

Minimization of Hydroboric Acid Containing Decontamination Solutions – 10198

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ABSTRACT

Tetravalent metal oxides were tested for their strontium uptake properties from 0.01 M HBF_4 solution. Antimony-doped tin dioxides showed high distribution coefficients for ^{85}Sr in batch experiments and also the materials' kinetic properties were found to be suitable for column operations. Extremely high decontamination factor ($\text{DF} > 1\,000$) levels were obtained in mini-column experiments. In addition, low quantities of iron (1 to 10 ppm) in fluoroboric acid didn't affect the DF-level. Decline in DF-levels were observed with 100 ppm Fe^{2+} content in the acid and the ^{85}Sr uptake was diminished with 1 000 ppm Fe^{2+} solution. The obtained results indicates that tin dioxide-based materials can be used effectively in stripping radioactive strontium from fluoroboric acid solution.

INTRODUCTION

Decommissioning and decontamination of nuclear power plants (NPP) has begun and the number of facilities to be decommissioned will increase in the near future. The decontamination of these facilities from radioactive materials and equipments requires different techniques and methods. A large variety of decontamination solutions have been tested from which fluoroboric acid (HBF_4), which has been used mainly in the electroplating industry, has shown extremely high decontamination factors. The Electric Power Research Institute (EPRI) has developed the DfD process (Decontamination for Decommissioning) based on fluoroboric acid; the acid is applied under controlled pH and redox potential to remove contamination from surfaces by dissolution of the underlying metal [1,2]. The main disadvantage of fluoroboric acid is the large amount of waste solutions it generates. Stripping the radioactive contaminants from these solutions is a challenge that has to be dealt before regeneration and recycling of the acid by an electrochemical process [3].

The use of selective ion exchange materials for stripping radioactive contaminants from HBF_4 solution is seen as highly advantageous due to the large volume of solution generated in the decontamination process. However, this solution is troublesome for inorganic ion exchange materials because of the acidity. Many highly selective inorganic ion exchange materials dissolve in acidic media or their pK_a values are so high that ion exchange doesn't occur. Tetravalent metal oxides are typically insoluble in mild acid solutions and their pK_a values are low, suggesting potential ion exchange properties in such solutions. For example tin dioxides are known to have good ion exchange properties for transition metals while manganese oxides are extremely selective for alkaline earth metals [4].

The focus of this study was on selective removal of strontium from fluoroboric acid solution which is considered as one of the best decontamination solutions used at nuclear power plants. Two tetravalent metal oxides (manganese and tin dioxides) and antimony pentoxide were chosen as uptake material due to earlier, promising results [5,6]. However, the pure forms of these metal oxides have also severe limitations, such as peptization of Sb_2O_5 and redox-based dissolution and pK_a of MnO_2 . These drawbacks were addressed by mixing the components in the synthesis phase, resulting in mixed oxides and solid solutions of metal oxides.

MATERIALS AND METHODS

The metal oxides were synthesized by alkali precipitation from acidic metal chloride solution with propriety additives. The precipitate was washed free from synthesis solution and dried at 70°C for 12 hours. X-ray diffraction patterns were collected with a Philips PW 1710 powder diffractometer (operating at 30 kV and 50 mA, Cu K α , 1.54 Å radiation) and the material was characterized as nanocrystalline tin dioxide.

Static batch experiments were used to evaluate the metal uptake properties of the material. In batch experiments 20 mg of solid ion exchange material was equilibrated in 10 ml of test solution in a constant rotary mixer (50 rpm) for 24 hours during which time the solid/solution system reached equilibrium. The solid phase was then separated by centrifuging the vials for 10 minutes at 3000 G, and 5 ml aliquots of the supernatant were pipetted and filtered through a 0.2- μ m filter (I.C. Arcodisc, Gellman Sciences) for measurements of strontium concentration by gamma spectrometric counting (Wallac 3" Wizard). The equilibrium pH was measured from the remaining solution. The results from batch experiments are presented as distribution coefficients (K_d , ml/g) that reveal how the element of interest is distributed between the initial sample solution and the solid material after 1 day equilibration time. It was calculated as follows:

$$K_d = \frac{(A_i - A_{eq}) * V}{(A_{eq}) * m} \quad (1)$$

where A_i = initial strontium concentration (activity) of the solution, A_{eq} = strontium concentration of the solution at equilibrium, V = volume of the solution, m = mass of the solid material.

The effect of Fe⁺² ions on the Sr uptake was tested under atmospheric conditions at room temperature and most probably some of the iron was also in its trivalent state.

Dynamic column experiments were done in mini-columns (BioRad, Bio-Scale MT2 with radius of 3.5 mm and 28- μ m support). In the column experiments, approx. 0.75 g of dry material, corresponding to 0.4 ml as bed volume, was placed in the minicolumn and solutions were pumped through the column using ~25 bed volumes per hour flow rate. The effluent was collected by a fraction collector using 120-min collection time. From the effluent fractions, the amount of strontium was measured using gamma counting. The results from column experiments are presented as decontamination factor (DF) that is the ratio of the element of interest in the solution before and after contact with the sorption material.

$$DF = \frac{A_i}{A_{eq}} \quad (2)$$

All reagents were of analytical grade. A radioactive tracer Sr-85 (γ , 514 keV) was added to the test solutions at trace concentrations.

RESULTS AND DISCUSSIONS

Batch experiments

Manganese dioxide-based materials showed extremely high distribution coefficients (K_d values) for strontium from 0.01M HBF_4 solution in static batch experiments (Table 1). The addition of antimony to manganese dioxide acidified the material so that ion exchange occurred at pH 2 which is considerably lower than the isoelectric point of pure manganese dioxides ($> \text{pH } 5$). However, the increase in antimony content and the change from the structure of manganese dioxide to the structure of antimony pentoxide (rutile to pyrochlore structure) decreased the K_d values substantially. Also the known peptization tendency of antimony pentoxide in dilute solutions discouraged further study of high Sb content materials.

The strontium uptake efficiency of tin dioxide was not as good as manganese-based materials, but still high K_d values, $< 10\,000 \text{ ml/g}$, were obtained with the material. Particularly, the good physical stability properties of tin dioxide overcame the good Sr uptake properties of other materials in view of the following column experiments.

K_d (ml/g)	Sb content (atomic%)
245 000	25
137 500	70
12 250	80

Interference of iron (II) on strontium uptake

One of the apparent interfering ions in the decontamination solution is iron and in the case of HBF_4 solution, particularly its divalent oxidation state. Fe^{2+} is a very troublesome ion for manganese dioxide which dissolves due to $(2\text{Fe}^{2+} + \text{Mn}^{4+} \rightarrow 2\text{Fe}^{3+} + \text{Mn}^{2+})$ electrochemical reactions. This was not a problem for tin dioxide materials and the interference of iron on strontium uptake was tested using 0.1, 1 and 10 ppm Fe^{2+} added to the 0.01M HBF_4 solution (Table 2). The interference of iron on strontium uptake was clear, but not as strong as anticipated. At 10 ppm Fe^{2+} content, the Sr uptake was decreased by approx. 50 % to K_d 4 800ml/g which was still quite promising, considering the materials used in the column operations.

K_d (ml/g)	Iron content (ppm)
10 600	0
9 700	0.1
8 670	1
4 830	10

Kinetic studies

Typically inorganic ion exchangers are slow in ion exchange kinetics which often prohibits their use in dynamic column operation. Tin dioxide-based material showed considerably fast strontium uptake kinetics reaching approx. 50% uptake after 4.5 hour of contact time (Table 3). This high uptake would allow a reasonable high flow rate in column use of the material.

Table 3. Kinetic experiments on antimony-doped tin dioxide. K _d values for ⁸⁵ Sr from 0.01M HBF ₄ .	
Contact time (h)	K _d (ml/g)
4.5	5 100
24	10 950

Column experiment

The strontium uptake began after a slow start, which is typical for inorganic materials, and achieved a DF level over 1 000 when the eluent was pure 0.01M HBF₄ (spiked with trace ⁸⁵Sr). The addition of 1 ppm and 10 ppm of Fe²⁺ to the fluoroboric acid didn't affect the DF level of the material. At 100 ppm Fe²⁺ content in the 0.01M HBF₄ solution, the DF level started to decrease at an almost constant rate. During the next ~1000 bed volumes from 3 500 to 4 500, the DF level decreased steadily from 1 000 to 100, indicating typical ion exchange competition between Fe and Sr ions. A 1 000 ppm concentration of iron in the eluent was enough to practically stop the strontium uptake and the DF dropped to 1 in the following 500 bed volumes. After exhaustion of the column due to high iron content, the solution was changed back to the initial solution (without iron) and pumping was continued. Part of the strontium uptake properties was regained and the experiment was stopped at a DF-level of 10 after 7 500 bed volumes.

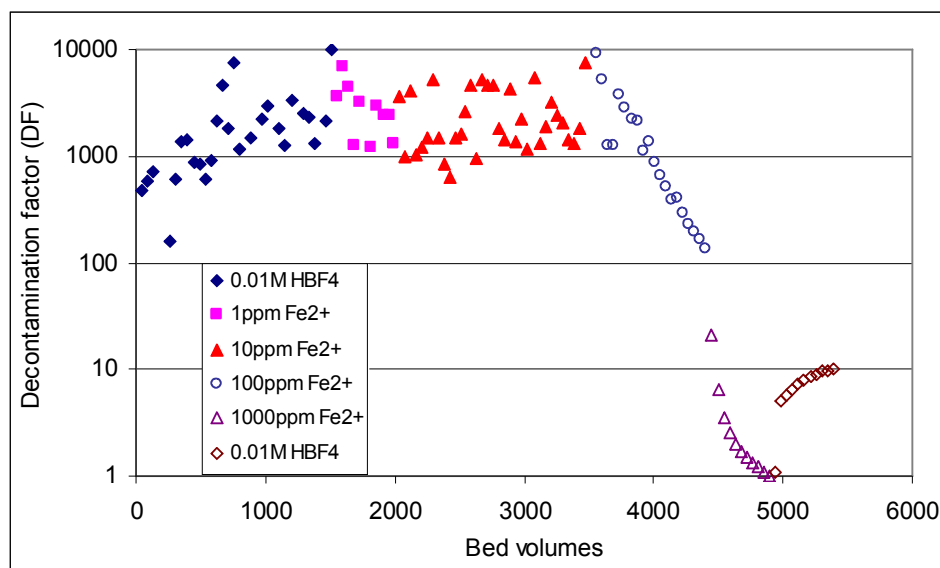


Fig. 1. Column experiment of antimony-doped tin dioxide for separation of ⁸⁵Sr from 0.01M HBF₄ solution with gradually increasing iron content. Treated bed volumes are along the x-axis and decontamination factors are along the y-axis.

CONCLUSIONS

Antimony doped-tin dioxide showed good strontium uptake properties from fluoroboric acid solution. The antimony addition to the tin dioxide structure acidified the material so that ion exchange occurred even at pH 2 (0.01M HBF₄). The static batch experiments resulted in high K_d values (up to 10 000 ml/g) in pure fluoroboric acid solution and the addition of iron (up to 10 ppm Fe²⁺) to the solution had only a moderate decreasing effect on the distribution coefficient, suggesting good ion exchange capacity for the material. Also experiments on the materials' ion exchange kinetics indicated suitability for dynamic

column operations. The real decontamination effectiveness of the material was tested in mini-column experiments where high decontamination factors ($DF > 1000$) were observed, even with 10 ppm of iron content. At 100 ppm iron content, the DFs decreased steadily from >1000 to 100 over the following 1 000 bed volumes. 1 000 ppm iron content diminished the strontium uptake properties rapidly. This study demonstrated that modified tin dioxide can be used for stripping radioactive strontium from acidic decontamination solution and that the materials selectivity and kinetic properties enables successful decontamination of fluoroboric acid solutions.

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