



## Macroporous LTA-monoliths for in-flow removal of radioactive strontium from aqueous effluents: Application to the case of Fukushima

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### ABSTRACT

Fukushima disaster has led to a large amount of contaminated seawater by radionuclides as caesium and strontium. <sup>137</sup>Cs is a beta–gamma emitter and <sup>90</sup>Sr is a beta-emitter with respective half-lives of 30 and 29 years. Innovative technologies are needed to treat such complex effluent: presence of competing cations (Ca<sup>2+</sup>, Na<sup>+</sup>), neutral pH (pH 7–8), together with an easy way of final disposal. We show here that a novel material appearing as a macroporous zeolite A monolith (named LTA-monolith) proves efficient for sorptive removal of Sr<sup>2+</sup> ions from salty aqueous solutions in continuous flow process. LTA-monolith shows high efficiency and selectivity for the in-flow treatment of radioactive water as simulated Fukushima seawater containing high amount of Na<sup>+</sup> (9.6 g L<sup>-1</sup>), Ca<sup>2+</sup> (0.4 g L<sup>-1</sup>), Mg<sup>2+</sup> (1.28 g L<sup>-1</sup>), K<sup>+</sup> (0.5 g L<sup>-1</sup>), and Sr<sup>2+</sup> (7.8 mg L<sup>-1</sup>), as well as radioactive <sup>90</sup>Sr<sup>2+</sup> (5.5 ng L<sup>-1</sup>, 28 kBq L<sup>-1</sup>). LTA-monolith in-flow process discloses a decontamination capacity four times higher in comparison to batch processes. Furthermore LTA-monolith can be directly used as storage radioactive matter without solidification to perform.

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### 1. Introduction

Nobody can forget March 11, 2011 with the disaster of Fukushima, which has led to a huge contamination of seawater by radioactive elements as Sr<sup>2+</sup> and Cs<sup>+</sup>. Cesium-137 is a beta–gamma emitter and strontium-90 is a beta-emitter with respective half-lives of 30 and 29 years. Different solutions have been envisaged to clean seawater and the use of zeolites is one of the promising solution for strontium removal ([1] and references herein). Zeolites with a Si/Al ratio of 1, as for example LSX or LTA, possess a high ion-exchange capacity. These zeolites have a high density of exchangeable ion sites and can accommodate a large amount of water molecules [2]. These two properties are important for an efficient ion exchange in aqueous medium. Furthermore LTA features a very high selectivity towards Sr<sup>2+</sup> with the following selectivity order: Sr<sup>2+</sup> > Ca<sup>2+</sup> > Mg<sup>2+</sup> > Cs<sup>+</sup> > Na<sup>+</sup> [3], which makes of LTA a highly suitable candidate to remove Sr<sup>2+</sup> from water containing competing cations such as in seawater where large amounts of sodium (9.6 g L<sup>-1</sup>) and also an important amount of calcium (0.4 g L<sup>-1</sup>) have been found. LTA has been the first zeolite that has been prepared by a synthetic process [4] and is nowadays the most produced zeolite by low-cost processes [5]. LTA is more known

for its application as ion-exchanger in washing powders, but LTA has also been proposed for the decontamination of radioactive wastewater [1]. Actually a mixture of LTA and natural chabazite has been used to take up Sr<sup>2+</sup> and Cs<sup>+</sup>, respectively, from contaminated water at Three Mile Island [6].

In addition to the high exchange capacity and the high selectivity of this zeolite, LTA features also a high resistance to radiation in contrast to more common acidic ion-exchange resins that can swell and generate hydrogen under irradiation, and precludes final disposal by vitrification. LTA synthesized by classical procedures features, as it is the case for most of the zeolites, micrometer size (2–10 μm) crystals, which prevent their use in flow processes due to critical accessibility, diffusion limitations and, above all, the development of very high drop pressures. For these reasons, studies of Sr<sup>2+</sup> removal from nuclear wastewater with LTA are classically performed in batch mode [1,3,6–10]. The process requires then a filtration step and a process for the radioactive waste treatment. Another way to proceed is to use inox or glass columns filled with ion-exchangers to avoid the filtration step and to flow the solution through the column. For the treatment of radioactive waste, ion-exchange resins (polymers, as Amberlite C-467 (amino-diacetate), Duolite IRC-718 (aminophosphoric acid), Diphonix-CS (styrene–divinylbenzene–diphosphonic acid, etc.)) [10] are normally used, as their implementation at the outflow of nuclear waste waters is simple. These systems are actually used for the treatment

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of radioactive effluents; however they show to have rather low efficiency and the drawbacks of danger cited above. Inorganic ion-exchangers as sodium titanate SrTreat (manufactured by Selion Oy, Finland) has been proposed instead of organic resins and are available as 0.30–0.85 mm particle size. Sodium titanates show a high ion exchange capacity of 5 meq g<sup>-1</sup> (dry base) [11]. This sodium titanate is very efficient for solutions with pH above 10 (for example, 0.5 mL SrTreat treats aqueous solution containing 1.3 mg Sr L<sup>-1</sup> and 55 g Na L<sup>-1</sup> at a flow rate of 25 bed volumes (BVs) h<sup>-1</sup> with an average decontamination factor (DF) of 4400 at 1500 bed volume (0.75 L)). DF corresponds to the ratio of the initial to the final concentration of Sr in solution. However, the sodium titanate shows lower performance at neutral pH and has a lower selectivity difference between strontium and calcium. LTA zeolite, which is efficient at neutral pH (6–8) [1] and features also a high ion exchange capacity (7 meq g<sup>-1</sup> (dry base) or 236 mg Sr g<sup>-1</sup> (wet base)) and a selectivity for strontium in comparison to calcium, has only been scarcely used in flow processes for nuclear waste water treatment because of the small size of the crystals. Preliminary attempts involving packed-bed columns have been performed (without sodium salt addition) using a mixture of zeolite A and X prepared from fly ash and featuring a particle size of 0.30 mm [1,8,9]. From non-radioactive solution (100 mg Sr L<sup>-1</sup>) it has been shown that a decrease in flow rate increases the volume treated efficiently by the column and that for 40–80 BV h<sup>-1</sup>, a bed capacity of 60–52 mg g<sup>-1</sup> is reached, respectively [1]. An alternative to packed-bed columns is to use zeolite monoliths featuring macropores as flow through pores, to avoid strong pressure gradients, and that can be directly used as storage radioactive matter without solidification to perform. Another advantage of LTA monoliths is that by their employment the amount of final waste matter could be decrease by a factor of 3, compared to packed-bed reactors filled with particles of 50 µm in size or with powders (5–10 µm particle size).

Different ways are known in order to shape zeolites as monoliths, (i) by washcoating the walls of ceramic monoliths (e.g. extruded cordierite honeycomb monoliths) with a slurry of zeolite particles, (ii) by extrusion of a paste composed of a mixture of crushed and sieved zeolites grains (~1 µm) with sacrificial binders such as methylcellulose (porogen) and a permanent binder such as colloidal silica or alumina, (iii) by the direct synthesis of zeolites onto a ceramic monolith support, and (iv) by the direct synthesis of pure zeolite monoliths [12]. Washcoating techniques are considerably complex and often dense layers are formed with small intercrystalline pores in which diffusion limitations may exist. Extrusion is also a demanding technique as defects may arise depending on the extrusion rate, heating rate and humidity. Washcoating, extrusion, and direct synthesis inside a monolithic support techniques are attractive because the synthesis of a variety of zeolites (ZSM-5, MOR, FER, BEA, etc.) on the support materials is possible, but it is often a time consuming multi-steps synthesis, with low final zeolite loading. Very recently the direct transformation of macroporous silica monoliths into macroporous LTA zeolite monoliths was achieved by a single hydrothermal treatment step [13]. The resulting macroporous LTA monolith features uniform 2 µm macropores and a 2 µm skeleton composed of 0.5–1.5 µm spherical LTA crystal aggregates. The efficiency of LTA-monoliths in continuous flow mode was evaluated for catalysis and revealed an increased productivity in comparison to packed-bed and batch reactors [13]. This result represented the first example of the use of macroporous monoliths with zeolite skeletons in flow process.

In the present paper, we evaluate the potentialities of this novel macroporous LTA-monolith for the sorptive removal of Sr<sup>2+</sup> ions from salty aqueous solutions and simulated contaminated seawater (as in the case of Fukushima) in flow processes. The capacity of LTA monolith is compared to other forms of LTA zeolite preparations.

## 2. Experimental

### 2.1. Chemicals

All the chemical reagents used are of analytical grade.

### 2.2. Synthesis of porous silica monolith

The synthesis of silica monoliths is adapted from a synthesis described in the literature by the group of Nakanishi [14]. Distilled H<sub>2</sub>O (46.3 g) and 4.6 g HNO<sub>3</sub> (68%, Aldrich) were mixed for 15 min at 0 °C and 4.79 g of PEO (20,000 kDa, Aldrich 99%) were added and stirred for 1 h. Then 37.7 g TEOS (Aldrich 99%) were added and the mixture was stirred for 1 h. The resulting solution was poured into PVC tubes of 10 cm length and 8 mm internal diameter and kept at 40 °C for 3 days. The monoliths were then washed in water and treated in an ammonia solution (0.1 M) at 40 °C for 20 h. The monoliths were then dried at 40 °C for 24 h and calcined at 550 °C for 8 h.

### 2.3. Synthesis of LTA-monolith

The synthesis of the LTA monoliths was performed by using previously described procedures [13]. A first solution was prepared by mixing 710 g H<sub>2</sub>O, 117 g TPAOH (20 wt.%), 13.8 g NaOH, and 158.9 g silica (Aerosil 200, Degussa). The mixture was shaken at 25 °C for 1 h and aged for 16 h at 100 °C. A porous silica monolith (7.8 cm, 6 mm diameter, 0.63 g) was then impregnated with a solution prepared by dissolving in distilled H<sub>2</sub>O (6.02 g), 0.369 g of the first solution with NaOH (0.06 g) and NaAlO<sub>2</sub> (2.16 g) to achieve a molar composition SiO<sub>2</sub>/NaOH/NaAlO<sub>2</sub>/H<sub>2</sub>O/TPAOH of 1/0.15/2.6/33/0.004. The impregnation was carried out in a Teflon-lined stainless steel autoclave, followed by hydrothermal treatment at 100 °C for 18 h. The monolith was then washed several times with water until neutral pH. The material was dried at 40 °C and calcined at 550 °C for 8 h. The macroporous LTA monolith is called thereafter LTA-monolith.

### 2.4. Synthesis of bulk powder LTA

The synthesis of bulk powder LTA was performed by using an adaptation of published process [3]. First a silica solution was prepared by dissolving 7 nm fumed silica (Aerosil 200 from Degussa) (7.9 g) into a basic solution containing 10.6 g of NaOH (for a ratio NaOH/SiO<sub>2</sub> = 2) and 105 g of deionized water. Then sodium aluminate solution (22.9 g of NaAlO<sub>2</sub> (Aldrich) in 140 mL of water) was introduced dropwise into the silica solution. After dissolution, the resulting gel was filtered, washed with deionized water and dried for 1 day at 80 °C.

### 2.5. Sr<sup>2+</sup> sorption experiments

Sr<sup>2+</sup> sorption experiments on both materials, bulk LTA powder and LTA-monolith, were performed first by using non-radioactive Sr<sup>2+</sup> containing solutions in order to compare these two materials and to investigate the sorption kinetics, and secondly with radioactive Sr<sup>2+</sup> containing aqueous saline solution simulating the Fukushima site. The saline solution (seawater) contains Na<sup>+</sup> (9.6 g L<sup>-1</sup>), Mg<sup>2+</sup> (1.28 g L<sup>-1</sup>), Ca<sup>2+</sup> (0.4 g L<sup>-1</sup>), K<sup>+</sup> (0.5 g L<sup>-1</sup>), and non-radioactive Sr<sup>2+</sup> (0.008 g L<sup>-1</sup>). Sorption experiments were performed in batch mode under shaking at room temperature and in flow mode for the LTA-monolith.

Batch experiments were carried out using bulk powder LTA and ground LTA-monolith with non-radioactive solutions. These two materials were compared using kinetics experiments at saturation. For this study, 10 mg of powder were shaken in 20 mL

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