

## Two-step synthesis, combining SC-CO<sub>2</sub> coating and hydrothermal conversion, applied to porous zeolite-based sorbent preparation for wastewater treatment

A. Hertz,<sup>a,\*</sup> A. Escamilla-Perez,<sup>a</sup> Y. Barre,<sup>a</sup> A. Grandjean<sup>a</sup>

<sup>a</sup> CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France

\*Corresponding author: [audrey.hertz@cea.fr](mailto:audrey.hertz@cea.fr)

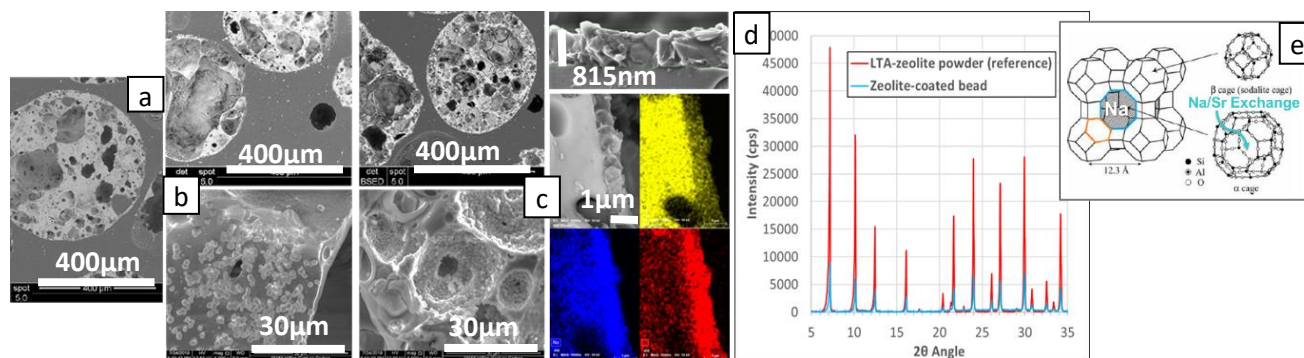
### 1. Introduction

Nuclear industry produces different types of wastewater containing radiotoxic radioelements (<sup>137</sup>Cs<sup>+</sup>, <sup>90</sup>Sr<sup>2+</sup> ...) that have to be treated. Sorption treatment by radioelement transfer from the wastewater to a solid substrate (sorbent) can reduce the final waste volume to be stored and facilitate their conditioning<sup>1</sup>. Implementation of this type of sorbent in a dynamic and compact process (fixed-bed/column) still represents, at this time, a challenge for efficient on-site treatment. Process efficiency is then dependent on sorption kinetics and sorbent selectivity for targeted elements<sup>2</sup>. These materials must allow an efficient wastewater flux into the column (macrostructure) and fast ion diffusion into the sorbent for ion exchange (microstructure). The porous network control, notably by mixing micro, meso and macro porosity, will limit the transport and diffusion issues; thus, enabling the radioactive species to access easily into the sorbent active sites<sup>3</sup>.

This study, funded by CEA and ORANO, focuses on the development of new hierarchical porous sorbents based on low-cost macroporous glass bead substrate and coated with LTA zeolite film (ion exchanger suitable for Sr sorption<sup>4</sup>). The zeolite film was produced by coupling two synthesis methods: a silica layer was first deposited on the substrates under supercritical CO<sub>2</sub> conditions and then transformed into zeolite by hydrothermal conversion.

### 2. Materials and Methods

Silica is coated by thermal decomposition of TEOS sol (iPrOH with HNO<sub>3</sub>), in SC-CO<sub>2</sub> (150°C 25MPa) in a batch mode reactor under mechanical stirring. Different operating conditions have been evaluated to improve precursor infiltration, silica film adhesion and thickness as well as final sorbent microstructure. Zeolite coating was then obtained by hydrothermal treatment of silica-coated beads in digestion vessels under classical conditions for LTA-zeolite crystallization. The hydrothermal treatment consist of SiO<sub>2</sub> local dissolution, aluminosilicate gel precipitation conserving SiO<sub>2</sub> film morphology (20h, 40°C) and gel crystallization into LTA-zeolite (24h, 70°C).



**Figure 1.** Scanning electron micrograph of (a) raw glass bead substrate, (b) after SiO<sub>2</sub> coating in SC-CO<sub>2</sub> and (c) after hydrothermal conversion of the SiO<sub>2</sub> film into LTA-zeolite. (d) Final zeolite-based sorbent X-ray diffractogram and (e) LTA-zeolite structure.

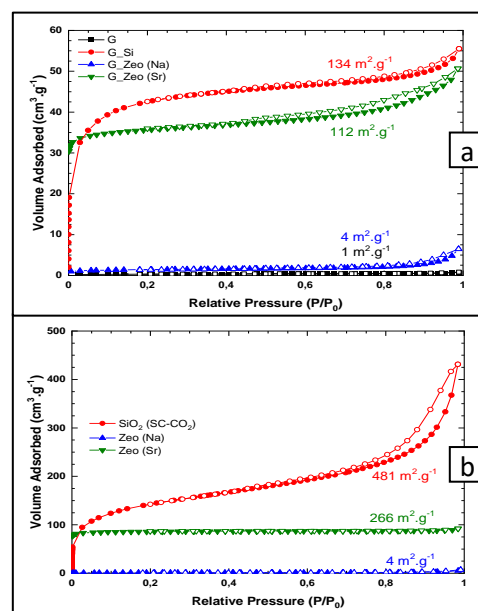
Silica and zeolite-based materials were widely characterized by XRD, N<sub>2</sub> adsorption/desorption and SEM (Fig. 1). Sr<sup>2+</sup> sorption properties of sorbents have been evaluated and compared to commercial LTA-zeolite sorbents. Kinetic and isotherm curves have been determined in batch mode while breakthrough curves have been obtained in lab-scale column process for various simulated wastewater containing Sr<sup>2+</sup> and competitive cations (Na<sup>+</sup>, Ca<sup>2+</sup>).

### 3. Results and discussion

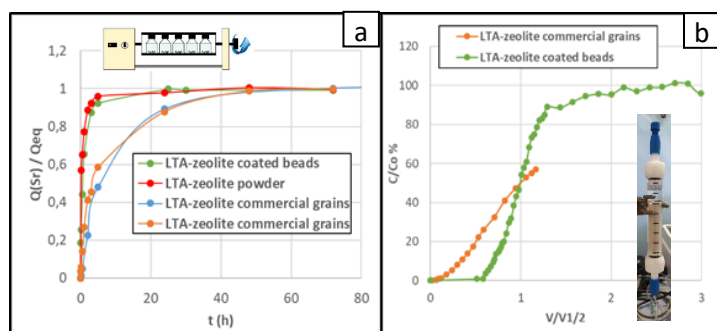
#### Optimized microstructure of the coated glass bead

For the silica layer deposition on the glass beads, the TEOS thermal decomposition in supercritical CO<sub>2</sub> at 150°C and 25MPa allowed the preparation of a homogeneous microporous silica film, well adherent to the overall surface of the substrate (Fig. 1b). The silica-coated beads present a high specific surface area (Fig. 2a) of around 135m<sup>2</sup>/g (1m<sup>2</sup>/g for the raw substrate). The associated silica powder presents a higher specific surface area of about 480m<sup>2</sup>/g (Fig. 2b). The composite contains around 30%<sub>weight</sub> of coated silica.

After hydrothermal conversion, one micron-thick film of LTA zeolite is produced (Fig. 1c). The specific surface area of the composite is reduced (4m<sup>2</sup>/g) because of diffusion issues of N<sub>2</sub> probe molecule due to the presence of Na in zeolite nanocages; only the external surface of zeolite particles is analyzed. After Na exchange with Sr, the N<sub>2</sub> molecule is allowed to diffuse and probe the micropore surface. The specific surface area of Sr-LTA-zeolite-coated beads is increased up to 110m<sup>2</sup>/g (Fig. 2a) while the associated powder surface area is about 265m<sup>2</sup>/g (Fig. 2b). The composite contains around 40%<sub>weight</sub> of zeolite.



**Figure 2.** N<sub>2</sub> adsorption/desorption isotherms for (a) silica and zeolite-coated beads and (b) powders obtained in same conditions.



**Figure 3.** (a) Kinetic curves (sorption capacities Vs time) for zeolite powder and composites and (b) breakthrough curves (Sr<sup>2+</sup> concentration after column treatment Vs treated volume), for zeolite composites.

#### Sr<sup>2+</sup> sorption properties of zeolite-based sorbents

The kinetic curves evaluation (Fig. 3a) evidences the good liquid transport and ion diffusion in LTA zeolite-coated beads (time to reach sorption equilibrium Q<sub>eq</sub> is similar than powder one), compared to LTA-zeolite commercial grains. The Q<sub>eq</sub> value is about 2.1meq/g while Q<sub>eq</sub> is about 4.8meq/g for powder, which confirms the presence of 40%<sub>weight</sub> of active LTA-zeolite in the composite. The good diffusion properties, in the prepared composite, lead to excellent behavior for treatment in fixed-bed process (Fig. 3b).

### 4. Conclusions

LTA-zeolite-based sorbents, with optimized structure and microstructure for Sr<sup>2+</sup> extraction in dynamic fixed-bed treatment process, have been prepared by a two-step method combining silica coating within SC-CO<sub>2</sub> and silica hydrothermal conversion into zeolite ion exchanger. The key of the success for this preparation method is related to the use of SC-CO<sub>2</sub> diffusion properties, which allow the infiltration of silica precursor in the complex macroporous substrate for homogeneous silica layer deposition. The microporous structure of the silica layer obtained with such a SC-CO<sub>2</sub> synthesis method is also of great interest for the quantitative transformation of the silica into LTA-zeolite during hydrothermal conversion step (kinetic balance between SiO<sub>2</sub> dissolution and aluminosilicate gel precipitation).

### References

1. H-C zur Loye et al., Chem. Mater. **2018**, 30, 4475–4488
2. A. Grandjean et al., Process Safety and Environmental Protection, **2020**, 134, 371-380
3. F. Akhtar et al., Journal of the European Ceramic Society, **2014**, 34(7), 1643-1666
4. A. Merceille et al., Separation and Purification Technology, **2012**, 96, 81-88