

SILICOTITANATES FOR STRONTIUM REMOVAL IN A CONTINUOUS PROCESS

Nuclear fuel reprocessing generates contaminated aqueous outflows after liquid-liquid extraction of uranium and plutonium through Purex process. These outflows contain a wide range of minor actinides and fission products and must be treated. Most of these radionuclides are separated from aqueous medium thanks to a precipitation in alkaline medium but some of them remain in solution, just like ^{137}Cs and ^{90}Sr . While treatment solutions exist in the case of Cs, others must be implemented in the case of Sr. Crystalline silicotitanates such as Sitinakite are promising materials due to the selective capture of Sr with regard to Ca. Sitinakite is an ionic exchanger with mobile sodium acting as charge compensator in the structure (**Fig. 1-left**).

This crystalline phase is obtained via hydrothermal reaction. During this synthesis, the variation of the Ti/Si ratio leads to a structural change of the species formed. For high values of Ti/Si (around 2), it is the sodium nonatitanate phase that is preferentially formed (**Fig1-right**). Although this phase is also known to capture Strontium, it does not show any selectivity towards Calcium. For Ti/Si ratios below 1.5, sitinakite is preferentially formed. As shown in **Fig1-right**, the lower the Ti/Si ratio, the less crystalline the sitinakite becomes, with smaller grain sizes resulting in higher and higher exchange rates between Strontium and sodium¹.

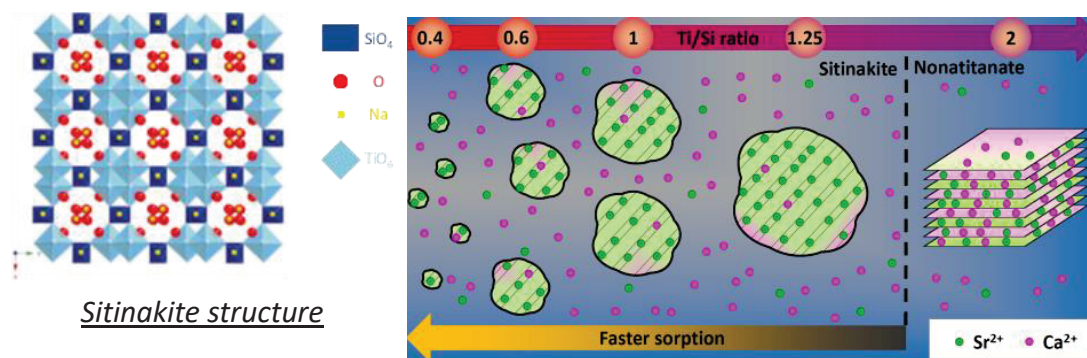


Figure 1. Left: Sitinakite crystalline structure ($\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}$). Right: Effect of Ti/Si ratio used during synthesis on the structure of the crystalline phase and on the Strontium uptake.

After exploring the synthesis of sitinakite powders from liquid Si and Ti precursors such as TEOS or TTIP, our team developed an alternative synthesis route using solid precursors such as TiO_2 or SiO_2 . This route has led to the formation of sitinakite powders, which are cheaper to synthesize and more feasible on an industrial scale. This work was the subject of a patent² and served as the basis for the next step, which concerns the formulation of porous materials that allow for column treatment of strontium-contaminated outflows. The aim is to transform preformed porous objects from TiO_2 into sitinakite while preserving the shape of the initial object. It has been

demonstrated that it is possible to carry out this pseudomorphic transformation on macroporous TiO_2 monolith foams or on extruded TiO_2 pellets produced industrially by the company CTI, Céramiques Techniques Industrielles (**Fig. 2**). The diffractogram indicates that the transformation to sitinakite is not complete and that approximately 10%wt of TiO_2 remains at the end of the reaction. This work is currently in the process of being patented³ and the prospects for development concern the improvement of the conversion yield and the increase in the specific surface area of the transformed objects.

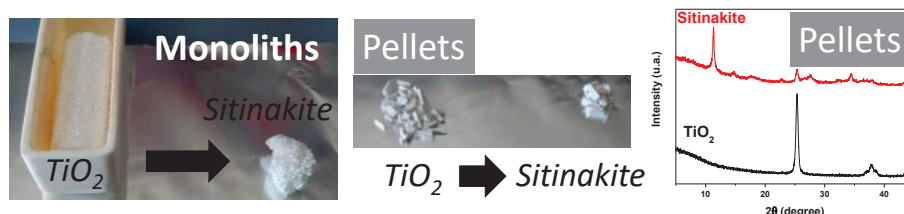


Figure 2. Pseudomorphic transformation of TiO_2 monoliths and pellets into sitinakite. XRD of the pellets before and after transformation

¹ T. Tratnjek, X. Deschanel, A. Hertz, C. Rey, J. Causse, **Ti/Si ratio as a tool to tailor the microstructure of titanate-based crystalline phases able to selectively trap strontium over calcium**, Journal of Hazardous Materials. 440 (2022) 129755

² J. Causse, T. Tratnjek, A. Hertz, **PROCÉDÉ DE PRÉPARATION D'UN MATÉRIAU SILICOTITANATE DE STRUCTURE SITINAKITE UTILISABLE POUR LA DÉCONTAMINATION D'UN EFFLUENT AQUEUX**, 2021, FD21638, FR2112208.

³ J. Causse, T. Tratnjek, A. Hertz, **Matériaux monolithiques granulaires de silicotitanate de structure sitinakite, leur procédé de préparation, et procédé de séparation les mettant en œuvre**, 2023, Patent demand ongoing,