



Mechanisms of strontium removal by a Ba-titanate material for the wastewater treatment



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ABSTRACT

Growing interest in radioactive effluent treatment, especially after the Fukushima nuclear accident, has led to the development of new, increasingly efficient mineral sorbents. The sorbents currently attracting the most attention are materials dedicated to strontium extraction. The Ba-titanate material investigated here, combining several sorption mechanisms, has a high capacity and selectivity for strontium with a distribution coefficient, K_d , of 863 mL g^{-1} , obtained from a batch sorption test with seawater ($[\text{Sr}] = 9 \times 10^{-5} \text{ mol L}^{-1}$; titanate concentration, 1 g L^{-1}). This K_d is six times higher than that of Na-titanate, one of the strontium sorbents used for multi-nuclide removal at the Fukushima-Daiichi nuclear power station. Upon contact with the sulfate-containing effluent, Sr extraction proceeds by ion exchange with the Ba ions inserted in the material and by coprecipitation with insoluble barium sulfate formed at the surface of the titanate grains.

1. Introduction

The number of studies devoted to the radioactive decontamination of wastewater has increased exponentially in the past few years in response to ever more stringent discharge standards. Among the elements present in radioactive effluents, ^{90}Sr is particularly radiotoxic because it emits high energy beta radiation and because its chemical similarity to calcium makes it attach readily to bone and bone marrow. Its half-life, 29 years, exceeds the safe timescale for decay and it must therefore be extracted from effluents. Coprecipitation is currently the most widely used method to treat effluents with low to intermediate concentrations of ^{90}Sr [1], even if some other technical processes as reverse osmosis desalination [2], integrated salt disposition process [3] or continuous electrodeionization [4] have also been studied. This typically involves the formation of barium sulfate, BaSO_4 , from the reaction between sodium sulfate Na_2SO_4 and a barium salt ($\text{Ba}(\text{NO}_3)_2$ or BaCl_2). Strontium ions coprecipitate on the surface of barium sulfate, which is continuously renewed by crystal growth [5,6]. This technique is simple to implement, robust (with respect to the salinity and composition of the effluent) and cost-effective. It is also the most selective process currently available for strontium extraction with distribution coefficients in seawater of about $20\,000 \text{ mL g}^{-1}$ against 46 mL g^{-1} for calcium for a mass/volume ratio (mass of BaSO_4 /volume of seawater) of 3.5 g L^{-1} [7]. However, the drawback of this approach is that it

produces large volumes of radioactive sludge. An alternative approach that produces much less waste is ion exchange in a fixed bed column. Numerous studies have already been carried out on the extraction of strontium by ion exchange with various inorganic compounds such as LTA (Linde type A) zeolites [8–12], silicotitanates [13–18] and sodium titanates [10,19–23]. However, at typical effluent pHs (7–8), while these materials do retain strontium effectively, they are poorly selective in the presence of other alkaline earth cations (e.g. calcium) in saline solutions [24,25], with, at best, strontium/calcium selectivity coefficients of around 1–10 [15,22,24].

The effluents targeted in this work are the low- and intermediate-concentration radioactive by-products of nuclear activities (e.g. nuclear power plants, reprocessing plants, dismantling activities) or the results of nuclear accidents (such as the contaminated groundwater and seawater generated during the Fukushima-Daiichi nuclear power plant accident). These aqueous effluents are characterized by a medium to high salinity (up to 35 g L^{-1}), a neutral to basic pH (6–8), and the presence of high concentrations of alkaline and alkaline earth cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} and, in the case of seawater, 8 mg L^{-1} of non-radioactive Sr^{2+}), various anions (chlorides, nitrates and especially sulfate ions) and traces of radioactive ^{137}Cs and ^{90}Sr . The high salinity and complexity of the effluents mean that highly efficient treatment processes selective for strontium are required. We have approached this problem by coupling ion exchange and coprecipitation using an

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inorganic sorbent. Strontium removal has recently been demonstrated using a Ba-silicate [26] and a Ba-zeolite [27]. Titanates have been extensively studied due to their potential applications in photocatalysis [28–31], ferroelectricity [32,33], thermoelectricity [34], lithium storage [35], gas sensing [36–38], biosensing [39] and sorption [40–45]. This paper investigates the extraction potential of a synthesized barium titanate material to complement the coprecipitation with sulfate ions present in solution. To the best of our knowledge, the chemical properties of this sorbent have not been studied before; we focus in particular on its selectivity towards strontium and the corresponding extraction mechanisms.

The sorption properties of the material were evaluated first in seawater and then in synthetic solutions, specifically by studying uptake kinetics and the effect of sulfate ions in solution. The effects of competitive cations (Ca^{2+} and Na^{+}) on the quantities of precipitated BaSO_4 and extracted strontium were assessed. X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption-desorption measurements were also performed to correlate the physical-chemical properties of the material with its sorbent behavior.

2. Materials and methods

2.1. Reagents

All the chemicals used in this study were supplied by Sigma Aldrich. The extraction mechanisms were studied using solutions of sodium nitrate, strontium nitrate, calcium chloride tetrahydrate, sodium sulfate and tetrabutylammonium sulfate. All the solutions were prepared with water with a resistivity of 15 $\text{M}\Omega\cdot\text{cm}$.

2.2. Synthesis

The sodium titanate sol-gel was prepared as described in the literature [23,46–48]. Titanium isopropoxide (25 g) was added rapidly to 27.2 g of a 50 wt% solution of NaOH before 20 mL of deionized water was added. This mixture was transferred to a Teflon vessel for hydrothermal pressure treatment. Heat treatment was performed at 160 °C for 22 h under autogenous pressure. The resulting gel was filtered, washed with deionized water to remove excess NaOH and dried at 80 °C for 24 h. The total Na content of the material was $3.70 \pm 0.74 \text{ mmol g}^{-1}$. The barium titanate sorbent was prepared by substituting the Na in Na-titanate ($\text{Na}_4\text{Ti}_9\text{O}_{20}$) with Ba. $\text{Na}_4\text{Ti}_9\text{O}_{20}$ powder was mixed in a 1 mol L^{-1} $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ solution for 24 h at a mass concentration of 1 g per 15 mL. The resulting Ba-titanate was then washed with distilled water and dried at 80 °C for 16 h.

2.3. Characterization

X-ray diffractograms were recorded using Cu $\text{K}\alpha$ radiation ($\lambda_{\text{K}\alpha 1} = 1,54056 \text{ \AA}$) for Bragg angles (2θ) varied between 5 and 70° at $0.01275^\circ \text{ min}^{-1}$ on a Panalytical X'Pert Pro powder device equipped with a Xcelerator type detector and operated at 45 kV and 40 mA. A Rietveld refinement was performed to calculate the cell parameters of the $\text{Ba}_{(1-x)}\text{Sr}_x\text{SO}_4$ precipitates using the initial structure determined by Goldish for $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{SO}_4$ [49]. The barium and strontium contents of the $\text{Ba}_{(1-x)}\text{Sr}_x\text{SO}_4$ precipitates were then deduced from the space group (Pbnm) and the calculated unit-cell parameters thanks to the relation between the latter and the composition of $\text{Ba}_x\text{Sr}_{1-x}\text{SO}_4$ powders published by Sitepu and Zaidi [50].

The specific surface area, pore size and pore volume of the Ba-titanate were measured by nitrogen adsorption-desorption analysis. The sample was degassed at 200 °C for 24 h before measurements were taken at 77 K using a Micrometrics ASAP 2020 analyzer.

Scanning electron micrographs and maps in chemical contrast were obtained using a Carl Zeiss MERLIN device equipped with an 80 mm²

Oxford Instruments X-MAX energy-dispersive X-ray analyzer (SEM-EDX). The samples were embedded in a non-conductive epoxy resin, polished using a GATAN Ilion+ cross-polisher and metallized with gold.

Size distribution of the Ba-titanate was determined by laser diffraction using a Malvern Mastersizer device. A suspension of Ba-titanate was prepared in distilled water and ultrasonication was applied to disperse the material before and during analysis.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Thermo Fisher Scientific iCAP 7400 DV, was used to determine the ion contents ($\text{Na}^{+}/\text{Ca}^{2+}/\text{Ba}^{2+}/\text{Sr}^{2+}/\text{S}$) of the solutions used for the sorption experiments after dilution in 2% nitric acid. The sulfate concentrations were calculated from the sulphur concentrations obtained by ICP-AES. Three replicate measurements were performed for each sample. To determine the chemical composition of the solids, 30 mg of each sample was mineralized by dissolution in hot HNO_3/HF . The Na, Ba and Ti contents of the resulting solutions were measured by ICP-AES with estimated uncertainties of the order of 20%.

2.4. Decontamination efficiency

The decontamination efficiency of the materials was evaluated as follows. The sorption capacity was calculated using Eq. (1):

$$Q_t = (C_0 - C_t) \times V / m \quad (1)$$

where Q_t is the sorption capacity of the sorbent at time t and Q_e is the sorption capacity at equilibrium (mg g^{-1} or meq g^{-1} of titanate); C_0 and C_t are respectively the initial and equilibrium concentration of the component (mg L^{-1} or meq L^{-1}); V is the volume of the solution (L); and m is the mass of the sorbent (g).

Distribution coefficients, K_d (mL g^{-1}), for different ion-sorbent combinations were calculated using Eq. (2),

$$K_d = Q / C_e \times 1000 \quad (2)$$

with high values indicating that the sorbent has a high affinity for the ion. K_d is constant at trace concentrations of the studied ion. The selectivity of the prepared Ba-titanate for Sr over Ca in the effluent was then calculated from the K_d ratio,

$$sK_{Ca}^{Sr} = K_d(\text{Sr}) / K_d(\text{Ca}) \quad (3)$$

with higher values indicating a greater selectivity.

Lastly, the decontamination efficiency was quantified using the decontamination factor (DF), the parameter commonly used in the nuclear industry:

$$\text{DF} = [\text{Sr}]_{\text{initial}} / [\text{Sr}]_{\text{final}} \quad (4)$$

For strontium decontamination, the target is usually a DF value of 100 (corresponding to the extraction of 99% of the Sr in solution).

2.5. Extraction tests

Strontium extraction tests were performed on solutions containing 1 g L^{-1} sorbent. The experiments were carried out in batch mode under stirring at ambient temperature in 60 mL polypropylene vials. The precipitation or extraction kinetics were measured by placing 20 mg of the sorbent in contact with 20 mL of each solution for 5 min to 24 h, with a separate experiment performed for each duration.

The remaining extraction experiments were performed for 3 h under stirring. All solutions were filtered using a 0.2 μm syringe filter. The extraction capacity, Q_e , was calculated from the measured initial and final Sr concentrations using Eq. (1). These values were also used to calculate the distribution coefficient at a given point in time. The sulfate concentrations measured in solution were used to calculate the concentration of the barium sulfate precipitates. To compare the amounts of Ba released in solution with the amounts of the ions sorbed in/on the solid, the concentrations were expressed as equivalent

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