalone (IE CNRS, projet CEA, 2020-2021) : Synthèse de phases minérales uranifères.
- Lara Di Mascio (IE CNRS, projet CEA, 2020-2021) : Conversion hydrothermale d'oxalates d'actinides.
- Dr Paul-Henri Imbert (IR CNRS, projet EJP EURAD, 2020-2022) : Lixivation d'échantillons frittés de UO₂ contenant des produits de fission en conditions d'entreposage direct.
- Morgan Zunino (IE CNRS, projet H2020 GENIORS, 2018-2020) : Synthèse et frittage d'oxydes mixtes à base d'uranium et d'éléments lanthanides et étude de leur dissolution en conditions de retraitement.
- Thomas Colombeau-Bedos (IE CNRS, 2022) : Développement de sondes à oxygène pour le sodium à base d'électrolyte hafnium dopé.

Doctorants affectés à l'ICSM

- Thomas Barral, (thèse CEA, 2020-2023) : Etude multiparamétrique de la dissolution d'oxydes mixtes (U,Ln)O₂ en milieu nitrique : impact de la composition et de la microstructure.
- Sofian Benarib, (thèse CEA, 2020-2023) : Apport des méthodes hydrothermales pour la préparation et le frittage direct d'oxydes hydratés d'uranium(IV) et de cérium.
- Thomas Dalger (thèse CEA, coll. DMRC, 2016-2019) : Rôle de l'acide nitreux sur la dissolution des oxydes à base d'uranium (IV) : Mécanisme et suivi operando de l'interface solide/solution.
- Mohammad Husainy (thèse CEA, 2021-2024) : Spéciation du molybdène dans UO₂ : impact sur la cinétique de dissolution en conditions de retraitement.
- Thibault Kaczmarek (thèse CEA, coll. DMRC, 2018-2021) : Impact des éléments platinoïdes et du molybdène dans les mécanismes de dissolution du dioxyde d'uranium.
- Jérémie Manaud (thèse ENSCM, coll. LHYS, 2017-2020) : Conversion hydrothermale d'oxalates d'actinides tétravalents : de la synthèse au frittage des poudres d'oxydes.
- Malvina Massonnet (thèse CEA, coll. DMRC, 2018-2021) : Impact de la méthode de préparation et des conditions de frittage sur les mécanismes de dissolution des oxydes mixtes (U,Ce)O₂.
- Théo Montaigne (thèse CEA, coll. DE2D, 2019-2022) : Mécanismes d'altération des combustibles MOX en conditions de stockage géologique.
- Danwen Qin (thèse CSC, 2016-2020) : Incorporation of tetravalent actinides in monazite-type ceramics : synthesis, sintering and long-term behavior.
- Alison Roche (thèse UM, 2020-2023) : Incorporation d'actinides tétravalents au sein de céramiques de structure monazitique : synthèse, frittage et comportement à long-terme.
- Victor Trillaud (thèse CEA, coll. L2ME, 2016-2019)) : Des systèmes simplifiés aux combustibles modèles : étude in situ du frittage d'oxydes d'actinides et de lanthanides.

Doctorants non affectés à l'ICSM

- Pierre Asplanato (thèse CEA, coll. CEA-DAM, 2019-2022) : Etude des mécanismes de formation par procédé hydrothermal et d'altération dans différents milieux de particules de référence d'oxydes d'actinides.
- Solène Bertolotto (thèse CEA, coll. DMRC, 2017-2020) : Etude de la réactivité d'échantillons monocristallins de UO₂ vis-à-vis des processus de dissolution en milieu acide nitrique.
- Claire Canas (thèse CEA, coll DTN, 2022-2025) : Mécanismes de corrosion de céramiques électrolytes par le sodium liquide.
- Rafael Caprani (thèse CEA, coll. DMRC, HZDR, 2020-2023) : Etude du comportement des produits de fission et de leur impact sur la microstructure des combustibles (U,Pu)O_{2-x}.
- Marie-Margaux Désagulier (thèse CEA, coll. DMRC, JRC Karlsruhe, 2020-2023) : Elaboration et mesure de propriétés thermodynamiques et structurales d'oxydes mixtes (U,Pu)O_{2-x} à forte teneur en plutonium.
- Lénaïc Desfougères (thèse CEA, coll. DMRC, Mines St-Etienne, 2016-2020) : Compréhension et modélisation de la conversion thermique d'oxalates d'actinides.
- Célia Gillet (thèse CEA, coll. DE2D, 2018-2021) : Etudes des effets de synergie entre irradiation et altération par l'eau des verres nucléaires.
- Charles Hours (thèse CEA, coll. DMRC, 2019-2022) : Couplage de la simulation de l'évolution de la microstructure de matrices céramiques combustibles et de la modélisation de la dissolution en milieu nitrique.
- Lucas Muller (thèse CEA, coll DMRC, 2022-2025) : Conversion de mélanges U(VI)-Pu(IV) par le peroxyde d'hydrogène en conditions hydrothermales.
- Aurélien Perrot (thèse CEA, coll DE2D, 2021-2024) : Etude des produits d'altération à la surface des oxydes mixtes (U,Pu)O₂ par imagerie Raman et marquage isotopique.

Apprentis:

- Kevin Balme (L3 Pro, projet CEA, 2021-2022) : Etude de la stabilité de H₂O₂ en conditions environnementales.
- Wassima Zannouh (DUT2, projet AIEA, 2021-2022) : Synthèse et étude de la durabilité de particules d'oxydes d'uranium.
- Laura Schuppe (L3 Pro, projet CEA, 2022-2023) : Conversion hydrothermale de carboxylates d'actinides.
- Marie Tronyo (L3 Pro, projet AIEA, 2022-2023) : Synthèse de microparticules d'oxydes mixtes à base d'uranium et étude de leur stockage sous forme de suspension.



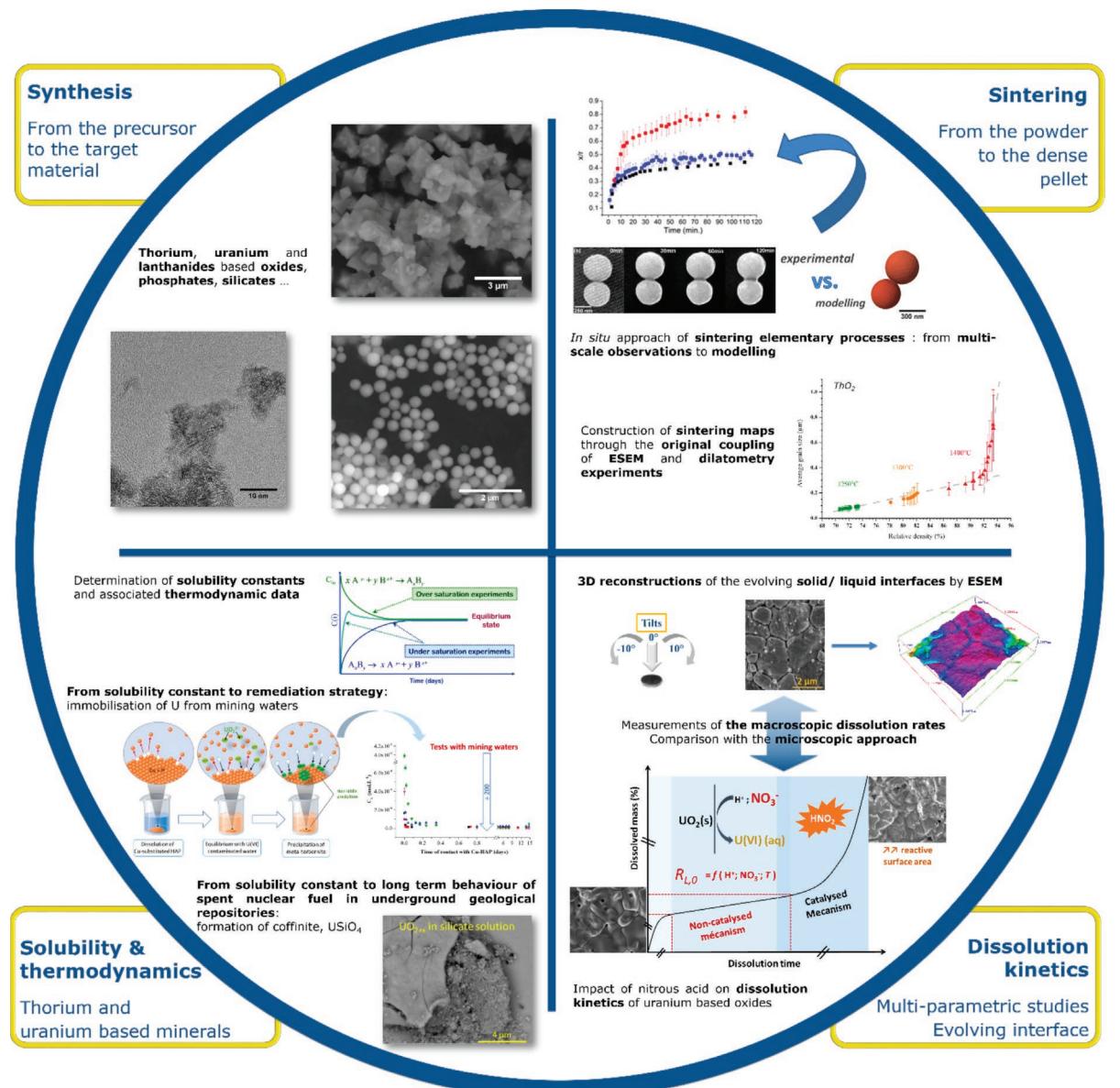


Fig. 1 Représentation de l'approche développée pour étudier les interfaces de matériaux en évolution

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 ou d'altération (lixiviation) sous contraintes (Figure 1).

Les expérimentations relatives aux interfaces solide/solide s'inscrivent dans l'étude du frittage

à travers la synthèse de poudres aux propriétés optimisées puis l'investigation des 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 qui étaient accessibles auparavant 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. L'étude de l'évolution des interfaces solide/liquide vise 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. La démarche expérimentale développée au LIME s'applique aux matériaux pour l'amont comme pour l'aval du cycle électronucléaire et doit permettre à terme leur optimisation.

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 ($U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_2$, $U_{1-x}Nd_xO_{2-y}$, $Th_{1-x}Y_xO_{2-y}$, ...) en privilégiant l'usage de précurseurs dont la réactivité dans le processus de frittage est améliorée par rapport aux oxydes préparés à haute température. Dans ce cadre, l'utilisation de méthodes de synthèse par voie humide, généralement favorables à l'amélioration de la distribution cationique au sein du solide, a également permis d'étendre le domaine d'existence de certaines solutions solides. Un effort particulier a porté sur la conversion de différents composés moléculaires d'actinides en conditions hydrothermales conduisant à la précipitation directe d'oxydes hydratés en solution (Thèses de Victor Trillaud, 2016-2019, de Jérémie Manaud, 2017-2020, de Sofian Benarib, 2020-2023 et de Lucas Muller, 2022-2025, projet H2020 Geniors). Ces travaux ont permis de préparer des composés de morphologie et de stœchiométrie en oxygène contrôlées et présentant de faibles teneurs en impuretés, qui ont conduit à poursuivre le développement de ce type de procédés dans une optique d'application industrielle (coll. ORANO – DMRC, CDD Lara Di Mascio 2020-2021). La maîtrise de la morphologie des poudres d'oxydes nous a également conduits à envisager la préparation d'échantillons de composition, d'isotopie et de taille contrôlées pouvant être utilisés comme matériaux de référence dans le cadre du contrôle des garanties nucléaires internationales opéré par l'AIEA (Thèse de Pierre Asplanato, 2019-2022). En outre, lorsque des précurseurs moléculaires ont été obtenus, leur conversion en oxyde a été examinée à travers le couplage de plusieurs techniques (diffraction, analyses thermogravimétriques, microscopiques et spectroscopiques). Par ce biais, les intermédiaires réactionnels successivement formés lors de la conversion ainsi que les transformations

chimiques et morphologiques de l'échantillon ont été identifiés (thèse ICSM-DMRC-EMSE de Lénaïc Desfougères, 2016-2020).

Sur la base de ces résultats, le frittage des oxydes mixtes $U_{1-x}Th_xO_2$, $U_{1-x}Ce_xO_2$, $U_{1-x}Nd_xO_{2-y}$ et $Th_{1-x}Y_xO_{2-y}$ a été étudié de manière à identifier les propriétés d'influence de la poudre initiale (surface spécifique, homogénéité, présence de carbone résiduel, ...). L'histoire d'un solide, c'est-à-dire le lien entre le précurseur utilisé, sa conversion en oxyde, et la microstructure finale du compact densifié a ainsi pu être établie (thèses de Jérémie Manaud, 2017-2020 et de Malvina Massonet, 2018-2021), par exemple au moyen de cartes de frittage permettant *in fine* de contrôler la microstructure des matériaux céramiques considérés (thèses ICSM-DTN de Yanis Cherkaski, 2015-2018 et de Claire Canas, 2022-2025).

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 de la thèse de Victor Trillaud (ICSM, 2016-2019) sur des composés modèles de morphologie sphérique contrôlée ont conduit à l'observation *in situ* par microscopies électroniques de la première étape du frittage (élaboration des ponts) des oxydes d'uranium et à l'acquisition de données cinétiques et thermodynamiques originales.

L'étude des interfaces solide/liquide s'inscrit principalement dans un contexte de retraitement du combustible nucléaire usé ou de stockage de matrices de conditionnement spécifiques des actinides (thèse de David Qin, China Scholarship Council, 2016-2020 ; post-doctorat de Mohammad Ruwaid Rafiuddin ANR X-MAS, 2018-2020). Plus récemment, ce cadre s'est également étendu au stockage direct de combustibles usés en formation géologique profonde (post-doctorat de Delphia Alby, projet SKB/Amphos21/Univ. Standford/ICSM, 2018-2019 ; thèse de Théo Montaigne, ICSM/DE2D, 2019-2022 en collaboration avec EDF et l'ANDRA) ou à leur entreposage en piscine sur de longues durées (CDD de Paul-Henri Imbert, EJP EURAD, 2020-2022, thèse d'Aurélien Perrot, ICSM/DE2D, 2021-2024 en collaboration avec EDF).

Concernant les études menées en conditions de retraitement, des tests multiparamétriques de dis-

solution ont été mis en place. Pour les solutions solides $U_{1-x}Th_xO_2$, 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 a été mise en évidence à la fois à l'échelle macroscopique par la variation des paramètres décrivant la cinétique (ordres partiels par rapport à l'activité en proton, énergie d'activation apparente) et à l'échelle microscopique par l'évolution de l'interface solide/solution suivie par MEBE *operando*. L'impact de la distribution cationique au sein d'oxydes mixtes $U_{1-x}Th_xO_2$ de composition hétérogène sur le comportement à la dissolution a également été mis en évidence à différentes échelles d'observation (thèse de Charles Hours, DMRC/ICSM/DEC, 2019-2022, en collaboration avec ORANO). Ainsi, des liens étroits ont été démontrés entre la microstructure du matériau et sa résistance à l'altération ou à la corrosion aqueuse. En outre, le rôle potentiellement catalytique d'espèces produites lors de la dissolution de ces solutions-solides en milieu acide nitrique (dont HNO_3) a été étudié (thèse de Thomas Dalger, ICSM/DMRC, 2016-2019). Parallèlement, le passage d'un régime de dissolution non-catalysé à un régime catalysé a été observé pour des échantillons monocristallins de UO_2 (Thèse de Solène Bertolotto, DMRC/ICSM, 2017-2020) permettant de s'affranchir de toute contribution microstructurale. Des observations menées à l'échelle micro et nanoscopiques ont permis de démontrer le rôle prépondérant des défauts structuraux dans l'initiation de la dissolution en milieu acide nitrique et la production d'espèces catalytiques azotées. Enfin, l'existence de faciès de dissolution spécifiques à l'orientation de la face cristallographique exposée à la solution a été mise en évidence.

Des études antérieures réalisées au LIME avaient montré que la présence d'éléments lanthanide trivalents au sein de la structure fluorine ($Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Nd_xO_{2-x/2}$) affectait significativement la durabilité chimique des solides en raison de la fragilisation du réseau cristallin consécutive à la formation des lacunes en oxygène. Le comportement des solutions solides $U_{1-x}Ce_xO_{2-x/2}$ et $U_{1-x}Ln_xO_{2-y}$ semble différer des oxydes à base de Th ou de Ce étudiés auparavant, notamment en raison de modifications de la spéciation redox de l'uranium induite par l'incorporation d'éléments trivalents (thèses de Malvina Massonet, ICSM/DMRC, 2018-2021 et de Thomas Barral, 2020-2023, projet H2020 Geniors, 2017-2021). De manière analogue, la présence d'éléments platinoïdes et de

molybdène au sein de UO_2 a été étudiée dans le cadre des thèses de Thibault Kaczmarek (ICSM/DMRC, 2018-2021) et de Mohammad Husainy (ICSM/DMRC, 2021-2024). Ces études ont souligné l'existence de phénomènes catalytiques significatifs, liés à la présence de ces éléments au sein du solide.

Un dernier aspect des travaux menés au sein du LIME concerne la caractérisation de phases uranifères ou thorifères d'intérêt aussi bien pour l'amont que pour l'aval du cycle du combustible. Dans ce cadre, la préparation de plusieurs phases uranifères est actuellement réalisée en partenariat avec ORANO et le CEA de Saclay en vue de constituer une banque de données associée à la réponse de ces phases par SLRT (CDD Eddie Anzalone, 2020-2021). Parallèlement, les phases silicatées à base de thorium et d'uranium (IV) font l'objet d'une collaboration internationale (Prof. A. Navrotsky, UC-Davis et Arizona State University, Prof. R.C. Ewing, Université de Stanford et X. Guo, Washington State University). Les études ont d'abord porté sur le système thorium – uranium – silicate puis sur la coffinite $USiO_4$, la stetindite $CeSiO_4$ et plusieurs silicates d'actinides (Th, Np, Pu) préparés en conditions hydrothermales. Les données thermodynamiques relatives à la solubilité de ces phases (K_s° , Δ_RH° , Δ_RG° , Δ_RS°) ont également été acquises aussi bien lors des tests de dissolution que par microcalorimétrie. Plusieurs phases phosphatées ont également été étudiées, dont le rhabdophane, la monazite et le xenotime (en tant que matrices de confinement spécifique de certains radionucléides). Initialement mené sur des phases purement lanthanidiques, ce travail a logiquement évolué vers l'incorporation d'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). Ainsi, des solutions solides incorporant du thorium ont été préparées, pour la première fois par voie humide, dans le cadre de la thèse de David Qin (China Scholarship Council, 2016-2020) puis ont été caractérisées afin d'aboutir à la détermination des données thermodynamiques associées (K_s° , Δ_RH° , Δ_RG° , Δ_RS°). Ce travail est actuellement poursuivi sur des phases incorporant de l'uranium dans le cadre de la thèse d'Alison Roche (thèse UM, 2020-2023). Une étude similaire a été menée en parallèle sur le système xénotime/thorite dans le cadre de l'ANR X-MAS (Post-Doctorat de Mohammed Ruwaïd Rafiuddin, 2018-2020).



The 'Evolving Interfaces in Materials' group (LIME) aims to describe and understand the various phenomena occurring at the solid/solid and solid/liquid interfaces in the field of the (current and future) nuclear fuel cycles. They are mainly related to the fabrication (powder synthesis and sintering) 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 preparation of inorganic powder samples with tailored properties (morphology, size, composition, ...) and the study of their sintering. 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 collect original data usually only accessible through modeling. Sintering maps (which represent the variation of the grain size vs. the densification rate) were also obtained, which resulted in an improved monitoring of the final microstructure of ceramics. 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 as models for nuclear fuels ($Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_{2-y}$, $U_{1-x}Nd_xO_{2-y}$, $Th_{1-x}Nd_xO_{2-x/2}$, ...). Wet chemistry routes based on the initial precipitation of crystallized precursors were generally considered for the synthesis in order to improve the reactivity and the sintering capability of the prepared powders, and to homogenize the cationic distribution. The thermal conversion leading to the final oxide form was then examined using various techniques (diffraction, spectroscopy, microscopy, ...), which allowed identifying the reaction intermediates as well as pointing out the chemical and morphological transformations of the samples. 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, especially using hydrothermal conditions (Ph.D. of Victor Trillaud, 2016-2019, Jérémie Manaud, 2017-2020, Sofian Benarib, 2020-2023 and Lucas Muller, 2022-2025, H2020 Geniors project). These studies led to the preparation of actinides oxides with controlled morphology and O/M stoichiometry, and low impurities contents, which

pave the way to the application of such processes to the fabrication of real fuel materials (coll. ORANO – DMRC, CDD Lara Di Mascio 2020-2021). Mastering the morphology of the oxide samples also led us to undertake the preparation of reference materials with controlled composition, size and isotropy, that could be used in the frame of the nuclear safeguards control operated by IAEA (Ph.D. of Pierre Asplanato, 2019-2022). Using this large set of samples, the sintering of $Th_{1-x}U_xO_2$, $Th_{1-x}Ce_xO_2$, $U_{1-x}Ce_xO_{2-y}$, $U_{1-x}Nd_xO_{2-y}$ and $Th_{1-x}YxO_{2-x/2}$ 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. 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 $Th_{1-x}YxO_{2-x/2}$ solid solutions (coll. ICSM-DTN, Ph.D. of Yanis Cherkaski, 2015-2018 and Claire Canas, 2022-2025). Also, *in situ* HT-ESEM and HR-HT-TEM observations undertaken in the frame of the Ph.D. work of Victor Trillaud led to the first experimental data concerning the kinetics and thermodynamics of the first step of UO_2 sintering (elaboration of necks between the grains).

The study of the solid/liquid interface mainly took place in the frame of spent fuel reprocessing and long-term storage of actinides waste forms (Ph.D. of David Qin, China Scholarship Council, 2016-2020 ; post-doctorate of Mohammed Ruwaïd Rafiuddin ANR X-MAS, 2018-2020). More recently, this scope was also extended to the direct storage of spent fuel in an underground repository (post-doctorate of Delphia Alby, projet SKB/Amphos21/Univ. Standford/ICSM, 2018-2019 ; Ph. D. of Théo Montaigne, ICSM/DE2D, 2019-2022) and to interim storage in nuclear pool (CDD of Paul-Henri Imbert, EJP EURAD, 2020-2022, Ph. D. of Aurélien Perrot, ICSM/DE2D, 2021-2024). Studies regarding the reprocessing of spent fuel were mainly based on multi-parametric dissolution tests. For $Th_{1-x}U_xO_2$ solid solutions, the modification of the driving dissolution mechanism (i.e. oxidation vs. surface reactions) as a function of the uranium content and the media acidity was evidenced both at the macroscopic and the microscopic scales, using *operando* ESEM observations. As such, links were established between the microstructure of the materials and their chemical durability (Ph. D. of Charles Hours, DMRC/ICSM, 2019-2022). Moreover, the catalytic role of chemical species produced during the disso-

lution of these samples in nitric media (including HNO_3) was studied (Ph.D. of Thomas Dalger, ICSM/DMRC, 2016-2019). In parallel, the transition from a catalyzed to non-catalyzed dissolution regime was observed for UO_2 single crystals, which allowed to avoid any bias coming from the microstructure (Ph. D. of Solène Bertolotto, DMRC/ICSM, 2017-2020). Micro- and nanoscale observations led to demonstrate the prevailing influence of point defects in the onset of dissolution, and to point out characteristic dissolution habits depending on the crystallographic orientation of the interface.

Previous works showed that the presence of lanthanide elements within the fluorite-type structure ($\text{Ce}_{1-x}\text{Nd}_x\text{O}_2$, $\text{Th}_{1-x}\text{Nd}_x\text{O}_2$) 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 comparison, the behavior of $\text{U}_{1-x}\text{Ce}_x\text{O}_{2-x/2}$ and $\text{U}_{1-x}\text{Ln}_x\text{O}_{2-x/2}$ solid solutions clearly differs, probably due to the modification of the uranium redox speciation provoked by the insertion of trivalent elements (Ph.D. of Malvina Massonet, ICSM – DMRC, 2018-2021 and Thomas Barral, 2020-2023, H2020 project Geniors, 2017-2021). In a similar way, the presence of platinum group metals and molybdenum within UO_2 was investigated (Ph. D. of Thibault Kaczmarek, ICSM/DMRC, 2018-2021 and Mohammad Husainy ICSM/DMRC, 2021-2024). Such experiments revealed the huge role of catalytic phenomena linked to the presence of PGM elements and molybdenum in the solid and in solution.

A last research topic deals with the characterization of U- and Th-bearing phases of interest for the front- and back-end of the nuclear fuel cycle. In this frame, a collaboration with ORANO and CEA Saclay aims to set up a spectroscopic database specifically linked with TRLFS spectra of uranium-based minerals. In parallel, 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, then were extended to stetindite (CeSiO_4) and several actinide silicates (Th, Np, Pu) prepared under hydrothermal conditions. Thermodynamic data of these silicate phases (K_s° , $\Delta_r^\circ \text{H}^\circ$, $\Delta_r^\circ \text{G}^\circ$, $\Delta_r^\circ \text{S}^\circ$) were collected, both from dissolution tests and calorimetry measurements. Determination of thermodynamic data was also undertaken for several phosphate-based compounds envisaged as host phases for actinides storage (including rhabdonite, monazite and xenotime).

The natural follow-up to this work then consists in the incorporation of tetravalent actinides through different coupled substitution, i.e. $2 \text{Ln}^{\text{III}} \leftrightarrow \text{An}^{\text{IV}}$ + M^{II} (monazite/cheralite solid solutions) or $\text{Ln}^{\text{III}} + \text{PO}_4 \leftrightarrow \text{An}^{\text{IV}} + \text{SiO}_4$ (monazite/huttonite solid solutions). Preparation of these samples was then achieved for the first time with $\text{An} = \text{Th}$ using a wet-chemistry route, while the synthesis of U-based samples is now under progress (in the frame of the Ph.D. of Alison Roche, 2021-2024). A similar study has also been developed on the xenotime/thorite system within the ANR X-MAS project (2018-2020).



7/ ETUDES DE LA MATIÈRE EN MODE ENVIRONNEMENTAL

Au 1^{er} décembre 2022, l'équipe est composée de 8 permanents:

- 1 ingénieur d'études CNRS responsable d'équipe (Dr Xavier Le Goff)
- 1 ingénieur de recherche CNRS (Dr. Renaud Podor)
- 1 ingénier-chercheur CEA/DES (Dr Diane Rebiscoul, mutation du LNER)
- 2 ingénieurs d'études CNRS (Sandra Maynadié, Joseph Lautru)
- 1 assistant-ingénieur CNRS (Guilhem Quintard, mutation NOEMI)
- 1 ingénieur CEA/DES (Henri-Pierre Brau)
- 1 ingénieur CEA/DRF (Michaël Odorico)

Et sur la période 2019-2022 de non-permanents:

Post-doctorants:

Ilyes Ben Kacem (Post-Doc. UM – Labex, 2018-19): Characterization of evolving solid/liquid interfaces during dissolution by 3D analysis at the microscopic scale by SEM.

Laëtitia Pinaud (projet PTC liqliqAFM, 2021-22): Réponse d'une interface liquide/liquide sous une pointe d'AFM.

CDD :

Helene Arena (prestation CEA, 2019)

Norma-Maria Pereira-Machado (CNRS, 2022-23)

Mélanie Taron (CNRS, 2022-2024)

Thésards:

Victor Trillaud (thèse CEA, 2016-19) : Premier stade du frittage du dioxyde d'uranium : une étude *in situ* par MEBE et MET à haute température.

Jérôme Mendonça (thèse CIFRE NewTEC Scientific à Nîmes, 2019-22) : Développement de micro-fourts haute température pour les Microscopes Electroniques à Balayage.

Apprentis:

Siham Hassak (M1-M2 instrumentation, 2020-22) : Reconstruction d'un microscope électronique à transmission



Le Laboratoire d'Etudes de la Matière en Mode Environnemental (L2ME) regroupe l'ensemble des techniques liées à la diffusion/diffraction et à la microscopie électronique. Cette combinaison de compétences et savoir-faire correspond à une volonté de coupler les informations microscopiques et macroscopiques obtenues par l'ensemble des techniques expérimentales disponibles au sein du L2ME.

Il est ainsi possible 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 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 supra-moléculaires 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, donne accès au suivi direct des mécanismes de rearrangement 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 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 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 in-

terfaces 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'IICSM. 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 caracté-

risation des matériaux via des environnements échantillons ou des programmes informatiques. 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. Le plugin SEraMic (intégré au logiciel ImageJ) permet l'analyse semi-automatique d'images acquises en microscopie électronique. L'équipe se tourne maintenant vers l'application de l'intelligence artificielle (apprentissage profond) pour l'analyse et le traitement d'images et de données. En parallèle, le projet de reconstruction d'un microscope électronique à transmission (MET) mené en interne à l'ICSM depuis plusieurs années est maintenant soutenu via un financement ANR LabCOM (NewTEM). La majorité de ces actions sont fortement appliquées et sont (ou seront) valorisées dans les années à venir aux travers de collaborations avec des acteurs économiques locaux, notamment avec la société NewTEC Scientific.



The Laboratory for the Study of Matter in Environmental Mode (L2ME) combines all the techniques related to scattering/diffraction and electronic microscopy. This combination of skills and know-how corresponds to a desire to couple microscopic and macroscopic information obtained by all the experimental techniques available within the L2ME. 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 charac-

terization 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.

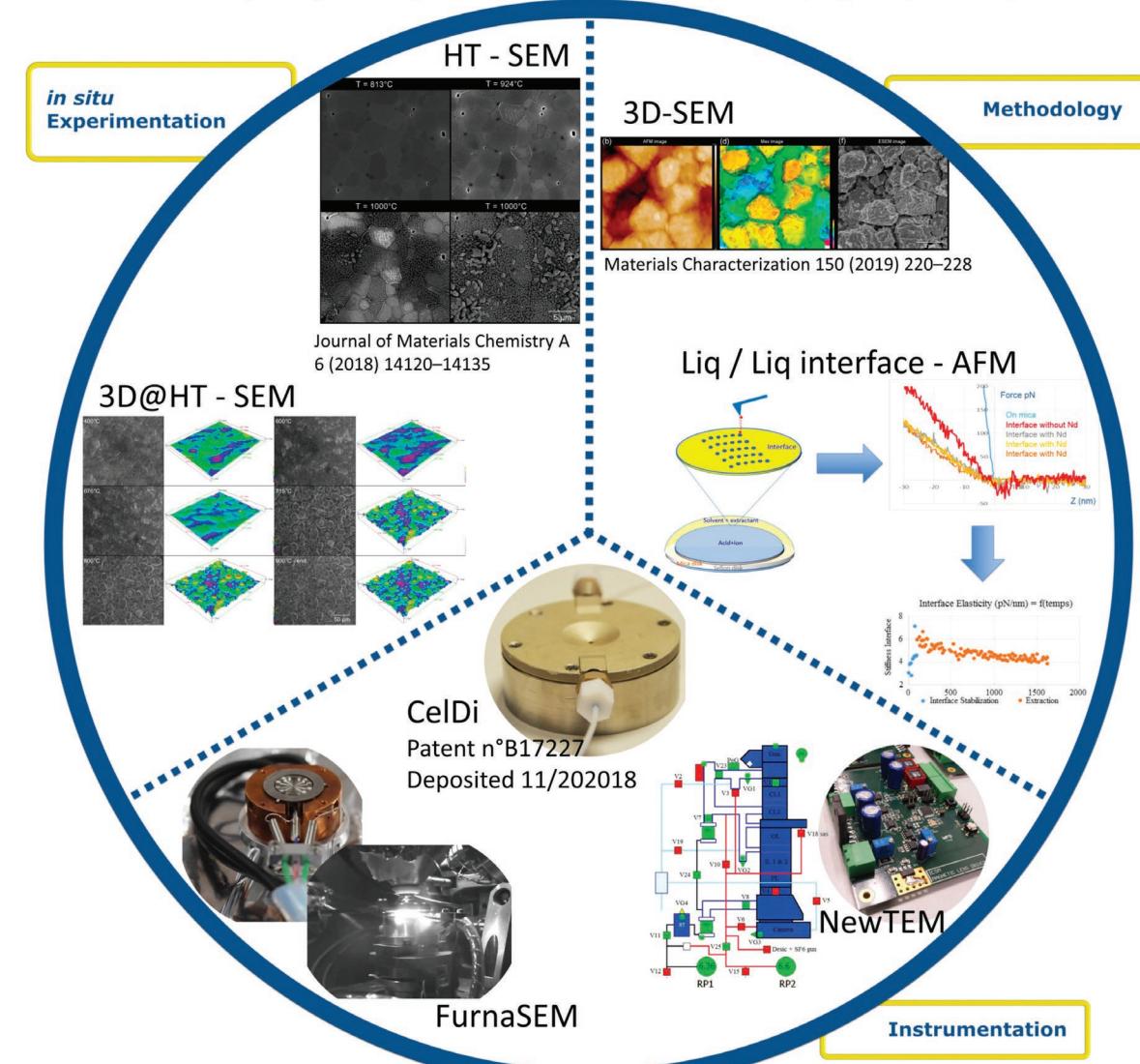
This approach is completed with the instrumental development of specific tools, based on the know-how of the lab team with the aim to answer specific research objectives. These developments can cover small tools (sample holders, etc), stages with dedicated applications or the complete refurbishing of 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 constraints 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 processes. 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 results deals with the development of specific tools for the characterization of materials (sample environments or computer programs). 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. The SEraMic plugin (integrated

into the ImageJ software) allows the semi-automatic analysis of images acquired by electron microscopy. The team is now turning to the application of machine learning (deep learning) for the analysis and processing of images and data. In parallel, the project aiming to the refurbishing of a TEM and fully funded by ICSM for several years, is now supported by ANR LabCOM funding (NewTEM). Most of these actions are highly applied and are (or will be) developed in the coming years thanks to collaborations with local economic players, in particular with the company NewTEC Scientific.

Instrumentation / capabilities: Environmental scanning electron microscope Quattro ESEM-FEG, TEM 200CX, Scanning electron microscope Vega3, 400 MHz NMR spectrometer, SEM/TEM Specimen preparation Lab, AFM Multimode 8, Small angle X-ray Scattering, D8 ADVANCE diffractometer (reflectivity, high temperature,...).



8/ MESOSCOPIC MODELLING AND THEORETICAL CHEMISTRY

L'équipe est constituée au 1^{er} novembre 2022 de :

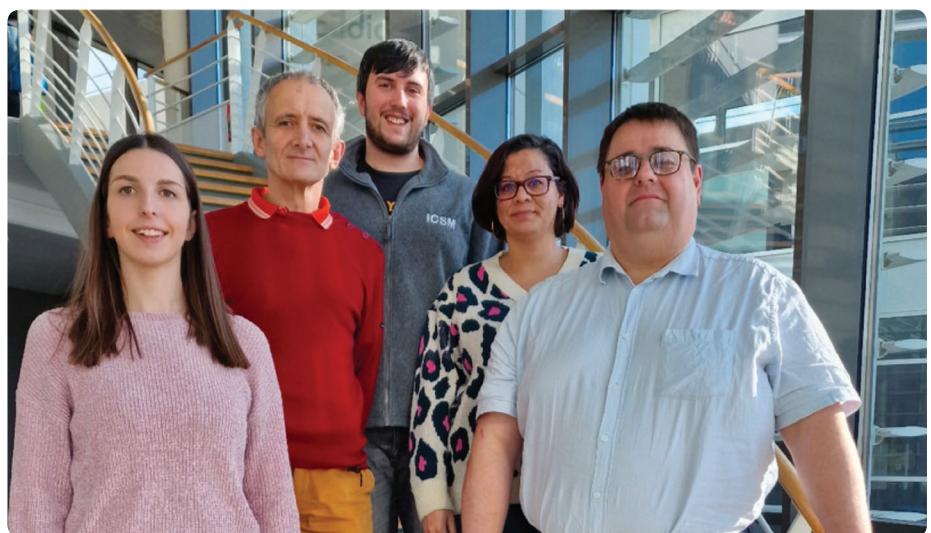
- 1 Professeur Université Montpellier, responsable d'équipe (Prof. Jean-François Dufrêche)
- 1 Chercheure CEA/DRF (Dr. Magali Duvail)
- 1 Chercheur-Ingénieur CEA/DES (Dr. Bertrand Siboulet)

Post-doctorants (2019-22) :

- Sébastien Le Crom (LABUM Université Montpellier, 2021-22) : Rationalisation par dynamique moléculaire des effets de structure dans les mécanismes d'extraction en milieu liquide ionique
- Yann Foucaud (CEA/DES, 2019-21) : Modélisation moléculaire de la SHG.

Doctorants (2019-22) :

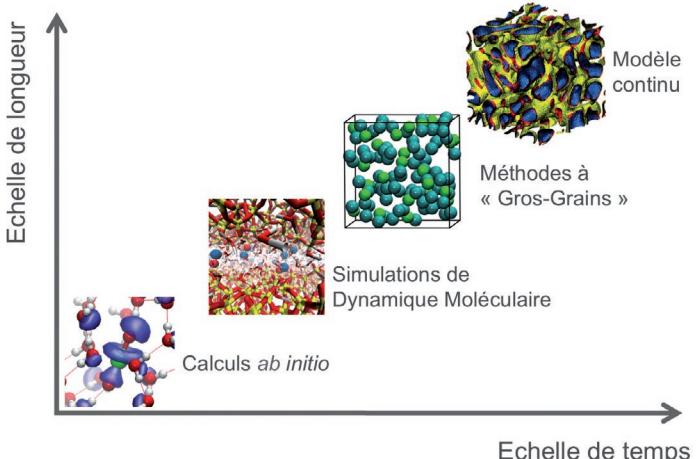
- Erwann Guillam (thèse CEA, coll. ISEC, 2022-) : Prédition moléculaire du transfert d'ions pour l'extraction
- Lara Žiberna (thèse CEA, coll. ISEC, 2022-) : Simulation de l'équilibre et du transport des ions aux interfaces liquide – liquide
- Thomas Colle (thèse Univ. Montpellier, ANR MULTISEPAR, 2020-22) : Modèle de microémulsion : Vers la prédition des procédés d'extraction liquide-liquide.
- Ludovic Jami (thèse Univ. Tours en collaboration avec ICSM, 2019-22) : Transport de molécules actives pour la communication entre insectes.
- Tristan Kunyu Wang (thèse Univ. Montpellier, 2019-22) : Simulation numérique pour les ions aux interfaces : corrélations ionique et dépollution des eaux.
- Marin Vatin (thèse CEA, coll. ISEC, 2018-21) : Modélisation multi-échelle de solutions organiques et systèmes interfaciaux pour l'extraction liquide-liquide.
- Lolita Hilaire (thèse CEA, coll. ISEC, 2018-21) : Modélisation de la coalescence : connecter les échelles - de l'approche déterministe à l'approche stochastique.
- Mathilde Coquil (thèse CEA, coll. ISEC, 2017-21) : Identification des contributions à l'origine de la sélectivité en extraction liquide/liquide.
- Amaury Coste (thèse Univ. Montpellier, ANR DYNAMISTE, 2016-19) : Modélisation moléculaire de solutions silicatées en milieux alcalins.
- Mario Spàdina (thèse CEA et ERC REE-Cycle, coll. Univ. Ljubljana, 2016-19) : Solvation et spécificité des ions en milieux complexes.
- Anne-Françoise de Guerny (thèse Labex CalSimLab à LJLL/UMPC, coll. ICSM, 2016-20) : Calcul mathématique des interactions faibles.



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 nano-échelles).

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 :

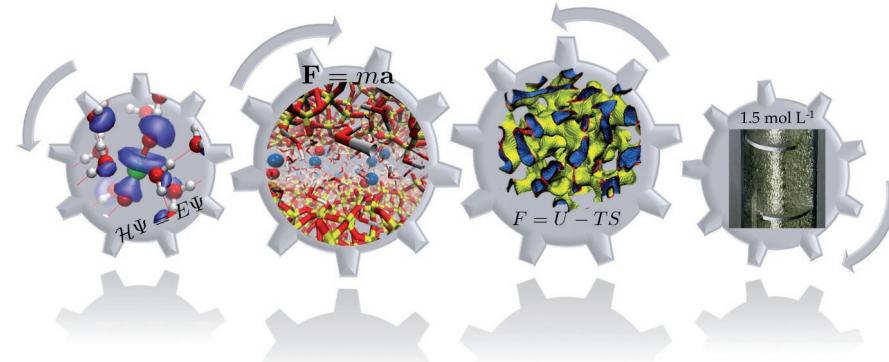
- Modélisation de l'extraction liquide-liquide. Une approche à gros grains permet de déterminer les propriétés thermodynamiques dans les différentes phases (aqueuse et organique). Cette méthode est peu à peu développée pour des systèmes de plus en plus complexes.
- Étude des milieux poreux, en particulier 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 explicits. 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 décou-

pler 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 et aussi une activité méthodologique propre.



The main goal of the modeling team is to study complex systems, particularly those involved in separation chemistry, from a multi-scale approach, with a particular focus on models at the intermediate scale (mesoscopic models or nanoscale).

The methodology is presented in the figure. The most fundamental description is that of quantum mechanics (ab initio calculations). It is capable of representing elementary events. It is particularly used to study complexation and can also be used to improve classical models. These can be studied by molecular dynamics to characterize the structure of the media, their equilibrium and transport properties, but only on rather small scales (a few nanometers and nano-seconds at most). Therefore, studies of complex media can only be conducted using intermediate scale methods («coarse-graining» models, continuous solvent theories, Brownian dynamics, integral equations, classical density functionals, mode coupling, interface theory, etc.) that are used (i) to describe the physical chemistry of the processes and (ii) to make the link with chemical engineering. The originality of the team stems from the fact that the scale transition is studied almost systematically. Most microscopic scales enable the improvement of the macroscopic models, not only by providing the values of physical parameters, but also by

directly improving the macroscopic fundamental equations.

Such a program is carried out in different contexts of separation chemistry and allows for the resolution of several open issues:

- Liquid-liquid extraction modeling. The thermodynamic quantities in the various phases (aqueous and organic solvent phases) can be calculated using a coarse-graining method. This method is being developed for increasingly complex systems.

- Porous Media, particularly those involved in separation (oxides, porous glasses, etc.). Here, the goal is to elicit as much information as possible from experiments while also characterizing the relevant underlying mechanisms. We also investigate clays for waste storage.

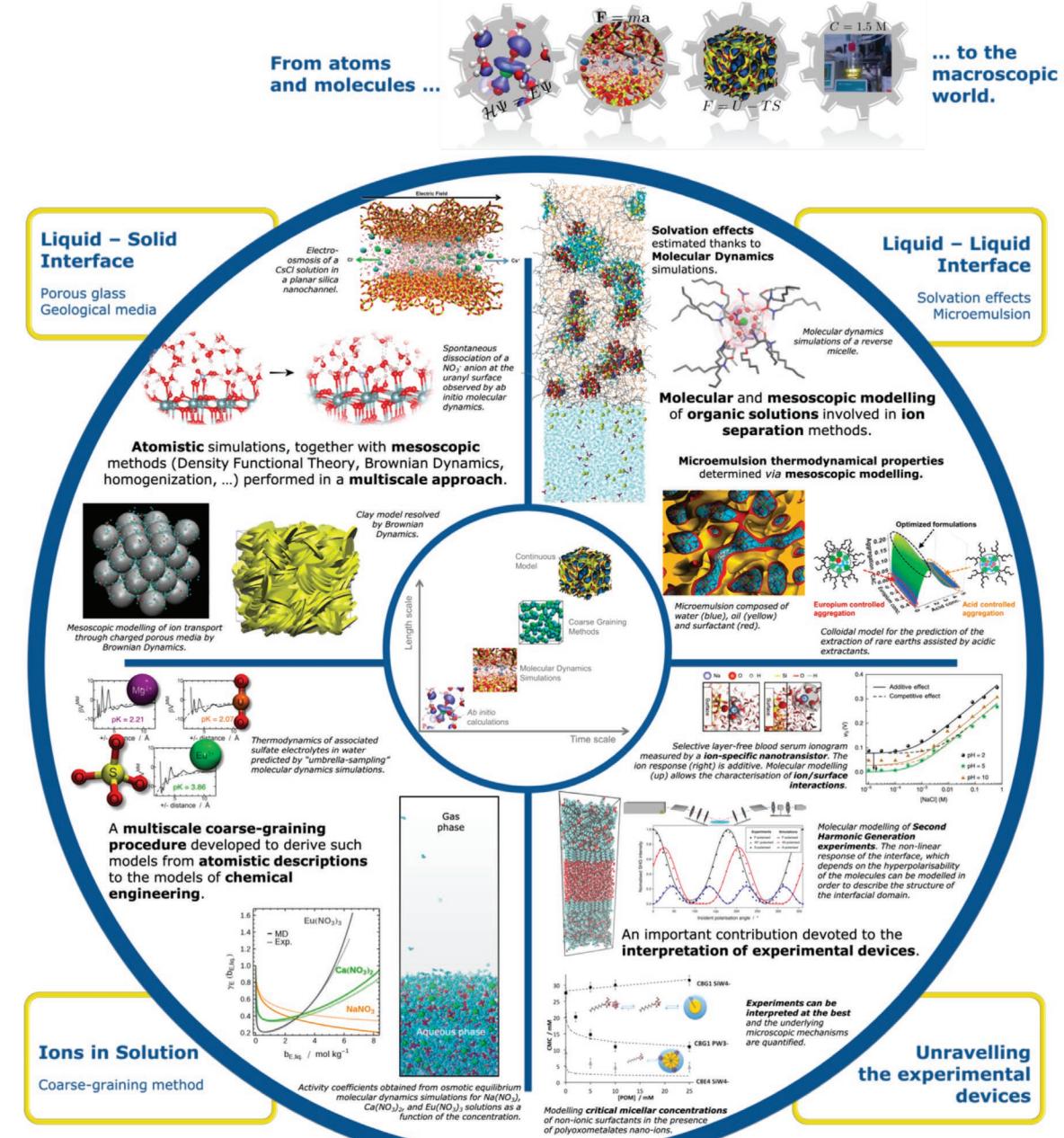
At the most fundamental level, we concentrate on electrolyte theory for transport and equilibrium properties. Some applications that have nothing to do with separation chemistry have been developed. In nanotechnologies, for example, the role of ionic noise has been studied in close connection with experiments involving one-electron transistors. Microemulsion models are also studied in order to model ternary phase diagrams.

These works have been performed in collaboration with experimentalists, particularly those of ICSM. The methods at the intermediate scales

can be validated by comparing them to the experimental results and molecular modeling results. The final idea would be to propose a global view of processes in which every mechanism is integrated into the most appropriate level of description, the link between the various models being explained. The fundamentals of statistical thermodynamics help us in understanding that such a project is at least a priori possible for the

equilibrium processes, but it is much more difficult for dynamical properties due to the need to uncouple the various time scales, which is not always possible.

Thus, the modeling group has activities that are directly related to the experimentalists at ICSM, as well as methodological activities on its own.





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 RECY- CLAGE

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



PRECIOUS METAL EXTRACTION, SEPARATION, RE-COVERY. THE PD CASE: FROM FUNDAMENTAL TO APPLIED RE-SEARCH

R. Mastretta, V. Lacanau, D. Bourgeois, D. Meyer - C. Contino-Pépin, F. Bonneté (Avignon Univ.) P. Wagner, M. Schmitt, F. Bihel (LIT, Strasbourg Univ.)

Palladium is a precious metal which is principally employed in autocatalysts. The increasing demand in palladium for this application combined with stable production has recently led to a sharp rise in palladium price as the market remains tight. Palladium price more than doubled over the last three years, and even, in January 2019, reached that of gold. Since then, palladium price regularly reaches record height, higher than 100 k€/kg (3000 \$/oz) in early March 2022. Palladium market is expected to go further in deficit and production from other secondary resources becomes a key to fulfil palladium needs. Supply from the so-called urban mine appears as a very attractive alternative to traditional mining, especially for Western countries, poorly endowed with natural mineral ores.

In this context and based on more fundamental studies already published, the LHys team has developed different hydrometallurgical approaches to recovering Pd from various wastes.^{1,2} We were able to lay the foundations for various process diagrams (Fig. 1).³

In collaboration with groups from University of Avignon and University of Strasbourg, we recently proposed to bridge the gap between growing needs for precious metals and difficulties to valuate e-waste, through the use of precious metal based catalysts directly prepared from e waste (Fig. 2).⁴

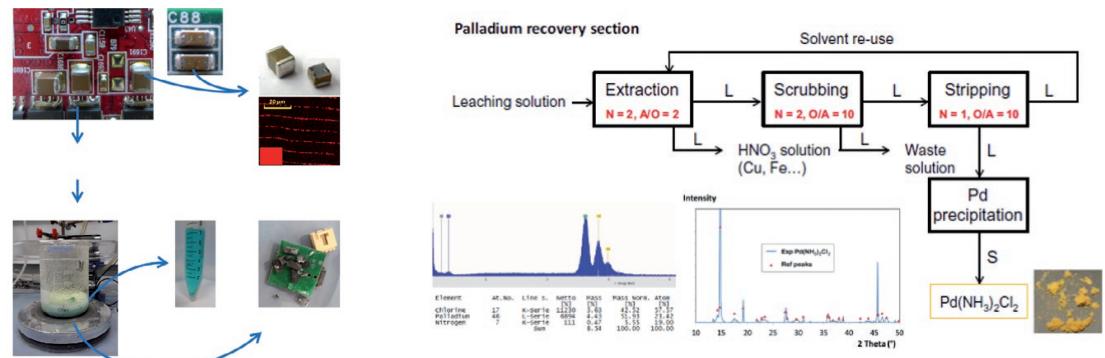


Figure 1: Pd recovery from PCB and related process diagram

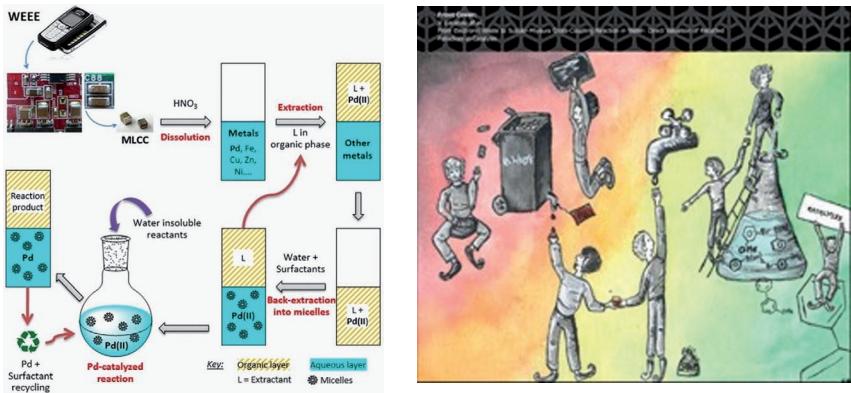


Figure 2: Direct use in micellar catalysis of Pd recovered from printed circuit board

¹ R. Mastretta, R. Poiré, D. Bourgeois, and D. Meyer «Palladium Isolation and Purification from Nitrate Media: Efficient Process Based on Malonamides», *Solvent Extraction and Ion Exchange*, 2019, 37, 2, 140-156.

² D. Bourgeois, V. Lacanau, R. Mastretta, C. Contino-Pépin and D. Meyer «A simple process for the recovery of palladium from wastes of printed circuits», *Hydrometallurgy*, 2020, 191, 105241.

³ D. Bourgeois, D. Meyer, PCT Int. Appl., WO2019048789A1, 07/09/2017; D. Bourgeois, D. Meyer, B. Braibant, PCT Int. Appl., WO2019048790A1, 07/09/2017; S.A. Moussaoui, A. Lélias, B. Braibant, D. Meyer, D. Bourgeois «Solvent extraction of palladi-um(II) using diamides: A performing molecular system established through a detailed study of extraction kinetics», *Sep. Purif. Technol.*, 2021, 119293.

⁴ V. Lacanau, F. Bonneté, P. Wagner, M. Schmitt, D. Meyer, F. Bihel, C. Contino-Pépin and D. Bourgeois «From Electronic Waste to Suzuki-Miyaura Cross-Coupling Reaction in Water: Direct Valuation of Recycled Palladium in Catalysis», *ChemSusChem*, 2020, 13, 5224-5230.

AN ORIGINAL OPEN AND CLOSED-LOOP RECYCLING METHOD FOR LI-ION BATTERIES THROUGH PRODUCTION OF METAL-ORGANIC FRAMEWORKS

M. Cognet, E. Lagae-Capelle, M. Carboni, D. Meyer

Energy storage is one of the biggest challenges for next decades. The management of renewable energy production requires efficient electrochemical energy storage devices to use it anytime and anywhere. In recent years, Li-ion batteries (LiBs) have been developed and successfully commercialized for portable devices (smartphones, laptops ...) or cars. A mixture of cobalt/nickel/manganese has been largely used in the development of the LiB (NMC batteries). Our team has recently proposed a recycling process by selective precipitations of these toxic metals as valuable materials (Metal-organic Frameworks (MOFs)) in batteries waste solution.^{1,2} Our previous works have shown an interest to use MOFs as active electrode materials for Li-ion batteries (Electrode material synthesis).³ (Figure 1)

process by forming MOFs. Poly(ethylene terephthalate) from plastic bottles was depolymerized to produce an organic ligand source (terephthalate), and Li-ion batteries were dissolved as a source of metals (Figure 2). By mixing both dissolution solutions together, selective precipitation of an Al-based MOF, known as MIL-53 in the literature, was observed.⁴

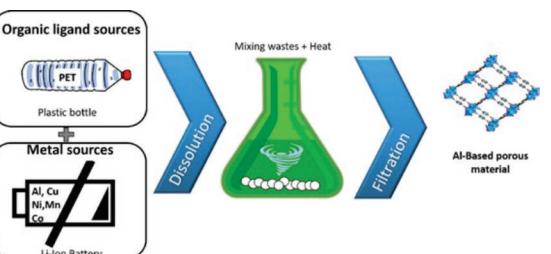


Figure 2: Combining organic and inorganic wastes to form MOFs

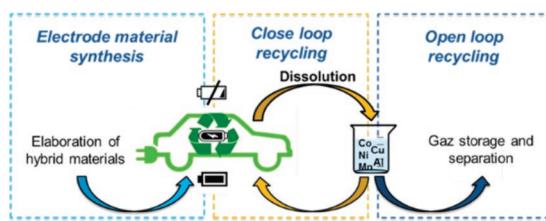


Figure 1: Strategy for the recycling of Li-ion batteries

A CoNiMn MOF obtained from simulant battery waste solution has been tested as electrode in a coin cell. It has revealed capacities as high as 460 mAh/g with a good cyclability over 50 charge/discharge cycles. Our recent studies have been focused on adapting this strategy by using real LiB wastes. It has been possible to obtain in large scale from LiB wastes some known MOFs, based on Al and Cu (the contactors of the battery) reported for their ability for gas storage (open loop recycling). This strategy can create an economical open loop recycling process to develop valuable materials from wastes in large scale.

Recently we also have reported a simple method to recycle plastic-bottle and Li-ion-battery waste in one

This strategy has been recently extended for the recycling of photovoltaic modules.⁵ The adsorption performances of these MOFs on cationic Methylene Blue and anionic Methyl Orange were determined to be ranging from 186.2 to 263.2 mg/g for MB, and 256.4 to 304.0 mg/g for MO. These results therefore suggest the potential of upcycling solar panels waste to form metal-organic framework for application in wastewater remediation to remove cationic and anionic dyes.

State of the art recycling of spent LIBs involving pyrometallurgy and hydrometallurgy processes generates considerable unwanted environmental concerns. Hence, alternative innovative approaches toward the green recycling process of spent LIBs are essential to tackle large volumes of spent LIBs in an environmentally friendly way. Such evolving techniques for spent LIBs recycling based on green approaches, including bioleaching, waste for waste approach, and electrodeposition, have been discussed here⁶ and are still in development with the SCARCE 2 project (collaborative work between CEA and NTU (Singapore)).

¹ Cognet M., Cambedouzou J., Madhavi S., Carboni M., Meyer D. - Targeted removal of aluminium and copper in Li-ion battery waste solutions by selective precipitation as valuable porous materials - *Materials Letters* (2020) 268, 127564.

² Cognet M., Condomines J., Cambedouzou J., Madhavi S., Carboni M., Meyer D. - An original recycling method for Li-ion batteries through large scale production of Metal Organic Frameworks - *Journal of Hazardous Materials* (2020) 385, 121603.

³ Cognet M., Gutel T., Gautier R., Le Goff X. F., Mesbah A., Dacheux N., Carboni M., Meyer D. - Pillared sulfonate-based metal-organic framework as negative electrode for Li-ion batteries - *Materials Letters* (2019) 236, 73-76.

⁴ Lagae-Capelle E., Cognet M., Madhavi S., Carboni M., Meyer D. - Combining Organic and Inorganic Wastes to Form Metal-Organic Frameworks - *Materials* (2020) 13, 441.

⁵ Pham H. K., Sim Y., Carboni M., Meyer D., Mathews N. - Generating metal-organic frameworks (MOFs) from photovoltaic modules for wastewater remediation - *Journal of Environmental Chemical Engineering* (2022) 10.

⁶ Roy J. J., Rarotra S., Krikstolaitis V., Zhuoran K. W., Cindy Y. D. I., Tan X. Y., Carboni M., Meyer D., Yan Q. Y., Srinivasan M. - Green Recycling Methods to Treat Lithium-Ion Batteries E-Waste: A Circular Approach to Sustainability - *Advanced Materials* (2022) 34, 210334

PILOTING SEPARATION IN LIQUID-LIQUID SYSTEMS

J. Durain, S.A. Moussaoui, A. Chevalier, D. Bourgeois, D. Meyer
M. Bertrand, A. Osypenko, J.M. Lehn (ISIS, Strasbourg Univ.)

One of the challenges for separative chemistry remains the control of flows of metal mixtures of variable composition. The primary intent is generally to separate everything, and the processes currently proposed are sequential. This strategy has its limits in the area of recycling because processes become too complex and generate too many effluents. In some cases, there is an interest in working on mixtures, without going till ultimate separation. We propose to approach this point by the development of multi-phase, adaptive systems, allowing to generate flows of controlled composition.

The LHYS has developed an expertise in the understanding of how a metal ion usually not soluble in an organic phase can be maintained into it by using classical extractants. We elucidated the impact of the interactions which take place at the molecular level, ie. chemical bonding and electrostatic interactions, and low energy second order interaction (H bonding, polarisation, dipole...) on several separation issues.¹

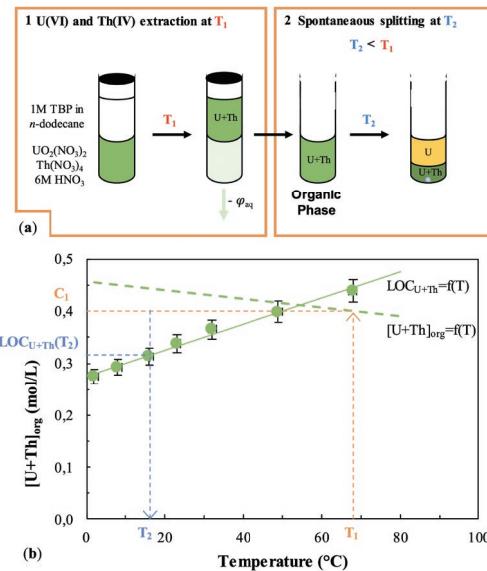


Figure 1: Principle of a. U-Th separation through organic phase self-splitting and b. piloting of the process using variation of Limiting Organic Concentration (LOC) according to temperature (T)

Amongst the approaches envisioned, the spontaneous phase splitting of an organic phase containing U and Th upon cooling was employed to design a non-proliferating

nuclear fuel reprocessing scheme employing classical tributyl phosphate (TBP) extractant (Fig. 1).² A first biphasic system is obtained after extraction of both U and Th at high temperature (T_1 , 70°C). The two phases are separated, then the organic phase loaded with U and Th is cooled below a critical temperature (about 50°C) where it segregates between a heavy and a light organic phase. Two fluxes are thus obtained: the first contains almost all of the Th in the presence of U in a controlled ratio, the second contains surplus U. The U/Th ratio in the heavy phase is controlled by the final temperature of the system (between 1°C and 20°C).

In another approach, completely different from the classical method where a single molecule is designed to extract metal cations under specific conditions, dynamic covalent chemistry has been exploited as a tool for inducing the generation of the extractant species. In collaboration with the LCS (ISIS), the LHYS team has implemented an adaptive dynamic covalent library to the liquid-liquid extraction of copper(II) nitrate: A dynamic library of acylhydra-zones constituents self-build and distribute through both phases of the system (Fig. 2).³

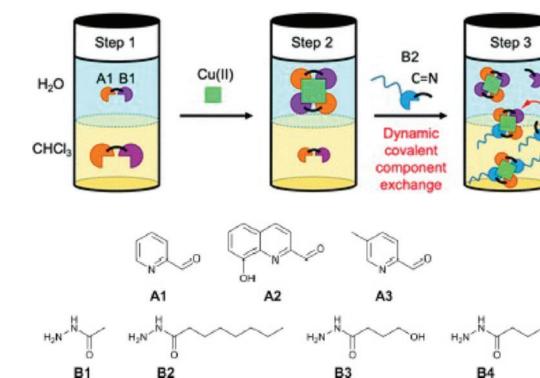


Figure 2: Principle of dynamic covalent chemistry in biphasic systems and reference library of aldehyde A1-A3 and hydrazide B1-B4 components

This work laid the foundation of a new liquid-liquid metal extraction-separation approach which opens the possibility of developing a system responding to several metal extraction-separation problems. The strategy is currently under further investigation at the LHYS in the frame of the PhD thesis of R. Moneuse. Latter work is dedicated to the study of dynamic acylhydrazones based biphasic systems encompassing metalizing cations such as Cu(II), Fe(III) and Pd(II).

¹D. Bourgeois, A. El Maangar, S. Dourdain, "Importance of weak interactions in the formulation of organic phases for efficient liquid/liquid extraction of metals", *Current opinion in colloid & interface science*, 2020, 46, 36-51.

²J. Durain, D. Bourgeois, M. Bertrand, D. Meyer, "Short Alternative Route for Nuclear Fuel Reprocessing Based on Organic Phase Self-Splitting", *Molecules*, 2021, 26, 6234.

³A. Chevalier, A. Osypenko, J.M. Lehn and D. Meyer. - «Phase transfer of metal cations by induced dynamic carrier agents: biphasic extraction based on dynamic covalent chemistry» *Chem. Sci.*, 2020, 11, 11468.

UNDERSTANDING THE EFFECT OF PHASE MODIFIERS ON THIRD PHASE APPEARANCE AND ON EXTRACTION PROPERTIES

A. El Maangar, Z. Lu, S. Dourdain, T. Zemb and S. Pellet-Rostaing

Phase modifiers are often added to solvent extraction processes to avoid the third phase formation. While this important issue of solvent extraction was attributed to sticky interactions between reverse aggregates, the structural effect of phase modifiers remains ambiguous.

As they are similar to reverse hydrotropes, phase modifiers may act as co-surfactant or as co-solvent in the organic phase in solvent extraction system. We therefore coupled a small-angle scattering approach to surface tension measurements on various extracting systems, to evaluate by which mechanisms phase modifiers repel the third phase and affects extraction properties.

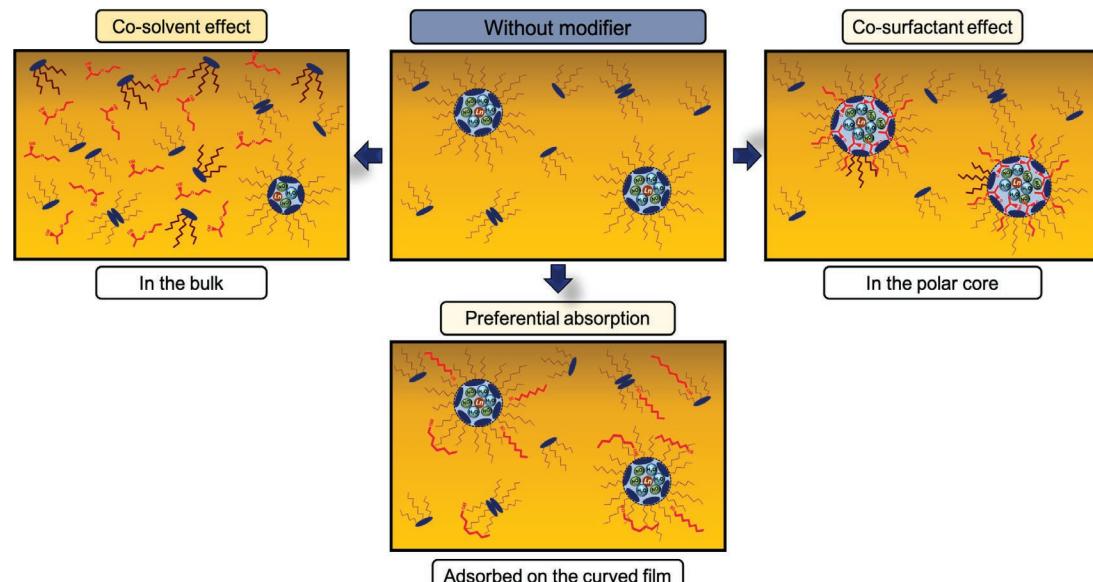


Figure 3: Illustration of the 3 possible effects of phase modifier on the organic phase structure

We showed that depending on the applied extractant molecules and phase modifiers, several mechanisms could be observed:

- A co-solvent effect was underlined when HDEHP and TOA extractant is considered with the hydrotrope PnP as modifier: The surface tension of the organic phase containing these extractants increases with the addition of phase modifier, and neutron scattering showed constant aggregation numbers and a decreased number of aggregates in the bulk.
 - A co-surfactant effect was shown for the extractant DMDOHEMA and DEHiBA. In this case, the surface tension decreases with the addition of the modifier and the aggregation is favored (the cac decreases). Neutron scattering confirmed a co-surfactant effect of PnP with a higher aggregation number in presence of PnP and larger deuterated polar core.
 - A preferential absorption at the aggregates interfaces was finally identified with TOA extractant and 1-octanol as modifier. In this unexpected case, the modifier is neither co-surfactant nor a co-solvent. It was shown to be located around the aggregates, forming a shielding barrier between the aggregates allowing to prevent for the 3rd phase formation.
- The consequences of the addition of phase modifier on extraction properties were also evaluated. We showed that for the two first examples, PnP can modify the extraction of water, acid and of the ion competitors allowing therefore to control the selectivity of the system by adjusting the size of the aggregates.

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-Asmae El Maangar, Sylvain Prévost, Sandrine Dourdain and Thomas Zemb, Molecular mechanisms induced by phase modifiers used in hydro-metallurgy : consequences on transfer efficiency and process safety, CRAS, in Press.

FROM IONIC SOLVENT TOWARD DILUENT-FREE SOLVENT EXTRACTION SYSTEMS

C. Micheau, C. Lopez, S. Le Crom, Z. Lu, E. Guerinoni, S. Dourdain, F. Giusti, G. Arrachart and S. Pellet-Rostaing

A recent challenge in solvent extraction is to replace conventional organic solvents (usually toxic and vola-tile), with ionic solvents (IL). Depending on the extraction systems studied, these new solvents can lead to better efficiency than the conventional ones.

An eco-friendly process was proposed based on ionic liquids 1a such as *N*-ethyl-*N*-alkyl-piperidinium bis(trifluoromethylsulfonyl)imide (EAPIp-NTf₂) or functionalized task specific ionic liquids (TSILs)^{1b} for the extraction and stripping of tantalum from sulfuric acidic medium that may come from e-waste. The study of the key parameters of the IL-based process was investigated including the effect of Ta concentration, H₂SO₄ concentration, equilibration time, temperature, IL partitioning... The recovery of other valuable metals such as Au and Pd from aqua regia leachate of e-waste was also demonstrated and a global flowsheet was pro-posed including the possibility to recover the metals thank to an electrodeposition process.^{1c}

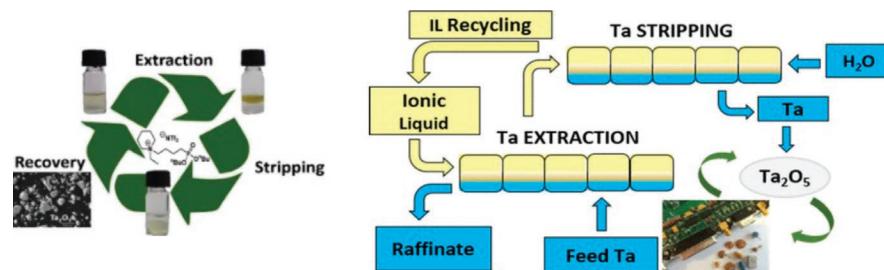


Figure 1. Ionic liquid extraction systems for efficient recovery of Ta from electronic wastes.

Rare earth extraction with DMDOHEMA in EApip Ntf₂ was also studied with a fundamental approach to evaluate the mechanisms of extraction in ionic liquids. It was observed with this extractant, that rare earth extraction is higher in IL than in conventional diluent, without any exchange of the IL anions or cations.² This very interesting behavior was investigated in more details with a coupled theoretical and experimental approach (Small Angle X Ray scattering and Molecular Dynamics) to evaluate the role of the IL structure in these better extraction efficiencies.³

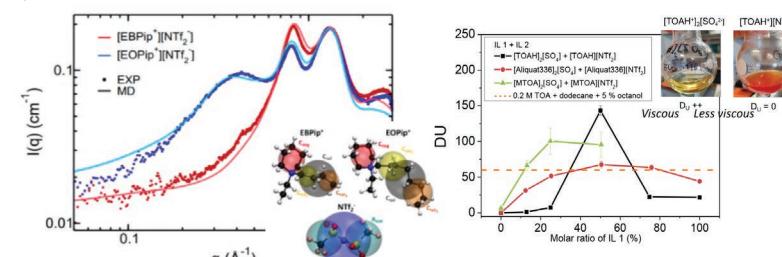


Figure 2. Coupled SAXS and molecular dynamic to understand structural effects in extraction mechanisms in ILs.

With a similar approach, we also designed a diluent-free IL system composed of a pure mixture of extractants which was shown to solve many problem of the industrial process used for U extraction: higher efficiency, no third phase, no organic compound evaporation.⁴ Nowadays, we believe that such ionic solvent, that can concern both ionic liquids or greener deep eutectic solvents are of high potential for solvent extraction.⁵

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³ Le Crom, S., Dourdain, S., Pellet-Rostaing, S., Duval, M., Long-Range Organization Study of Piperidinium-Based Ionic Liquids by Polarizable Molecular Dynamics Simulations, J. Phys. Chem. B, 126, 17, 3355-3365, (2022)

⁴ Z. Lu, G. Arrachart, S. Dourdain, S. Pellet-Rostaing, F. Giusti. Procédé d'extraction de l'uranium des milieux sulfuriques au moyen de mélanges d'ammonium quaternaires, FR3116936A1, WO2022117942A (2022).

⁵ G. Arrachart, J. Couturier, S. Dourdain, C. Levard, S. Pellet-Rostaing. Recovery of Rare Earth Elements (REEs) Using Ionic Solvents, Pro-cesses 9 7 (2021) 1202 ; ⁷ B. Villeméjeanne, S. Legeai, E. Meux, S. Dourdain, H. Mendil-Jakani, E. Billy, Halide based ionic liquid mixture for a sustainable electrochemical recovery of precious metals, Journal of Environmental Chemical Engineering 10 1 (2022) 107063

EFFECT OF CHIRALITY ON SOLVENT EXTRACTION PERFORMANCES AND MECHANISMS

N. Félines, D. Lemire, M. Thimotée, F. Giusti, S. Dourdain, G. Arrachart and S. Pellet-Rostaing

It is well established that solvent extraction performances result from a combination of the affinity of the ligand towards the targeted element and the ability of the ligand to cluster and trap this element into reverse aggregates¹. So, it is not trivial to note that most of branched ligands commonly used in hydrometallurgical processes, are mixtures of stereoisomers, namely enantiomers and diastereoisomers carrying one or several chiral centers (see fig. A). At the opposite of enantiomers, diastereoisomers are not expected to show the same chemical (chelation) and physical chemical (aggregation) properties, thus two main interesting questions could be: i) Does chirality may affect the performances of liquid-liquid extraction ? ii) What is the extent of this effect ? In order to address those concerns, we initiated, in collaboration with the DMRC group (CEA Marcoule), a new project aiming at developing diastereopure ligands and assessing their extracting properties regarding their absolute configuration. As preliminary results, pioneering works reported in N. Félines Ph. D. thesis² deal with the synthesis of diastereopure stereoisomers of *N,N*-bis(2-ethylhexyl)butyramide (DEHBA) and the studies of their extraction properties towards uranium (U) and plutonium (Pu) at low or high acidity in the context of the spent nuclear fuel cycle. The results yielded after solvent extraction experiments showed that chirality did not affect the distribution ratio

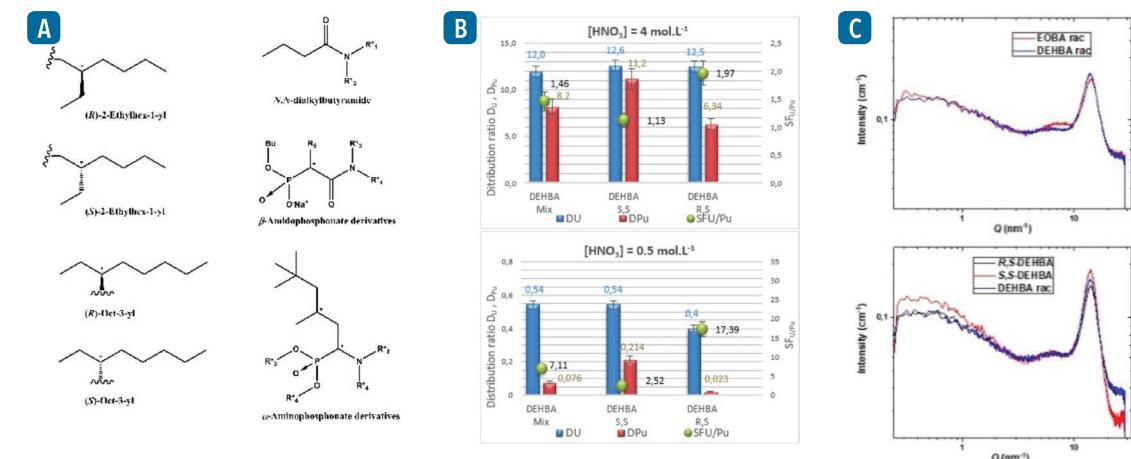


Figure. A) Structures of targeted ligands. Chiral carbons are labeled with *. R*₁ and R*₂ are the same or opposite enantiomer of the 2-ethylhex-1-yl or the oct-3-yl. R*₃ and R*₄ are the same or opposite enantiomer of the 2-ethylhex-1-yl. R*₅ is indifferently an alkyl or an aryl group. B) Comparison of results yielded after U, Pu extraction performed with racemic and diastereopure stereoisomers of DEHBA at two different concentrations of nitric acid in the aqueous layer. SF_{U/Pu} = D_U/D_{Pu} is the selectivity factor for the element U. C) Small angle X-ray scattering spectra of DEHBA isomers diluted at 2.5 g.L⁻¹ in dodecane after contact with a 2.5 g.L⁻¹ aqueous solution of uranyl nitrate. EOBA is the N-(2-ethylhexyl)-N-(octan-3-yl)butyramide.

¹ Zemb T., Bauer C., Bauduin P., Belloni L., Déjugnat C., Diat O., Dubois V., Dufrêche J.-F., Dourdain S., Duval M., Larpent C., Testard F., Pellet-Rostaing S. - Recycling metals by controlled transfer of ionic species between complex fluids: en route to "ienanics" - Colloid Polymer Science (2015) 293, 1-22.

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ORGANIC RESINS AS SORBENT MATERIALS FOR THE EXTRACTION OF STRATEGIC METALS

C. El Khoueiry, E. Lelong, G. Mossand, R. Oye Auke, F. Bekkar, C. Arrambide, G. Arrachart, S. Pellet-Rostaing

Extraction of specific targeted species from industrial (mining deposit, desalination plant, urban mining), nuclear effluents or natural surface water (seawater, river) is an important issue in the valorisation, recycling of strategic metals or decontamination processes.

A large number of organic solids, chelating or ion-exchanging materials, have been developed for selective ionic separation by solid / liquid process.

The aims of this project was the syntheses of chelating original systems and then the preparation of specific resole-type phenolic resins. The covalent introduction of specific ligands into the backbone of the resin, in addition to their robustness, makes it possible to increase the selectivity towards a metal target by the nature of the chelating agents, their coordination sites and their rigidity.

The objective focus on the one hand the development of an efficient methodology for the preparation of these organic materials and on the other hand, their implementation in the solid-liquid extraction of metal targets. The synthesis of the phenolic precursors by integrating specific ligands allowed the use of resin for the recovery of various strategic metals such as germanium,¹ rare earths elements,² uranium,³ platinoids... The versatility of this approach allows the implementation of sorbent materials in various form such as dense materials, foam but also as function of the crosslinked network led to water soluble polymers which can be involved in filtration assisted by complexation processes.

Further investigations are focused now on the synthesis of phenolic resins, fully free of formaldehyde, from nontoxic and potentially biobased chemicals.⁴

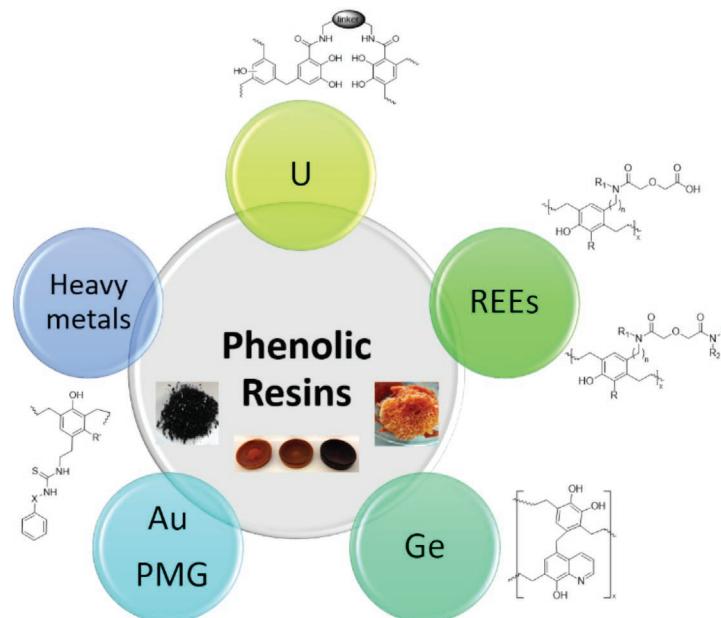


Figure. Overview of application of phenolic resins.

¹ Arrambide Cruz C., Marie S., Arrachart G., Pellet-Rostaing S. - Selective extraction and separation of germanium by catechol based resins - *Separation and Purification Technology* (2018) 193, 214-219.

² Arrambide C., Arrachart G., Berthalon S., Whebie M., Pellet-Rostaing S. - Extraction and recovery of rare earths by chelating phenolic copolymers bearing diglycolamic acid or diglycolamide moieties - *Reactive and Functional Polymers* (2019) 142, 147-158.

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⁴ Oye Auke R., Arrachart G., Tavernier R., David G., Pellet-Rostaing S. - Terephthalaldehyde-Phenolic Resins as a Solid-Phase Extraction System for the Recovery of Rare-Earth Elements - *Polymers* (2022), 14, 311.

SONOCATALYTIC OXIDATION OF ORGANIC COMPOUNDS

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

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^\bullet 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. Even if using ultrasonic irradiation with Pt based catalyst gives interesting result, and clearly points out a synergistic effect, the use of scarce and expensive materials like platinum should be avoided.

Within this framework, a new approach was developed based on the employment of noble free catalyst such as $\text{Co}_3\text{O}_4/\text{TiO}_2$ for the degradation of EDTA.¹ [1] The EDTA degradation was studied under high ultrasonic frequency at 345 kHz in the presence of Ar/O₂ gas mixture at various temperatures (from 20 to 50 °C).

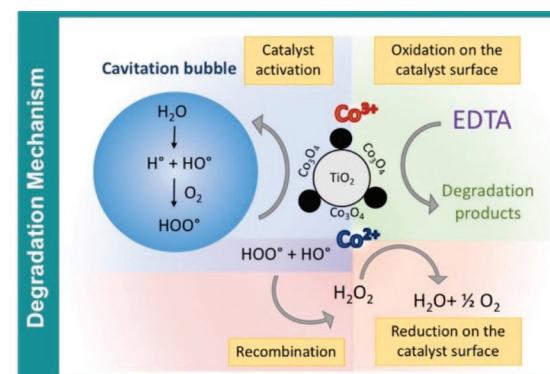


Figure 1 - Mechanism of EDTA sonocatalytic degradation on $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst in the presence of oxygen.

In all experiments 200 mL f 5 mM EDTA solution were ultrasonically irradiated in presence of 1 g/L of 1 to 6 wt% $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalysts. The results clearly indicate that the $\text{Co}_3\text{O}_4/\text{TiO}_2$ 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 Figure 1 and implies the oxidation of EDTA with Co^{3+} catalyst site and reoxidation of Co^{2+} with in situ formed radicals.

Similarly, significant acceleration of EDTA degradation was achieved during sonication in the presence of Ti⁰ NPs and Ar/20%O₂ gas mixture (Figure 2).^{2,3} Coating of Ti⁰ with TiO_2 nanocrystalline shell reduces sonocatalytic activity. Pristine TiO_2 anatase nano-particles do not show a sonocatalytic activity in studied system. Suggested mechanism of EDTA sono-catalytic degradation involves two reaction pathways: (i) sonochemical oxidation of EDTA by $\text{OH}^\bullet/\text{HO}_2^\bullet$ radicals in solution and (ii) EDTA oxidation at the surface of Ti⁰ NPs in the presence of oxygen activated by cavitation event. Ultrasonic activation most probably occurs due to the local heating of Ti⁰/O₂ species at the cavitation bubble/solution interface.

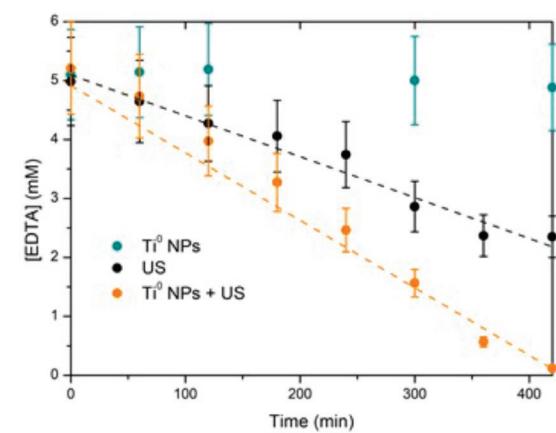


Figure 2 - Evolution of EDTA concentration over time in presence of Ti^0 NPs (2 g/L) at 40 °C under Ar/O₂ (20%) with or without 345 kHz ultrasonic irradiation.

¹ 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 $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst - *Applied Catalysis B: Environmental* (2019) 241, 570-577.

² El Hakim S., Chave T., Nikitenko S.I. - Sonocatalytic degradation of EDTA in the presence of Ti and $\text{Ti}@\text{TiO}_2$ nanoparticles - *Ultra-sonics Sonochemistry* (2021) 70, 105336.

³ El Hakim S., Chave T., Nikitenko S.I. - Photocatalytic and Sonocatalytic Degradation of EDTA and Rhodamine B over Ti-0 and $\text{Ti}@\text{TiO}_2$ Nano-particles - *Catalysts*. (2021), 11 (8), 928

NANO-IONS SPECIFIC EFFECT: SUPERCHAOTROPY

P. Bauduin, L. Girard, A. Jonchère, C. Pasquier et O. Diat

We have found that large-size ionic species with low-charge density, like polyoxometalates (POMs) or (metal-)boron clusters, behave differently from conventional ions regarding their surface properties at liquid interfaces. Indeed, they have a strong propensity to adsorb at neutral polar (hydrated) interfaces through non-specific interactions, an effect referred to as "super-chaotropy".¹ The super-chaotropy increases as the nano-ions charge density decreases. The study of the cloud point (temperature) variation of some non-ionic organic species in water was suggested as a straightforward method for assessing and categorizing nano-ions according to their super-chaotropy. Depending on where they are on the superchaotropcity scale, they interact more or less strongly with non-ionic, polar molecules or supramolecular structures in bulk solutions or at interfaces in the sub-millimolar range. Soft-matter research has new avenues

to be explored thanks to our understanding of this property.² It is indeed possible to induce phase transitions in self-assembling systems, to structure aqueous phases as or with hydrotopes. The superchaotropic behavior of nano-ions makes it possible to control molecular co-assembly constituted of non-ionic oligomers or polymers or proteins by changing concentrations and the choice of their counterions. Physico-chemical properties of non-ionic compounds can be strongly altered by nano-ions. For example, the water solubility of sparingly soluble organic molecules or the stability of non-ionic foams can be significantly improved. The use of super-chaotropic behavior of nano-ions opens then opportunities in separation science, catalysis, and the design of nanostructured hybrid materials. In physical chemistry of solutions, nano-ions close the gap between ions and (charged-) colloids, because of their nm size.

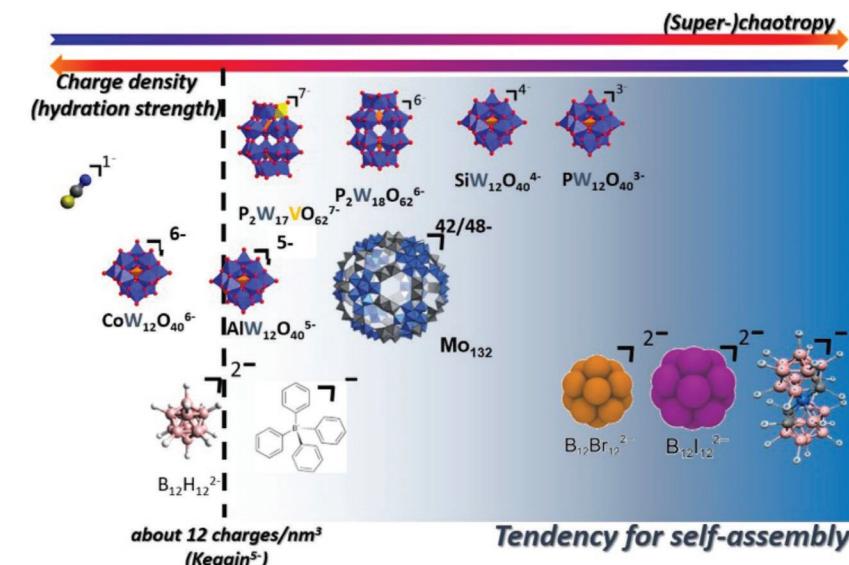


Figure. Various types of inorganic anionic clusters such as the heteropolyoxometalates (Keggin, Dawson, Klaproth...), the bismuthide and derivatives, dodecaraborate ($B_{12}Y_{12}^{2-}$, Y= H, Br, Cl, I), and organic ones such as tetraphenylborate are distributed as a function of their superchaotropcity and beyond the Hofmeister series on the "chaotropes" side with the thiocyanate, SCN^- , on the left upper side.

¹Girard L., Naskar B., Dufreche J. F., Lai J., Diat O., Bauduin P. - A thermodynamic model of non-ionic surfactants' micellization in the presence of polyoxometalates - Journal of Molecular Liquids (2019) 293.

²Hohenschutz M., Grillo I., Diat O., Bauduin P. - How Nano-Ions Act Like Ionic Surfactants - Angewandte Chemie-International Edition (2020) 59, 8084-8088.

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Schmid P., Hohenschutz M., Grass X., Witzmann M., Touraud D., Diat O., Pfitzner A., Bauduin P. - Counterion effect on a Keggin polyoxometalates in water: The peculiar role of H⁺ on their salting-in effect and co-assembly with organics - Journal of Molecular Liquids (2022) 359.

SUPERCHAOTROPIC ION FLOTATION

K. Skorzewski, L. Girard, C. Pasquier, A. Jonchère and P. Bauduin

Ions are extracted and separated by foams in the industrial process known as «ion foam flotation.» The classical ion flotation method makes use of ionic foaming agents (surfactants) to selectively remove ions through electrostatic interactions. As explained in previous pages, superchaotropicity is the general property of low charge density nanometric size ions (nano-ions) that adsorb onto neutral hydrated surfaces. This property could become a driving force in a nano-ions flotation process using non-ionic surfactant, converting this process into pure nonelectrostatic, a "superchaotropic ion flotation". For example, the large size and low charge density of some polyoxometalates (POMs), compared to classical ions, are responsible for this peculiar superchaotropic behavior. The goal of this thesis project was to provide a proof-of-concept evidence for an ion flotation process for which the driving force and selectivity would arise from the affinity of superchaotropic nano-ions for uncharged hydrated surfaces in a non-ionic surfactant foam. The need for novel, straight-forward, eco-friendly extraction techniques to stop environmental damage in the mining industry led to the selection of molybdenum as targeted species. Indeed, at low pH, molybdate forms low charge density polyoxometalate species such as $Mo_{36}O_{112}^{8-}$, also known as Krebs anion. $Mo_{36}O_{112}^{8-}$ has a low charge density and present superchaotropic characteristic. For this study, the following chemical system was used: molybdate and polyoxyethylene (10) oleyl ether (BrijO10®) surfactant in aqueous solution. The effects of pH and Mo and surfactant concentrations on Mo extraction with foam and its specification were investigated by SAXS and Raman spectroscopy. The objective was achieved as superchaotropic flotation of molybdate by a non-ionic surfactant has been shown to be effective. Molybdate could also be selectively separated from tungstate and copper ions and a separation factor of 2 or 3 was achieved without any further optimization. Superchaotropic flotation appears to be an innovative method for the extraction and separation of metalate species.

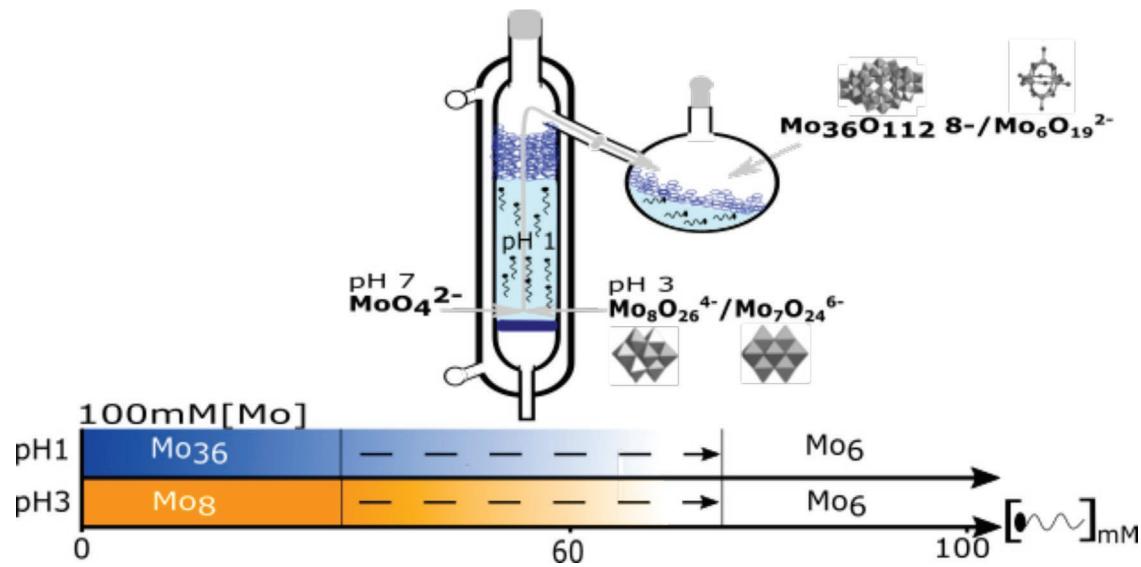


Figure. Extraction process of molybdate species by superchaotropic ion flotation (top). Change in the speciation of molybdate species upon addition of non-ionic surfactant. This change in the speciation is driven by the affinity and stabilization of the superchaotropic nano-ions with non-ionic surfactant

SOLUBILIZATION PROPERTY OF NANOIONS: THE CASE OF METALLA-BIS-(DICARBOLLIDES)

I. Chazappi, T. Merhi, L. Girard, A. Jonchère, C. Pasquier, O. Diat and P. Bauduin

Metalla-bis-(dicarbollides), such as the COSAN anion $[Co(C_2B_9H_{11})_2]^-$, are fully inorganic and non-amphiphilic ionic boron clusters. COSAN derivatives have attracted much attention in biology (BNCT for Boron Neutron Capture Therapy or inhibition of cell activity) or in separation science as extractant of radioactive caesium. We know from our previous studies that these anionic clusters are nano-ions with a very low charge density (below around 12 charges/nm³) with a strong superchaotropic character (see previous page). Moreover, among nano-ions, COSAN can self-assemble as surfactants in aqueous media, due to its extremely low charge density. Recent studies have explored the solubilization of poorly water-soluble molecules (i.e. hydro-phobic) using this type of nano-ions. Molecular solubilization of hydrophobic compounds in water is commonly made by the addition of organic solubilizers through (i) micellar association or hydrotropic solvent pre-structuration using amphiphilic molecules, (ii) co-solvency using water-soluble solvents, and (iii) host-guest complexation using macrocycles. We show that the cobalta-bis-dicarbollide and their derivatives (COSANS), efficiently act as solubilizers of model hydrophobic compounds (medium-chain alcohols with logP values between around 0.6 and 1.5) in water. COSAN, in contrast to surfactants, is an effective solubilizer

when it is monomeric, or at concentrations that are significantly below the critical aggregation concentration. Spectroscopic and scattering methods were used to disclose this novel solubilization mechanism, which is based on the production of thermodynamically stable COSANs/alcohol anisotropic co-assemblies. We have also shown that the COSANs/2-butanol co-assemblies can be used to solubilize more hydrophobic compounds with logP values up to around 6.¹ The same strategy and methods were applied to demonstrate that, depending on concentration, COSAN could solubilize glucosides chemicals by co-assembling. Indeed, we have demonstrated that COSAN binds to glucoside C₈G₁ monomers or onto C₈G₁ supramolecular self-assemblies. COSAN adsorbs onto C₈G₁ micelles above the CMC through the superchaotropic effect. At high COSAN concentrations, it breaks C₈G₁ micelles, resulting in co-assemblies that resemble COSAN micelles but contain only a small quantity of solubilized C₈G₁.² The disruptive effect and/or solubilization properties of these nano-ions are now being explored to either separate macromolecules or disperse hydrophobic compounds in water. An extension of this study was also explored to solubilize phospholipidic bilayers; it will be discussed soon.³

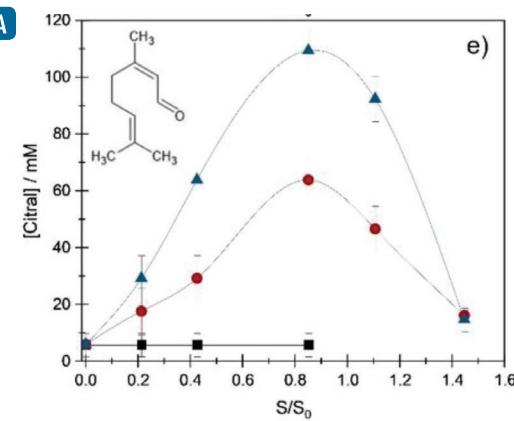


Figure. A) Solubility of citral as a function 2-BuOH concentration (S/S_0) and for different NaCOSAN concentrations: 0 (dark squares), 0.01 (red circles) and 0.02 mol L⁻¹ NaCOSAN (blue triangles). B) Sketch of alkyl glucoside surfactant solubilization with COSAN molecules above Surfactant Micellar Concentration (upper sketch) below CMC (lower sketch).

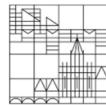
¹Chazapi et al, J. Coll. Int. Sci. accepted

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³To be submitted

PHASE SEPARATION OF BINARY MIXTURES AND MICROEMULSIONS INDUCED BY SOFT CENTRIFUGATION

Universität Konstanz



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W. Kunz, D. Horinek (Uni Regensburg), S. Prevost (ILL-Grenoble) and S. Marčelja (ANU-Canberra)

Centrifugation is one of the most common methods to separate emulsions and microparticles; In the colloid domain, when particles and droplets to sediment are well below 100 nm, centrifugation is not efficient enough to separate in species at acceptable cost in energy, time and effluent volume. In this domain for which chromatography is nowadays still the least inefficient and costly. Ultra-centrifugation would be the method of choice but for preparative separation, but it is only used since the Nobel works of Svedberg a century ago for analytics. The recent understanding of surfactant-free microemulsions has opened the possibility of a technological breakthrough in the form of soft centrifugation (< 2000 g) with separative performance of Ultracentrifugation and extremely fast kinetics, due to the large transient fluctuations present near phase boundaries of complex fluids.

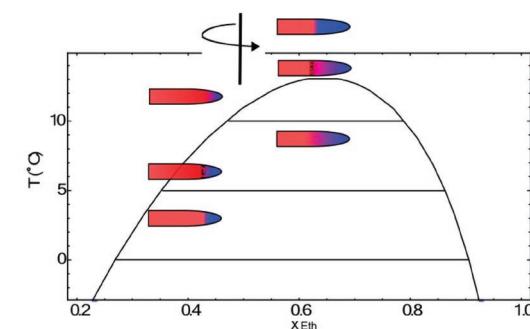


Figure 1: In the model binary system ethanol-dodecane that shows a LCST AT 15C, phase separation induced by centrifugation close to as well as far from the critical point. Centrifuge-induced separation occurs with a meniscus while centrifuge-induced criticality appears as a turbid zone near the middle of the test tube¹.

Progress in these domains requires understanding of the competition of centrifugal fluids with mixing entropy and fluctuations in structurations at nano-scale. "strange" behaviour was signalled since fifty years, but there was no predictive theory available for separation beyond the well known centrifugation in nearly-critical fluids. We have determined experimentally and developed a parameter-free general theory for binary fluids, as well as for regular solutions. In both cases, near-critical instabilities are enhanced by centrifugation near the critical point. Far from the critical point, emulsification in the form of "ouzo" droplets is predicted also in ternary fluids that are close to regular solutions. Test of the effects predicted by a parameter free "Boltzmann-Archimedes-Gibbs" theory developed on the nearly regular solution².

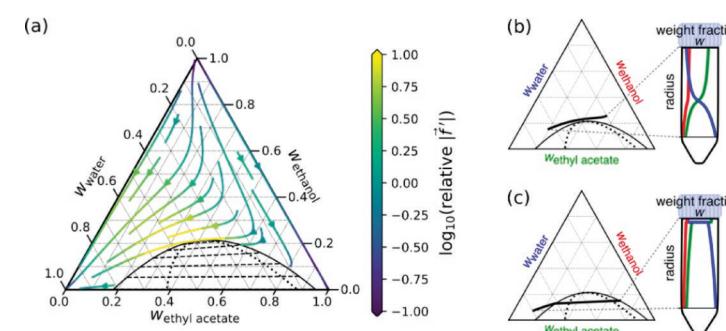


Figure 2.: left: phase diagram water/ethanol/ ethyl acetate system that is used for green extraction in the food and pharmacy are in progress. There is a critical point around 20% Weight of ethanol at room temperature; Coloured vector field shows the concentration gradients appearing under centrifugation: near the critical point, the water/oil ratio fluctuates, while far from the critical point, when composition reaches the miscibility gap, spontaneous emulsification is induced by the centrifugation.

¹Zemb, T., Rosenberg, R., Haffke, D., Kunz, W., Dufrêche, J.-F., Horinek, D. and Cölfen, H., "Phase separation of binary fluids in centrifugal fields" PCCP (2021) 2021, 23 (14), 8261-8272

²Stempflinger, S.; Prevost, S.; Zemb, T.; Horinek, D.; Dufrêche, J.-F. Theory of Ternary Fluids under Centrifugal Fields. J. Phys. Chem. B 2021, 125 (43), 12054-12062. doi.org/10.1021/acs.jpcb.1c05875.



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 MATÉRIAUX POUR L'ÉNERGIE

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).



SYNTHESIS OF ACTINIDE OXIDE COMPOUNDS BY COMBUSTION SYNTHESIS PROCESS

Anna Hautecouverture, Cyrielle Rey, Julien Monnier, Xavier Deschanel
Paul Estevenon (DES/ISEC/DMRC CEA MARCOULE)

As part of the development of generation IV nuclear reactors, solution combustion synthesis is studied to convert actinide nitrates into a solid solution of actinide mixed oxides¹. Solution Combustion Synthesis (SCS) involves the self-propagation of an exothermic reaction in a media composed of organic fuels (glycine, citric acid...) and a metal nitrate dissolved in water. After mixing, a thermal treatment leads to the dehydration of the precursors as a gel, finally the ignition occurs at very low temperature ($\sim 200^\circ\text{C}$) to produce the metal oxide powder. The fuel/nitrate ratio is a key parameter that changes the reactivity and flame temperature of the reaction. This ratio determines the characteristics of the powders obtained, namely the residual carbon content, the crystallinity, the specific surface and can induce a phase transition in the final oxide.

In a first stage, this reaction was employed with actinide substitutes. The conversion of $\text{Gd}(\text{NO}_3)_3$ to Gd_2O_3 with glycine and citric acid as fuel, was successfully obtained at low temperature ($\sim 210^\circ\text{C}$) about 200°C lower than that of a classical denitration reaction. Gd_2O_3 monoclinic phase powders with a high specific surface (10-20 m^2/g), a low amount of residual carbon and a good crystallinity were obtained.

Based on these results, studies on the conversion of actinides/lanthanides nitrates were done to obtain solids solutions of UCeO_{2+x} and U-PuO_{2+x} . For these elements which have several redox states, different phases have been obtained depending on the fuel/nitrate ratio. For example,

in the case of the citric acid (CA) and uranyl nitrate (U) system, the fluorine phase was obtained for $0.6 < \text{CA}/\text{U} < 0.7$ and a mixture of fluorine phase and U_3O_8 phase in variable proportions for $0.3 < \text{CA}/\text{U} < 0.6$ or $0.7 < \text{CA}/\text{U} < 1$. The origin of these structural changes has not yet been clearly established, it is likely that they result from a combination of the temperature reached and the gases produced by the thermal decomposition of the precursors (NH_3 , CO/CO_2) which set the operating redox conditions. It was also possible to obtain powders of solid solution $\text{U}_y\text{Pu}_{1+y}\text{O}_{2+x}$ by SCS reaction for $0.9 < y < 0$. The cell parameters of these compounds are presented in figure 1. Post-treatment under a reducing atmosphere was necessary to obtain stoichiometric compounds. The powders obtained have a porous morphology (figure 2).

Sintering at 1600°C under reducing conditions ($\text{Ar}/5\%\text{H}_2$) of SCS uranium oxide and uranium-cerium oxide powders was carried out. The pellets have a high density ($> 90\%$) and good microstructural characteristics (grain size less than $10\ \mu\text{m}$).

To conclude, the synthesis by combustion in solution allows an easy conversion of actinide nitrates into oxides. The solid solutions obtained by this route have good chemical homogeneity over a wide range of composition (eg. $\text{U}_y\text{Pu}_{1+y}\text{O}_{2+x}, 0.9 < y < 0$), a low residual carbon content ($C < 0.1\%$ for CA-U system). These characteristics are interesting for the fabrication of MOx fuels. The sinterability of the powders requires further studies.

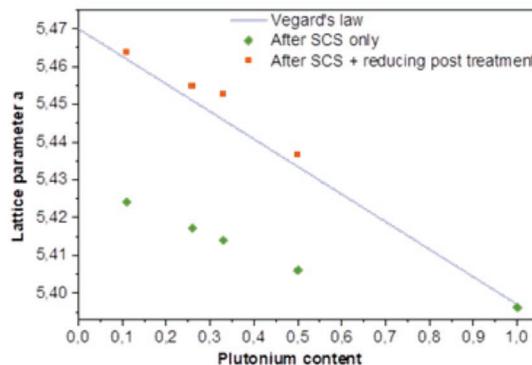


Figure 1. Cell parameters of U-Pu powders synthesized by SCS with CA fuel

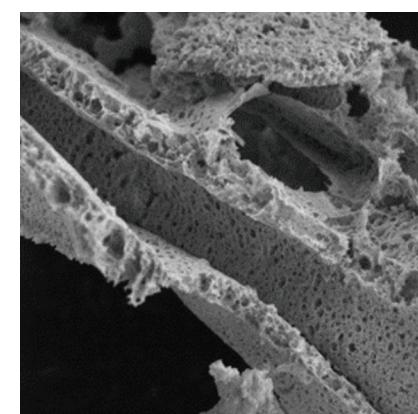


Figure 2. SEM image of PuO_{2+x} powders synthesized by SCS ($\text{CA}/\text{Pu}=1$)

¹ Monnier, J., C. Rey, S. C. Mohan, J. Causse, E. Welcomme and X. Deschanel - Conversion of actinide nitrate surrogates into oxide using combustion synthesis process: A facile approach - Journal of Nuclear Materials (2019) 525: 14-21.

² Monnier J., PhD, University of Montpellier, 2019.

³ Hautecouverture A., PhD, University of Montpellier, in preparation.

DEVELOPMENT OF NEW ACTINIDE-BASED HYBRID MATERIALS

E. Ré, B. Mortada, X. Le Goff, D. Meyer, J. Maynadié, M. Carboni, D. Bourgeois

In the nuclear industry, materials and more particularly those based on actinides are omnipresent. To increase our knowledge of this type of materials, it seems essential to develop new simple and effective synthetic strategies for the production of model materials or precursors of model materials. In this context, actinide-based hybrid materials appear to be good candidates presenting modular physico-chemical properties. This project deals with the conception of new structured actinide-based hybrid materials, which can display unusual properties with respect to the bulk inorganic counterpart. In this way, we are focused our attention on the development of new bottom-up synthesis strategies.

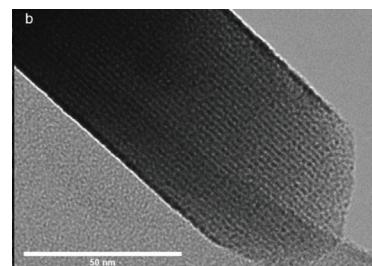


Figure 1. TEM image of actinide-based nano-sheet

Table 1. $d_{\text{U}-\text{U}}$ calculations and interlamellar distances measured by TEM and SAXS of nano-hybrids formed with different linkers

	Naphthalene-2,6-dicarboxylic acid	1,4-Phenylene diacrylic acid	4,4'-Stilbene dicarboxylic acid
Molecules			
$d_{\text{U}-\text{U}} (\text{nm})$	1.37	1.62	1.81
TEM (nm)	1.65	1.83	1.90
SAXS (nm)	1.60	1.88	1.94

Table 1. Table of inter nano-lamellae distances

First, we developed a one-pot approach in order to control the nano-structure of the material.¹ Using a ternary molecular system (dicarboxylic acid, oleylamine, dibenzyl ether), it is possible to obtain nano-sheets displaying an internal nanometric structuration in which UO_x nano-lamellae (around 1 nm) are separated by organic linkers (Figure 1). In the nano-sheets, the inter- UO_x nano-lamellae distance could be adjusted in accordance with the length of the employed dicarboxylic acid linker (Table 1). Moreover, the stacking distance between two nano-sheets could be modulated by adjustment of the

synthesis temperature. Using this synthesis methodology, it is possible to modulate the structure of materials at the nanometric scale by adjusting some parameters intrinsic to the reaction. This approach is currently developed in the team for the synthesis of new NMC (Ni/Mn/Co) hybrid materials for Li-ion batteries.²

A second strategy, based on the self-assembly of functionalized nanoparticles, is developed.³ This strategy starts with the well-known synthesis of metal-oxide nanocrystals (UO_2 , ThO_2 or MO_x) stabilized with oleic acid.⁴ This method permits to obtain well-defined monodisperse nanoparticles with an average size of 4.5 nm for UO_2 and 3.5 nm for ThO_2 (Figure 2 top). Then, the surface of the pre-synthesized nanoparticles is modified using capping agents having reactive pendant functionality (alkyne, azide, ionic moiety) without modification of the morphology of the nanoparticles. To obtain the final materials, the crosslinking of modified nanocrystals could be operated through a click-chemistry step catalyzed by Cu(I) or electrostatic interactions (Figure 2 bottom). The final goal consists in the formation and the characterization of heterometallic nano-hybrid superlattices.

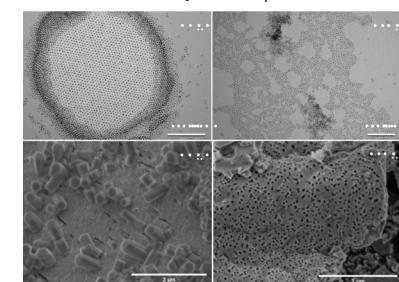


Figure 2. Top: TEM images of UO_2 (left) and ThO_2 (right) nanocrystals / Bottom: SEM images of functionalized nanoparticles self-assemblies (UO_2 (left) and ThO_2 (right))

The third strategy is developed with the goal to produce actinide-based hybrid materials using complex organic phases from liquid-liquid extraction processes. Currently, in the spent fuel cycle, the liquid-liquid extraction step is followed by stripping one. To avoid this latter, it could be interesting to induce direct controlled precipitation in the complex organic phase (metal ions + extractant + dodecane), using simple ditopic organic linkers (as oxalic acid or 2,5-dihydroxy-1,4-benzoquinone) to promote the formation of coordination polymers or MOF potentially having adjustable properties (structure, morphology, texture, robustness). These materials could be envisaged as new precursors for the preparation of actinide-based oxide materials used in the nuclear fuel cycle.

¹ Elisa Ré, Xavier Le Goff, Guillaume Toquer, Jérôme Maynadie and Daniel Meyer, "Linker-assisted structuration of tunable urani-um-based hybrid lamellar nanomaterials", New J. Chem., 2020, 44, 8463.

² Thèse T. Riant.

³ Thèse E. Ré.

⁴ Damien Hudry, Christos Apostolidis, Olaf Walter, Thomas Gouder, Eglantine Courtois, Christian Kübel and Daniel Meyer, "Non-aqueous synthesis of isotropic and anisotropic actinide oxide nano-crystals", Chem. Eur. J., 2012, 18, 8245

SYNTHESIS AND THERMODYNAMICS OF ACTINIDE SILICATES

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In collaboration with CEA DES/ISEC/DMRC, Washington State University, Soleil and ESRF synchro-trons

Actinides, including plutonium, are the main contributors to the long-term radiotoxicity of spent nuclear fuels. In geological conditions, the interactions between these radioelements and silicate species could influence their mobility in environmental conditions and could affect the safety of the storage facilities. Especially, the formation of actinide silicate, AnSiO_4 , has to be considered carefully, since Th and U silicates are rather abundant in environmental silicate rich media and under reductive conditions^{1,2}. Moreover, the natural formation mechanism of coffinite USiO_4 , which involves the alteration of UO_2 in reductive and silicate rich media, raise important questions about the radionuclides' behavior under geological repository conditions.² Additionally, the formation of actinide oxy-hydroxysilicate colloids has been observed for Th, U and Np in weakly basic carbonate media at room temperature, which are suspected to play a huge role on the An mobility (including Pu) in environmental conditions.

However, the conditions of PuSiO_4 formation remained poorly understood. They were reexamined by the way of the 3 surrogate elements (Th, U and Ce), which are considered to represent Pu(IV) aqueous chemistry and to form zircon-type silicates MSiO_4 (S.G. I4₁/amd). For each surrogate element, optimized conditions have been determined through multiparametric study. ThSiO_4 was formed by two different optimized sets of conditions: in acidic media without any complexing agent or in weakly basic media in the presence of large quantities of carbonate ions. Contrarily, USiO_4 coffinite was only prepared in weakly basic carbonate media. For CeSiO_4 , the

use of Ce(IV) as starting precursor did not succeed due to the rapid hydrolysis of Ce(IV). On the contrary, the use of Ce(III) reactants led to the formation of CeSiO_4 in very specific conditions in terms of pH, concentrations and temperature.¹ Using solid Ce(III) silicate precursors, promoted the formation of cerium silicate complexes, which counterbalanced the hydrolysis of Ce(IV) and allowed the formation of pure CeSiO_4 .^{1,4}

The transposition of the 4 optimized protocols to the plutonium system was conducted in the ATA-LANTE facility. While it failed when applying the protocols developed for ThSiO_4 and USiO_4 , it succeeded starting from solid Pu(III) silicate precursors, as observed for cerium. Thus, the study provided key information on the formation of silicate based phases and enabled to identify differences in terms of reactivity between Pu and the surrogate elements. Since the conditions of synthesis allowing the formation of PuSiO_4 were very close to those obtained for CeSiO_4 (Fig 1), it may be inferred that Ce constitutes the best surrogate of Pu in silicate ions rich environments. Moreover, experiments performed in alkaline conditions also confirmed that Pu-silicate based colloids can be formed and exhibit the same structure as Th, U and Np.⁶

Based on the results obtained for all the actinide end-members, the synthesis and characterization of new kinds of zircon-type solid solutions involving actinide and zirconium are now under study to mimic phases also formed during melted nuclear fuels (corium) consequently to severe nuclear accidents.

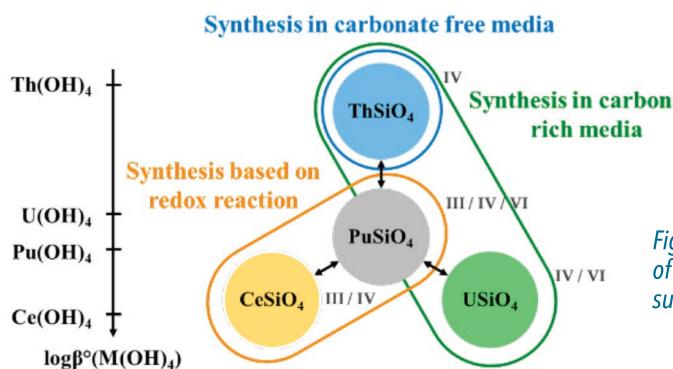


Figure 1. Conditions of synthesis of MSiO_4 for plutonium and its surrogate elements (Ce, U, Th).⁵

¹ Estevenon, P., Kaczmarek, T., Vadot, F., Dumas, T., Lorenzo Solari, P., Welcomme, E., Szenknect, S., Mesbah, A., Moisy, P., Poinsot, C., Dacheux, N. - Formation of CeSiO_4 from cerium (III) silicate precursors - *Dalton Trans* (2019) 48, 10455.

² Szenknect, S., Alby, D., Garcia, M.L., Wang, C., Podor, R., Misqueré, F., Mesbah, A., Duro, L., Zetterstrom-Evans, L., Dacheux, N., Bruno, J., Ewing, R.C. - Experimental evidence for coffinite formation from UO_2 - *Scientific Reports* (2020) 10, 12168.

³ Estevenon, P., Causse, J., Szenknect, S., Welcomme, E., Mesbah, A., Moisy, P., Poinsot, C., Dacheux, N. - In situ study of the synthesis of thorite (ThSiO_4) under environmental representative conditions - *Dalton Trans* (2020) 49, 11512.

⁴ Strzelecki, A.C., Kriegsman, K.W., Bourgeois, C., Zhao, X., Estevenon, P., Wei, N., Szenknect, S., Mesbah, A., Wu, D., Ewing, R.C., Dacheux, N., Guo, X. - Thermodynamics of CeSiO_4 : implications for actinide orthosilicates - *Inorg. Chem.* (2020) 59, 13174.

⁵ Estevenon, P., Welcomme, E., Tamain, C., Jouan, G., Szenknect, S., Mesbah, A., Poinsot, C., Moisy, P., Dacheux, N. - Formation of PuSiO_4 under hydrothermal conditions - *Dalton Trans* (2020) 49, 6434.

⁶ Estevenon, P., Dumas, T., Lorenzo Solari, P., Welcomme, E., Szenknect, S., Mesbah, A., Kvashnina, K.O., Moisy, P., Poinsot, C., Dacheux, N. - Formation of Pu(IV) silicate species in very alkali-line reactive media - *Dalton Trans* (2021) 50, 12528.

HYDROTHERMAL CONVERSION OF ACTINIDES CARBOXYLATES

S. Benarib, J. Manaud, P. Asplanato, L. Di Mascio, J. Maynadie, A. Mesbah, N. Dacheux, N. Clavier.
In collaboration with CEA/DAM/SRCE, CEA/DES/DMRC, IAEA/Safeguards Analytical Services and Orano

Innovative methods for oxide fuels preparation are frequently based on wet-chemistry routes, involving the precipitation then the calcination of crystallized precursors. Despite the advantages of these methods, the resulting oxide powders suffer from some drawbacks, including morphology poorly adapted to sintering, and residual traces of carbon in the final samples. In order to avoid these potential issues and to get rid of the thermal conversion step, we investigated the use of hydrothermal conditions to convert tetravalent actinides bearing carboxylates and directly achieve actinide dioxide precipitation from solution.

The conditions of formation of An(IV) hydrated dioxides were first determined from the conversion of thorium¹ and uranium² oxalates. For U(IV)-based compounds, the lowest temperatures explored (typically from 180 to 200°C) led to stabilize $\text{UO}_{2+x}/\text{U}_3\text{O}_9$ mixtures with a O/U ratio of 2.38 ± 0.10 , while higher temperatures (220-250°C) led the latter

to decrease. Increasing the temperature also improved the elimination of residual carbon species, down to less than 200 ppm. Hydrothermal conversion of $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ also opened the way to tune the powders morphology from bipyramidal aggregates (up to pH = 1), microspheres (2 ≤ pH ≤ 5) then to nanometric powders (pH > 5). Finally, a kinetics study showed that uranium oxides were obtained within few hours, hydrothermal conversion proceeding as a two-step mechanism composed by the oxidative decomposition of U(IV) oxalate followed by the reduction of uranium by organic moieties and then by its hydrolysis.

A preliminary study dedicated to sintering revealed the good densification ability of the oxides produced³. The sintering map of different uranium oxide samples presenting various morphologies was established and paves the way to the control of the microstructure of final pellets. The hydrothermal conversion of oxalates is now extended to $\text{U}_{1-x}\text{Ce}_x\text{O}_2$ solid solutions, cerium being used as a plutonium surrogate.

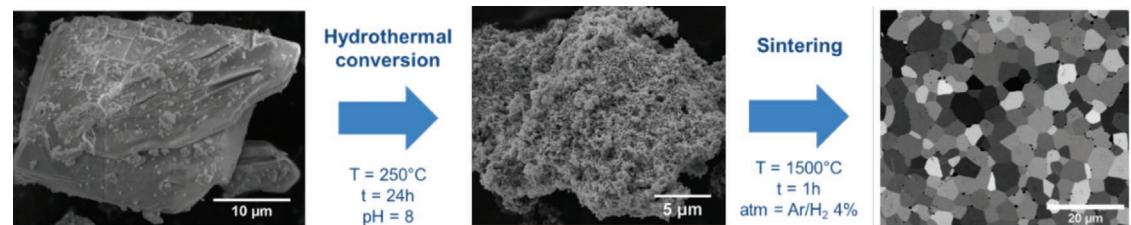


Figure 1. Fabrication of a UO_2 model fuel through hydrothermal conversion of $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$.

Similar methodology was used to study the hydro-thermal conversion of An(IV) aspartates (An(IV) = Th, U), with the aim to develop an original and versa-tile wet chemistry route to AnOx reference materials, to be used in isotopic measurements of nuclear materials. Indeed, the detection and the measurement of the isotopic composition of nanometer- to micrometer-sized particles provide currently a key tool for safeguards verification by the International Atomic Energy Agency (IAEA). Because of the low number and extremely small size of the particles of interest, particles analyses are always an analytical challenge, which requires reference materials representative of the analyzed samples. Such materials are typically actinide oxide particles with well-known sizes, densities and isotopic compositions, which could be used for optimization and qualification of analytical methods and instruments. With this aim, uranium-thorium mixed oxide micro-spheres

were synthesized through the hydro-thermal conversion of aspartate precursors⁴. This latter was performed at T = 160°C and led to mixed dioxide micro-particles with controlled spherical morphology and size, up to 5 mol.% in thorium. In order to remove impurities, densify the micro-particles, and control the chemical form of the final com-pounds, heat treatments were performed under various atmospheres. Nearly stoichiometric (U, Th) O_2 dioxides were obtained under reducing conditions (Ar-4% H₂) while U_3O_8 -based samples were formed under air, with thorium incorporated in the structure up to 2 mol%. Last, the homogeneity of the cation distributions was evaluated by LG-SIMS analyses of individual particles. It led to consistent results, which paves the way to use these mixed oxide particles in the field of nuclear safeguards. The chemical durability of these particles is also under study to evaluate their stability when stored as a suspension.

¹ Manaud J., Maynadie J., Mesbah A., Hunault M. O. J. Y., Martin P. M., Zunino M., Dacheux N., Clavier N. - Hydrothermal Conversion of Thorium Oxalate into $\text{ThO}_{2.6}\text{H}_2\text{O}$ Oxide - *Inorganic Chemistry* (2020) 59, 14954-14966.

² Manaud J., Maynadie J., Mesbah A., Hunault M. O. J. Y., Martin P. M., Zunino M., Meyer D., Dacheux N., Clavier N. - Hydrothermal Conversion of Uranium(IV) Oxalate into Oxides: A Comprehensive Study - *Inorganic Chemistry* (2020) 59, 3260-3273.

³ Manaud J., Podor R., Le Goff X. F., Maynadie J., Dacheux N., Clavier N. - Direct sintering of UO_{2+x} oxides prepared under hydro-thermal conditions - *Journal of the European Ceramic Society* (2021) 41, 6697-6707.

HIERARCHICALLY POROUS 3D SHAPING OF METAL-ORGANIC FRAMEWORK

F. Lorignon, S. Medjouel, D. Pianca, M. Carboni, A. Gossard, D. Meyer

Metal-Organic Frameworks (MOFs) have attracted a lot of attention over the past two decades mainly because their unique set of properties, notably their high porosity and surface area, are useful for gas storage and separation, but these materials are also well suited to the de-contamination of liquid effluents. They are synthesized as crystalline solid powders but, for a broad applicability, producing MOFs as handleable materials is crucial. Furthermore, the main challenge for their use in fix bed processes consists in creating and controlling a meso- and macroporous network in the body of the material while ensuring the MOF's micropores remain accessible.¹ Different routes have been proposed to shape MOFs in this way, namely various mechanical processes (granulation, pressing, extrusion or spray drying), finely controlled metal-organic gel formation, thin film deposition, and sacrificial templating.

Our strategy was shaping MOF monolith by using Pickering emulsions.² The emulsions are stabilized by MOFs solid particles with a high internal phase emulsions (HIPE) (Figure 1). Then, by growing a solid skeleton in the continuous phase to support the global structure and eliminating the internal phase, a macro porous material can be obtained with the pore size defined by the size of the initial drop-lets of the emulsion.

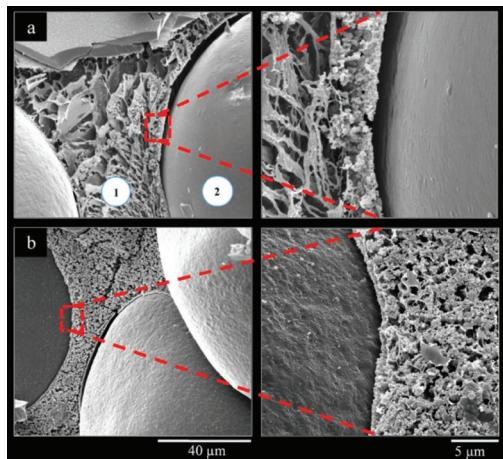


Figure 1. Cryo scanning electron micrographs of emulsions with a paraffin volume ratio of 0.8 v/v and MOFs concentrations of (a) 1 wt.% and (b) 3.5 wt.%. (1) Continuous aqueous phase concentrated in MOFs and (2) oil droplet.

¹ Lorignon F., Gossard A., Carboni M. - Hierarchically porous monolithic MOFs: An ongoing challenge for industrial-scale effluent treatment - *Chemical Engineering Journal* (2020) 393, 124765.

² Lorignon F., Gossard A., Carboni M., Meyer D. - From wastes to interconnected porous monolith: Upcycling of Al-based metal organic framework via pickering emulsion template - *Materials Letters* (2021) 296.

³ Lorignon F., Gossard A., Carboni M., Meyer D. - Microstructural and rheological investigation of upcycled metal-organic frameworks stabilized Pickering emulsions - *Journal of Colloid and Interface Science* (2021) 586, 305-314.

⁴ Pianca D., Carboni M., Meyer D. - 3D-Printing of porous materials: Application to Metal-Organic Frameworks - *Materials Letters-X* (2022) 13, 100121.

Controlling the properties of the emulsion was crucial both to optimizing the microstructural design of the MOF-functionalized materials and to ensuring that the fluid is workable into an appropriate structure (e.g. by extrusion or additive manufacturing) without any degradation of the internal microstructure and to obtain a rigid monolith (Figure 2).³

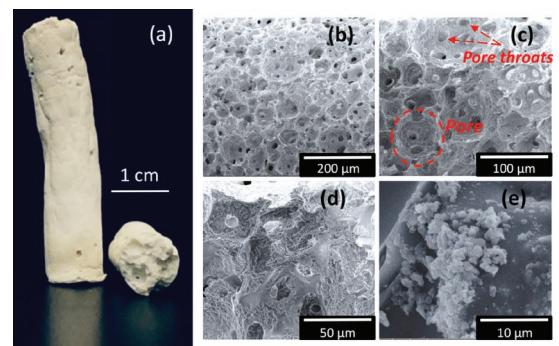


Figure 2. (a) Photograph of the M100/10/0.5 monolith, seen from the front and from below; (b-e) SEM images of the M100/10/0.5 monolith at different magnifications

We are also developing method to shape porous MOFs materials by using 3D-printers.⁴ Different strategies are ongoing but our first effort has been focused on direct-ink writing (DIW). In this technique, the extruder of the printer will be replaced to support a syringe connected to a peristaltic pump to deposit directly a paste (ink) containing the MOF on the hot bed of the printer conducting to the solidification of the ink. Additive formulation are often composed of solvent/thermosetting polymers/adhesive polymers. Such formulation is close to those that we have used to form monoliths by Pickering emulsion and need a research effort to optimize and characterize the viscosity and other rheological properties of the ink to optimize the deposition.

Although relatively few studies have been published to date, the field is expanding fast in terms of the techniques proposed and the understanding of the stability of MOFs and their performances as hierarchically porous materials rather than powders.

PREPARATION, REACTIVITY AND MULTI-SCALE CHARACTERIZATION OF ACTINIDE OXIDE NANOPARTICLES

M. Virot, S. I. Nikitenko
T. Dumas, P. Moisy CEA DES/ISEC/DMRC

Actinide (An) research at the nanoscale is gaining fundamental interest due to environmental and industrial issues. Much effort is currently dedicated to the preparation of well-defined nanoparticles (NPs) and related nanomaterials that could tailor specific properties in comparison to their bulk analogues. Sonochemistry has been widely used for the preparation of NPs and offers new perspectives in the nuclear domain. The sonication of PuO₂ powder under reducing atmosphere was found to yield very stable intrinsic Pu(IV) colloidal suspensions composed of NPs with a PuO₂-like structure and offering striking similarities and differences with colloids obtained by hydrolysis.¹ This observation started persistent studies dedicated to the characterization of the multi-scale properties of PuO₂ NPs (i.e. size, shape, local structure, formation...).

Small angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) were combined on an innovative analytical bench on SOLEIL/MARS synchrotron beamline to characterize Pu(IV) intrinsic colloids. The structural properties of the NPs were found to be strongly influenced by the synthesis route. Both SAXS and XAS approaches converged in the description of Pu colloids as core-shell NPs made up of a PuO₂ core covered with a size-dependent disordered Pu-O shell possibly solvated with counter ions from the medium.²

More recently, the synthesis and relevant characterization of PuO₂ and ThO₂ NPs displayed as dispersed colloids, nanopowders or nanostructured oxide powders, allowed to establish a clear relationship between the size of the nanocrystals composing these oxides and their corresponding local structure (XAS).³ Particularly, an analogous behaviour was noticed for nanosized Pu and Th oxides confirming that the often observed splitting of the Pu-O shell on the Fourier transformed EXAFS signal of PuO₂ samples is attributed to a local structural disorder driven by a NP surface effect rather than to the presence of controversial PuO_{2+x} species.³

New insights were recently provided about the formation mechanism of PuO₂ NPs by investigating an unprecedented kinetic isotope effect observed during their hydrolytic synthesis in H₂O or D₂O and attributed to

OH/OD zero point energy difference.⁴ The signature of a Pu(IV) oxo-hydroxo hexanuclear cluster, appearing as an important intermediate during the formation of the 2 nm PuO₂ NPs (syn-chrotron SAXS/XAS), was further revealed indicating that their formation is controlled by H-transfer reactions occurring during hydroxo to oxo-bridge conversions.

The significant dissolution of refractory ThO₂ NPs was observed under 20 kHz ultrasound (Ar/(20%)O₂) in dilute 0.5 M H₂SO₄. It was shown to result from a combination of physical effects provided by low frequency ultrasound, sulfate complexations and sonochemical generation of H₂O₂.⁵ Surprisingly, the extended ultrasonic treatment allowed to observe the partial precipitation of a secondary phase attributed to an unprecedented Th peroxy sulfate, Th(O₂)(SO₄)(H₂O)₂, exhibiting 1D morphology. The crystalline structure of this compound was studied and later resolved.⁶

The preparation of U intrinsic colloids was obtained by 20 kHz sonolysis of UO₃ powder in pure H₂O under Ar/(10%)CO at 20 °C. These conditions allowed the partial conversion of powdered UO₃ into a stable colloidal suspension made out of NPs (HR-TEM, XAS) exhibiting a schoepite-like crystallographic structure.⁷

More generally, these results offer new insights about the preparation and thorough characterization of An oxide NPs. The state-of-the-art and recent advances in the topic were recently summarized in two reviews.^{8,9}

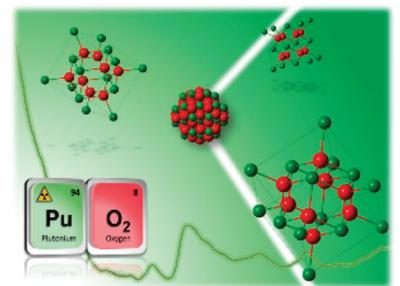


Figure 1. Cover picture used for *Nanoscale Advances* journal for a Review article

¹ Dalodière E., Virot M., Morosini V., Chave T., Dumas T., Hennig C., Wiss T., Dieste Blanco O., Shuh D. K., Tyliaszak T., Venault L., Moisy P., Nikitenko S. I. Insights into the sonochemical synthesis and properties of salt-free intrinsic plutonium colloids - *Sci. Rep.* (2017) 43514.

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³ Bonato L., Virot M., Dumas T., Mesbah A., Dalodière, E., Dieste Blanco O., Wiss T., Le Goff X., Odorico M., Prieur D., Rossberg A., Venault L., Dacheux N., Moisy P., Nikitenko S. I. Probing the local structure of nanoscale actinide oxides: a comparison between PuO₂ and ThO₂ nanoparticles rules out PuO_{2+x} hypothesis - *Nanoscale Adv.* 1 (2020) 214-224.

⁴ Cot-Auriol M., Virot M., Dumas T., Diat O., Menut D., Moisy P., Nikitenko S. I. First observation of [Pu₆(OH)₄O]₄¹²⁺ cluster during the hydrolytic formation of PuO₂ nanoparticles using H/D kinetic isotope effect - *Chem. Commun.* 58 (2022) 13147-13150.

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⁷ Cot-Auriol M., Virot M., Micheau C., Dumas T., Le Goff X., Den Auwer C., Diat O., Moisy P., Nikitenko S. I. Ultrasound-assisted conversion of uranium trioxide into uranium(VI) intrinsic colloids - *Dalton Trans.* 50 (2021) 11498-11511

⁸ Virot M., Dumas T., Cot-Auriol M., Moisy P., Nikitenko S. I. Synthesis and multi-scale properties of PuO₂ nanoparticles: recent advances and open questions - *Nanoscale Adv.* (2022) 4, 4938-4971.

⁹ Nikitenko S. I., Virot M., Moisy P. Sonochemistry of actinides: from ions to nanoparticles and beyond - *Radiochim. Acta* (2022) 110, 453-470.

SONOCHEMICAL SYNTHESIS OF NANOMATERIALS FOR ENERGY AND ENVIRONMENT

S. El Hakim, T. Chave, X. Le Goff, S.I. Nikitenko

A.A. Nada, S. Roualdes (Institut Européen des Membranes, Montpellier)

Ultrasonic cavitation can be applied in a wide range of experimental conditions and even during hydro-thermal treatment. Ti@TiO₂ core-shell nanoparticles (NPs) have been obtained using simultaneous action of hydrothermal conditions (100–214 °C, auto-genic pressure P = 1.0–19.0 bar) and 20 kHz ultra-sound, called sono-hydro-thermal (SHT) treatment, on metallic Ti0 NPs in pure water. The influence of the 3 hour treatment temperature on the final composition of the material was studied and compared to classical hydrothermal treatment.¹ Pristine Ti⁰ is composed of quasi-spherical particles (30–150 nm) of metallic titanium coated with a meta-stable titanium suboxide Ti₃O which can still be observed for temperature treatment below 150 °C. SHT treatment at 150–214 °C leads to the oxidation of this Ti3O and also to the partial oxidation of Ti0 followed by formation of nanocrystalline shell (10–20 nm) composed of TiO₂ anatase (Figure 1). Rietveld refinement analyses revealed that SHT drastically increase this oxidation rate of Ti₃O and Ti(0) into crystalline TiO₂ compared to hydrothermal conditions without ultrasound.

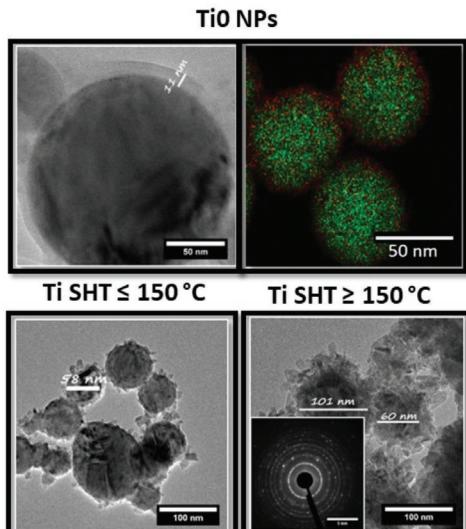


Figure 1. TEM images of Ti@TiO₂ NPs obtained after a SHT treatment for 3 hours at various temperatures compared to pristine material with elemental mapping showing the presence of oxygen (red dots) at the surface of titanium core (green dots).

Photocatalytic performances of obtained material were then assessed for the hydrogen production in presence of sacrificial reagents. It was shown that Ti@TiO₂ NPs exhibit a strong photothermal effect during the photocatalytic process of hydrogen production from aqueous solutions of glycerol. The effective electron-hole separation between Ti core and nanocrystalline TiO₂ anatase shell in Ti@TiO₂ NPs was confirmed by photoluminescence spectroscopy. In the same way, kinetic study highlights the importance of TiO₂ nanocrystalline shell for the efficient H₂ generation as shown in Figure 2. Apparent activation energy equal to Eact = 32 ± 2 kJ mol⁻¹ indicates that the thermal effect is more related to the diffusion of reaction intermediates at catalyst surface rather than to the activation of chemical bonds. However, recent studies on the photothermal hydrogen production using the H/D kinetic isotopic effect revealed the involvement of the hole-mediated O-H bond cleavage in the limiting stage of this process at the active site of the photocatalyst.³

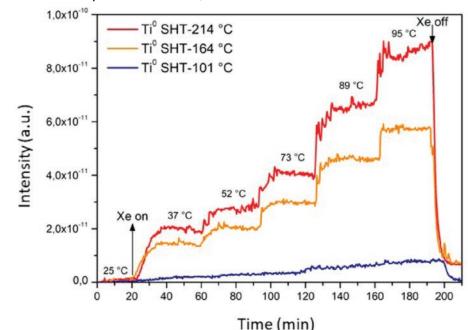


Figure 2. Hydrogen signal evolution during the 0.5 M Glycerol solution photocatalytic treatment (Xe lamp 8.9 W) at various temperatures in the presence of the different Ti@TiO₂ catalysts (0.12 g/L top). Graphical sketch of suggested mechanism of H₂ photocatalytic formation in presence of sacrificial reagents like alcohols (bottom).

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³ El Hakim S., Chave T., Nikitenko S.I. - Deciphering the reaction mechanisms of photothermal hydrogen production using H/D kinetic isotope effect. Catalysis Science & Technology, (2022), 12, 5252.

PHOSPHATE-BASED MATRICES FOR THE SPECIFIC CONDITIONING OF ACTINIDES

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In collaboration with University of California, Davis and Arizona State University



For long, phosphates-based ceramics appeared as promising candidates for the specific conditioning of tetravalent and trivalent actinides as well as for plutonium excess coming from dismantled nuclear weapons. Such interests come from their good resistance to radiation damage, interesting sintering capability, and extremely high chemical durability. These materials are known to be widespread minerals with a general formula REPO₄ (REE = Ln, Sc, Y).

Monazite is encountered for light rare-earth elements (LREE) with larger ionic radii (Ln from La to Gd) and crystallizes with the monoclinic P2₁/n structure type. Xenotime is formed for heavier and smaller elements (Y and Ln from Tb to Lu) and crystallizes with the zircon type structure in the tetragonal system (I4₁/amd). The incorporation of actinides within these structures goes through different substitution mechanisms (Fig. 1).

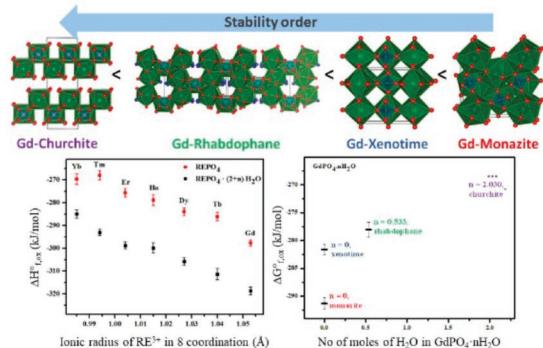


Figure 2. Thermodynamic properties of GdPO₄·nH₂O with various structures

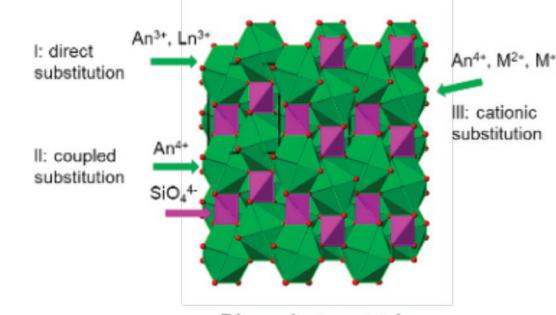


Figure 1. Substitution ways in monazite and xenotime structures

These materials are currently synthesized by solid-state routes. These protocols require successive grinding steps which can be considered as an important drawback when handling radioactive materials. For this reason, we developed various promising wet chemistry routes, in order to prepare single-phased and homogeneous compounds. The synthesis of the target materials is operated by precipitation of low-temperature precursors, such as rhabdophane or churchite for LREE or HREE, respectively. This wet chemistry route was first developed for the preparation of monazite end-members.

¹ Subramani T., Rafiuddin M.R., Shelyug A., Ushakov S., Mesbah A., Clavier N., Qin D., Szenknect S., Elkaim E., Dacheux N., Navrotsky A. - Synthesis, Crystal Structure, and Enthalpies of Formation of Churchite-type REPO₄·2H₂O (RE = Gd to Lu) Materials - Crystal Growth & Design (2019) 19, 4641-4649.

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³ Rafiuddin, M.R., Seydoux-Guillaume, A.M., Deschanel, X., Mesbah, A., Baumier, C., Szenknect, S., Dacheux, N. - An in-situ electron microscopy study of dual ion-beam irradiated xenotime-type ErPO₄ - Journal of Nuclear Materials (2020) 539, 152265.

⁴ Qin D., Mesbah A., Clavier N., Szenknect S., Dacheux N. - From Th-Rhabdophane to Monazite-Cheralite Solid Solutions: Thermal Behavior of Nd_{1-2x}Th_xCaxPO₄·nH₂O (x = 0–0.15) - Crystal Growth & Design (2019) 19, 2794-2801.

⁵ Qin, D.W., Mesbah, A., Lautru, J., Szenknect, S., Dacheux, N., Clavier, N. - Reaction sintering of rhabdophane into monazite-cheralite Nd_{1-2x}Th_xCaxPO₄ (x=0-0.1) ceramics - Journal of the European Ceramic Society (2020) 40, 911-922.

⁶ Qin, D., Shelyug, A., Szenknect, S., Mesbah, A., Clavier, N., Dacheux, N., Navrotsky, A. - Chemical and environmental stability of monazite-cheralite solid solutions Ln_{1-2x}CaxTh_xPO₄ (Ln = Pr, Nd; x = 0–0.15): A thermodynamic study - Applied Geochemistry (2023) 148, 105504.

RADIATION EFFECTS IN MESOPOROUS MATERIALS - APPLICATION TO NUCLEAR WASTE PACKAGING

Jun Lin, Yu Lou, Sandrine Dourdain, Cyrielle Rey, Jérémie Causse, Guillaume Toquer, Pierre de La-harpe, Bertrand Siboulet, Xavier Deschanel, Sylvain Peuget, Hélène Arena (DES/ISEC/DPME/SEME CEA MARCOULE)

Considering their large interfacial surface, nanoporous materials offer interesting perspectives for the study of the evolution of damage induced by irradiation¹. In order to study this phenomenon, thin films (IPC, ICC) (figure 1) and pellets of mesoporous silica (SBA15, MCM41) produced by sol-gel process were irradiated at JANNUS, SIRIUS and GANIL facilities. The irradiations conditions are as following (i) Xe-0.55 to 0.71 MeV/A, C-0.98 MeV/A, Ca-9.17 MeV/A, Ar-0.98 MeV/A, Kr-0.86 MeV/A and 2 MeV electrons, corresponding to electronic damage processes (ii) Au-0.0025/0.06 MeV/A corresponding to ballistic processes. The porous structure was analyzed by X-Rays Reflectivity or gaseous adsorption-desorption iso-therms and the silica wall network by various spectroscopy IR and NMR. All of the experimental results demonstrated that the ordered porous structure was damaged and a significant collapse of the mesoporosity inducing a compaction was observed^[2-4]. The radius of the tracks representative of the damage to the structure is shown in figure 2 as a function of the total stopping power of the ions. As could be expected, higher is the stopping power larger are the track radius. For a same total stopping power, non-porous silicas have a greater damage radius than mesoporous one, that is mean that porous silicas present a better radiation tolerance than non-porous material. This conclusion is supported by the results of IR spectroscopy which demonstrate that the IR changes caused by irradiation on silica network in the porous material are less than that observed in non-porous silica at the same dose. However, as previously indicated, when the irradiation dose becomes sufficiently high, the mesoporous structure of the silica collapses.

From a technological point of view, mesoporous silica can be used to develop a new strategy for the treatment of radioactive effluents based on the use of a porous functionalized support. After functionalization, this support would allow both the separation of the radionuclide, and their encapsulation after the collapse of the porosity by irradiation effect. This new concept would result in obtaining a primary wasteform matrix. Mesoporous silicas will be used as support materials, because the nanometric size of their pores allows easy closure. 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. The ANR Automact project aims to study the potential collapse of a mesoporous silica doped with a radioactive element (238Pu). Another field of application concerns the evolution during aging of the mesoporosity formed in the alteration gel of nuclear glasses. This mesoporosity is a factor aggravating the dissolution of the wasteform matrix. The effects of irradiation could lead to a closure of this mesoporosity, inducing self-healing of the gels. A thesis began in 2022 on this subject in the laboratory.

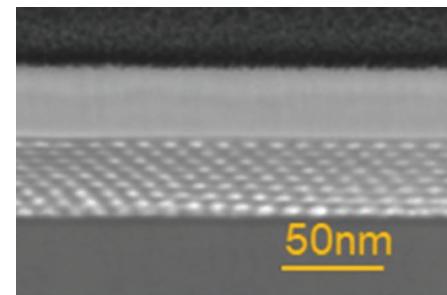


Figure 1. SEM image of SiO_2 mesoporous ordered thin film (IPC).

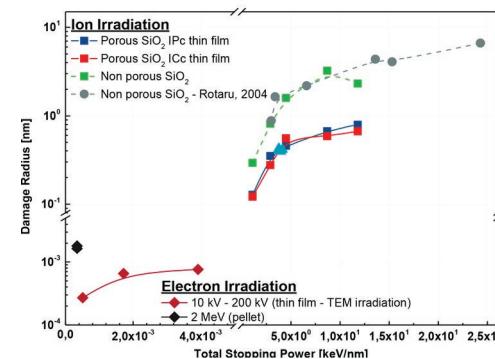


Figure 2. Summary of damage radius of the track induced by radiation damage as a function of total stopping power of the projectile (ions or electrons).

¹ P. Makowski, X. Deschanel, A. Grandjean, D. Meyer, G. Toquer and F. Goettmann - Mesoporous materials in the field of nuclear industry: applications and perspectives - *New J. Chem.*, 36 (2012) 531.

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IMPACT OF SPECIATION IN URANIUM BASED MIXED OXIDES ON THE DISSOLUTION KINETICS

M. Massonnet, T. Barral, S. Szenknect, L. Claparède, N. Clavier, R. Podor, N. Dacheux.
In collaboration with CEA DES/ISEC/DMRC

Uranium-plutonium mixed dioxide $(\text{U},\text{Pu})\text{O}_{2-\delta}$ is currently used as a fuel in several pressurized-water reactors worldwide, and constitutes one of the reference fuels for some of the concepts developed for the fourth generation of nuclear reactors, including sodium-cooled fast reactor (SFR).

In order to reprocess the spent $(\text{U},\text{Pu})\text{O}_{2-\delta}$ assemblies, the quantitative dissolution step must be mastered before any operation of partitioning. Nevertheless, if the dissolution of UO_2 has been extensively documented, that of $(\text{U},\text{Pu})\text{O}_{2-\delta}$ mixed oxides remains less understood. Furthermore, the links between the dissolution rate and the cation speciation in the solid are generally not studied. These latter are of particular importance owing to the complex redox properties of actinide cations. Indeed, while uranium and plutonium are mainly tetravalent in the pristine fuel, they can endure either oxidation or reduction during irradiation, respectively. Also, the presence of aliovalent cations such as soluble fission products (Nd, La, ...) in the UO_2 matrix is expected to impact the uranium redox speciation.

As a result, the fuel matrix mainly consists of a mixture of U(IV), U(V) and even U(VI), on the one hand, and Pu(IV) and Pu(III) on the other hand, which gives rise to a large variety of O/M ratios (with M = U+Pu). In order to fill this gap, highly homogeneous $(\text{U},\text{Ce})\text{O}_{2-\delta}$ and $(\text{U},\text{Nd})\text{O}_{2-\delta}$ sintered samples were prepared by wet-chemistry route. HERFD-XANES spectroscopy led to determine accurately the O/M ratios (with M = U + Ce). Under reducing atmosphere ($\text{PO}_2 \sim 6 \times 10^{-29}$ atm), the oxides were found to be close to O/M = 2.00 while the O/M ratio varied with the sintering

conditions under argon ($\text{PO}_2 \sim 2 \times 10^{-6}$ atm). They globally appeared to be hyper-stoichiometric (i.e. O/M > 2.00), the departure from the dioxide stoichiometry decreasing with both the cerium content in the sample, and the sintering temperature¹.

In order to show the impact of the sintering atmosphere on the chemical durability of the $(\text{U},\text{Ce})\text{O}_{2-\delta}$ samples, solid solutions were densified under Ar and Ar-H₂ at 1400°C for 10h. The two pellets exhibited densification rates close to 94%. The evolution of the normalized mass losses and of the relative mass losses obtained during the dissolution in 2 mol.L⁻¹ HNO_3 at room temperature is reported in figure 1 with the monitoring of the solid-liquid interface by ESEM.

ESEM images evidenced the preferential dissolution of the grain boundaries for the densified compound under Ar-H₂. This result could be due to a slight Ce-enrichment in the grain boundaries, thus explaining the slight pulse observed during the first days of dissolution. This preferential dissolution subsequently resulted in the removing of some grains. For samples prepared under inert atmosphere, the dissolution seemed smooth across the surface. Dissolution thus revealed the crystalline orientation of the grains and some kinetic differences then emerged between the grains, some of them disappearing more quickly than others. A similar approach was also used for $(\text{U},\text{Nd})\text{O}_{2-\delta}$ sintered samples².

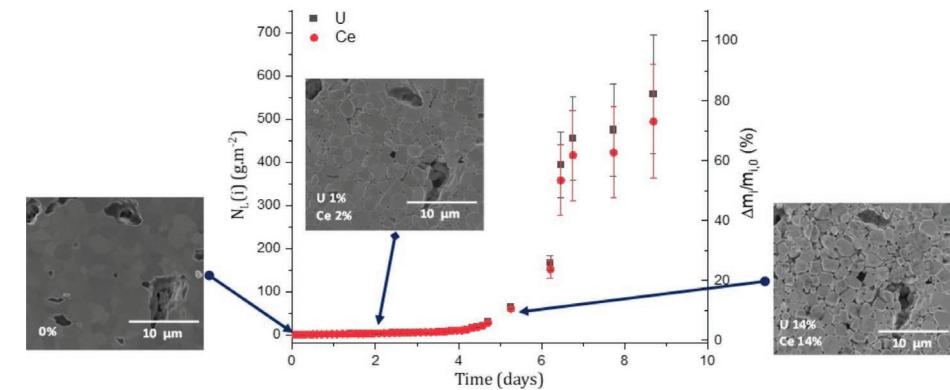


Figure 1. Evolution of the normalized weight losses and of the solid-liquid interface monitored by ESEM during dissolution of sintered $\text{U}0.89\text{Ce}0.11\text{O}_2$ samples sintered (Ar-H₂) in 2 mol.L⁻¹ HNO_3 at RT

¹ M. Massonnet, L. Claparède, J. Martinez, Ph. Martin, M.O.J.Y. Hu-nault, D. Prieur, A. Mesbah, N. Dacheux, N. Clavier - Hydrothermal Influence of sintering conditions on the structure and the redox speciation of homogenous $(\text{U},\text{Ce})\text{O}_{2-\delta}$ ceramics : a synchrotron study - *Inorganic Chemistry* (2023) submitted.

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DISSOLUTION OF PLATINUM GROUP METALS BEARING UO₂

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In collaboration with CEA DES/ISEC/DMRC

Reprocessing of spent nuclear fuels (SNFs) for the recovery of uranium and plutonium is currently achieved in France using the plutonium uranium reduction by extraction process (PUREX). Although SNF is composed of about 96 wt. % of UO₂, its composition and microstructure display an extreme complexity due to the presence of more than 30 fission products. Fission products found as metallic precipitates (named ε -phase) in the SNF are mainly composed of the noble metals Ru, Rh, Pd, Mo and Tc. The first step of the PUREX process is the dissolution of the SNF in hot and concentrated nitric acid. However, until recently, the specific impact of the presence of these fission products on the kinetics of dissolution of the UO₂ matrix received less attention.

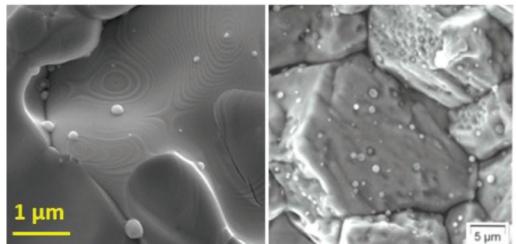


Figure 1. Cleavage surface of UO₂ pellet doped with 3 mol.% Rh and of a real SNF (Noirot, 2009)

The multiparametric study of dissolution revealed that the dissolution rate of UO₂ pellets doped with metallic particles of PGMs was systematically higher than that of UO₂. Moreover, this effect was more pronounced for HNO₃ concentrations less than 1 mol L⁻¹. For higher HNO₃ concentrations, the impact of the PGMs particles was mitigated by the predominant oxidation of U(IV) by nitrate ions. The decrease of the apparent activation energy associated to the reaction of dissolution revealed the catalytic activity of the PGMs particles. The monitoring of the microstructural evolution of the pellet surface by Environmental Scanning Electron Microscopy (ESEM) during dissolution supported the existence of reactions taking place at the metallic particles/UO₂ solid/solid interface².

Furthermore, assessment of mechanistic understanding was achieved from dedicated dissolution experiments. These experiments were designed to evaluate the spe-

In this context, our group has developed a multiparametric study of the dissolution kinetics of UO₂ based model compounds incorporating 3 mol. % of platinum group metals (PGMs: Ru, Rh, Pd) metallic precipitates¹. These compounds were prepared by hydroxide precipitation. The prepared precursors were converted to oxides, pelletized and sintered to create dense UO₂ pellets incorporating PGMs metallic particles. The speciation, the morphology as well as the spatial distribution of PGMs in the sintered samples were determined. For this large panel of materials, the final microstructure was representative of SNF (Fig. 1).

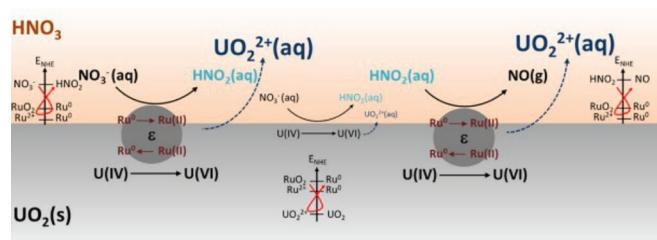


Figure 2. Proposed mechanism for the catalytic effect of RuO nanoparticles incorporated in the UO₂ matrix during dissolution in nitric acid.

cific impact of Ru, Rh, Pd or Mo metallic particles on the dissolution rate of UO₂.³ Ru and Rh had a positive impact, Pd had virtually no effect, whereas Mo had a negative impact on the dissolution rate of UO₂. These differentiated impacts were linked to the redox potentials of the various species in the systems. The redox properties of Ru and Rh, the high electric conductivity and the nanometric dimension of the metallic particles allowed electronic transfer from the nitric acid solution to UO₂ (Fig. 2). In contrast, Mo acted as a competitor to U(IV) oxidation by nitrates due to the redox potentials of MoO₃/Mo and U(VI)/U(IV) couples, respectively. In addition, reduction of U(VI) by Mo metal at the solid/liquid interface can also contribute to slow the UO₂ dissolution kinetics. To evaluate the contribution of these mechanisms, dissolution studies of UO₂ pellets incorporating Mo in various amounts and different chemical forms is currently ongoing.

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SONOCHEMICAL DECONTAMINATION OF HETEROGENEOUS SYSTEMS

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A. Leybros, Y. Barré (DMRC/STDC/LPSD)

High-power ultrasound (US) has been widely used for de-greasing, biological decontamination, scaling, and more simply, 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 are treated without addition of concentrated chemicals avoiding restrictive, laborious and often dangerous handling of materials. In nuclear industry, US-assisted decontamination of materials can be of particular interest for dismantling and decommissioning ending life nuclear facilities. 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 benefits.

UNGG cladding nuclear wastes constitute a huge volume of Mg-based materials raising economic and safety concerns, particularly due to their radioactivity coupled to the potential generation of H₂ gas under disposal. Their significant decontamination would result in more secure and less expensive storage, with a better containment of the separated long-lived radioisotopes that could enter in a classical channel. Preliminary experiments demonstrated the unprecedented structuring of extended Mg surfaces in mild conditions under high-frequency US.¹ "Golf ball"-like extended morphologies were prepared in dilute oxalic solutions at 20 °C under high-frequency US (200 kHz). An original approach carried out through iterative 3D reconstruction of treated surfaces was used to describe their evolution, characterize the formed microstructures and investigate the formation mechanism. A screening

of the sonication experiments clearly pointed out an US frequency dependency for the effects generated at the surface. Later, 345 kHz sonication (0.01 M H₂C₂O₄, 20 °C) of genuine UNGG cladding materials (Mg/Zr alloy) allowed the analogous structuring of their surfaces with the observation of homogeneously distributed craters of 20–40 μm .² After a thorough characterization and comparison of the US effects generated at the surface, several samples were artificially contaminated and characterized before sonication. The complete and rapid sono-chemical decontamination of Mg-based materials was observed, in addition to the removal of the carbon layer promoting corrosion on the inner side of the cladding. Such a behaviour was attributed to the US-controlled dissolution of the Mg-based surface. The extension of sonication allowed neoformed phases (brucite) to accumulate on the surface. This contributed in a slight but continuous surface recontamination attributed to the re-adsorption of U(VI) from the solution which can be avoided by optimizing the treatment duration. US, coupled to ion exchange, was also successfully applied to remove Cs⁺ from contaminated vermiculite clay.³ At room temperature, sonication was found to greatly accelerate the desorption process, by more than a factor of 20, but the desorption yield remained limited. In contrast, the elevated temperature and autogenic pressure under hydrothermal treatment contributed to Cs⁺ desorption rates of up to 55 % at 200 °C and almost complete desorption was achieved under sonohydrothermal treatment at 200 °C, highlighting the potential of this process for the remediation of Cs⁺ contaminated soils. Sonohydrothermal treatment at 100 °C was found to be as efficient as hydrothermal treatment at 200 °C, suggesting that sonication can also be used to minimize energy consumption while maintaining the same operating efficiency.

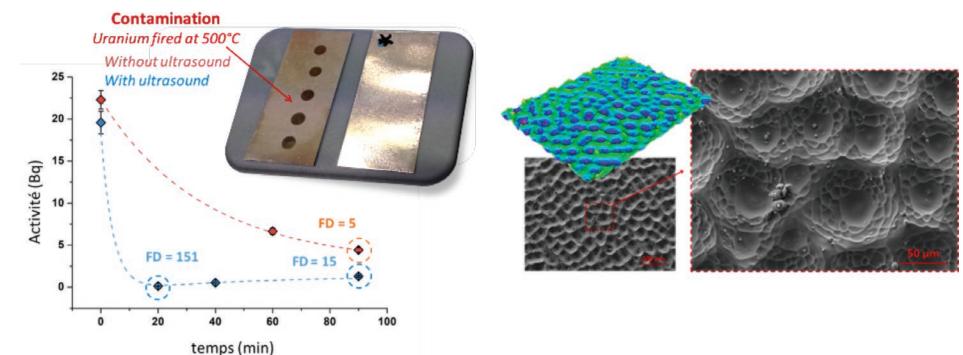


Figure 1. Decontamination of Mg surfaces under 345 kHz US in dilute oxalic medium (0.01 M, Ar, 20 °C, 100 rpm, 40 W). Left image: evolution of the surface activity as a function of the treatment duration. Right image: "golf-ball" shape micro-structure with 3D reconstructions.

¹ 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 - *Ultrason. Sonochem.* (2018) 40, 30-40.

² Ji, R., Virot, M., Pflieger, R., Nikitenko, S. I. Sonochemical decontamination of magnesium and magnesium-zirconium alloys in mild conditions *J. Hazard. Mater.* (2021) 406, 1-14.

³ Herr, S.; Leybros, A.; Barre, Y.; Nikitenko, S.; Pflieger, R. Desorption of Cs from vermiculite by ultrasound assisted ion exchange - *Chemosphere* (2022) 303 Part 3, 135175

COLLOIDAL PHYSICAL CHEMISTRY TOWARDS ELECTROPHORETIC DEPOSITION (EPD)

F. Didier, P. Alastuey, M. Odorico, X. Deschanel, G. Toquer

Electrophoretic deposition (EPD) is known as an important tool for the production of wide range of coatings but which is extended to the nanoscale¹ in this work. The final target is here to control, through a bottom-up approach², the formation of nanostructured material associated with selective optical properties designed for photothermal solar collectors³. This study is focused first on stable charged colloidal dispersions, which are electrodeposited on substrate with tunable thickness, density and morphology. Carbon nanotubes (CNTs), deposited by electrophoretic deposition (EPD), are thus investigated as selective solar absorbers. First, various kinds of CNTs with different aspect ratios, are disper-

sed by ultrasound in an aqueous solution of pyrocatechol violet (PV). PV couples to the CNT's outer walls via π - π stacking interactions and acts as a dispersing agent as well as a charging agent. PV adsorption isotherms on CNT combined with N_2 physisorption isotherms are performed to optimize the CNT/PV ratio. In this way, Zeta potentials up to -40 mV are obtained for the dispersed CNTs, which are deposited on platinized silicon wafers by EPD, forming a film. The EPD kinetics are then investigated as a function of the applied electric field (in the 8–20 V cm⁻¹ range) and are explained through a Sarkar & Nicholson model type (see fig. 1).

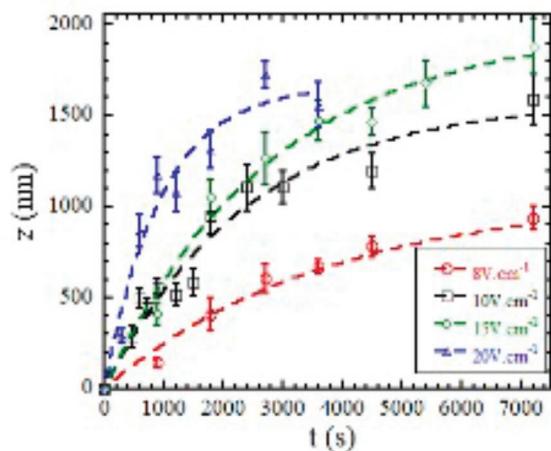


Figure 1. EPD kinetic of SWCNT coating

X-ray reflectivity is performed to characterize the coating density around 1.3 g cm⁻³, and film cohesion is probed by nanoindentation coupled to atomic force microscopy images (see fig. 2). The hemi-spherical reflectance of the samples is measured by spectrophotometers equipped with an integrating sphere, and following from spectra, the absorptance (α) and emittance (ϵ) are calculated⁴. The selectivity of the deposits, based on α and ϵ values, is then discussed as a function of the applied electric field and the coating thickness. Single-walled CNT de-

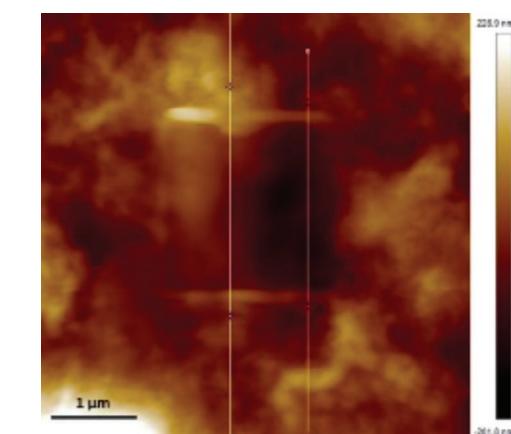


Figure 2. Nano-indentation constraint of 3×10^2 MPa leading to 10% of the film compacting

positions are found to have a solar absorptance of 0.91 and thermal emission of 0.05. Thermal annealing experiments reveal that the coatings could withstand up to 300 °C while sustaining selective properties and losing only 21% of the initial yield. The calculated efficiency of the tandem material would be also enhanced by adding an anti-reflective layer⁵. Advances in the understanding of deposition mechanisms are crucial to finally select the most promising coatings acting as an efficient solar absorber.



¹ Charlot A., Deschanel X., Toquer G. – Submicron coating of SiO₂ nanoparticles from EPD – *Thin Solid Films* (2014), 553, 148-15

² S Shehayeb S., Deschanel X., Karame I., Ghannam L., Toquer, G. – Spectrally selective coatings obtained from electrophoretic deposition of CuO nanoparticles – *Surface & Coatings Technology* (2017), 322, 38-45

³ Shehayeb S., Lautru J., Karame I., Ghannam L., Odorico M., Deschanel X., Toquer, G. – Thin polymeric CuO film from EPD designed for low temperature photothermal absorbers – *Electrochemical Acta* (2019), 305, 295-303

⁴ Shehayeb S., Deschanel X., Ghannam L., Karame I., Toquer, G. – Tandem selective photothermal absorbers based on EPD of CuO suspension coupled with dip-coated silica – *Surface & Coatings Technology* (2021), 408, 126818

⁵ Didier F., Alastuey P., Tirado M., Odorico M., Deschanel X., Toquer, G. – Solar absorbers based on electrophoretically deposited carbon nanotubes using pyrocatechol violet – *Thin Solid Films* (2022), 764, 139614



METHODOLOGIES AND THEORIES IN SEPARATION CHEMISTRY

MÉTHODOLOGIES 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).



MÉTHODOLOGIES ET THÉORIES POUR LA CHIMIE SÉPARATIVE

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



STRUCTURE AND THE THERMODYNAMICS OF COMPLEX SOLUTIONS

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V. Dru, Ch. Sorel (ISEC/DMRC), A. Poulesquen (ISEC/DPME), I. Billard, M. Plazanet (Univ. Grenoble Alpes)

Understanding solvent extraction-based purification and recycling approaches requires detailed information on different thermodynamic properties of phases in order to develop a sustainable and clean industry.

The use of non-standard diluents to replace conventional organic solvents is a key challenge in liquid-liquid extraction. Ionic liquids (ILs) provide economic and environmental benefits due to their very low volatility. They also enable much higher extraction performances than traditional solvents. We recently addressed a complete picture of the microscopic mechanisms leading to temperature-induced phase separation in IL-based acidic aqueous biphasic solutions, which represent a breakthrough in the field of metal recycling¹. Small-angle neutron scattering revealed an unusual property of tributyl-tetradecylphosphonium chloride ($[P_{4444}Cl]$), acid, and water mixture, with a lower solution critical temperature that leads to phase separation as temperature rise. This was explained by the increasing disorder of the short aliphatic chains surrounding the IL ions, allowing chloride ions to attract to the micelle surface and thus increasing the screening of electrostatic repulsion that maintains the micelles in suspension. At the same time, Molecular Dynamics (MD) simulations and small-angle X-ray scattering (SAXS) were combined to investigate the structure of two piperidinium- and (trifluoromethyl-sulfonyl)imid-based ILs ($[EBPip^+][NTf^2]$ and $[EOPip^+][NTf^2]$) differing in the alkyl chain length of their cation that are used for the extraction of rare-earth². The detailed analysis of the different contributions of the X-ray scattering data highlighted the correlations responsible for the low-q peak observed for the long-chain alkyl cations, as well as the angular correlation between anions at large distances (Fig. 1). The apolar microdomain volume decrease for piperidinium-based ILs compared to imid-azolium-based ILs could be attributed to chain alignment, which could explain the difference in extraction performance.

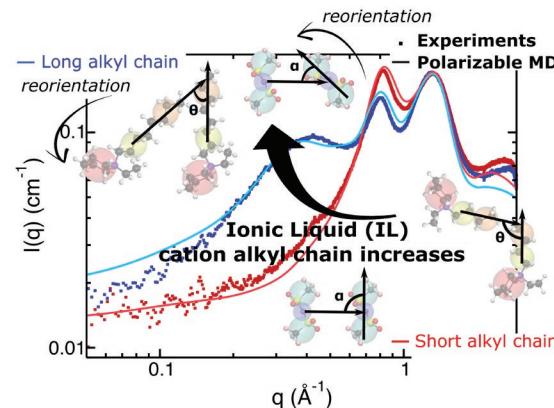


Figure 1. MD simulations combined with SAXS spectroscopy to explain the ILs supramolecular organization.

This approach which combines MD simulations and wide-angle X-ray scattering (WAXS) spectroscopy, has also been used to characterize other types of complex solutions, such as alkali activation solutions of aluminosilicates used in geopolymer applications³. The validation of the MD force fields, made by the comparison with the experiments, allowed us to address the thermodynamic properties of the electrolytes in solution, such as the association constant. It is indeed crucial to determine and predict such thermodynamic properties in order to accurately describe all the mechanisms involved in processes. Binary data for ruthenium(III) nitrosylnitrate, for example, have been reported for a molality range from 0 to 18 mol kg⁻¹. However, due to the complex chemistry of this electrolyte, a combination of methods, including the simple solution concept and the Kusik-Meissner-Tester method, has been used to determine the binary data of an electrolyte exhibiting a deviation from the simple behavior when using the simple solution concept⁴. As a result of a mathematical approach, the deviation has been estimated, and the Vdovenko and Ryazanov equation used to compute the density has been corrected, allowing it to be used for mixtures that deviate from the simple behavior.

¹ Meyer G., Schweins R., Youngs T., Dufrêche J.-F., Billard I., Plazanet M. – How Temperature Rise Can Induce Phase Separation in Aqueous Biphasic Solutions – *Journal of Physical Chemistry Letters* (2022) 13, 2731-2736

² Le Crom S., Dourdain S., Pellet-Rostaing S., Duvail M. – Long-Range Organization Study of Piperidinium-Based Ionic Liquids by Polarizable Molecular Dynamics Simulations – *Journal of Physical Chemistry B* (2022) 126, 3355-3365

³ Coste A., Poulesquen A., Diat O., Dufrêche J.-F., Duvail M. – Investigation of the Structure of Concentrated NaOH Aqueous Solutions by Combining Molecular Dynamics and Wide-Angle X-Ray Scattering – *Journal of Physical Chemistry B* (2019) 123, 5121-5130.

⁴ Dru V., Sorel Ch., Dufrêche J.-F. – Activity of Ruthenium(III) Nitro-sylnitrate Aqueous Solution: Using Ternary Mixtures to Get Binary Data – *Journal of Molecular Liquids* (2021) 329, 115464

MOLECULAR APPROACHES FOR UNRAVELING THE LIQUID-LIQUID EXTRACTION

M. Duvail, M. Vatin, M. Coquil, S. Stemplinger, C. Poulin-Ponnel, J.-F. Dufrêche
Ph. Guilbaud, T. Dumas, C. Berthon B.

The majority of efficient ion separation methods are based on equilibria between complex fluids, typically aqueous and organized organic phases. Understanding the thermodynamics in both phases is therefore crucial for optimizing separation processes. Although the aqueous solutions are now thoroughly described, understanding the thermodynamic properties of ions in organic phases remains a challenge. Indeed, ions migrate from the aqueous to the organic phase thanks to amphiphilic surfactant or extractant molecules in the organic phase, where they are trapped in reverse micelles or aggregates. Modeling such processes remains quite difficult due to the numerous phenomena involved: complexation, solvation, electrostatic interactions, van der Waals forces, polarization forces, entropy, curvature, etc¹.

The main goal of this research is to understand the effect of these phenomena on the ion transfer between both phases. To access the structural, dynamic, and thermodynamic features of ions in solution, molecular dynamics (MD) simulations coupled with experiments, such as EXAFS², SWAXS³, and NMR⁴ techniques, are preferred (Fig. 1).

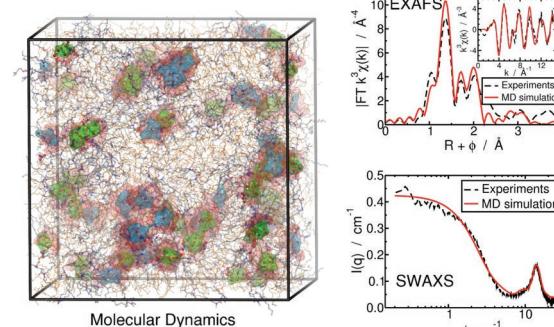


Figure 1. MD simulations coupled with EXAFS and SWAXS spectroscopies

Indeed, it allows for providing realistic pictures of ion solvation, which is a first step needed to access their thermodynamic properties.

Weak association and diluent effects on solvent extraction mechanisms have been investigated by MD simulations and it was revealed that while it can affect the structural properties of the aggregate², typically inside the polar core of the aggregate, it has little effect on curvature properties⁵. Furthermore, MD simulations were used to investigate aggregation properties in order to better understand the role of extractant molecules in the supramolecular properties of solvent extraction phases⁶. Based on association criteria between molecules in the solution and the graph theory, this robust procedure allows for the easy calculation of fundamental structural and physicochemical quantities such as equilibrium constants, enthalpies of formation, and aggregation numbers (Fig. 2).

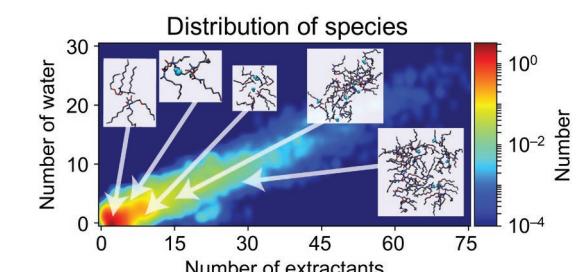


Figure 2. Distribution of water-DMDOHEMA aggregates calculated from MD simulations

¹ Coquil M., Boubals N., Duvail M., Charbonnel M.-C., Dufrêche J.-F. – On Interactions in Binary Mixtures Used in Solvent Extraction: Insights From Combined Isothermal Titration Calorimetry Experiments and Molecular Dynamics Simulations – *Journal of Molecular Liquids* (2022) 345, 116985

² Sukhbaatar T., Duvail M., Dumas Th., Dourdain S., Arrachart G., Solari P.L., Guilbaud Ph., Pellet-Rostaing S. – Probing the Existence of Uranyl Trisulfate Structures in the AMEX Solvent Extraction Process – *Chemical Communications* (2019) 55, 7583-7586

³ Duvail M., Dumas Th., Paquet A., Coste A., Berthon L., Guilbaud Ph. – UO₂⁺ Structure in Solvent Extraction Phases Resolved at Molecular and Supramolecular Scales: A Combined Molecular Dynamics, EXAFS and SWAXS Approach – *Physical Chemistry Chemical Physics* (2019) 21(15), 7894-7906.

⁴ Poulin-Ponnel C., Duvail M., Dumas Th., Berthon C. – Contribution of Molecular Dynamics in pNMR for the Structural Determination of AnV and AnVI Complexes in Solution – *Inorganic Chemistry* (2022) 61, 15895-15909

⁵ Stemplinger S., Duvail M., Dufrêche J.-F. – Molecular dynamics simulations of Eu(NO₃)₃ salt with DMDOHEMA in n-alkanes: Unravelling curvature properties in liquid-liquid extraction – *Journal of Molecular Liquids* (2022) 348, 118035

⁶ Vatin M., Duvail M., Guilbaud Ph., Dufrêche J.-F. – Thermodynamics of Malonamide Aggregation Deduced From Molecular Dynamics Simulations – *Journal of Physical Chemistry B* (2021) 125, 13, 3409-3418

ORGANIC PHASES MESOSCOPIC MODELING FOR SOLVENT EXTRACTION

M. Duvail, S. Gourdin, M. Špadina, S. Stemplinger, Th. Zemb, J.-F. Dufrêche
D. Horinek (University Regensburg), K. Bohinc (University of Ljubljana), M. Gradzielski (Technische Universität Berlin)

Identifying and understanding the motors of selectivity and efficiency of hydrometallurgical processes based on liquid-liquid extraction is crucial for rare-earth elements recycling and nuclear waste management. One essential aspect is understanding the aggregation processes in organized organic solvent phases in contact with aqueous electrolyte solutions. In such approaches, the organic solvent phases are assumed to behave like microemulsions, which are thermodynamically stable mixtures of oil, water, and surfactant¹.

Despite their importance in chemical engineering and separation science, the forces that drive solute transfer are still poorly understood. Indeed, molecular forces and entropy drive ion phase transfer (Fig. 1).

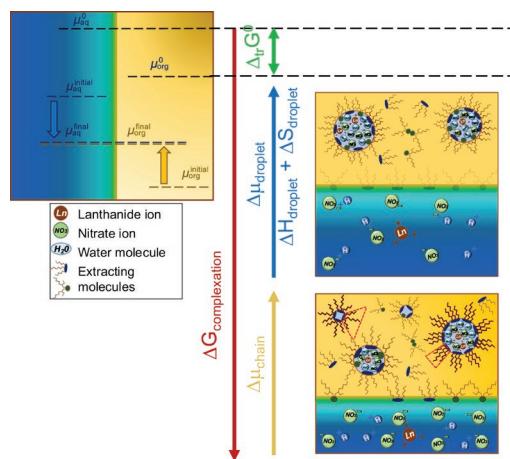


Figure 1. Molecular forces at work in LL extraction

Extraction is thus a combination of high-energy interactions related to short-range forces like ion pairing or complexation forces and low-energy interactions related to supramolecular and nanoscale organizations that are similar to long-range solvent-averaged interactions².

Modeling such complex systems is difficult because the domains are coupled, and the resulting free energy of extraction is around $k_b T$ to ensure the process's reversibility. Nonetheless, quantification is possible. The resulting free energy of transfer is rationalized by combining terms representing strong complexation energies, counterbalanced by various entropic effects and the confinement of polar solutes in nanodomains dispersed in the diluent, together with interfacial extractant terms^{3,4}.

Furthermore, rather than assuming a simple complexation reaction with predefined stoichiometries, we developed a minimal thermodynamics model combining supramolecular chemistry and mesoscale, in which metal salt extraction is triggered by complexation and quenched by the associated necessary reorganization of the structured solvent phase, which is assumed to be a microemulsion⁵ (Fig. 2).

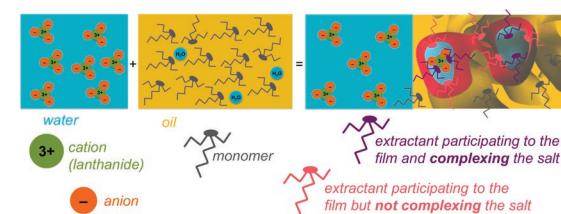


Figure 2. Minimal thermodynamics model

Finally, in order to obtain coherent descriptions of colloidal equations of state, colloidal interactions such as hydration and depletion forces must be considered. This differs significantly from the standard DLVO paradigm, which combines electrostatics and dispersion forces⁶. For example, based on classical density functional theory, we recently developed a general theoretical description of ternary solutions of small molecules in a centrifugal field that could be used to predict analytical experiments or large-scale industrial separation chemistry⁷.

¹ Gradzielski M., Duvail M., Malo de Molina P., Simon M., Talmon Y., Zemb Th. – Using Microemulsions: Formulation Based on Knowledge of Their Mesostucture – *Chemical Reviews* (2021) 121, 5671-5740

² Špadina M., Dufrêche J.-F., Pellet-Rostaing S., Marčelja S., Zemb Th. – Molecular Forces in Liquid-Liquid Extraction – *Langmuir* (2021), 37, 10637–10656

³ Špadina M., Bohinc K., Zemb Th., Dufrêche J.-F. – Synergistic Solvent Extraction Is Driven by Entropy – *ACS Nano* (2019) 13, 13745-13758

⁴ Špadina M., Bohinc K., Zemb Th., Dufrêche J.-F. – Colloidal Model for the Prediction of the Extraction of Rare Earths Assisted by the Acidic Extractant – *Langmuir* (2019) 35, 3215-3230

⁵ Gourdin-Bertin S., Dufrêche J.-F., Duvail M., Zemb Th. – Microemulsion as Model to Predict Free Energy of Transfer of Electrolyte in Solvent Extraction – *Solvent Extraction and Ion Exchange* (2022) 40, 28-63

⁶ Zemb Th., Rosenberg R., Marčelja S., Haffke D., Dufrêche J.-F., Kunz W., Horinek D., Cölfen H. – Phase Separation of Binary Mixtures Induced by Soft Centrifugal Fields – *Physical Chemistry Chemical Physics* (2021) 23, 8261-8272

⁷ Stemplinger S., Prévost S., Zemb Th., Horinek D., Dufrêche J.-F. – Theory of Ternary Fluids Under Centrifugal Fields – *Journal of Physical Chemistry B* (2021) 125, 12054-12062

LIQUID/LIQUID INTERFACE OR INTERPHASE

L. Girard, J. Wang, M. Duvail A. Jonchère and O. Diat
P. Guilbaud (ISEC CEA-Marcoule)
P-M. Gassin, G. Martin-Gassin (ICGM, Montpellier)

A crucial step in many commercial hydrometallurgy applications, especially for the reprocessing of nuclear fuel, is ion separation via liquid-liquid extraction (LL) or solvent extraction. In order to better understand the ion transfer between an aqueous and an organic phase in this type of process, it is important to know precisely i) the speciation of the different ionic and molecular species in each of the two phases in contact which defines the differences in chemical potential between the two phases (the ienaics concept) and ii) all the molecular and supramolecular interactions at the interface which are at the origin of the potential barriers that can influence the kinetics of ion transfer. Several results from volume phase experiment can now be explained structurally by molecular dynamics simulations. However, there hasn't been much research done on a similar experimental/simulation coupled method at the interface containing ligands and in equilibrium with neighboring volumes. Thanks to a collaboration between L2IA and LTSM teams and a laboratory in Montpellier, we first synthesized a diamide extractant containing a chromophore (MAD, figure A) in order to be able to exalt the nonlinear optical signal in a second

harmonic generation experiment, a technique that has proven to be relevant for probing buried fluid interfaces. The different physico-chemical and extracting properties of this molecule were studied as well as its response in nonlinear optics (see figure B). Parallel to this work, molecular dynamics simulation boxes were built with LMCT and the LILA team at CEA/DES/ISEC on a reference diamide in a solvent but also with the new chromophore ligand (see figure C) allowing us to visualize as a function of time the equilibrium of ligand distributions between the organic phase and the LL interface. The goal of comparing the simulated and experimental SHG signals of the simulation boxes has not yet been achieved because the SHG response of this novel ligand revealed a chiral response that depended on the interfacial concentration of the ligand, making it more complex. However, it was reasonable to hypothesize from this work that for a more amphilic extractant, which is more likely to organize at LL interfaces and to aggregate in solution, a depletion layer near the interface might produce a potential barrier, resulting in a more kinetic than diffusive ion transfer.

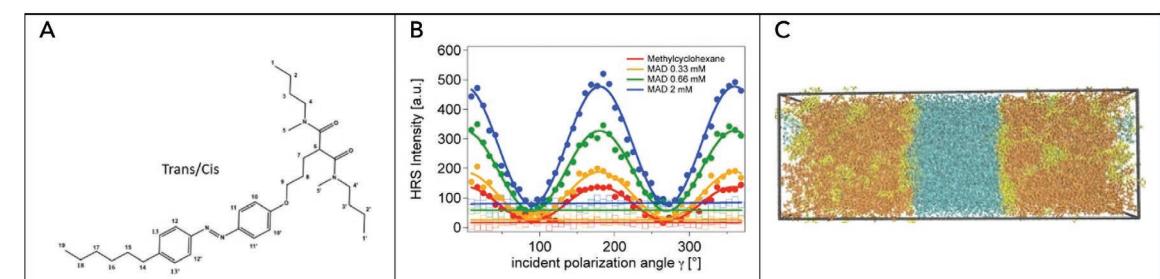


Figure. A) Chemical structure of synthesized chromodiamide (MAD). B) Hyper Ralleigh Scattering signal from MAD versus the incident polarization and concentration. C) Molecular dynamic simulation box of water/ MAD containing methyl-cyclohexane (0.4M).

¹ W Wang J., Arrachart G., Giusti F., Gaëlle M. G., Gassin P. M., Jonchère A., Diat O., Girard L. – Synthesis and Characterization of a Chromo-Extractant to the Probe Liquid-Liquid Interface in a Solvent Extraction Process – *Journal of Physical Chemistry C* (2020) 124, 10916-10923.

OXIDES INTERFACIAL SYSTEMS AND THEIR ENVIRONMENT

B. Siboulet, K. Wang, J.-F. Dufrêche, D. Rébiscoul, M. Duvail, L. Girard

Ions at oxide-charged interfaces are ubiquitous and widely studied. Most of the continuous models for such interfaces are due to Smoluchowski (1872-1917) and are still applied in the field. Simulations, classical or quantum, have the virtue of reducing the extent of conjectures required for the interpretation of experiments.

Indeed, the simulation of oxide interfaces is a powerful tool, both in the fundamental knowledge of these interfaces, as well as in the interpretation of experiments.

We performed various studies, describing the interface with more accuracy than it is usually done in most studies including simulations. We have shown¹ that a high affinity between ions in a dissolved salt promotes the ion adsorption at the surface, which then occurs substantially in the form of pairs. The difference between the pair adsorption of BaCl_2 and MgCl_2 is significant. Experiments on the insertion of MCl_2 solution in silica nanochannels under XRR³ show that the fluid mobility in the channel is impaired in the case of BaCl_2 , in contrast with MgCl_2 or CaCl_2 .

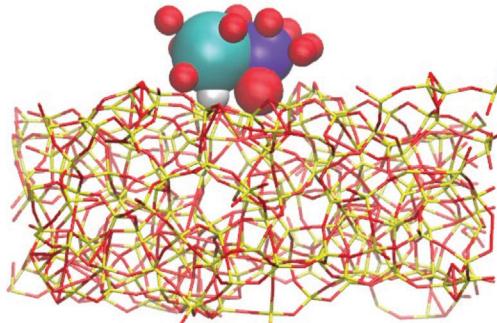


Figure 1. The cation-anion interaction at the surface encourages cation adsorption.

The question of whether this results from ion surface interaction or interionic interaction in bulk is answered by simulation: the association in the bulk is the driving factor of this observation, and this is in line with solubility tendencies. The information on ion distribution at charged interfaces is generally indirect (electrokinetic phenomena, titration), but there is a direct method, the X-Standing Wave Reflectivity (XRSW).³ Although direct and selective, these experiments take advantage of adjusting on molecular simulations rather than on the Gouy-Chapman-Stern model. Cation adsorption selectivity on amorphous silica is shown to be a result of hydration at surface⁴, and, in the variety of sites occurring on an amorphous solid, the selectivity of any site can be deduced from simple steric considerations. Simulation identifies unambiguously charge reversing as a result of divalent adsorption, as well as its cancellation upon the addition of a monovalent cation, namely sodium.

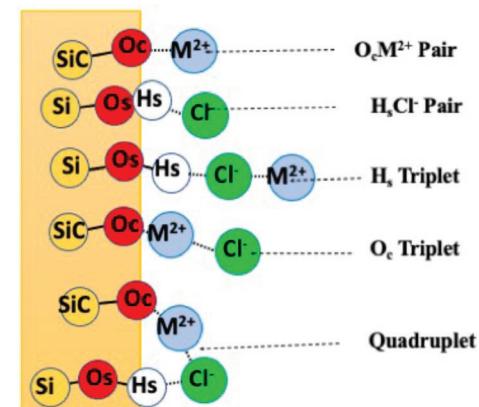


Figure 2. Doublet (site-ion), triplet, and quadruplet ion clusters at silica surface.

¹ Wang K., Siboulet B., Rébiscoul D., Baum M., Daillant J., Malloggi F., Girard L., Dufrêche J.-F. - How ion pair formation drives adsorption in the Electrical Double Layer: Molecular Dynamics of charged silica-water interfaces in the presence of divalent alkaline earth ions - *The Journal of Physical Chemistry C* (2021) 125, 20551-20569.

² Rébiscoul D., Baum M., Wang K., Tardif S., Larrey F., Siboulet B., Dufrêche J.-F., Rieutord F. - Experimentally probing ionics in extreme confinement - *Journal of Colloid and Interface Science* (2021) 614, 396-404.

³ Malloggi F., Ben Jaballah S., Girard L., Siboulet B., Wang K., Fontaine P., Daillant J. - X-ray Standing Waves and Molecular Dynamics Studies of Ion Surface Interactions in Water at a Charged Silica Interface - *The Journal of Physical Chemistry C* (2019) 123, 30294-30304.

⁴ Döpke M. F., Lützenkirchen J., Moulton O. A., Siboulet B., Dufrêche J.-F., Padding J. T., Hartkamp R. - Preferential Adsorption in Mixed Electrolytes Confined by Charged Amorphous Silica - *The Journal of Physical Chemistry C* (2019) 123, 16711-16720.

TEST VEHICLE: A NEW EXPERIMENTAL TOOL TO STUDY PROCESSES OCCURRING AT THE SOLID-LIQUID INTERFACE

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The physical-chemical processes occurring at the solid-liquid interface such as adsorption, complexation, species transport, dissolution, condensation, precipitation and electrochemical reaction, drive the evolution of bulk or porous materials when their surface are in contact with an aqueous solution. Thus, it is important to describe these processes to *in fine* predict the material surface behavior in solution.

To study the process occurring at the solid-liquid interface, we used since few years, the so-called test vehicle. A test vehicle is defined as the use of a model sample presenting a distinctive signal when it is analyzed with a specific characterization tool. From this distinctive signal, with or without the use of a fitting model, it is possible to have a precise quantification of values characteristic of a process. Several examples are presented on the Figure 1. Among these examples, the highly ordered silica meso-

pores such as SBA15 and MCM41, *in situ* characterized by Small Angle X-ray Scattering have allowed the quantification of the kinetics of dissolution of the silica pore wall and the solution diffusion through its microporosity⁶. Another example is the silica nanochannels with a height of 3 or 5 nm made of etched grooves in silica films, coupled to the interface X-ray reflectivity analysis using hard X-rays that directly provides the ion distribution of the nanochannel-confined solution. Using this combination and probing the filling kinetics of the nanochannels with ionic solutions XCl_2 1 M having cations presenting increasing kosmotropic properties ($\text{X} : \text{Ba} < \text{Ca} < \text{Mg}$), we directly evidence the interface, i.e. the interaction existing between ions and the surface and show that the formation of ion pairs may result in dramatic changes of solution properties in extreme confinement².

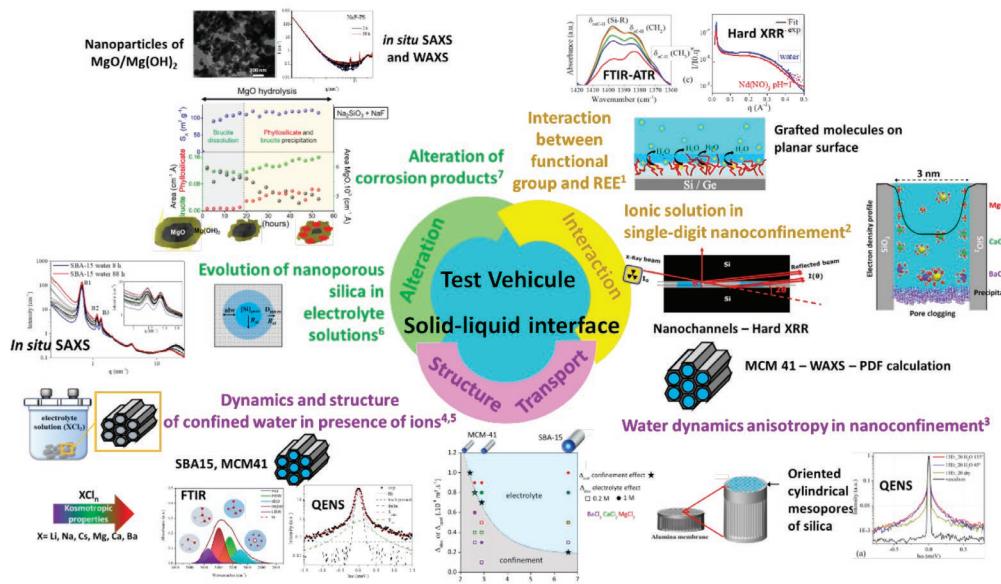


Figure 1. Illustration of test vehicle used for the study of the solid-liquid interface.

¹ Walker O., Rébiscoul D., Odorico M., Tardif S., Pellet Roistaing S., Arrachart G. - Toward a method of understanding the complexation of REE by functionalized organosilanes in aqueous media, submitted.

² Rébiscoul D., Baum M., Tardif S., Wang K., Siboulet B., Dufrêche J.-F., Rieutord F. - Experimentally probing ionic solutions in single-digit nanoconfinement, *Journal of Colloids and Interface Science*, *Journal of Colloids and Interface Science* (2022) 614, 396-404.

³ Khoder H., Zanotti J.-M., Ollivier J., Le Goff X., Podor R., Rébiscoul D. - Anisotropy of water dynamics confined in model silica material, in preparation.

⁴ Baum M., Rébiscoul D., Rey C., Juranyi F., Rieutord F. - Dynamical and Structural Properties of Water in Silica Nanoconfinement: Impact of Pore Size, Ion Nature, and Electrolyte Concentration, *Langmuir*, (2019) 35, 10780-10794.

⁵ Baum M., Rébiscoul 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 C*, (2018) 122, 19857-19868.

⁶ Baum M., Rieutord F., Rébiscoul D. - Underlying Processes driving the Evolution of Nanoporous Silica in Water and Electrolyte Solutions, *Journal of Physical Chemistry C* (2020) 124, 27, 14531-14540.

⁷ Rébiscoul D., Boubon R. - Evolution of Mg-based corrosion products in porous solutions extracted from geopolymers, in preparation.

MULTI-SCALE STRUCTURAL CHARACTERISATION OF FOAM

J. Lamolinairie, A. Jonchère, C. Pasquier, L. Girard, P. Bauduin and O. Diat

To investigate foam structure and because there is currently no one approach that can gather the essential data concurrently over all pertinent length scales, studies have been conducted sequentially, with each technique investigating a separate foam sample. However, because each sample is distinct, the results are not comparable. Additionally, the experimental demonstration of theoretical foam destabilization mechanisms was previously hampered by the lack of a comprehensive perspective of the evolution of the foam structure with aging.

The idea was to develop a device capable of probing the same sample of foam with multiple techniques within a single experiment.

The developed device consists of a quartz column – based on the FOAMSCAN model produced by Tecnis Scientific within which the foam sample is produced. A wide range of data is then collected from the nano to the centimeter scale through the simultaneous use of three techniques: electronic conductivity, macro-photography and small-angle neutron scattering (SANS). Analysis of the simultaneous data acquired by the device has enabled the first multi-scale characterization of the structural evolution of foam, significantly improving understanding of the underlying aging processes.

The average thickness of foam films, obtained using SANS data, combined with the repulsion between facing foam films, deduced from the curvature of plateau borders in the image data, has allowed the first quantification of pres-

sure inside the foam. The pressure measured in the foam has been found to differ by a factor of 10 from the pressure measured on a single film, despite the fact that a thin-film pressure balance is typically used to measure pressure on a single film. This finding further demonstrates the unreliability of combining results from various experimental set-ups. «The ILL's D33 diffractometer was constructed and equipped with not one but two detectors, one closer and one further from the sample, giving it a particularly wide Q-range. With this setup, it is possible to probe the entire structure of foam in a single experiment, from hundreds of nanometers to one nanometer. The neutron beam's comparatively large 15 mm diameter enables non-destructive probing of hundreds of bubbles at once, guaranteeing that the results are statistically significant. Additionally, the ILL's neutron output, which is the world's highest continuous neutron flux, has an unparalleled temporal resolution that makes it possible to closely monitor the foam's structural development.

For the device's development, the Partnership for Soft Condensed Matter (PSCM) at ILL was crucial. «At the PSCM, extensive preliminary work was done to characterize foam using all available methods. The PSCM is crucial to ensuring that neutrons are only utilized when their contribution is vital because they are an expensive probe, according to Dr Leonardo Chiappisi.

The new device represents an important milestone in the quest to understand foam and opens new perspectives for the field.

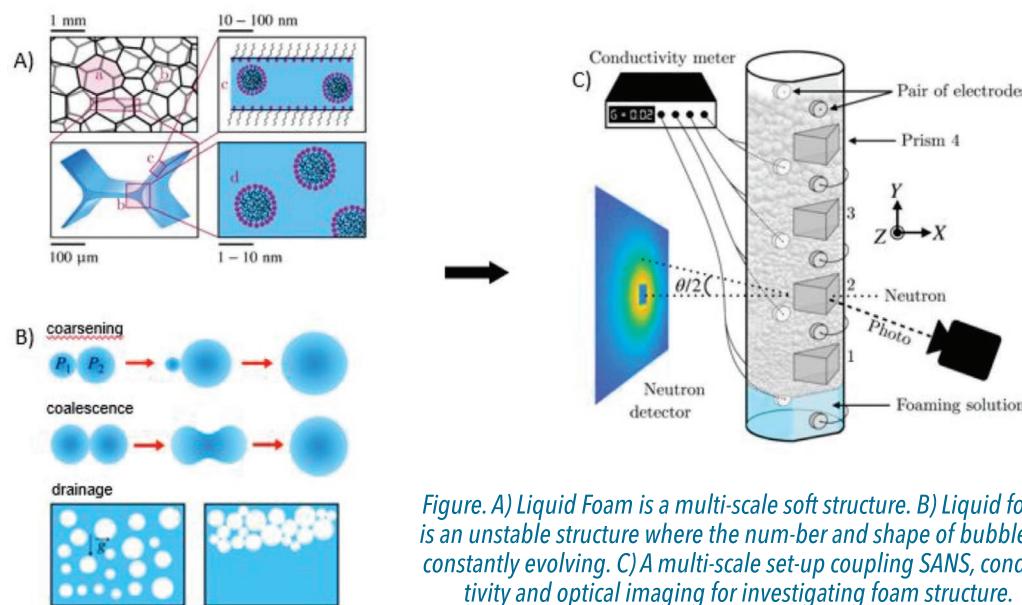


Figure 1. A) Liquid Foam is a multi-scale soft structure. B) Liquid foam is an unstable structure where the number and shape of bubbles is constantly evolving. C) A multi-scale set-up coupling SANS, conductivity and optical imaging for investigating foam structure.

¹ Lamolinairie J., Dollet B., Bridot J. L., Bauduin P., Diat O., Chiappisi L. - Probing foams from the nanometer to the millimeter scale by coupling small-angle neutron scattering, imaging, and electrical conductivity measurements - *Soft Matter* (2022) 18, 8733-8747.

SPECIFIC ANALYSIS OF HIGHLY ABSORBING NANOPOROUS POWDER BY SMALL-ANGLE X-RAY SCATTERING

L. Zjie, D. Rébiscoul, T. Narayanan, T. Zemb

The characterization of nanoporous powders of highly absorbing compounds such as transition metals, rare earths, lanthanide and actinide elements, by Small-angle X-ray scattering involves overcoming several difficulties before quantitative information related to the porous texture can be derived. In this context, we worked on a new method that overcomes these difficulties to obtain the scattering intensity in absolute scale and to quantify for the first time, the specific surface and the porous volume of these materials¹.

For these highly absorbing materials, absorption effect has to be corrected and three components has to be distinguished in the measured intensity: the "leaked" beam i.e. the beam that does not cross the material due to its high absorption, the scattered and the reflected beam. To minimize the reflectivity contribution choosing the most appropriate grain size, mathematical expressions of the scattered and the reflectivity fractions of the measured intensity were established for one single spheri-

cal grain. Using these two mathematical expressions, several experimental cases with various highly absorbing grain properties (size and specific surface) can be calculated and the most appropriate grain size chosen.

Generally, in order to minimize the absorption effect, high resolution synchrotron radiation source at 16 keV can be used to characterize highly absorbing materials. However, with a classical laboratory X-ray source with Mo at 17.4 keV, the absorption problem still exists. Regarding this problem, we proposed a new and robust experimental method to correctly determine the scattering intensity in absolute scale of the highly absorbing granular samples. This method allows to calculate accurately the porous volume and the specific surface using the Porod's law and the invariant without using a synchrotron instrument. This last result opens new perspectives for the characterization of the volume and the surface of highly absorbing actinide oxide powders.

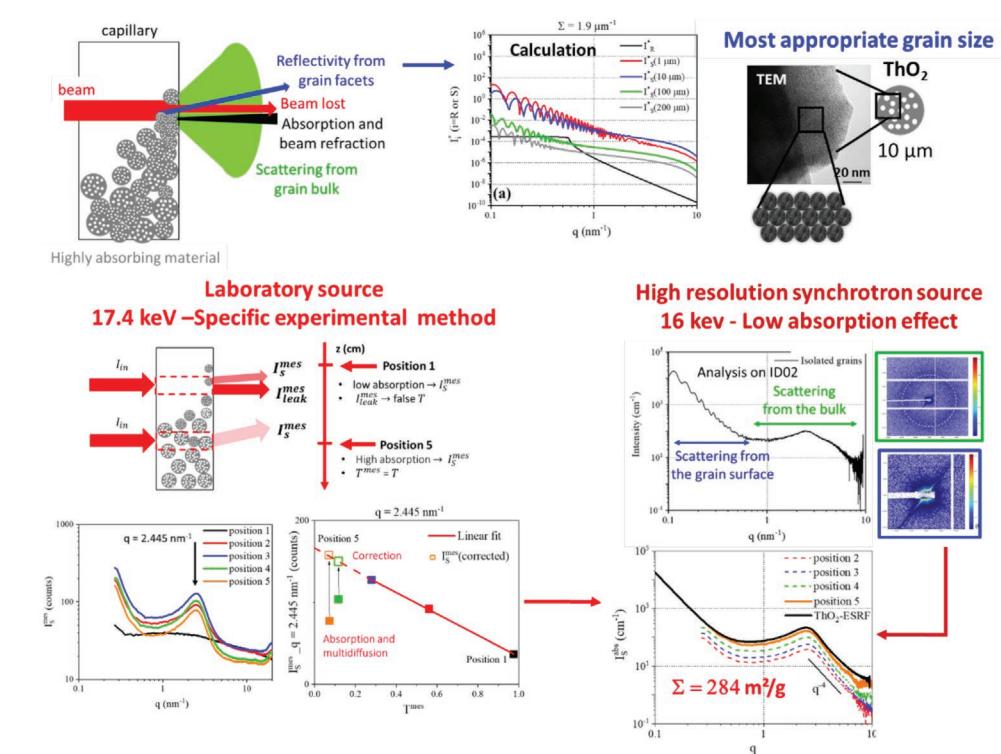


Figure 2. Method developed to characterize the highly absorbing materials using the example of ThO_2 microporous materials².

¹ Lu Z., Rébiscoul D., Narayanan T., Zemb T. - Specific analysis of highly absorbing nanoporous powder by small-angle X-ray scattering - *Journal of Applied Crystallography* (2022) 55, 1154-1163.

² Lu Z., Zemb T., Le Goff X., Clavier N., Khoder H., Lautru J., Rébiscoul D. - Facile Preparation of Macro-Microporous Thorium Oxide via a Colloidal Sol-Gel Route toward Safe MOX Fuel Fabrication- *ACS Applied Materials Interfaces* (2022) 14, 47, 53165-53173

SERAMIC: A SEMI-AUTOMATIC METHOD FOR THE SEGMENTATION OF GRAIN BOUNDARIES

R. Podor, X. Le Goff, J. Lautru, H.P. Brau, N. Clavier

The SEraMic method¹, implemented in the SEraMic plugin for Fiji or ImageJ softwares, has been developed to calculate a segmented image showing the grain boundaries from a ceramic cross-section. This method has been used to accurately and automatically determine the grain boundary positions – and further assess the grain size distribution - of monophasic ceramics or metals / alloys. The only required sample preparation is a mirror polished cross-section. The SEraMic method is based on the recording of at least 6 backscattered electron (BSE) SEM images with different tilt angles ranging between -5° to $+5^\circ$, of a unique region of interest, which emphasize the orientation contrasts of the grains (Fig. 1). As this latter varies with the incident beam angle with the sample, the set of images contains the information relative to all the grain boundaries. The SEraMic plugin calculates and builds automatically the segmented image of the grain boundaries from the set of tilted images (Fig. 2). The SEraMic method is com-

pared with the classical thermal etching methods. It is applied to the determination of grain boundaries for different types of materials (oxides, phosphates, carbides, alloys). The method remains easy to use and accurate when the average grain diameter is higher or equal to 0.25 μm .

The SEraMic method saves a lot of time (about 90-95%) in the tedious analysis steps of sample preparation (annealing for thermal etching in particular) and determination of the average grain size in ceramics. It is independent of the operator. It allows working on large quantities of grains (from 800 to 2000). Finally, this method will be adapted to work on multiphase materials.

It is currently being used in numerous projects currently underway at ICSM to characterize ceramics or establish sintering maps.

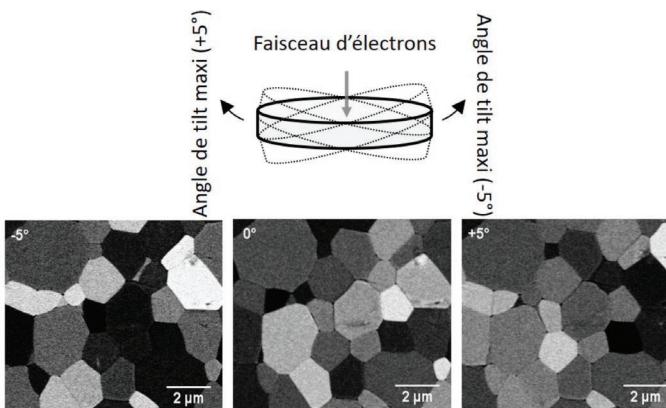


Figure 1. Principle of the SEraMic method:
recording of tilted BSE image series.

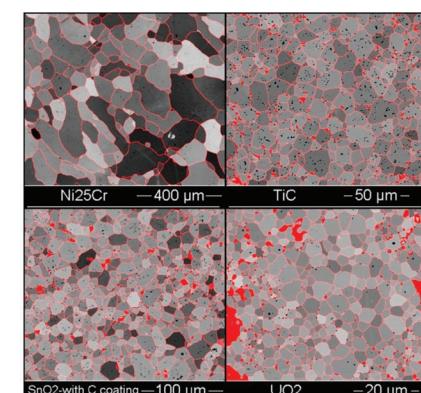


Figure 2. Segmented images for different
types of materials using the SEraMic method.

NANOPARTICLES, NANOSTRUCTURES AND NANODEFECTS IMAGING WITH AFM

M. Odorico, R. Podor, L. Bonato, M. Virot, S.I. Nikitenko, A.H. Anamul, S. Peugot, J.-L. Pellequer

In numerous scientific fields such as life, materials and earth sciences, there is a need for a precise description of the materials features at the nano-metric scale. Atomic Force Microscopy (AFM) is one of the dedicated techniques for probing material morphology and topography down to the atomic scale. This technique has been used at ICSM to characterize nanoparticles, nanostructures and nanodefects.

- Nanosphere standard particles (PS22) given at a reference diameter of 22 ± 2 nm were precisely characterized

by AFM and several other techniques during an inter-comparison experiment with the goal to measure sizes of several nanoparticles¹ (Fig. 1a-c).

- AFM was used to emphasize the evolution of the nanoscale architecture of ThO_2 samples during a heat treatment². The absence of nanostructure is evident for Th oxalate precursors, confirming the temperature dependence of the ThO_2 nanostructure.

- Several types of local defects generated by electron and particle irradiations at high energies and doses were characterized by AFM.

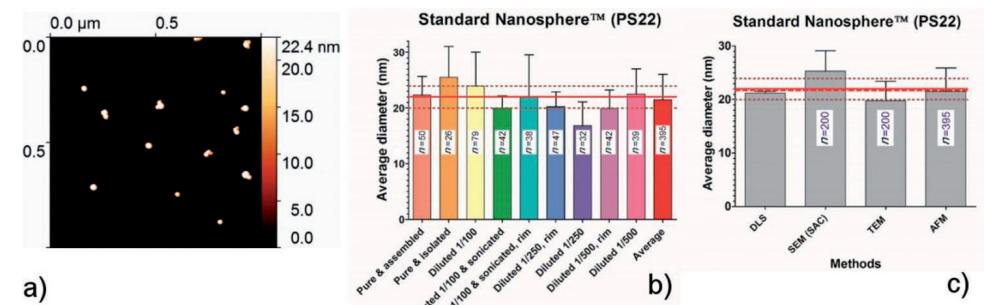


Figure 1. Nanosphere standard particles a) AFM view, b) AFM analyses, c) other techniques analyses

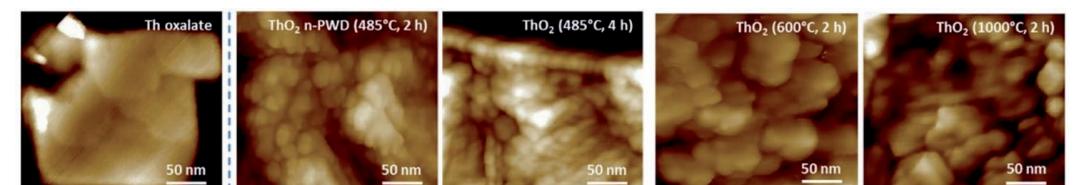


Figure 2. AFM images showing the nanoscale architecture of ThO_2 samples during heat treatment

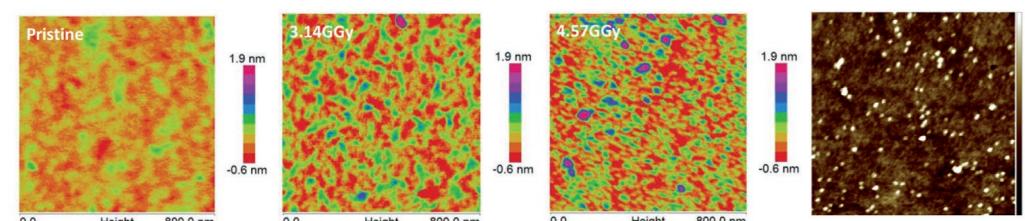


Fig. 3. a) AFM images obtained on the surfaces of pristine (1), 3.14 GGy (2) and 4.57 GGy (3) sample (2.3 MeV electrons irradiation). b) AFM image of ion tracks on the surface of the BS3 glass irradiated with 10^9 MeV U ions up to 7×10^{10} ions. cm^{-2} .³

¹ Teulon J.M. et al. - On the operational aspects of measuring nanoparticle sizes - *Nanomaterials* (2019) 9, 18.

² Bonato L. et al. - Probing the local structure of nanoscale actinide oxides: A comparison between PuO_2 and ThO_2 nanoparticles rules out $\text{PuO}_{2+\alpha}$ hypothesis- *Nanoscale Advances* (2020) 2, 214-224.

³ Mir A.H., Peugot S. - Using external ion irradiations for simulating self-irradiation damage in nuclear waste glasses: State of the art, recommendations and prospects- *Journal of Nuclear Materials* 539 (2020) 15224618.

CHARACTERISATION OF BUBBLES, OF THE SONOCHEMICAL PLASMA AND COMPARISON WITH OTHER PLASMAS

R. Pflieger, S. Herr, S.I. Nikitenko
M. Ashokkumar (University of Melbourne)
M. Draye (University Savoie Mont-Blanc)
M.A. Courty (Institute PROMES)

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^\bullet 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 or that can be monitored to follow the evolution of the sonicated system.¹

The combination of SL measurement with pulsed ultrasound can be used to monitor the dissolution of bubbles and to estimate bubble size distribution from it. A strong effect of the gas nature was observed at 362 kHz, with cavitation bubble sizes of 3.0 μm for Ar, 1.2 μm for He,

Finally, the sonochemical plasma can be used as a tool to try and understand naturally occurring chemical reactions. This is done in the framework of the project LINA, led by Marie-Agnès Courty from PROMES institute and supported by Region Occitanie, that aims at understanding the long-term transfer of nanoparticles produced by ionisation in the atmosphere to bee hives via pollen, nectar, propolis, water and their transformations by honey bees into polymer nanocomposites. The latter are either stored in the hive or eliminated, depending on their toxicity. It is shown that similar nanocomposites can be formed by the sonochemical approach and by other plasma techniques. Mechanisms in nature are under investigation.

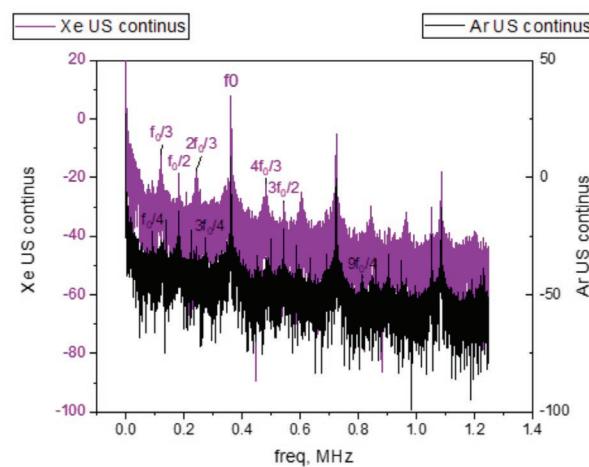


Figure 1. Acoustic spectra measured in water saturated with Ar or Xe and sonicated at $f_0 = 362$ kHz.

¹ R. Pflieger; M. Lejeune; M. Draye - Sonoluminescence Spectra in the First Tens of Seconds of Sonolysis of [BEPip][NTf₂], at 20 kHz under Ar - *Molecules* (2022) 27(18), 6050

² R. Pflieger, G. Audiger, S.I. Nikitenko, M. Ashokkumar - Impact of bubble coalescence in the determination of bubble sizes using a pulsed US technique: Part 2 - Effect of the nature of saturating gas - *Ultrasonics Sonochemistry* (2021) 73, 105537

³ S.I. Nikitenko, M. Brau and R. Pflieger - Acoustic Noise Spectra Under Hydrothermal Conditions - *Ultrasonics Sonochemistry* (2020) 67, 105189; Herr, S ; Leybros, A ; Barre, Y ; Nikitenko, S ; Pflieger, R - Desorption of Cs from vermiculite by ultrasound assisted ion exchange - *Chemosphere* (2022) 303 Part3, 135175

FURNASEM: A NEW METALLIC FURNACE FOR HT-SEM

J. Mendonça, H.P. Brau, D. Nogues, A. Candeias, R. Podor

In situ high-temperature experimentation in a Scanning Electron Microscope (SEM) is an advanced technique for the study of matter that allows the visualization of the dynamics of microstructural transformations that a material undergoes during heat treatment. The implementation of this technique requires the use of a micro-furnace allowing the heating and observation of the samples. The work carried out with the industrial partner NewTEC Scientific (Readynov FurnaSEM project and Cifre thesis of J. Mendonça) is to design, produce and test a new micro-furnace, called FurnaSEM, capable of heating and cooling rapidly (about 10°C/s) a millimetre-sized sample up to 1300°C, under high vacuum and reduced gas pressure. The design choices for the microfurnace (flat furnace with a sample on top) are based on extensive literature research. The materials used to manufacture the various elements of the microfurnace are chosen according to their physical and chemical properties. The geometry of the furnace and the materials selected are implemented in a digital model, called a digital furnace, and the shape of the parts is optimised by thermal calculations. In parallel, the FurnaSEM microfurnace was manufactured, tested and characterised in a test bench specially

developed for this work (Fig. 1). The experimental results validated some of the numerical model results and discussed their limitations (Fig. 2). The technical operational characteristics of the FurnaSEM microfurnace have been precisely established and are in accordance with the specifications. Numerical calculations and measurements in the test bench show that the positioning of a sample on FurnaSEM can generate a temperature jump. Effective solutions to limit this artefact are proposed. The FurnaSEM microfurnace is used to perform in situ experiments in a SEM up to 1340°C, under vacuum and gas. All the technical characteristics of FurnaSEM have been validated under operating conditions and many new results have been obtained.^{1,2} A new generation of microfurnaces has been developed based on the coupling of a numerical and experimental approach. Recommendations for the future user on the geometry of the samples and their positioning on the furnace are given on the basis of quantifiable elements. Finally, the geometry of the furnace can be adjusted on demand using numerical simulations. The FurnaSEM 1300 furnace is currently marketed by NewTEC Scientific.

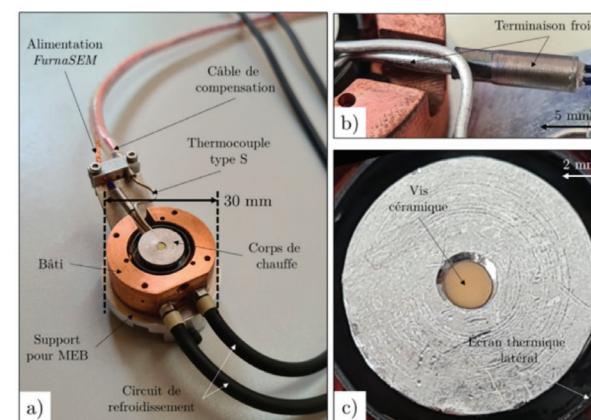


Figure 1. View of the FurnaSEM 1300 furnace.

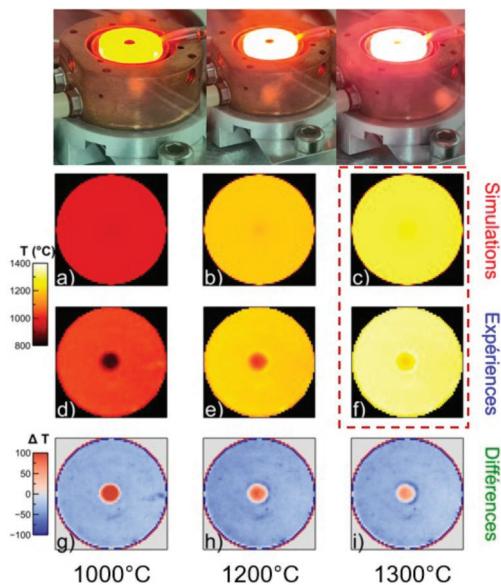


Figure 2. Experimental and numerical views of the FurnaSEM 1300 device under operating conditions at 1000, 1200 and 1300°C.

¹ Podor, R., Mendonça, J., Lautru, J., ..., Mathieu, S., Vilasi, M. - Evaluation and application of a new scintillator-based heat-resistant back-scattered electron detector during heat treatment in the scanning electron microscope - *Journal of Microscopy* (2021) 282(1), 45-59.

² Trillaud, V., Podor, R., Gossé, S., ..., Dacheux, N., Clavier, N. - Early stages of $\text{UO}_{2+\delta}$ sintering by in situ high-temperature environmental scanning electron microscopy - *Journal of the European Ceramic Society* (2020) 40(15), 5891-5899.

NEW IMAGING MODES FOR HIGH TEMPERATURE SCANNING ELECTRON MICROSCOPY

R. Podor, J. Lautru, J. Mendonça, H.P. Brau, X. Le Goff, D. Nogues, A. Candeias

The use of the FurnaSEM device opens new opportunities in terms of imaging conditions due to its flat configuration and its fully metallic conception. For example, the working distance between the sample and the objective lens can be reduced (thus improving the signal-to-noise ratio of the images and improving the resolution) or new detectors can be associated with the furnace.

First of all, the working distance between the sample and the objective lens can be minimized. Thus, low voltage images (up to 3kV) could be recorded under residual gas pressure at high temperature. They allow observing surface details of a $(\text{Ce}, \text{Gd})\text{O}_2$ -Ag thin film as low as 30 nm, during thermal treatment at $T=350^\circ\text{C}$ (see Fig. 1). Second, the design of a fully metallic furnace makes it possible to reduce the outgassing of the furnace during the heat treatments. This property allows the direct observation of the microstructural evolution of metallic materials and opens new perspectives in the field of metallurgy. Third, the furnace can be tilted relative to the primary electron beam and series of tilted images can be recorded at high temperature. These images are then used to reconstruct a 3D image of the sample surface directly at high temperature. These images can be recorded continuously and allow the topographic variations of a sample during heat treatment to be described quantitatively. This technique have been used to study the surface variations of an Al-Si coating deposited on a steel substrate during a heat treatment (Fig. 2)¹. Last, a backscattered electron detector that can be used at high temperature, developed by the Czech company Crytur, was adapted to the SEM and used to study phase transformations at high temperatures (Fig. 3)². These methodological developments open up new avenues of study for understanding the behavior of materials at high temperatures (sintering, oxidation, reactivity of glasses, etc.).

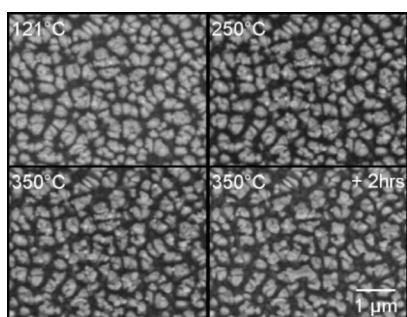


Figure 1. Microstructural evolution of a $(\text{Ce}, \text{Gd})\text{O}_2 + \text{Ag}$ thin film during a heat treatment observed at $E_0 = 5\text{kV}$.

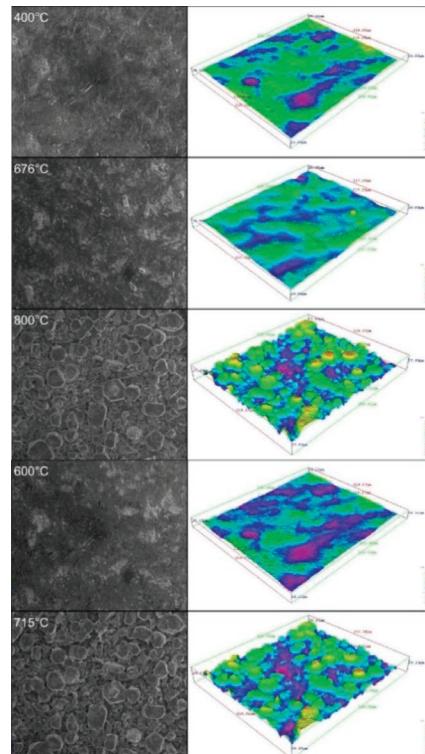


Figure 2. 3D images of Al-Si coating deposited on a steel substrate during a heat treatment.

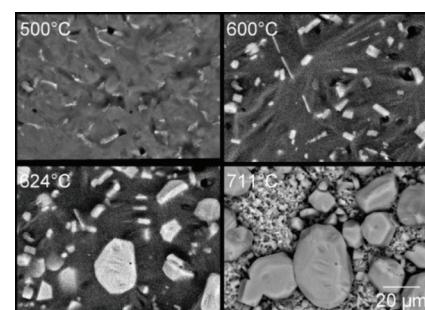


Figure 3. BSE images of Al-Si coating deposited on a steel substrate during a heat treatment.

¹ Podor, R., Mendonça, J., Lautru, J., (...), Mathieu, S., Vilasi, M. - Direct Observation of the Surface Topography at High Temperature with SEM-Microscopy and Microanalysis (2020) 26(3), 397-402.

² Podor, R., Mendonça, J., Lautru, J., (...), Mathieu, S., Vilasi, M. - Evaluation and application of a new scintillator-based heat-resistant back-scattered electron detector during heat treatment in the scanning electron microscope - Journal of Microscopy (2021) 282(1), 45-59.



INTERNATIONAL PROJECTS



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MICROEMULSIONS: UNIFICATION OF ULTRA-FLEXIBLE, FLEXIBLE AND RIGID CASES

Th. Zemb, M. Duvail, J-F. Dufrêche

Michael Gradzielski, Paula Malo de Molina, Miriam Simon (TU-Berlin)

Ishi Talmon (Technion, Haifa)

Microemulsions are dispersions of two fluids stabilized by a molecular layer of surfactants. They are optically inactive and differ from mini and macro-emulsions by their thermodynamics stability. They are ubiquitous in important application, not only in the nuclear fuel cycle, but also in the food, agriculture, pharmacy and home care domains. There are more than thousand scientific papers and hundred patents a year dealing with some kind of microemulsions. We review the properties of the three classes of microemulsions, depending on the flexibility of the surfactant film: the rigid,

the flexible and the newly recognized ultra-flexible microemulsions. The latter had several names in the litterature, such as surfactant-free microemulsions or mesoscopic solubilisation. Ultra-flexible microemulsions are distinguished by the order of magnitude of bending constant and solvation forces versus thermal free energy¹. The rigid microemulsions, most used in pharmaceutical applications and inorganic nanoparticle stabilization are shown below with their topology on the figure 1A on the left below.

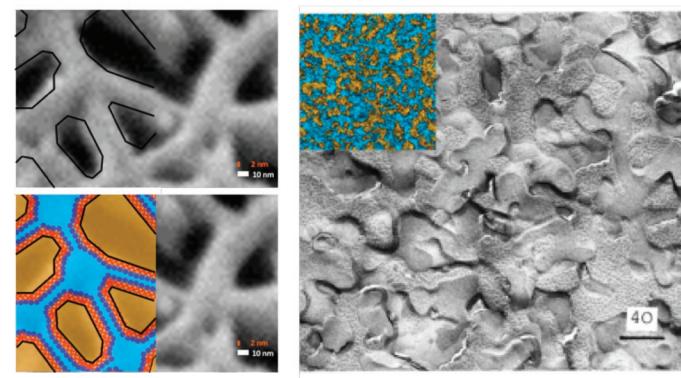
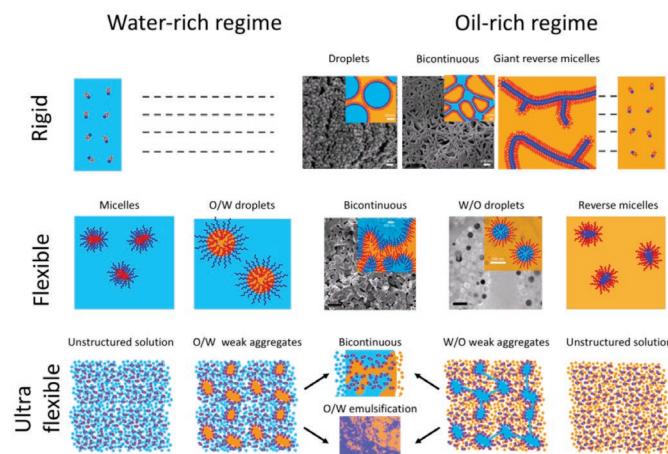


Figure 1: (A, left) the low-water regime in cationic surfactant/water/oil ternary microemulsions: bending rigidity imposes the presence of thin connected water channels of high conductivity that vanishes upon addition of water. (B, right): the bicontinuous flexible case obtained with typical alkyl ethyl oxide ethers with similar chain and head volume: spontaneous curvature is low and induces a randomly bending of the surfactant film at any polar/apolar volume ratio.



Depending on the solvent to water relative rations, all nanostructures shown on the left can be obtained w/o droplets, bicontinuous and w/o².

The variation of topology and hence solubilizing power is crucial for formulation and allows to optimize performance in applications , as well as designing the best surfactant mix and couple of solvents used, at peculiar points in the ternary phase prism.

¹ Dufreche J. F., Zemb T. - Bending: from thin interfaces to molecular films in microemulsions - *Current Opinion in Colloid & Interface Science* (2020) 49, 133-147.

² Michael Gradzielski, Magali Duvail, Paula Malo de Molina, Miriam Simon, Yeshayahu Talmon and Thomas Zemb, **Using Microemulsions: Formulation Based on Knowledge of their Mesostructure**, *Chem. Rev.* 2021, 121, 5671–5740

SPONTANEOUS "OUZO" EMULSIONS ARE IN DYNAMIC COEXISTENCE COEXIST WITH "PRE-OUZO" AGGREGATES

Th. Zemb, O. Diat, D. Horinek, W. Kunz (Université de Regensburg) S. Prevost (ILL)

In ternary solutions containing two slightly miscible solvents and a hydrotrope, mesostructures appear close to the phase boundary. Near the critical point, hetero-phase fluctuations dominate while on the water-rich side, "pre-ouzo" aggregates of 30_300 solvent molecules are present on the water-rich side while three dimensional w/o networks shown in the figure to the right predominate in the solvent-rich corner of the triangular phase diagram.^{1,2}

When water is added on the water-rich side with 10 to 40 percent of ethanol to ternary solutions containing pre-ouzo aggregates, spontaneous emulsification known as ouzo-effect is produced we have investigated this. We have made the first real-time studies of emulsification and shown that emulsion and ultra-flexible microemulsions in dynamic equilibrium coexist once formed. The emulsions formed contain a significant amount of water and are structured solutions.

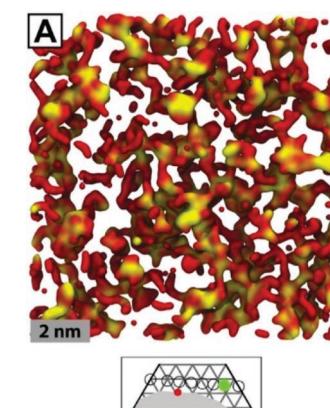


Figure 1: molecular dynamics snapshot showing the network morphology of ethanol, water and octanol hydroxy-groups at the composition point shown in green on the ternary phase diagram, water-octanol-ethanol

The extremely common dispersive liquid-liquid emulsion method (DLLME) used in analytics since 15 years may be explained from this knowledge of the link for nano-scale and meso-scale self-assembly.

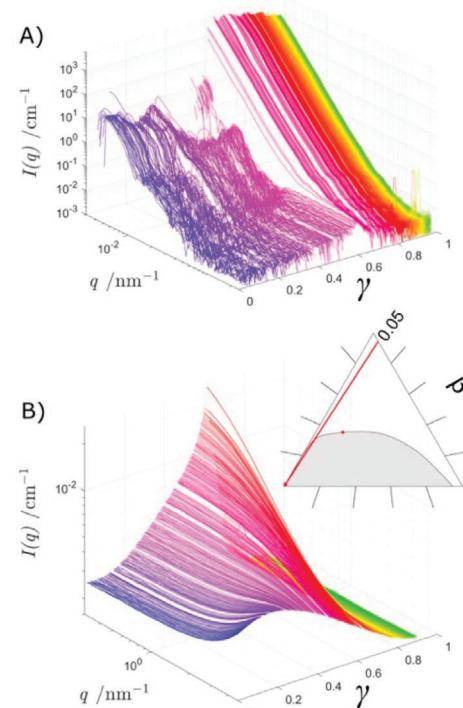


Figure 2: water is added progressively to an initial solution containing 5% of octanol and ethanol. A) shows the ultra-small angle X-ray scattering versus time and B) shows the middle-q range SAXS (on ID02 at ESRF): the low-q date measures the spontaneous emulsion droplet size and number per volume, while SAXS demonstrates the existence of small "pre-ouzo" aggregates in the large aqueous fraction of the sample.

¹ Schöttl S., Lopian T., Prévost S., Touraud D., Grillo I., Diat O., Zemb T., Horinek D. - Combined MD/SAXS analysis of organization on a nanometer-scale in ternary solvent solutions containing a hydrotrope - *JCIS* (2019) 540 pp. 623-633

² Prévost S., Krickl S., Marcelja, S. ; Kunz W., Zemb T., Grillo I. - Spontaneous Ouzo emulsions coexist with pre-ouzo ultra-flexible microemulsions - *Langmuir* 2021, 37, 3817–3827

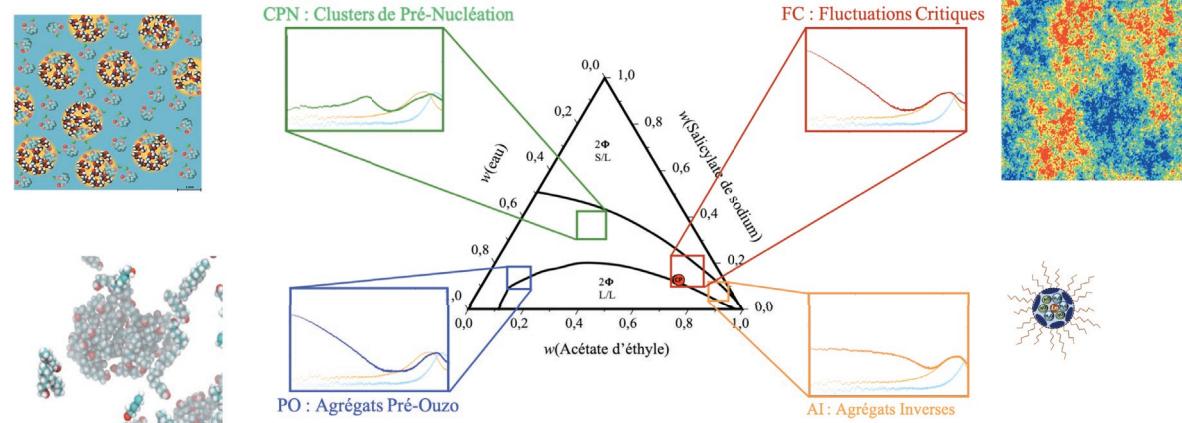


SODIUM SALICYLATE: AN EXTRAORDINARY HYDROTROPE !

Th. Zemb, A. El Maangar, P. Dégot, D. Touraud and W. Kunz (Université de Regensburg)

The ternary system water, ethylacetate and sodium salicylate presents at room temperature a large single phase domain in between a common liquid-liquid miscibility gap and stable dispersions of microcrystallites in a liquid-solid regime. In this single phase region, four types of dominant microstructures are identified by their characteristic SAXS pattern and schematized near the phase triangle shown.

- in the water-rich corner "pre-ouzo" aggregates as clusters of 20-50 molecules are in dynamic equilibrium near the phase boundary.
- in the ethylacetate-rich corner, very common aggregates that are similar to supra-molecular complexes form around isolated water molecules.



WHAT HAPPENS WHEN DIRECT IONIC MICELLES CANNOT ELONGATE DUE TO STERICAL CONSTRAINTS ?

Th. Zemb, A. El Maangar, P. Denk and W. Kunz (Université de Regensburg)

We examine the properties of a class of "triblock" anionic surfactants with the general formula CiEiR-A^+ the peculiarity of having the same amount of CH_2 and $(\text{C}_2\text{H}_4\text{O})$ groups in the head has profound consequences: the cost in free energy of interfacial bending of the commonly observed sphere to rod transition for linear ethoxy is too high to occur. These ionic surfactants are miscible with water without phase separation nor formation of lyotropic liquid crystals. When diluted more than 20% w in

water, these micelles exist like classical core-shell micelles (L'_1). Above 30% w, the heads interdigitate and all water is in the first hydration shell of the head-groups; there is no free water and with this type of surfactant, direct o/w exist without the presence of any bulk water (L'_1). These (L'_1). These micelles can be crosslinked with divalent ions, and produce a new type of nematic phase of prolate ellipsoids.

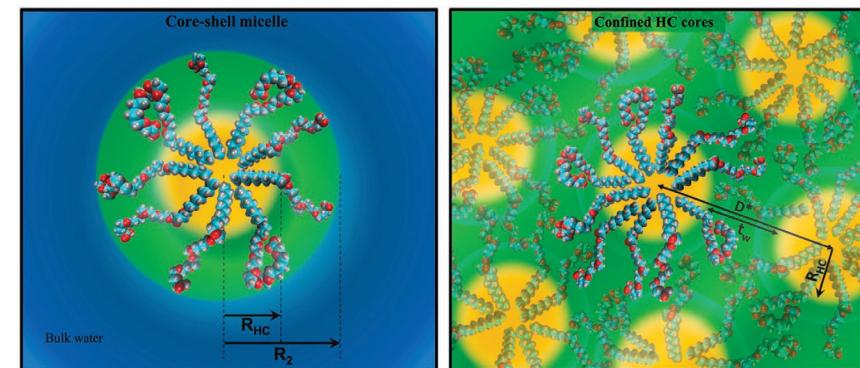
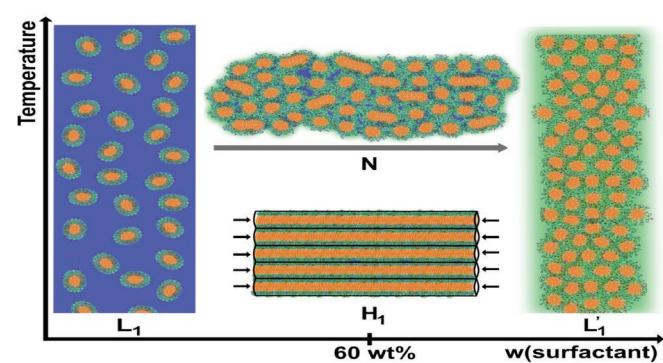


Figure: (above)The micellar shape of octyl ether octaethylene oxide carboxylic acid ($[\text{H}^+][\text{C}_8\text{E}_8\text{C}]$) is restricted to spheres. A classical core-shell micellar regime (L_1) at lower surfactant concentrations transitions into a regime of head-group interdigitated micelles (L'_1) at higher concentrations. (below) In the surfactant's sodium or calcium salts the micelles are deformed from spherical to slightly prolate spheroidal. The formation of a hexagonal (H_1) phase within the transition regime between L_1 and L'_1 is possible by a reduction of the area per molecule by counterion bridging. An increase in temperature decreases the influence of ion bridging and 'melts' the H_1 phase into a nematic phase (N) consisting of shorter chains of prolate micelles with a preferential orientation (grey arrow).



¹El Maangar, A.; Dégot, P.; Huber, V.; Causse, J.; Berthault, P.; Touraud, D.; Kunz, W.; Zemb, T. Pre-Nucleation Cluster Formation upon Ethyl Acetate Addition to an Aqueous Solution of an Anionic Hydrotrope. *Journal of Molecular Liquids* 2020, 310.

²Dégot, P.; Huber, V.; El Maangar, A.; Gramueler, J.; Rohr, L.; Touraud, D.; Zemb, T.; Gschwind, R. M.; Kunz, W. Triple Role of Sodium Salicylate in Solubilization, Extraction, and Stabilization of Curcumin from Curcuma Longa. *Journal of Molecular Liquids* 2021, 329.

¹Denk, P.; El Maangar, A.; Lal, J.; Kleber, D.; Zemb, T.; Kunz, W. Phase Diagrams and Microstructures of Aqueous Short Alkyl Chain Polyethylene Glycol Ether Carboxylate and Carboxylic Acid Triblock Surfactant Solutions. *JCL* 2021, 590, 375-386.

²Denk, P.; El Maangar, A.; Lal, J.; Kleber, D.; Zemb, T.; Kunz, W. Phase Diagrams and Microstructures of Aqueous Short Alkyl Chain Polyethylene Glycol Ether Carboxylate and Carboxylic Acid Triblock Surfactant Solutions. *JCL* 2021, 590, 375-386.

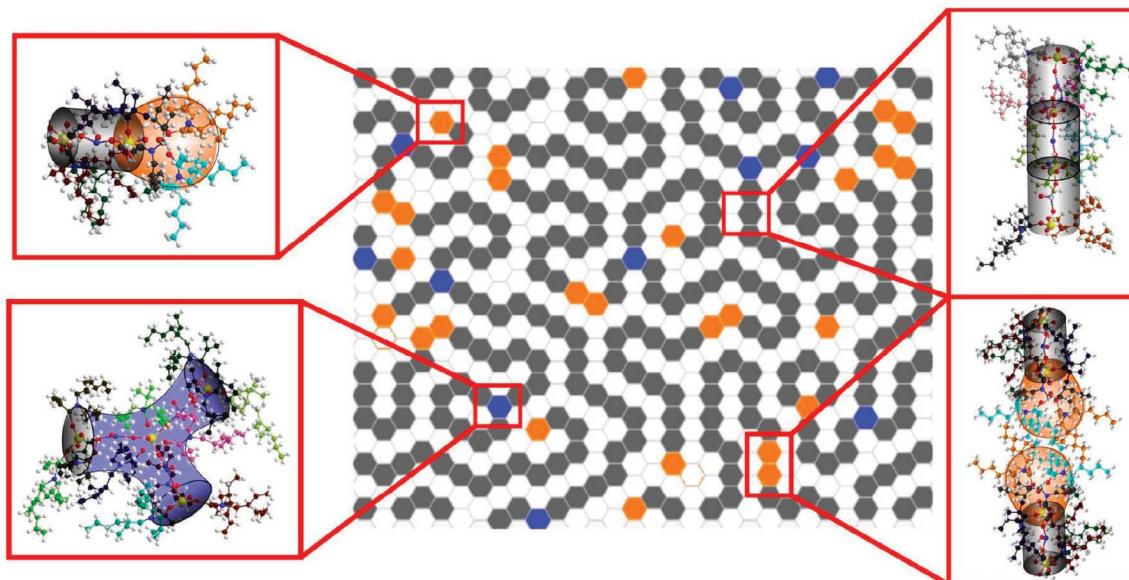
A MINIMAL THERMODYNAMIC MODEL PREDICTING DIRECT AND REVERSE GIANT MICELLE VISCOSITY

Th. Zemb, A. El Maangar, P. Denk and W. Kunz (Université de Regensburg)

The viscosity increase of the organic phase observed when liquid-liquid-extraction processes are intensified causes designing safe difficulties for processes on industrial scale. When acidity or "load" in uranium for example increases, most extractant formulations used in applications exhibit strong increase of viscosity is extracted in the organic phase. We have tackled this problem using as a model system, the family of N,N-dialkylamides with different topologies of the hydrocarbon chain in presence of uranyl experimentally. SWAXS experiments done in Marcoule have detected for the first time the peak due to U-U distance in the solvent phase.

We have developed a minimal model at nanoscale based on the "microphase" concept introduced in biochemistry by Charles Tanford, 40 years ago and never used in the context of chemical engineering. The coexisting microphases are contact-points, end-caps and rigid w/o cylinder (see fig.). Using only measurable parameters such as spontaneous curvature and chain flexibi-

lity allows to rationalize all the experimental values observed and does show predictive power : qualitative trends in viscosity variation observed when cation content is increased, and this is dependent on the packing parameter of the extractant used. This model explains why some molecules behave "better" than others and the moderate effect of diluent formulation.¹ Surprisingly, the model also applies in the o/w case: in the domain of body care, the viscosity increase linked to additives such as salts or fragrances 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 other organic additives.². In the case of widely used surfactants in home washing machines with different chemical "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



¹Denk, P.; El Maangar, A.; Lal, J.; Kleber, D.; Zemb, T.; Kunz, W. Phase Diagrams and Microstructures of Aqueous Short Alkyl Chain Polyethylene Glycol Ether Carboxylate and Carboxylic Acid Triblock Surfactant Solutions. *JCIS* 2021, 590, 375-386.

²[2] Denk, P.; El Maangar, A.; Lal, J.; Kleber, D.; Zemb, T.; Kunz, W. Phase Diagrams and Microstructures of Aqueous Short Alkyl Chain Polyethylene Glycol Ether Carboxylate and Carboxylic Acid Triblock Surfactant Solutions. *JCIS* 2021, 590, 375-386.

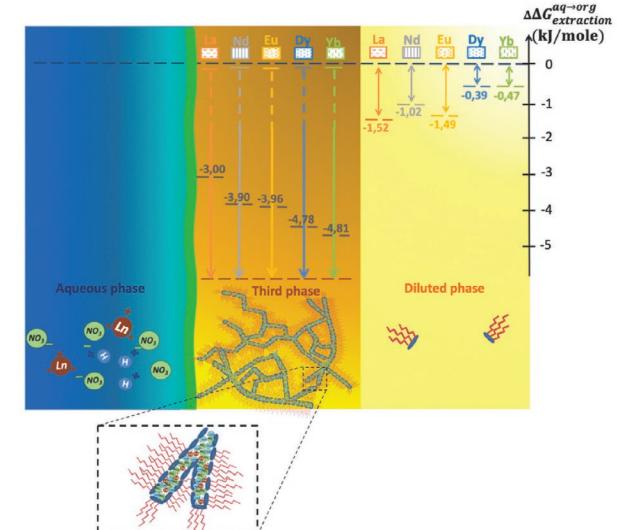
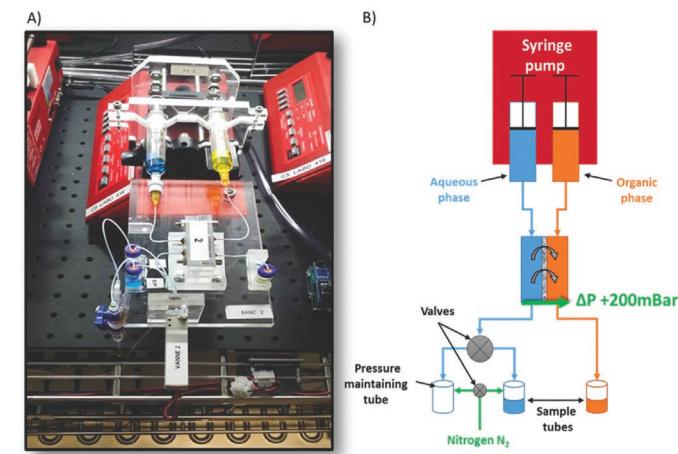
³[3] Pleines M., Kunz W., Zemb T., Benczedi D., Fieber W. - Molecular factors governing the viscosity peak of giant micelles in the presence of salt and fragrances - *Journal of Colloid and Interface Science* (2019) 537, 682-693.

A MICROFLUIDIC STUDY OF SYNERGIC LIQUID-LIQUID EXTRACTION OF RARE EARTH ELEMENTS

El Maangar, A.; Theisen, J.; Penisson, C.; Zemb, T.; Gabriel, J.-C.

The microfluidic device shown on the left has been coupled with X-ray fluorescence in order to investigate the origin of the so-called synergy effect observed in liquid-liquid extraction of rare earth elements (REEs) when special combinations of two extractants – one solvating and one ionic – are used. The setup enables kinetic studies by varying the two phases' contact time. The results obtained are compared with those obtained using a standard batch extraction method at identical contact time. We can therefore determine with unprecedented precision the Gibbs energy free energies of transfer for five rare earth cations competing with a non-target ion (Fe^{3+}) at different pH. Analysis of the effect of temperature and of surface charge density of the coexisting cations allows separating electrostatic effects from complexation effects¹. We finally show that all non-linear (synergic) effects are quadratic in mole fraction. This demonstrates that in-plane mixing entropy of the bent extractant film, is the determining term in the synergy effect.

Surprisingly, even when the third phase is present, free energies of transfer could still be measured in the dilute phase, which is reported for the first time, to our knowledge. The crucial measurement is the distribution ratio of an element: therefore the quantity left in the minor phase is crucial to determine Gibbs energy of transfer. Due to the unprecedented precision of the measure, we could show that the extractive power of the dense third phase is stronger than that of conventional reverse aggregates in equilibrium with excess water (shown on the bottom figure).²



¹ El Maangar, A.; Theisen, J.; Penisson, C.; Zemb, T.; Gabriel, J.-C. A Microfluidic Study of Synergic Liquid-Liquid Extraction of Rare Earth Elements. *Physical Chemistry Chemical Physics* 2020, 22 (10), 5449-5462.

² Maurice, A.; Rai, V.; Theisen, J.; Olivier, F.; El Maangar, A.; Duhamet, J.; Zemb, T.; Gabriel, J.-C. On-line X-ray fluorescence characterisation of liquid/liquid extraction in microfluidics. *NanoSelect*, 2021, 1-12.

³ El Maangar, A.; Theisen, J.; Penisson, C.; Zemb, T.; Gabriel, J.-C. A Microfluidic Study of Synergic Liquid-Liquid Extraction of Rare Earth Elements. *PCCP* 2020, 22 (10), 5449-5462.

INTERNATIONAL RESEARCH PROJECT I.R.P. CNRS-MPG -UNIVERSITY OF REGENSBURG "NISI" 2018-2021

From January 1, 2018, a collaboration between Marcoule/Montpellier, Potsdam associated with Regensburg has evolved to the "NISI" French-German International Research Project (ex-LIA). This program is indeed built around Nano-Ions in interaction with Soft Interfaces.

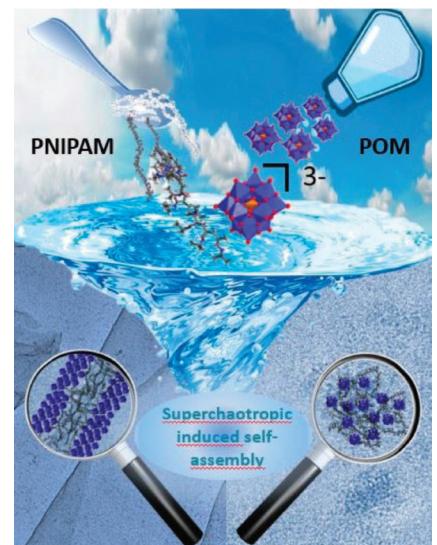
P.I., Olivier Diat (ICSM), co-P.I., Emanuel Schneck (MPI Potsdam) & Dominik Horinek (Univ. Regensburg)

For several years, we worked to decipher the mechanism of polar or ionic species transfer between two immiscible fluid phases. These studies have caused us to concentrate on how specific salt (composed of a large anion) behaves when it interacts with polar/apolar interfaces. We have been able to show that there is sometimes a complex equilibrium between the adsorption of nanometric ionic clusters at these interfaces and the release of adsorbed water molecules. The term «superchaotropy,» which refers to an effect exclusive to ions, has been used to describe this equilibrium. Our research has mostly focused on understanding this phenomenon, classifying many inorganic chemicals that have it, and exploring the multiple potential uses that could be based on it.

TASK 1: SELF-ASSEMBLIES

We have shown for the first time that short chain poly(N-isopropylacrylamide) PNIPAM, one of the most famous thermo-responsive polymers mixed with Keggin-type polyoxometalate (POM) $H_3PW_{12}O_{40}$ (PW), self-assembles in water to form (i) discrete nm-globules and (ii) micrometric sheets with nm-thickness. The type of self-assemblies is controlled by PW concentration: at low PW concentrations and the length of the polymeric chain. The PW/PNIPAM self-assembly arises from a solvent mediated mechanism associated to the partial dehydration of PW and of the PNIPAM, which is related to the general propensity of POMs to adsorb on neutral hydrated surfaces. This effect, known as superchaotropy, is further highlighted by the significant increase in the lower critical solubilization temperature (LCST) of PNIPAM observed upon the addition of PW in the mM range. The influence of the POM nature on the self-assembly of PNIPAM was also investigated.¹

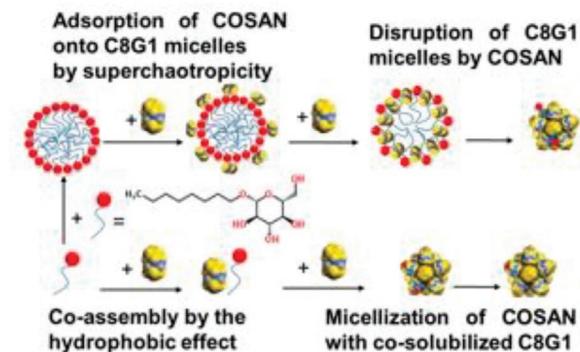
We have also shown that nano-ions at low concentrations (μM range), similarly to anionic surfactants, induce the spontaneous transformation of a swollen lyotropic lamellar phase of non-ionic surfactant into a vesicle phase. This transition occurs when



the neutral lamellae acquire charges, either by adsorption of the nano-ions onto, or by anchoring of the ionic surfactant into the lamellae. Contrarily to ionic surfactants, nano-ions dehydrate strongly the neutral surfactant assemblies. As a conclusion, purely inorganic nanometric ions act here as alternatives to the widely used organic ionic surfactants.²

¹ Buchecker T, Schmid P, Grillo I, Prevost S, Drechsler M, Diat O, Pfitzner A, Bauduin P. - Self-Assembly of Short Chain Poly-N-isopropylacrylamid Induced by Superchaotropic Keggin Polyoxometalates: From Globules to Sheets - *Journal of the American Chemical Society* (2019) 141, 6890-6899.

² Hohenschutz M, Grillo I, Diat O, Bauduin P. - How Nano-Ions Act Like Ionic Surfactants - *Angewandte Chemie-International Edition* (2020) 59, 8084-8088.



The carboranes clusters, and more especially the metalla-bis-(dicarbollide) anions like COSAN, are additional fascinating nanoions to study in addition to the low charged polyoxometalates. It has applications in many different sectors, including catalysis, materials, ionic separation, environmental research, and medicine (together with its derivatives). It is one among the most superchaotropic ones due to its extremely low charge density (especially for the iodo-derivative species). We have studied the interactions of COSAN with the glucose moiety that is ubiquitous at biological interfaces. Octyl-glucopyranoside surfactant (C8G1) was chosen as a model as it self-assembles in water and creates a hydrated glucose-covered interface. At low COSAN content and below the critical micellar concentration (CMC) of C8G1, COSAN binds to C8G1 monomers through the hydrophobic effect. Above the CMC of C8G1, COSAN adsorbs onto C8G1 micelles through the superchaotropic effect. At high COSAN concentrations, COSAN disrupts C8G1 micelles and the assemblies become similar to COSAN micelles but with small amount of solubilized C8G1. Therefore, COSAN binds in a versatile way to C8G1 upon either the hydrophobic or superchaotropic effect depending on their relative concentrations.¹

In the continuity of these researches, some investigations were carried out 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 was to make a link between experiments results and simulations using current models derived from the approach developed by Schwierz and Horinek. We again focused mainly on dicarbollide anions and their interactions with biological functions and support with some cancer therapy applications. This study was extended to a compressed Langmuir monolayer containing glycolipids over a subphase containing various concentration of COSAN and also other types of nano-ions such as polyoxometalates. Varying the headgroup chemistry (one or two galactoside functions) and the alkyl chain saturation, we observed different behaviour of nano-ion in interaction with the subsurface of the glycolipids and this as a function of the surface pressure. Using synchrotron techniques, we found superchaotropic nano-ions interact preferentially with species in gas or in the liquid expanded phases than with the solid phase whose crystalline structure is not affected. Lower the charge density of the nano-ions and weaker the lateral interaction between the sugar head groups, stronger is the interaction between the nano-ions and the glycolipids (non published results).

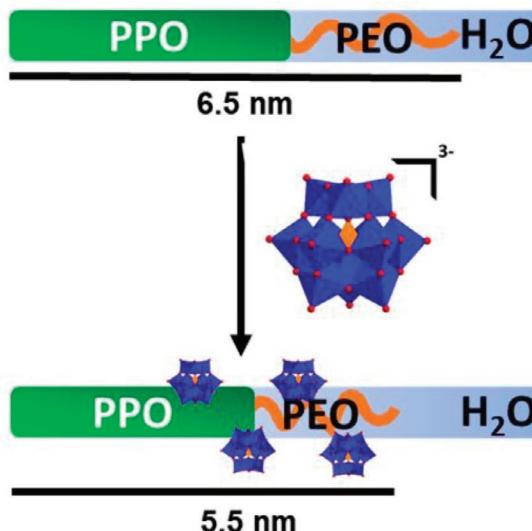
¹ Merhi T, Jonchere A, Girard L, Diat O, Nuez M, Vinas C, Bauduin P. - Highlights on the Binding of Cobalta-Bis-(Dicarbollide) with Glucose Units - *Chemistry-a European Journal* (2020) 26, 13935-13947.

² Schmid P, Buchecker T, Khoshima A, Touraud D, Diat O, Kunz W, Pfitzner A, Bauduin P. - Self-assembly of a short amphiphile in water controlled by superchaotropic polyoxometalates: H4SiW12O40 vs. H3PW12O40 - *Journal of Colloid and Interface Science* (2021) 587, 347-357.

TASK 2: THERMODYNAMICAL STUDIES

We have shown that the CMC variation of the non-ionic surfactant in presence of Keggin POM can be positive or negative as a function of the polar head/POM couple. Indeed, either a stabilization of the micelle for $C_8G_1/[PW_{12}]^{3-}$ and $C_8E_4/[SiW_{12}]^4$ system, a stabilization of the monomeric form for $C_8G_1/[SiW_{12}]^4$ and even a coacervate for $C_8E_4/[PW_{12}]^{3-}$ was observed. Thermodynamic approaches were used to quantitatively describe the CMC shift. A classical pseudo-phase model was used when the surfactant monomer form was stabilized (CMC increase) whereas a lateral equation of state was applied when the POM adsorption onto the micelles was the dominant effect (CMC decrease).¹

Our research advances knowledge of the non-electrostatic interactions between POMs and non-ionic amphiphilic molecules in water and can be used to many types of nanoions in interactions with hydrophilic surfaces or interfaces. It serves as a cornerstone for the CHAOPOM ANR's ongoing development of novel materials with distinctive nanostructures and useful characteristics.



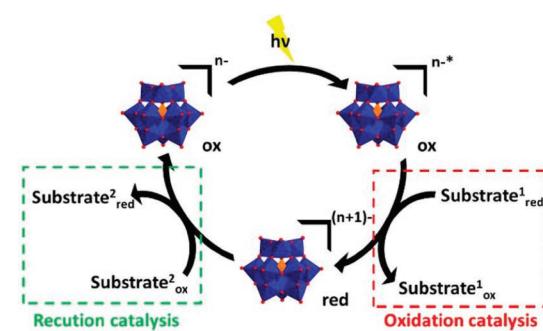
We also investigate the chaotropic effect of α -PW₁₂O₄₀³⁻ (or PW) on the triblock copolymer P84 exhibiting an ABA architecture (A: ethylene oxide, B: propylene oxide). The combination of phase diagrams, spectroscopic (nuclear magnetic resonance) and scattering (small angle neutron/X-ray scattering) techniques reveals: (i) below the micellization temperature of P84, PW exclusively binds to the propylene oxide moiety of P84 unimers and (ii) above the micellization temperature, PW mostly adsorbs on the ethylene oxide micellar corona. Nevertheless, PW was found to penetrate the micellar core (propylene oxide) partially. In conclusion, the poorly hydrated propylene oxide moiety and PW interact due to the chaotropic effect. After micellization, the hydrophobic and chaotropic effects battle for control of the dehydration of propylene oxide, resulting in the majority of PW being driven into the ethylene oxide corona. This study stresses the delicate balancing act between two assembly motives, the chaotropic effect and the hydrophobic effect, and advances our understanding of the function of hydration and dehydration in the chaotropic effect.²

We have also shown how PW in their acidic form can turn classical salting-out salts into highly salting-in salts and therefore (partially) invert the classical Hofmeister series, as previously observed by addition of classical salt on the Cloud Point (CP) of proteins like lysozyme. Although, the often overlooked counterion effects of POMs have a strong effect on the solubility of POMs, we have shown that the type of alkali counterion (Li⁺, Na⁺, K⁺) of α -Keggin type POMs PW₁₂O₄₀³⁻ (PW) and SiW₁₂O₄₀⁴⁻ (SiW) does not change their (superchaotropicity-driven) association with the non-ionic surfactant C₈E₄ as well with short-chain amphiphile C₃P₂. In both systems, SiW and PW produced a strong CP increase with alkali counter-cations (Li⁺, Na⁺, K⁺). However, a steeper CP increase was observed for PW compared to SiW as expected from its lower charge density, i.e. stronger (super)chaotropic effect. However, combining a low charge density nano-ion (PW) with proton as counterion, enables to turn salting-out anions (with a basic character) into apparently salting-in anions, i.e. inverting the Hofmeister effect of classical salts.³

Understanding how the organic and inorganic assemblies interact at the nanoscopic scale is of utmost fundamental importance to the design of highly ordered hybrid systems. Within an extra-collaboration with university of Versailles/Saint-Quentin we demonstrate that the presence of γ -CD promotes aggregation of molybdate ions under reducing conditions. Solution studies supported by solid state analyses were consistent with mechanisms mostly directed by the chaotropic effect while this work demonstrates that the Mo-blue ring-shaped anion must be classified as the highest chaotrope in the Hofmeister extended series. Thus, such a property gives rise to important consequences corresponding to the significant increase of the formation rate of {Mo154} or to the formation of related hierarchical multi-component architectures.¹

TASK 3: APPLICATION

We have demonstrated the simultaneous use of PW in acid form as an oxidation and reduction (photo-)catalyst in a liquid-liquid biphasic system that distinguishes between oxidizing and reducing conditions in each of the phases.



This method is called the «2-stages 2-reactions 1-catalyst» concept because it involves performing two reactions in two phases with a single catalyst. We did discover that the commercially available α -Keggin POM PW predominantly distributes in organic alcohol phases in a water:alcohol biphasic system (1-HexOH, 1-OctOH, and 2-Me-2-HexOH). SiW, on the contrary, was shown to distribute most-

ly in the aqueous phase. We used these opposite distributions to separate PW³⁻ (organic phase) and photoreduced PW⁴⁻ (aqueous phase) which has the same distribution towards water as SiW. Owing to the oxidative and reductive properties of PW³⁻ and PW⁴⁻ respectively, we could therefore separate an oxidizing environment (PW3-organic phase) and a reducing environment (PW4-aqueous phase) in a biphasic system.²

We now understand that nanometer-sized anions (nano-ions), such as polyoxometalates and boron clusters, display the so-called superchaotropic behavior, which defines their potent clinging to hydrated non-ionic materials in water. Thus, in collaboration with Aachen University, we are able to demonstrate that nano-ions, at millimolar concentrations, significantly increase the viscosity and cause gelation of aqueous solutions of non-ionic cellulose ethers (CEs), a class of widely used polymers known for their thickening and gel-forming ability. The traditional thickening effects of ionic surfactants and classical salts are considerably outweighed by the innovative and universal physical crosslinking motif for CE-solutions that emerges from superchaotropic nano-ion binding.³

¹Girard L., Naskar B., Dufreche J. F., Lai J., Diat O., Bauduin P. - A thermodynamic model of non-ionic surfactants' micellization in the presence of polyoxometalates - *Journal of Molecular Liquids* (2019) 293.

²Schmid P., Grass X., Bahadur P., Grillo I., Diat O., Pfitzner A., Bauduin P. - Polymeric Surfactant P84/Polyoxometalate alpha-PW12O403-A Model System to Investigate the Interplay between Chaotropic and Hydrophobic Effects - *Colloids and Interfaces* (2022) 6.

³Schmid P., Hohenschutz M., Grass X., Witzmann M., Touraud D., Diat O., Pfitzner A., Bauduin P. - Counterion effect on α -Keggin polyoxometalates in water: The peculiar role of H⁺ on their salting-in effect and co-assembly with organics - *Journal of Molecular Liquids* (2022) 359.

¹ Yao S., Falaise C., Ivanov A. A., Leclerc N., Hohenschutz M., Haouas M., Landy D., Shestopalov M. A., Bauduin P., Cadot E. - Hofmeister effect in the Keggin-type polyoxotungstate series - *Inorganic Chemistry Frontiers* (2021) 8.

²Schmid P., Jost G., Grass X., Touraud D., Diat O., Pfitzner A., Bauduin P. - {2-Phases 2-reactions 1-catalyst} concept for the sustainable performance of coupled reactions - *Green Chemistry* (2022) 24, 2516-2526.

³Hohenschutz M., Bauduin P., Lopez C. G., Förster B., Richtering W. - Superchaotropic Nano-ion Binding as a Gelation Motif in Cellulose Ether Solutions - *Angewandte Chemie Int. Ed.* (2022) accepted.

BEHAVIOUR OF SPENT NUCLEAR FUEL (SNF) PELLETS UNDER INTERIM STORAGE CONDITIONS IN EUROPEAN JOINT PROGRAMME ON RADIOACTIVE WASTE MANAGEMENT (EURAD)

In the EURAD project, the Laboratory of Evolving Interfaces in Materials (LIME) is involved in the Work Package Spent fuel characterization and evolution until disposal (and more precisely in the subtask on the behaviour of Spent Nuclear Fuel (SNF) pellets under interim storage conditions). In this WP, our goal is to better understand the behavior of UO₂ based model compounds during leaching tests representative for long-term interim storage in nuclear pools. Especially, the impact of various Fission Products on the chemical durability and on the surface reactivity of the sintered materials is examined. With this aim, we first developed the synthesis of a large variety of sintered UO₂ samples doped with FP. Then we applied a micro-/macro- dual methodology in order to examine the role of several families of FP on the behavior of the sintered samples during leaching tests. It includes not only the analysis of the released elements in the solution, but also the monitoring of the solid/liquid interface during multiparametric leaching/

alteration tests, this latter being possible by coupling various techniques such as AFM, ESEM, GI-XRD. A particular attention is focused on the evaluation of some potential modifications in terms of reactive surface area during the leaching tests as well as on the quantification of the dissolved preferential zones (grain boundaries, triple junctions, pores, ...) through the development of 3D reconstructions performed on leached/ altered materials.

In the same WP, we are also involved in the preparation of a large panel of sintered uranium-lanthanide oxide based samples for CEMHTI – Orléans. The aim of this second task is to follow the consequences of the incorporation of lanthanide elements in terms of defects formed within the material. The characterization of the samples specifically involves positron annihilation spectroscopy (PAS) in order to probe, as instance, the potential vacancy defects induced by such incorporation in the fluorite structure.

GEN IV INTEGRATED OXIDE FUELS RECYCLING STRATEGIES (GENIORS)

The main objectives of the Work Package of the GENIORS project¹ in which ICSM is involved, i.e. *solid/liquid interface chemistry*, is to better understand the phenomena occurring at the solid/ liquid interfaces during spent nuclear fuel reprocessing in order to support potential processes. It is divided in two main topics.

The first task is devoted to the dissolution step. It is examined not only considering the direct interactions between the chemical species coming from the solid and the solution, but also through the development of catalytic reactions at the interface. This task is devoted to the better understanding (then control) of the mechanisms occurring at the solid/liquid interface during dissolution. Several kinds of actinide oxide based solid solutions, including (U,Ce)O₂, (U,Ln)O₂, are prepared by wet chemistry routes then finally submitted to various dissolution tests. Then, the effects of structural, microstructural and morphological parameters, coming from the “material history” are particularly examined with the help of multiparametric dissolution tests. For both solid solutions, the particular role of redox reactions on the overall dissolution

mechanism is examined by combining macroscopic and microscopic approaches (including ESEM, AFM, XRR and Raman spectroscopy).

The second task is focused on the uptake of actinides from solution by precipitation in new kinds of precursors then on the final conversion to oxide based samples by heating (i.e. wet chemistry routes). In this field, various precursors of (U,Ce)O₂ and (U,Ln)O₂ are prepared by using novel types of ligands yielding to original metal-organic architectures with designed morphology. Their conversion into the final oxides are followed by a large panel of techniques including HT-ESEM (Environmental Scanning Electron Microscopy). Shaping then sintering of these precursors leading to the final oxides by heating are then studied by conventional techniques (dilatometry, HT-ESEM, density measurements). The same methodology is also applied for (U,Ce)O₂ and (U,Ln)O₂ samples prepared by direct conversion of the precursors to oxides under weak hydrothermal conditions or by denitration process.

¹www.geniors.eu

TOWARD SUSTAINABLE BATTERIES BASED ON SILICON, SULFUR AND BIO-MASS DERIVED CARBON AS 2BOSS PROJECT IN ERAMIN2 EUROPEAN CALL

Closing the circular economy loop by recycling raw materials to create new components is especially important in a fast-expanding and strategic industry like energy storage. Because batteries are a crucial component of portable electronics and electric vehicles, it is important to create efficient and cost-effective recycling methods to keep up with the industry's rapid expansion. Although lithium-ion batteries are currently the most popular technology, they have a number of inherent limitations that prevent their production from being sustainable. These limitations include their moderate specific energy capacity and durability, their heavy reliance on a number of essential raw materials (CRMs) for the EU, and the difficult and expensive recycling of these CRMs due to their dispersion and metal-metal mixing. Toward sustainable batteries based on silicon, sulfur, and carbon obtained from biomass (2BoSS) will concurrently develop an innovative battery technology and the related recycling strategies to enable a circular reuse of raw materials that ensures a sustainable manufacturing.

By focusing on these four key areas, 2BoSS will create environmentally friendly batteries that are appropriate for the circular economy: 1) creation and testing of a silicon-sulfur battery technology that offers optimum performance, reduces the need for CRMs, and permits the circular use of resources. 2) defining and validating efficient recycling techniques that enable raw material separation and reuse; 3) assessing the cost, life cycle, and environmental, health, and safety impacts; and 4) designing high-performance products and scaling up their production. A battery technology supported by a cobalt-free Li₂S-based cathode and a graphite-free silicon-based anode will be optimized and validated by 2BoSS.

The consortium gathers the FUNDACIO INSTITUT DE RECERCA DE L'ENERGIA DE CATALUNYA, the Department of ENVIRONMENT, LAND AND INFRASTRUCTURE ENGINEERING (DIATI) in Turin (Italy), the Commissariat à l'énergie atomique et aux énergies alternatives (CEA / France) with the participation of ICSM/LHYS team and Cleopa GmbH / Innovation Energy Efficiency in Jülich (Germany)

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 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 elements 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:

- Development of process parameters for selective leaching of rare earth metals from WEEE (Waste Electrical and Electronic Equipments - NdFeB magnet and fluorescent lamps).
- Design of suitable solvent-extractant combination (e.g. task specific ionic liquids) using molecular modeling techniques.
- 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).
- 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.
- Conduct large scale trial of the complete process developed for scrap magnets and fluorescent lamps.



ANR ICSM 2019 - 2022

AGENCE NATIONALE DE LA RECHERCHE



CADET PROJECT ANR-ANDRA-RTSCNADAA160014

(MARCH 2016 - SEPT. 2019)
"CAVITATION-ASSISTED DECONTAMINATION"



Partners:
ICSM-LSFC
Institute Jean Le Rond d'Alembert (D'ALEMBERT) UMR 7190 (Coordinator)

ICSM : Dr Serguei Nikitenko

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 PIA-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 personnel. 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.

CARAPASS PROJECT ANR-16-CE08-0026

(NOV. 2016 - OCT 2020)
"CARBIDE & CARBONITRIDE NANOCOMPOSITE BASED PHOTO-THERMAL SOLAR ABSORBERS"



Partners:
IEM Montpellier, UMR5635 (coordinator)
IEM Montpellier
SPCTS Limoges
PROMES Odeillo
CRM² Nancy
ICSM - Marcoule

ICSM : Dr Xavier Deschanel

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 industriel» (theme «Matériaux et procédés» 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 ≤ x ≤ 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 specia-

lists 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.

DYNAMISTE PROJET ANR-15-CE07-0013-01

(OCTOBER 2015 - MARCH 2020)

DYNAMICS OF ALUMINO-SILICATES FLUIDS



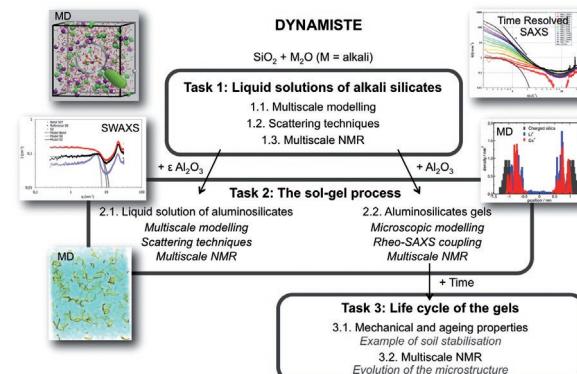
Dr Magali Duvail

Partners:
ICSM-LMCT (coordinator)
CEA-DES-DE2D Marcoule
Laboratoire Charles Coulomb Montpellier
Wöllner GmbH & Co.KG (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 PROJECT ANR-17-CE06-0004

(DEC. 2017 - NOV 2020)

"XENOTIME: A MATERIAL FOR ACTINIDES SPECIFIC STORAGE"



Dr Adel Mesbah

Partner:
ICSM-LIME, CEA Marcoule

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 ($\text{Ln} = \text{Tb-Lu}$) 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 $\text{Ln}_{1-x}\text{An}_x\text{PO}_4$. Whereas with tetravalent actinides (Th, U), two different mechanisms will be explored leading to the formation of $\text{Ca}_x\text{An}_{x-1}\text{Ln}_{1-2x}\text{PO}_4$ et $\text{An}_{x-1}\text{Ln}_{1-x}(\text{SiO}_4)_{x-1}(\text{PO}_4)_{4-1-x}$ 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.

DECIMAL PROJECT PIA 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:
ICSM-LNER (coordinator)
DEN, CEA Marcoule
INSA Rennes
IRCP
ORANO (industriel)

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 geopolymers 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.

FOAMEX PROJECT ANR-17-CE08-0016

(FEV. 2018 - FEV. 2022)

« MOUSSES DE LIXIVIATION POUR L'EXTRACTION DE MÉTAUX DES DÉCHETS ÉLECTRONIQUES »



Dr Olivier Diat

Partners:
ESPCI (Coordinateur)
ICSM-L2IA
BRGM
EXTRACTHIVE (start-up)

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.

AUTOMACT PROJECT ANR-18-CE05

(OCT. 2018-OCT. 2022)

«SOLID FIXATION AND AUTO-CONDITIONING OF ACTINIDE ELEMENTS COMING FROM CONTAMINATED LIQUID OUTFLOWS»



Dr Xavier Deschanel

Partners:
ICSM-LNER (coordinator)
CIMAP GANIL Caen
IRAMIS Saclay
ICG Montpellier

The objective of this basic research project (Fundamental Research-PRC) 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 traditional 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 (^{244}Cm , ^{238}Pu). 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.

MULTISEPAR PROJECT ANR-15-CE07-0013-01

(FEB. 2019 - AUG. 2022)

«MODELISATION MULTI-ÉCHELLE DES PHASES ORGANIQUES POUR L'EXTRACTION LIQUID-LIQUIDE »



Pr Jean-François Dufrêche

Partners:
ICSM-LMCT (coordinator)
DEN/DMRC CEA Marcoule
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.

RECALL PROJECT ANR-20-CE04-0007

(FEV. 2021 - MARS 2025)

« SUSTAINABLE RECOVERY OF VALUABLE METALS IN BAUXITE RESIDUE »



Partners:

CEREGE Centre européen de recherche et d'enseignement de géosciences de l'environnement (Coordinateur)
ICSM-LTSM
AMSE Aix Marseille School of economics
HYMAG'IN (start-up)
ALTEO (Industriel)

Dr Stéphane Pellet-Rostaing

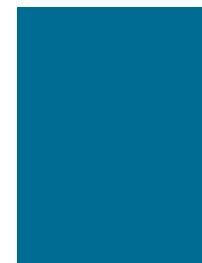
The RECALL project, supported by the French Institute of Circular Economy (INEC), aims at recovering selectively critical metals and valorize the iron from bauxite residue with the overall goal of reducing the pressure on natural mineral resources. To reduce the environmental footprint of the extractions, this interdisciplinary and intersectorial project aims at developing sustainable processes (in aqueous media at relatively low temperature and without solvents and strong mineral acids) as an alternative to traditional pyro- and hydrometallurgy processes and to value the economic impact of this technological change in terms of social welfare where potential environmental and health impacts are taken into account. This interdisciplinary project is built on 5 hypothesis: (i) environmentally friendly extraction processes rely in part on selective leaching in mild conditions compared with current technologies that uses significant energy to decompose the entire matrix. (ii) Selectivity can

be achieved by coupling a good knowledge of waste composition and the speciation (chemical form) of the targeted critical metals and the choice of the appropriate extractant and extraction methodology. (iii) The use of biological molecules can selectively leach targeted critical elements at reasonable extent. (iv) Iron and critical metals can be co-valorized to reduce the quantity of waste generated by the alumina extraction industry and generate economic value. (v) New processes, can lead to an increase of social well-being compared to traditional approaches. Beyond a potential impact (negative or positive) on the private profit of the industrial implementing new technologies, the valuation of social well-being associated with new processes will be a crucial information for policy makers and citizens. In social well-being is included externalities associated with the process and other sources of economic inefficiency impacting welfare at the aggregate (society wide) level.

BIOULLPS PROJECT ANR-21-CE06-0010

(OCT. 2021 - MARS 2025)

« MOLECULAR FORCES AND LIQUID-LIQUID PHASE SEPARATION IN SOLUTIONS OF BIOLOGICAL MACROMOLECULES»



Partners:

Institut de Biologie structurale (Coordinateur)
ICSM-LTSM
Institut Laue Langevin

Nom Prénom

Many membrane-less cellular compartments are formed by liquid-liquid phase separation (LLPS). This process is related to the flexibility and effective charge of macromolecules. The underlying mechanisms and driving forces are still poorly understood. BioLLPS is based on a well-defined biological system used by the rabies virus to build viral factories in the infected host cell (called Negri bodies in the case of rabies). This system has unique properties for a biophysicist, as it separates into two liquid phases in a reversible and reproducible manner, and the highly concentrated protein phase remains in a liquid state without aggregation, crystallization, or gelation. This system also has the ability to control the partitioning of other macromolecules between phases. This system offers the possibility to be characterized in terms of structure and colloidal forces, allowing the identification of factors that control LLPS in biological systems....

The objective of BioLLPS is to decipher some of the underlying physicochemical principles by which proteins induce LLPS leading to membrane-free organelles in cells. In a bottom-up approach, we will establish a minimalist model system that recapitulates the essential properties of these virus-induced organelles: (1) appearance of a dense liquid phase and (2) partitioning of macromolecules....

ALUPLAT PROJECT ANR-21-CE08-0013

(NOV. 2021 - NOV 2025)

« DÉGRADATION DE REVÊTEMENTS D'ALUMINURE SUR SUPERALLIAGES RÉELS ET MODÈLES CONTENANT DU PLATINE »

Partners:

IJL Institut Jean Lamour
LaSIE Laboratoire des Sciences de l'Ingénieur pour l'Environnement (Coordinateur)
Pprime Institut P' : Recherche et Ingénierie en Matériaux, Mécanique et Energétique
ICSM / L2ME

Nom Prénom

Ni-based superalloys of aeronautical gas turbines possess adequate mechanical resistance at high temperatures. Additional mechanical strength can be achieved by incorporating Pt into new superalloys. Like with the equilibrium α/β coatings (Pt deposited and diffused in the alloy), the oxidation and hot corrosion resistance of the superalloy should also be improved. Mechanical degradation (mostly by fatigue) may originate at corroded and/or oxidized surfaces. Addition of Al, Si and reactive elements (RE) to the surface could thus impair corrosion and oxidation resistance. However, the environmental and mechanical interactions of the Al-based coatings with these new poor Pt-containing superalloys are unknown, let alone in brand new biofuel environments. This requires fundamental investigations with model alloys prior to extrapolation to real superalloys.

The aim of "ALUPLAT" is to study the combined environmental and mechanical degradation of very new Pt-containing Ni-based superalloys ("TROPEA" alloys) in the uncoated and Al/Si/RE-coated conditions. No studies on the topics covered by ALUPLAT are reported in the open literature.

The originality lies in the study of the interfacial interactions between a coating that delivers Al, Si and reactive elements to a bulk that contains Pt in low amounts rather than producing "conventional" NiPtAl or γ/γ' coatings, i.e. trying to establish the frontier at which mechanical and environmental are

optimal. To the best of our knowledge, this has never been reported in the literature. Another innovative aspect is that ALUPLAT will also compare the effect of the impurities released by the biofuels (constraint imposed to the airlines after COVID19 and in line with Europe's goal on carbon neutrality) against the "conventional" hot corrosion. The approach of investigation will first follow separated environmental and mechanical degradation and then combined modes of degradation. This will allow to identify the critical onset of failure in relation with the corroding and oxidizing media and loading conditions. A very original approach will reside in tailoring the coating compositions to avoid interdiffusion zones that could mechanically degrade the superalloy. The concept of "flash aluminizing" will be applied, whereby thin diffusion coatings could be deposited in very short times and/or by placing Ni interlayers, which has never been studied before.

The project is purely scientifically focused but could have in the future potential applications in protecting superalloy components employed in aeronautical engines. Keywords of "ALUPLAT" match perfectly most of the ones of the strategic goal of "metallic and inorganic materials and associated processes" including functional and mechanical properties, innovative synthesis, microstructures, surfaces, interfaces, degradation, fatigue, corrosion and coatings...

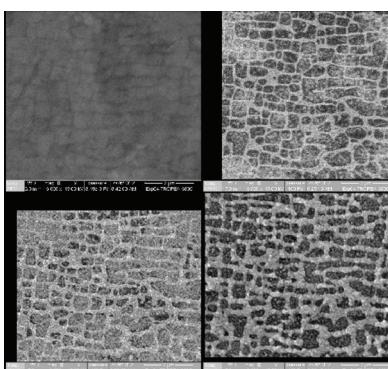


Figure 1. Series of images showing the oxidation of the TROPEA alloy during heating up to 680°C (left) and during the isothermal oxidation (right).

CAREME PROJECT ANR-21-CE06-0010

(OCT. 2021 - MARS 2025)

« CATALYSE PAR DES MÉTAUX ISSUS DU RECYCLAGE : VALORISATION DIRECTE DE DÉCHETS »

Partners:

IRCE Lyon (Coordinateur)
ICSM-LHYS (Coordinateur)
Institut Laue Langevin

Nom Prénom

complètement les catalyseurs à base de métaux précieux préparés directement à partir de déchets électroniques, sans isolation des métaux, avec une analyse minutieuse de chaque étape de la vie des catalyseurs. Le projet apportera des connaissances utiles sur les synergies et antagonismes possibles entre le métal ciblé et les impuretés. La réponse à cette question scientifique originale est la clé de la bonne gestion du profil des impuretés pendant tout le processus de traitement des déchets électroniques et de la détermination des niveaux acceptables de ces impuretés en fonction des applications ciblées. S'appuyant sur ces résultats, le projet inclura comme objectif technologique la préparation à grande échelle d'un lot de catalyseurs, afin d'obtenir une validation dans un environnement pertinent (TRL 5) suffisamment détaillée pour permettre une évaluation technique et économique de l'approche proposée.

Si un procédé de traitement approprié peut conduire à un flux de métaux de composition contrôlée, qui à son tour permet la fabrication d'un catalyseur efficace, les déchets électroniques pourront être validés comme une source alternative de métaux précieux. Si ce catalyseur peut alors être intégré dans les processus industriels existants, y compris les processus de régénération et de recyclage, alors la démonstration sera faite que des circuits économiques courts peuvent être mis en place dans notre société. Cette approche réduira notre dépendance envers de certains pays pour ces matières premières critiques.

ITALLIX PROJECT ANR-22-CE29-0023

(DEC 2022 - DEC 2026)

« TRANSPORT D'IONS À TRAVERS UNE INTERFACE LIQUIDE-LIQUIDE
EN VUE DE PROCESSUS D'EXTRACTION MÉTALLIQUE »

Partners:

LIPHY (Coordinateur)
ICSM-LMCT
LEPMI

Nom Prénom

Recycler sans polluer est un des défis actuels de la chimie nécessitant des systèmes innovants d'extraction liquide-liquide. De plus, une séparation optimale dans un processus continu à grande échelle de solutions en écoulement, plutôt que de bains statiques, doit être examinée lorsque de nouveaux systèmes chimiques sont proposés. Suite à la récente obtention de systèmes biphasiques aqueux acides, nous proposons avec ITALLIX un projet expérimental et théorique qui abordera des questions fondamentales sur le transport ionique à travers l'interface entre deux solutions non miscibles mais néanmoins aqueuses. Les origines de la différence de potentiel chimique ressentie par les ions entre les deux phases et permettant naturellement le transport d'une phase à l'autre, fortement dépendantes de l'acidité et de la force ionique de la solution, doivent être clarifiées. De plus, des relations fines entre différents effets sont attendues : viscosité, tension de surface, glissement, advection ou polarisation des concentrations, couplées à des instabilités de l'interface liquide-liquide.

Nous proposons ici d'aborder ces questions enchevêtrées en étudiant trois systèmes différents qui permettront d'aborder séparément l'effet des interactions électrostatiques, de l'entropie et de l'encombrement moléculaire. Ces solutions ternaires sélectionnées subissent toutes une séparation de phase lors de l'augmentation de la température, c'est-à-dire qu'elles présentent un Lower Solution Critical Temperature (LCST). Dans un premier temps, une caractérisation complète de la structure, de la dynamique des ions et de la cinétique de nucléation sera effectuée. Ensuite, afin de rendre l'expérience réalisable sur une échelle de temps et de durée adaptée au laboratoire, nous utiliserons un système microfluidique à co-

flux équipé de caractérisations optiques (spectroscopie UV/vis) et rayons X (SAXS, XAS) des profils de l'écoulement. Les surfaces des canaux permettront d'aborder l'origine de la nucléation dans différentes conditions. Nous caractériserons ensuite la structure de la solution et de l'interface, les profils de concentration et les coefficients de diffusion. Enfin, la combinaison des paramètres géométriques et des conditions de viscosité (composition de la solution) offrira la possibilité de créer des instabilités de surface et de déterminer leur rôle sur le transport ionique à travers l'interface.

En parallèle, une description théorique des systèmes sera donnée par la simulation MD et la modélisation mésoscopique, offrant une complémentarité des deux échelles de description. Cela comprend la simulation tous-atomes de l'interface liquide/liquide, et des simulations de dynamique moléculaire hors-équilibre pour modéliser les phénomènes de transport (hydrodynamique, longueur de glissement, diffusion) au niveau mésoscopique. Tous les résultats théoriques seront systématiquement comparés entre eux et avec les expériences. Une telle approche permettra de prédire les différentes contributions thermodynamiques et les interactions microscopiques qui régissent le transport ionique.

ITALLIX permettra de démêler l'influence des paramètres physico-chimiques (acidité, charges, hydrophobie...) et des différents effets hydrodynamiques (glissement, advection vs diffusion, instabilités de surface...). Chacun de ces effets peut potentiellement être tourné à l'avantage d'un transport amélioré, c'est-à-dire d'une efficacité d'extraction accrue. Le but du projet est de développer une nouvelle voie pour la chimie séparative via des interfaces liquide-liquide à très faible tension de surface.

PROMENIX PROJECT ANR-22-CE06-0026

(DEC 2022 - DEC 2026)

« LES NANO-IONS COMME OPPORTUNITÉ POUR L'ÉTUDE DES PROTÉINES MEMBRANAIRES »

Partners:

I2BC Institut de Biologie Intégrative de la Cellule
ICSM / L2IA (Coordinateur)
IBS Institut de Biologie Structurale
MTS/Li2D

Nom Prénom

Les protéines membranaires (PMs) sont la cible de 60% des médicaments actuellement sur le marché. Leur caractérisation au niveau moléculaire est ainsi essentielle pour le développement de nouveaux médicaments. L'étude des PMs repose sur leur extraction des membranes par des détergents. Cette étape d'extraction est un verrou dans l'étude des PMs, car ils conduisent souvent à une dénaturation des protéines. Nous voulons évaluer le potentiel d'ions de taille nanométrique, «nanions», pour la solubilisation et l'étude fonction-

nelle/structurale des PMs de divers organismes, p. ex. procaryotes et de cellules de mammifères. Les NIs sont inorganiques et n'ont pas la séquence amphiphile classique (hydrophile-hydrophobe) des détergents organiques. Cependant, leurs propriétés tensioactives ont été récemment découvertes, ouvrant des opportunités pour de nombreuses applications. Notre projet permettra de mieux comprendre les interactions complexes entre les NIs, les membranes et les protéines.

LABCOM NEWTEM: REFURBISHING OF TRANSMISSION ELECTRON MICROSCOPES

R. Podor, X. Le Goff, H.P. Brau, D. Nogues, A. Candeias

Transmission electron microscopes (TEMs) are very expensive tools of main importance for the characterization of materials in many scientific domains (physics, chemistry, geology, biology, etc). These microscopes are often shut down permanently after 20 years period of use due to electronic failures considered as unre-pairable by the manufacturers. However, the main parts of these microscopes remain operational and their performance is fully compatible with the actual needs of the majority of users. The main objective of the NewTEM LabCOM is to fight against the obsolescence of old scientific equipments by recycling them and restoring their value. It thereby aims to respond to very current societal challenges. The NewTEM LabCom will involve the Institut de Chimie Séparative de Marcoule (ICSM - academic partner) and the NewTEC Scientific company (NewTEC - industrial partner).

NewTEC Scientific is a small business company located in the Gard region, based near Nîmes, which has developed in a few years an original and recognized know-how and skills in the field of scientific instrumentation associated with scanning electron microscopes (SEM) and the nucleарization of SEM. This project aims to develop and diversify the company's activities and to enable it to conquer new markets.



Figure 1. General view of the NewTEM prototype microscope.

The Institut for Separative Chemistry of Marcoule (ICSM) is a mixed research unit, based in Marcoule (Gard), created in 2007 with the aim of bringing out breakthrough technologies in the field of separative chemistry. The « Study of Matter in Environmental Mode » (L2ME) team involved in the project develops new analytical methods and the associated scientific instrumentation in various fields, including electron microscopy. This project will enable it to develop these activities and implement new methodologies.

The refurbishment of the microscopes, as proposed, will be based on the complete reconstruction of the associated electronics and the development of the TEM piloting software. It requires the development of scientific instrumentation based on extremely severe technical constraints with regard to the electronic part. It is part of a desire to make it accessible to as many users as possible to control complex microscopes through control software designed for them. Finally, as the re-commissioning will be free from the constraints of the historical manufacturers, expert users will be able to configure the refurbished microscopes with complete freedom of control and thus access unusual configurations. These different points constitute the building blocks of the NewTEM project. These developments will be carried out by the ICSM team and then transferred to NewTEC, which will ensure their industrialization and marketing.

This project is part of a long-term vision. The first step is to develop and launch a new product that meets the real expectations of TEM users (Fig. 1). Then it is a question of proposing simple, user-friendly and scalable software for the management of the refurbished TEMs. In the medium term, the aim is to create a new tool that can be adapted to the needs of users, facilitating scientific and technical developments and enabling the training of students and researchers (Fig. 2).

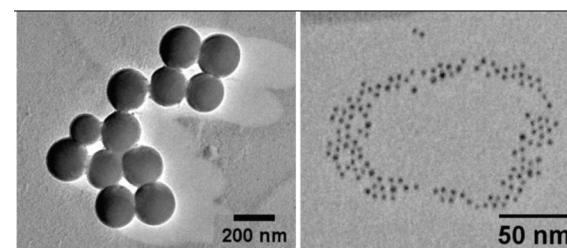


Figure 2. Bright field images recorded with the NewTEM microscope.





LABEX CHEMISYST



FROM LABEX CHEMISYST TO MUSE'LAB CHEMISTRY

Till 2019, the four Balard institutes of chemistry from Montpellier University Scientific, ICGM, IBMM, IEM and ICSM plus a team of "soft matter" physicists, of the Laboratory Charles Coulomb (UM) and the Centre of Materials of l'Ecole des Mines were associated around a laboratory of excellence, a Labex, entitled **CheMISyst**. This association was devoted to molecular and interfacial chemistry with a focus on the non-covalent long-range forces driving self-assembly. The related research was 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 was 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 main topics underlying all the studies were: 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 was 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

In 2017, the reorganization of the Montpellier university around the "Montpellier University of Excellence" a new association, an I-SITE that gathers the forces of 19 institutions towards a common ambition: create in Montpellier a thematic research-intensive university that will be internationally recognized for its impact in the fields of agriculture, environment and health. For all its consortium members, this university strives to act as the academic partner they can establish strong ties with, and on which they can fully rely. Through the project construction named MUSE and in perspective of the end of the Labex project Chemisyst planned in 2021, the four institutes of the "Pôle de Chimie Balard" targeted the development of their own structure towards a **Lab'MUSE** starting in 2019 and taking into account a chemistry for man and his environment, i.e. a chemistry thought out differently, accompanying changes in concepts and practices for a controlled management of resources, a protected environment and sustainable health.

Whether it is a question of nutrition, environmental protection or health, it is absolutely necessary to design products that are effective, resistant but non-toxic, degradable after use, and environmentally friendly. With the permanent concern for a chemistry that respects the principles of «green chemistry» and «green engineering» for a judicious and sustainable development, the concept of adaptive molecular systems whose properties are governed by the principles of «cooperation, synergy and diversity of intermolecular interactions» makes the originality of Montpellier's chemistry. Whatever the required application, the aim is to understand and then to control how a set of molecules or supramolecular entities interact (communicate and behave collectively) to create complex systems with properties far beyond those of the individual constituents. This change of paradigm should contribute to this «green revolution», based on transdisciplinary cooperation for which chemistry must be a source of progress for :

- Promoting an innovative agriculture to contribute to food security and environmental quality and thus meet the challenges of modern agronomy. The aim here is to design active molecules and systems for environmentally friendly agriculture, to study and synthesize plant molecules useful for human health, to recover agricultural waste and to use biomass as a raw material.

- Promoting a transition to an environmentally friendly society to provide complementary solutions to the restoration and protection of the environment but also to eliminate and/or recycle wastes (primary or secondary). The aim here is to design systems capable of producing or storing clean energy, develop processes for the synthesis of molecules that are more environmentally friendly, develop processes for the treatment of contaminated effluents, and implement processes for the reasoned recycling of recoverable materials.

- Improving human health in changing environments by gaining a thorough understanding of physio-pathological mechanisms at the molecular level, designing active molecules, delivery systems, targeting, transport for targeted treatments, drawing inspiration from nature and using living organisms for healing.

PRocédé vert pour la dépollution DE SiTes mINIers : Separation superchaotropique de tungstène/molybdène par des mousses (PREDESTINE)

	NOM	PRENOM	INSTITUT
Responsable	BAUDUIN	Pierre	ICSM/L2IA
Co-responsable 1	SZENKNECT	Stéphanie	ICSM/LIME
Doctorant	LEGRAND	Valentin	
Date de démarrage du projet	01/11/2022		
Date de fin du projet	31/10/2025		

L'adsorption des POMs à l'interface eau/air en présence de tensioactifs non-ioniques permet d'envisager leur extraction/concentration dans des mousses, c'est la flottation ionique par superchaotropie (voir fiches bleues). Actuellement, tous les procédés de flottation ionique se réalisent avec un tensioactif (collecteur) ionique de charge opposée à l'ion métallique à extraire, l'extraction dans la mousse se faisant ainsi par formation de paires d'ions (collecteur/ion métallique) à l'interface eau/air. Dans le cas de la flottation ionique par superchaotropie l'utilisation d'un tensioactif neutre permet uniquement l'extraction de nano-ions superchaotropes et non des ions simples, ce qui permet d'envisager un nouveau mécanisme de séparation des espèces ioniques (ions/nano-ions) et donc de métaux en solutions. Des résultats préliminaires récents nous ont permis de valider ce nouveau concept de flottation ionique par superchaotropie. L'intérêt principal de la flottation ionique est son faible coût d'exploitation par l'utilisation de l'air comme phase extractante, la simplicité des réacteurs utilisés qui se présentent principalement sous forme de cuves ou de colonnes, mais également sa facilité de mise en œuvre. Par ailleurs, l'absence

ou le faible ajout de matières organiques, permettant la séparation ou la génération de la mousse, réduit grandement **l'impact sur l'environnement** contrairement à l'extraction par solvant qui nécessite de grandes quantités de phase extractante et de diluant organique.

Les mines de tungstène d'Anglade, commune de Salau (Occitanie, Ariège), ont été fortement exploitées dans les années 70 et 80. Depuis la fermeture de ce site minier en 1986, environ 150 mille tonnes de résidus, encore riche en tungstène / W (et molybdène/Mo) sont restées sur site à flanc de montagne, créant un risque environnemental important. Des procédés plus respectueux de l'environnement et efficaces pour permettre le traitement de tel résidus, avec un double but de dépollution et de valorisation, sont donc à trouver. L'objectif de cette thèse est de proposer une solution innovante à une extraction sélective du W et du Mo en couplant (i) la méthode de flottation ionique par superchaotropie pour l'extraction/séparation de tungstène/molybdène et (ii) une méthode douce (acide organiques) de lixiviation de résidus miniers riches en tungstène/molybdène.

Molecular dynamics to rationalize structural effects on extraction mechanisms in ionic liquid (RAMELI)

	NOM	PRENOM	INSTITUT
Responsable	DUVAIL	Magali	ICSM
Co-responsable 1	DOURDAIN	Sandrine	ICSM
Post-Doctorant	LE CROM	Sébastien	ICSM

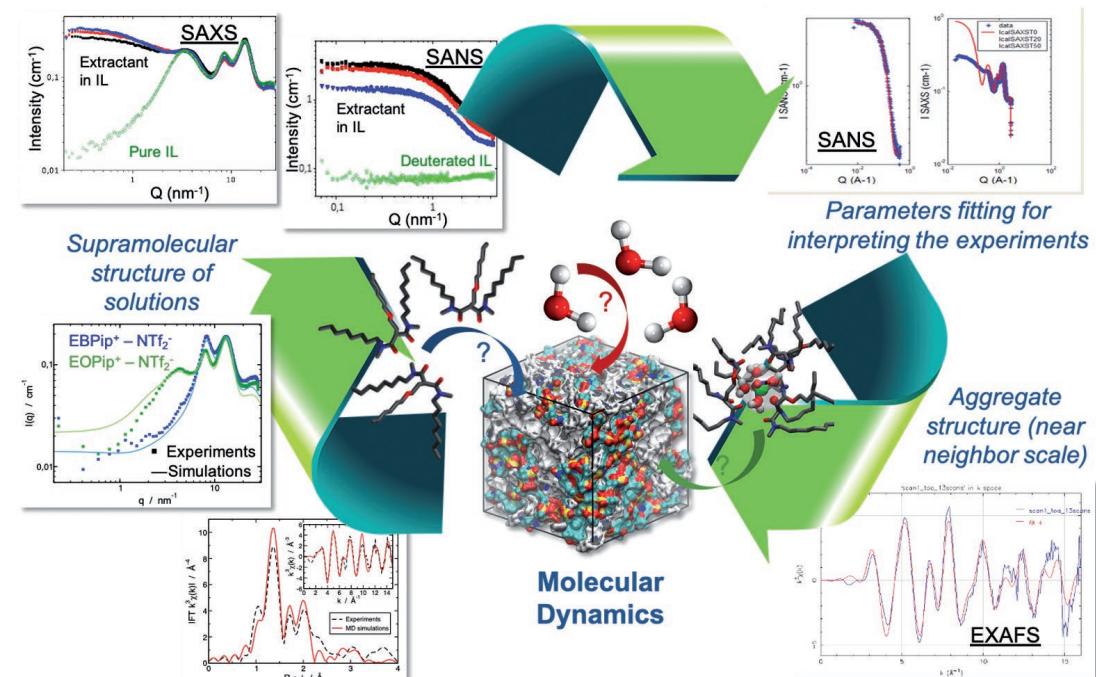
Date de démarrage du projet	1 ^{er} février 2021
Date de fin du projet	31 août 2022

As part of an approach applied to the recycling of metals of interest, an essential challenge in liquid-liquid extraction today consists in replacing conventional organic solvents by non-conventional diluents, typically ecofriendly solvents like ionic liquids. This study will be based on studies performed at ICSM in an attempt of developing extraction processes in ionic liquids, which demonstrated that the best extraction performances in ionic liquid media are not only due to different complexation mechanisms, but also to different structural properties. The objective of this project is to understand the mechanisms occurring in liquid-liquid extraction processes performed in ionic liquid media by developing multi-scale theoretical approaches based on molecular dynamics.

It will allow a better understanding of the thermodynamic properties of aggregates in ionic liquid media in order to rationalize the phenomena associated with the transfer of ions involved in liquid-liquid extraction processes.

• Scientific driving question, in the context of system chemistry:

The objectives of this project will provide insights on the structuring and the mechanisms of aggregation of the extracting molecules in ionic liquid media by understanding the effect of the solvent structure on the extraction performances. Applied to the extraction of metals of interest, this project will also allow identifying ionic liquids in which the extraction performances will be improved.

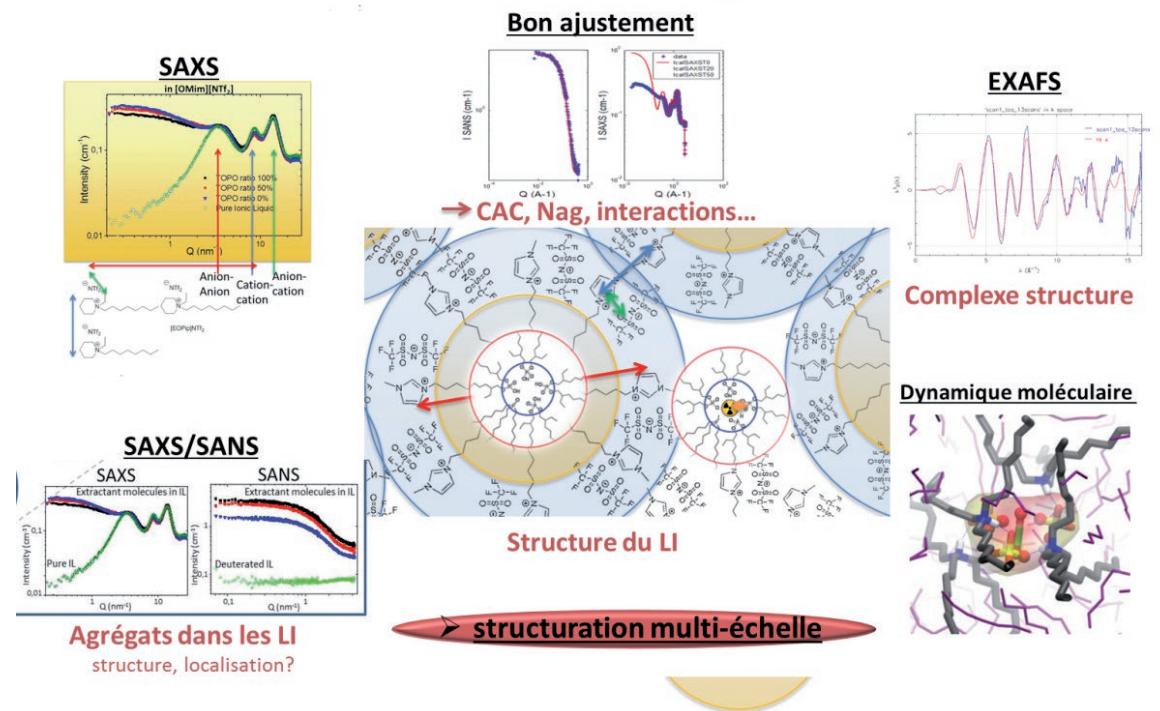


Extraction mechanisms in Ionic Liquid medium for the extraction of metals of interest (MERLIN)

	NOM	PRENOM	INSTITUT
Responsable	DOURDAIN	Sandrine	ICSM
Co-responsable 1	ARRACHART	Guilhem	ICSM
Co-responsable 1	CAMBEDOUZOU	Julian	IEMM
Post-Doctorant	AUGUSTO LOPEZ	Cesar	ICSM
Date de démarrage du projet	1 ^{er} mai 2018		
Date de fin du projet	1 ^{er} novembre 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.

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.



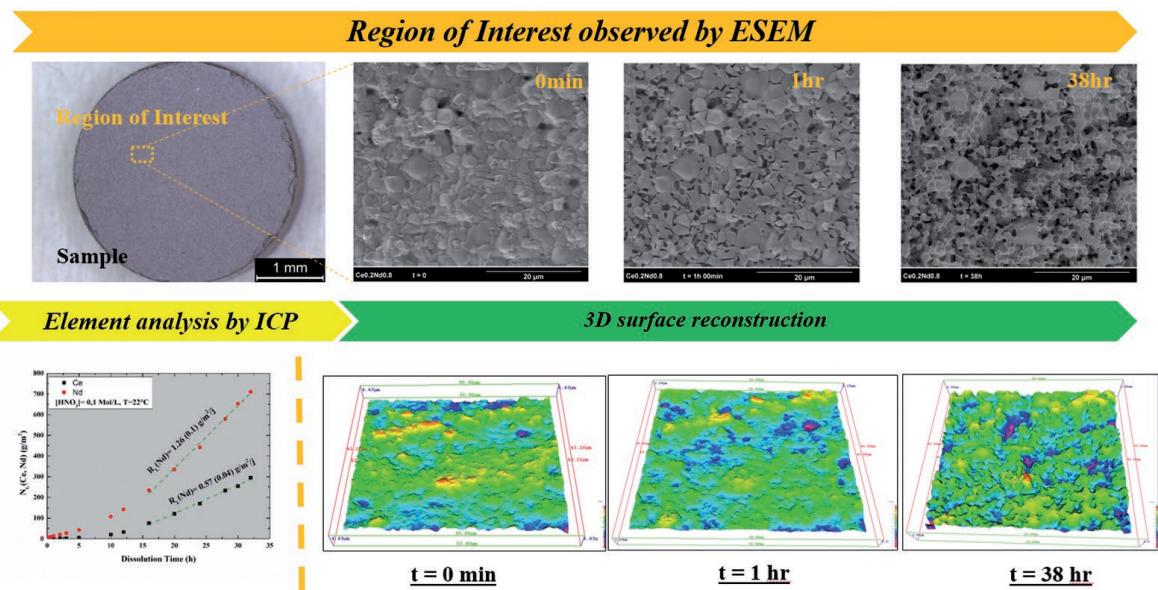
Characterization of evolving solid/liquid interfaces during dissolution by 3D analysis at the microscopic scale by SEM (Disso3D)

	NOM	PRENOM	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	8 janvier 2018
Date de fin du projet	7 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 $\text{CeO}_2\text{-Nd}_2\text{O}_3$ binary system. This system allows preparing materials with variable crystal structures and microstructures, depending on 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.



Self-assembly of Ammonium Borane hybrid alkanes in organic solvents (A4)

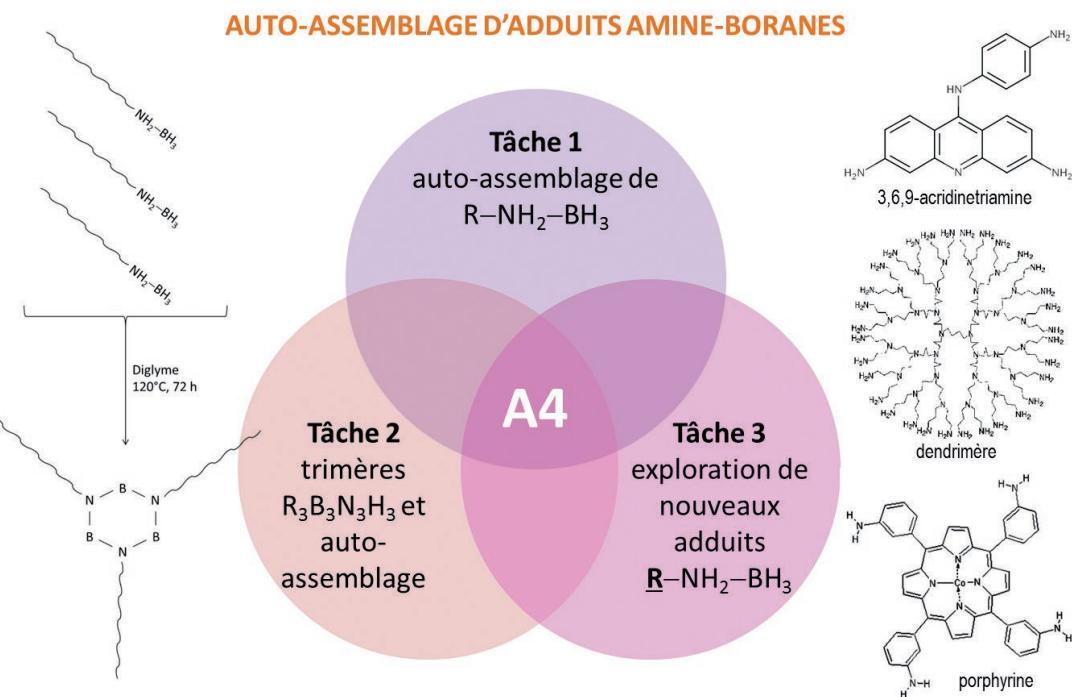
STAGES LABEX

	NOM	PRENOM	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	1 ^{er} mars 2018
Date de fin du projet	1 ^{er} octobre 2019

The A4 project aims at developing molecules having $-\text{NH}_2\text{-BH}_3$ groups (with protic hydrogens together with hydridic hydrogens, *i.e.* $\text{H}^\delta+$ versus $\text{H}^\delta-$) within the context of the supramolecular chemistry. Our idea is to study the interactions $\text{H}^\delta+\cdots\text{H}^\delta-$ 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.





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 and training 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 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 in 2020. 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 CheMSyst 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 school of SURFACES AND NUCLEAR SCIENCES

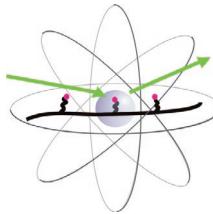
as well as for "NEUTRON AND X-RAY REFLECTIVITY" and "SMALL ANGLE X-RAY AND NEUTRON SCATTERING" were organized by ICSM jointly with the European Membrane Institute (and University of Avignon for SAXS). These thematic schools were largely appreciated by the participants and they will be recurrent. An international workshop around "model and simulation" organized by LMCT under the CECAM certification was also successful.

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).



ECOLE THÉMATIQUE SURFACES ET NUcléAIRE

19-22 JUIN 2022 (MÉJANNES LE CLAP)

Après 2012, 2015, 2018, la quatrième édition des écoles thématiques « Surfaces et Nucléaire » a permis de réunir dans une ambiance conviviale **17 participants et 11 intervenants** provenant de différents cette de recherche (Subatech Nantes, CIRIMAT Toulouse, IJC Lab Paris, CEA Marcoule, ICSM, CEA Saclay, CEA Cadarache).

L'objectif de cette école était de former les participants aux techniques d'analyse des surfaces et des interfaces appliquées aux problématiques spécifiques du domaine du nucléaire au travers de cours théoriques. Ces cours ont permis de donner une vue globale des potentialités d'un grand nombre de techniques utilisables dans différents domaines de recherche du nucléaire.

Pour la première fois cette école a participé à l'animation scientifique de deux groupes structurés dans différentes communautés scientifiques dont l'ICSM est membre. Il s'agit principalement du **GDR SCINEE** (Sciences Nucléaires pour l'Ener-

gie et l'Environnement) et du **GDR PROMETHEE** (Procédés Hydrométallurgiques pour la Gestion Intégrée des Ressources Primaires et Secondaires). Ce dispositif d'école thématique est parfaitement adapté puisque la formation proposée se positionne à l'intersection de 2 thèmes principaux : la caractérisation des surfaces et des interfaces et les problématiques spécifiques en sciences des matériaux et procédés pour le nucléaire. Les participants appartiennent 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. De plus, la volonté de l'école est de pousser les participants à créer des liens pour promouvoir de futures collaborations. Le lieu choisi est donc isolé et les infrastructures (salle de conférence, chambres sur le site...) sont idéales pour ce type de manifestation.



A noter la programmation du prochain rendez-vous en 2025.

Organisatrices : Stéphanie Szenknect (LIME), Sandrine Dourdain (LTSM), Diane Rébiscoul (L2ME)



ECOLE THÉMATIQUE DE DIFFUSION DES RAYONS X ET DES NEUTRONS AUX PETITS ANGLES

15-17 JUIN 2022



L'école thématique de diffusion des rayons X et des neutrons aux petits angles a permis de réunir dans une ambiance conviviale **24 participants et 6 intervenants** provenant de différents centres de recherche (ISCR Rennes, ISTO Orléans, Univ. Strasbourg, Clermont-Ferrand, CIRIMAT Toulouse, CEA Grenoble, Marcoule-ICSM, Saclay, ...).

Le premier objectif de l'école était de former les participants aux **principes théoriques de la diffusion, à son utilisation, au traitement des données ainsi qu'à leur exploitation au travers de cours et de travaux pratiques**.

Le second objectif était de permettre aux participants de se faire connaître via des présentations courtes et de nombreux échanges, et d'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, qui ont convenu en fin de session qu'il serait intéressant de formaliser la mise en place d'un **réseau sur la diffusion aux petits angles**.

Devant le nombre de demandes, nous prévoyons une nouvelle édition en juin 2024.



Organiseurs: Julien Cambedouzou (IEM), Sandrine Dourdain (CEA-ICSM), Pierre Bauduin (CEA-ICSM), Olivier Diat (CEA-ICSM), Alain Gibaud (Univ. Le Mans), Françoise Bonneté (IBPC, Paris Cité)

ECOLE D'AUTOMNE DE RÉFLECTIVITÉ DES RAYONS X ET DES NEUTRONS

05-08 OCTOBRE 2021



La réflectivité des rayons X ou des neutrons est une technique de caractérisation des surfaces, des couches minces, voire de dépôts multicouches, qui permet d'obtenir des informations sur les **épaisseurs, les rugosités et les densités** à proximité de la surface étudiée.

Cette école thématique, organisée du 5 au 8 octobre 2021 à l'ICSM par Sandrine Dourdain et Diane Rébiscoul (ICSM) et Arie Van der Lee (IEM, Montpellier), avait pour objectif de **former les participants aux principes de la réflectivité**. Cette école a permis de réunir dans une ambiance conviviale **11 élèves** provenant de différents centres de recherche (Université Aix-Marseille, Université de la Sorbonne, Université Paris-Saclay, du Laboratoire d'Analyse et d'Architecture des Systèmes, Institut de Chimie de la Matière Condensée de Bordeaux, du CEA Marcoule et de l'ICSM) appartenant à la communauté des chercheurs et des doctorants pratiquant ou allant pratiquer la réflectivité pour l'analyse des surfaces.

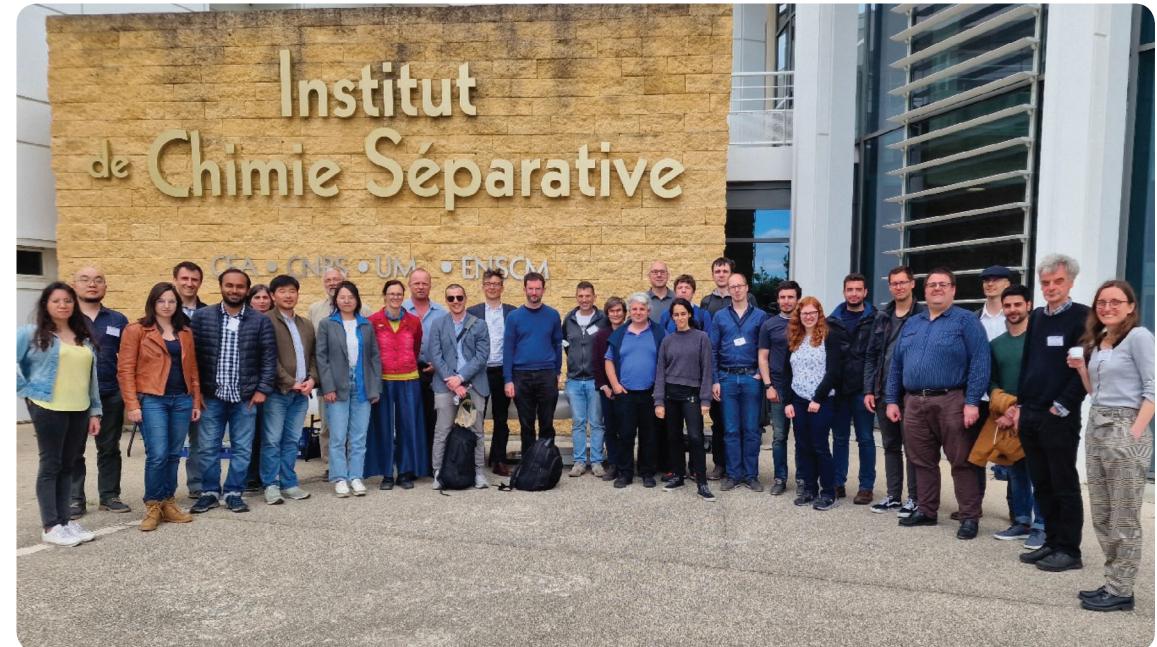
Cette école d'automne a permis de former les participants **aux principes théoriques de la réflectivité**, à ses potentialités d'utilisation, aux traitements des données et à leur exploitation **au travers de cours et de travaux pratiques** (analyses des échantillons sur un appareil et simulation des données à l'aide du logiciel Reflex). Des échanges enrichissants et motivants entre les participants et les intervenants sur les différents types d'échantillon analysés ont permis d'initier de nouvelles collaborations et de proposer des pistes d'adaptation du logiciel Reflex à des cas spécifiques.

Prochaine école : rendez-vous en 2024 !!

Organiseurs: Sandrine Dourdain - LTSM (CEA-ICSM), Diane Rébiscoul -L2ME (CEA-ICSM), Arie Van der Lee (IEM).

ATELIER CECAM ION ADSORPTION AND ELECTROKINETIC TRANSPORT AT INTERFACES

MAY 4, 2022 - MAY 6, 2022



Le domaine des interfaces solide-liquide chargées présente un intérêt particulier en physico-chimie car il concerne de nombreux domaines et applications scientifiques : électrochimie, biologie, géologie, dépollution, formulation, etc. Les phénomènes électrocinétiques sont à l'origine de la conception de dispositifs nanofluidiques contrôlés qui sont très utilisés par les sciences de l'ingénieur.

L'atelier du Centre Européen de Calcul Atomique et Moléculaire (CECAM) « Ion adsorption and electrokinetic transport at interfaces », organisé par Jean-François Dufrêche (ICSM, France), Remco Hartkamp (Delft University of Technology, Pays-Bas), Laurent Joly (Université Lyon 1, France) et Milan Předota (University of South Bohemia, République Tchèque) a eu lieu du 4 au 6 mai 2022 à l'Institut de Chimie Séparative de Marcoule (ICSM). Cet atelier avait pour but d'établir un état des lieux de la modélisation des interfaces chargées solide/liquide impliquées dans de nombreux procédés naturels et industriels, et en particulier dans les sciences de l'énergie. Il a permis de réunir dans une ambiance conviviale 45 participants de 15 pays européens différents et des Etats-Unis. Les participants, parmi les meilleurs experts en modélisation du domaine, ont ainsi pu comparer et améliorer leurs approches et développer des projets sur ces thématiques.

<https://www.cecam.org/workshop-details/1141>

FORMATION : INITIATION AUX TRAITEMENTS D'IMAGES AVEC LE LOGICIEL IMAGEJ / FIJI

12-14 SEPTEMBRE 2022
(MONTPELLIER)

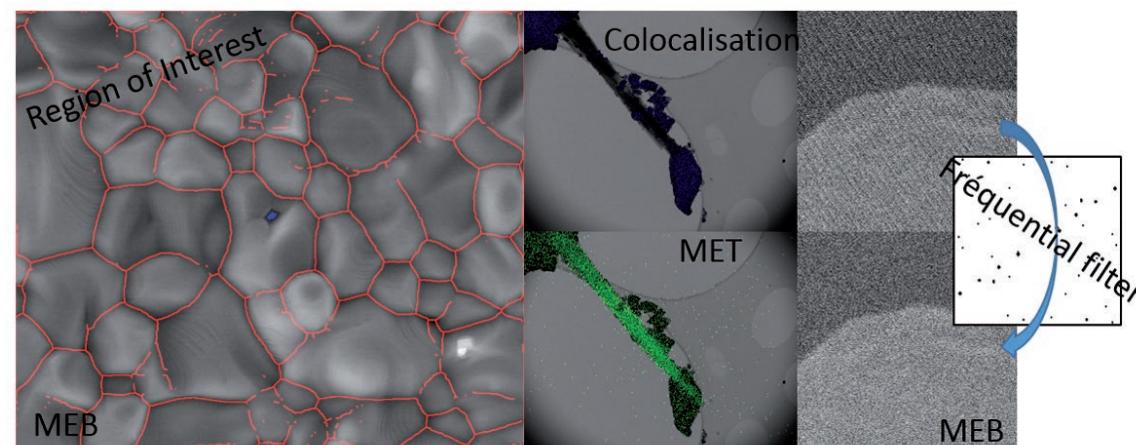


Avec l'avènement de l'ère numérique, les images sont aujourd'hui des données numériques multi-dimensionnelles qui peuvent être traitées et analysées quantitativement pour en extraire davantage d'informations. Le logiciel open source **ImageJ/Fiji** est un outil puissant disponible pour traiter et analyser les images numériques. Il permet également d'automatiser l'analyse d'images avec des macros et des plugins personnalisés.

Depuis 2015, nous proposons une formation via la **formation permanente de la délégation Occitanie Est du CNRS** (Montpellier). A chaque session, **8 à 10 personnes sont formées**. Cette formation a pour vocation de donner l'ensemble **des notions et connaissances nécessaires pour réaliser des traitements d'images**. D'une durée de **3 jours**, la formation se déroule principalement par des **travaux pratiques encadrés par deux personnels de l'ICSM** (CEA et CNRS).

La formation permet de donner un **ensemble d'outils**, de **méthodes** pour la segmentation d'images et un aperçu rapide de **l'apprentissage automatique** à cette fin. Cette formation se concentre sur l'analyse d'images de microscopie mais s'adresse à toutes les personnes engagées dans la recherche qui souhaitent commencer à utiliser ImageJ/Fiji pour l'analyse d'images en général.

La prochaine session est programmée du **26-28 septembre 2023**.



Formateurs: Henri-Pierre Brau (L2ME), Joseph Lautru (L2ME), Xavier Le Goff (L2ME)



OUTLOOK



Olivier Diat, Stéphane Pellet-Rostaing et Marielle Asou-Pothet

This scientific report summarises the achievements made in the fields of recycling and nanoscience for energy over the last four years. With still about three hundred publications but a number of external citations per year of about 2000 (according to web of science) which has slightly decreased during the COVID period, ICSM remains an active institute in terms of innovation with 20 patents over this period. This specific scientific activity has also developed strongly on a global scale around the widespread development of the circular economy. The ICSM is still a reference in this field, although facing more challenges to maintain its position at the top due to its competence in this area, which has been capitalized since its founding. The direction of scientific and technical efforts, initially defined by several reports from the Academy of Sciences in the early 2000s, must be redefined for future years but depends on an agreement between each supervisory body. This in no way prevents the ICSM from remaining dynamic and responding to numerous regional, national and European calls for projects through numerous academic and industrial collaborations.

One of the reasons of the success is that a significant contribution in the three hundred primary scientific papers in "A" ranked journals, the sustained rate of patent filings and the important number of co-authorship with colleagues from R/D CEA departments in charge of applications, of international collaboration and with activities that meet either the demands of industrial partners such as ORANO or a more prospective researches (TRL 1-4). Last but not least, more than half of the articles are co-signed by complementary teams within the Institute. To our best knowledge, this is a unique case of pluridisciplinary approach.

Since its creation, the ICSM has always balanced between "understanding" - i.e. demonstrating the predictive capacity of models built on known 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"). As a result, an area of expertise and collaboration within the institute focused on

«Innovation in Extraction and Recycling» keeps growing, as evidenced by the creation of synergism in solvent formulation or water-saving technologies and would not excel without a close link between observation and theory. Within a second cluster of "**Methodologies and theory in separation chemistry**", 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 are still explored. The development to support recent developments in electron microscopy, which enable direct 2D observation (and 3D reconstruction) and the complex characterization of physico-chemical properties to advance our understanding of self-healing, sintering, dissolution, and chemical reactivity through in situ experiments, is also significant. No separation process can be made without knowledge of the "durability of materials", i.e. materials that should withstand to extreme constraints and long usage. This is true in the nuclear fuel area and along its life-cycle, but also for all materials used in other decarbonated 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 deeply investigated from the initial state of the precursors (dispersed molecular clusters, colloids, emulsions...) to the final state of the final material (sintered, porous, powder, thin film) since the physical and chemical properties of these materials (durability, robustness, extraction, confinement...) depend on their evolution during synthesis and on their life-cycle. In order to target the dissolution impact, a specific attention has been placed on chemical or physical heterogeneities within the matter in recent years.

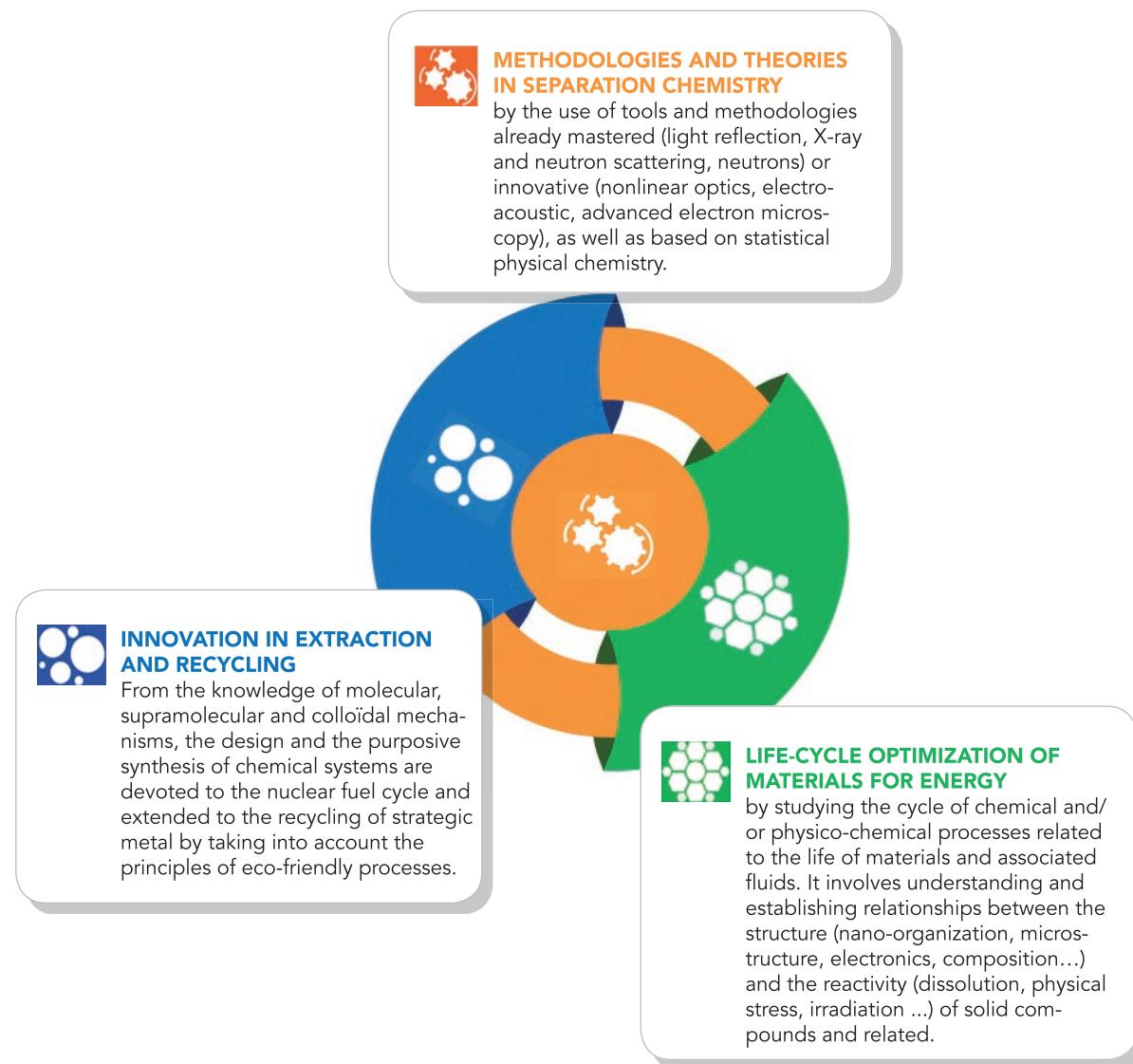
To facilitate the understanding of the underlying profound unity within the institute, our research projects are presented in this booklet under those three clusters.

The question stands: what comes next? What evolution for 2030 horizon? A roadmap will be proposed by the direction of ICSM to the scientific council end of 2023 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 2021-2026 contractual goals of research in energy, using all facets of recycling.

Stéphane Pellet-Rostaing

Olivier Diat

THE CONNECTED CLUSTERS OF INNOVATION AT ICSM



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.





LIST OF PUBLICATIONS ICSM (2017-2020)

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Photo conseil scientifique du 29 Juin 2021

De gauche à droite (Membres et Invités) :

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PLAN D'ACCÈS ICSM

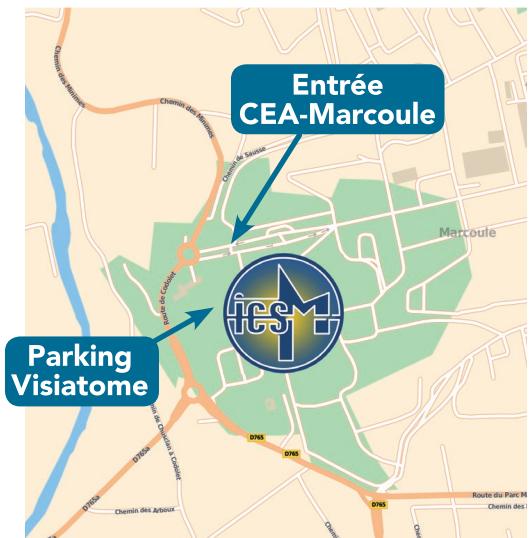
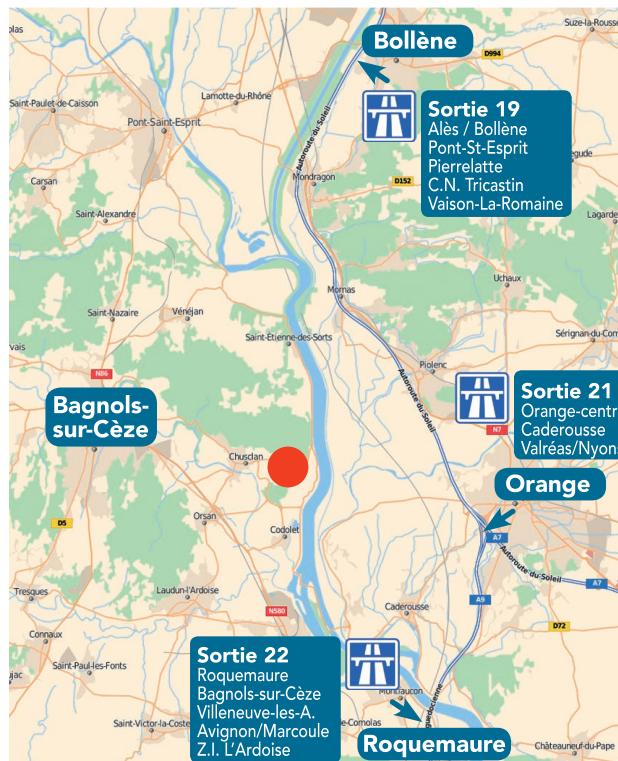
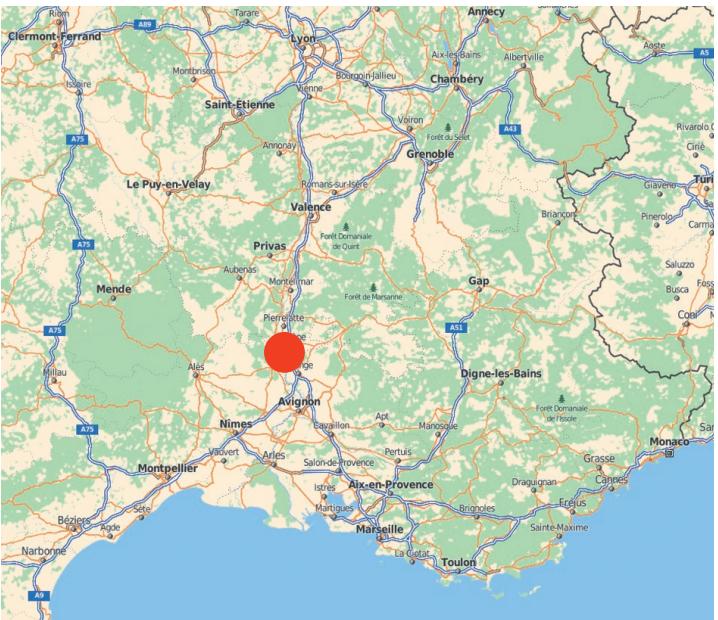
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• Depuis Montpellier, rejoindre l'A9 en direction de Nîmes/Lyon. Prendre la sortie 22 et continuer sur la N580 direction Bagnols-sur-Cèze. Après la traversée de L'Ardoise, prendre la direction de Marcoule sur la D138a.

• 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 droite la N580 en direction de Bagnols-sur-Cèze jusqu'à la traversée de L'Ardoise et prendre la direction de Marcoule sur la D138a.





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