

## Adsorption of strontium, europium and americium(III) ions on a novel adsorbent Apatite II

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**Abstract** A novel material, Apatite II, obtained from a natural source, has been determined to be a good adsorbent for radionuclides of strontium, europium and trivalent actinides, but not caesium, from neutral aqueous solutions containing common chelating agents and inorganic salts at moderate concentrations. This inexpensive, easily available material seems to be a promising backfill for engineered barriers in nuclear waste repositories. However, encapsulation of the sorbent grains loaded with radiostrontium in the Portland cement matrix results in undesirably high leaching rate for this particular radionuclide.

**Key words** adsorption • americium • Apatite II • europium • hydroxyapatite • nuclear waste • strontium

### Introduction

Multibarrier systems which prevent migration of long-lived radionuclides from nuclear waste repositories to the environment usually include various inorganic ion exchangers which strongly adsorb ions of radioactive metals [7]. Among the most troublesome radionuclides of nuclear wastes we can distinguish  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$  and long-lived isotopes of transplutonium elements (minor actinides), mainly trivalent americium and curium. Inexpensive materials of high adsorption efficiency toward these radionuclides are strongly desired. Natural zeolites are often used as effective adsorbents for radiocaesium and radiostrontium [9], however, still better adsorbents are required. A novel material, Apatite II, specially-processed from a natural source [4], was shown to be an excellent adsorbent for ions of toxic heavy metals [3, 5].

Apatite II, of the nominal composition  $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{OH})_2(\text{CO}_3)_x$  where  $x < 1$  [14], is a special form of the mineral hydroxyapatite, developed and proprietary by UFA Ventures Inc. It has the optimal physical and chemical properties for remediation of heavy metal ions [3, 5]. Its high reactivity towards numerous metal ions results from: its generally amorphous structure of high internal micro-porosity making it the best non-specific surface adsorbent of all apatites, but with random nanocrystals of well-crystalline apatite serving as nucleation sites for precipitation of new metal-apatite phases; fully carbonated structure with no fluorine in the hydroxyl position; little or no trace metals initially in the structure [4, 5]. For these reasons Apatite II is an adsorbent superior to traditional phosphate ores and cow bone, charred or not. This inexpensive [3, 5] material, available in large amounts, has also been suggested to be a good adsorbent for several other metals including strontium and actinides [3, 14].

The aim of this work was to study the properties of Apatite II as a potential backfill for various engineered barriers in nuclear waste repositories.

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Received: 30 September 2003, Accepted: 20 October 2003

## Experimental

### Materials

Apatite II of grain size  $0.1 \div 0.3$  mm was used. Twice distilled water and analytical grade chemicals were used in the experiments. The radiotracers were purchased as acidic aqueous solutions, either from Polatom, the Centre for Isotope Production at Świerk, Poland ( $^{137}\text{Cs}$ ,  $^{85}\text{Sr}$  and  $^{152,154}\text{Eu}$ ) or from Amersham International, UK ( $^{241}\text{Am}$ ).

### Equipment

The pH was measured using a Teleko N5172 (Poland) pH/ion Meter with a Hydromet Semi-Micro Combination glass electrode. The reference cell was filled with  $3.0 \text{ mol dm}^{-3}$  NaCl solution. Calibration of the system was performed using pH 4.00, 7.00 and 10.00 standard buffer solutions (Chempur, Poland).

The radionuclidic purity of the radiotracers was checked by  $\gamma$ -spectroscopy using a HPGe detector connected to a 4096 channel multichannel analyzer (ORTEC). The gamma activities of solution aliquots were measured using a counter with a well-type NaI(Tl) detector.

### Adsorption procedure

Adsorption properties of Apatite II towards microamounts ( $10^{-9} \div 10^{-8} \text{ mol dm}^{-3}$ ) of the radionuclides of Cs, Sr, Eu(III) and Am(III) were investigated in batch experiments at room temperature,  $21 \pm 3^\circ\text{C}$ . Small samples of the adsorbent grains (0.050 g each) were shaken in  $20 \text{ cm}^3$  plastic vials with the solutions studied ( $10 \text{ cm}^3$ ) for about 20 h, i.e. longer than the time required to reach equilibrium. The vials were then centrifuged for 3–5 minutes, followed by filtering the solutions through paper filters. Duplicate samples of  $1.00 \text{ cm}^3$  were taken from each aqueous phase for the radioactivity measurement, and an aliquot of ca.  $2 \text{ cm}^3$  – for the pH measurement. The distribution ratios,  $K_d$  ( $\text{cm}^3 \text{ g}^{-1}$ ), were calculated using the following equation:

$$(1) \quad K_d = \frac{(a_i - a_{\text{eq}})V}{a_{\text{eq}}m}$$

where:  $a_i$  denotes the initial radioactivity of the solution;  $a_{\text{eq}}$  – radioactivity of the solution at equilibrium;  $V$  – solution volume ( $\text{cm}^3$ );  $m$  – mass of the adsorbent (g).

## Results and discussion

### Radionuclide adsorption

It comes from Fig. 1 that the Apatite II is a very efficient adsorbent for  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$ , particularly from neutral and moderately acidic solutions. Moreover, it is a good adsorbent for  $\text{Sr}^{2+}$  ions from neutral and moderately alkaline solutions.  $\text{Cs}^+$  was practically not adsorbed on the Apatite within the whole pH range studied. Due to a similar behaviour of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  on the adsorbent (Fig. 1),

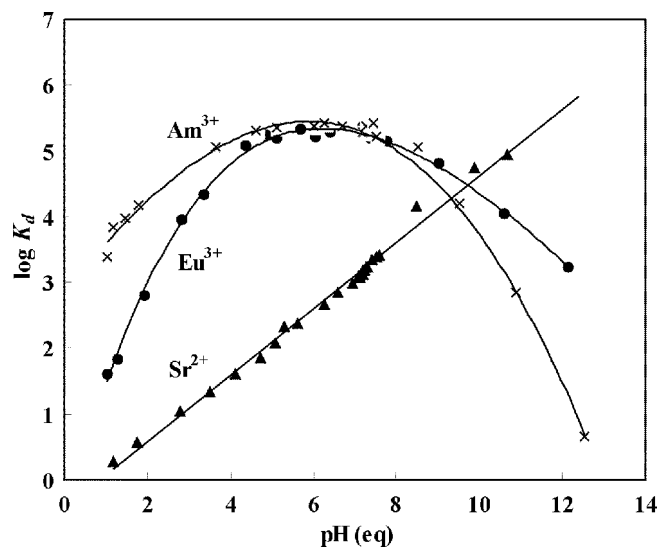


Fig. 1. Adsorption of radionuclides of  $\text{Sr}^{2+}$  (▲),  $\text{Am}^{3+}$  (x) and  $\text{Eu}^{3+}$  (•) on Apatite II from  $0.01 \text{ mol dm}^{-3}$   $\text{NaNO}_3$  aqueous solution vs. pH at equilibrium.

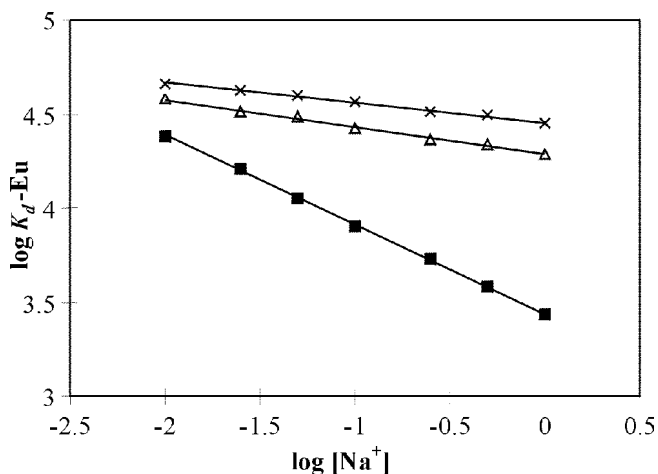
further studies were carried out with  $\text{Sr}^{2+}$  and  $\text{Eu}^{3+}$  only. Studies on the kinetics of adsorption of microamounts of  $\text{Sr}^{2+}$  and  $\text{Eu}^{3+}$  ions at pH 7 show that the respective equilibria are attained within 0.5 and 5 h. The observed rates of adsorption are much higher than those reported for much larger Apatite II grains [3], as well as for synthetic crystalline hydroxyapatites commercially available, even of smaller grains [6].

### The effect of salts and chelating agents on adsorption

Adsorption efficiency of metal ions is affected by the presence of inorganic salts and chelating agents – the common components of nuclear wastes and leaching solutions. Typical composition of liquid radioactive waste treated at the Department of Radioactive Waste Management of the Institute of Atomic Energy, Świerk (Poland), is as follows: EDTA (45 ppm), oxalic acid (50 ppm), citric acid (50 ppm),  $\text{CaCl}_2$  ( $0.1 \text{ g dm}^{-3}$ ),  $\text{Na}_2\text{SO}_4$  ( $1 \text{ g dm}^{-3}$ ) and KOH ( $1 \text{ g dm}^{-3}$ ) [2]. Therefore, our studies were focused on the effect of the concentration of the above components.

Adsorption of  $\text{Sr}^{2+}$  and  $\text{Eu}^{3+}$  ions slightly decreases with increasing concentration of  $\text{Na}^+$ . The slopes of the straight line dependence of  $\log K_d(\text{Sr}^{2+})$  on  $\log [\text{Na}^+]$ , observed within the range of  $10^{-2}$  to  $1 \text{ mol dm}^{-3}$   $[\text{Na}^+]$ , are equal to about  $-0.3$ , regardless of the kind of anion studied. However, the dependence of  $\log K_d(\text{Eu}^{3+})$  on  $\log [\text{Na}^+]$  observed for sodium chloride and sodium nitrate is smaller (the slope of ca.  $-0.1$ ), and greater (the slope of ca.  $-0.45$ ) for sodium sulphate (Fig. 2). This different effect of the anions on  $\text{Eu}^{3+}$  adsorption is obviously due to the formation of moderately stable sulphate complexes [11].

Calcium ions strongly reduce  $\text{Sr}^{2+}$  adsorption. The slope of the relationship  $\log K_d(\text{Sr}^{2+})$  vs.  $\log [\text{Ca}^{2+}]$ , equal to  $-1.0$  (Fig. 3), can be explained in terms of a cation exchange mechanism of sorption. Such mechanism has already been suggested, at least as prevailing, for sorption of numerous divalent *d*- and *p*-block metal ions on various hydroxyapatites [6, 12, 13]. The slope of the relationship

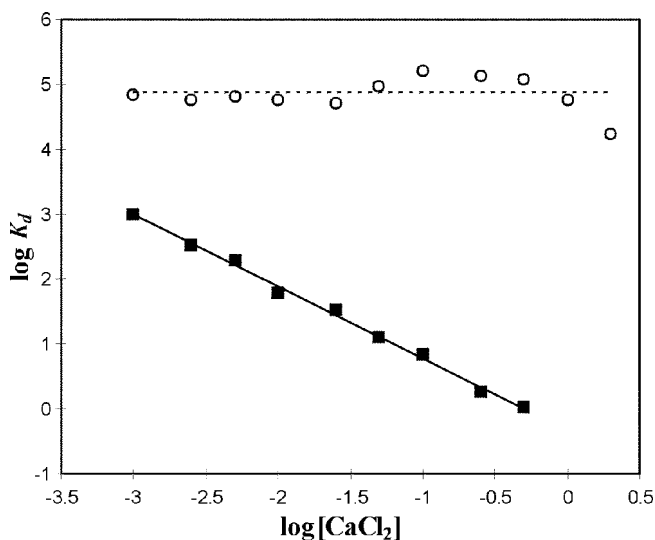


**Fig. 2.** Distribution of  $\text{Eu}^{3+}$  ions between Apatite II and neutral (pH 7) aqueous solutions of sodium salts: x – chloride;  $\Delta$  – nitrate;  $\blacksquare$  – sulphate; vs. molar concentration of sodium ions.

$\log K_d(\text{Sr}^{2+})$  vs. pH (Fig. 1), that is much lower than the 2.00 expected for a simple cation exchange mechanism, and the low slope of the  $\log K_d(\text{Sr}^{2+})$  vs.  $[\text{Na}^+]$  relationship (Fig. 2) are not inconsistent with this suggestion. The presence of different types of cation exchange sites in hydroxyapatites has been already well recognized [6, 12, 13]. Numerous weak acidic cation exchange sites in the Apatite II: phosphates, carbonates and hydroxides [3], protonated to a different extent, make the ion exchange a very complex process, strongly affected by protonation/deprotonation equilibria [6]. The ion exchange characteristics of hydroxyapatites towards divalent metal cations are enhanced with increasing content of carbonate ions in the lattice [8]. However, other mechanisms of cation adsorption can also contribute to the retention of metal ion on hydroxyapatites [10, 15]. Conca *et al.* [3] suggested precipitation of insoluble phosphates of multivalent cations on the surface of amorphous Apatite II, nucleated on nanocrystals present in the structure.

On the other hand, the adsorption of  $\text{Eu}^{3+}$  and  $\text{Am}^{3+}$  on Apatite II from acidic and neutral solution is much more effective than that of  $\text{Sr}^{2+}$  but it decreases substantially with increasing pH (Fig. 1). This strong adsorption is in line with the higher charge of the  $\text{Eu}^{3+}$  and  $\text{Am}^{3+}$  ions, while the ionic radii of all three ions fit the optimal range for sorption on hydroxyapatites very well [10, 12]. On the other hand, the  $\text{Cs}^+$  ion is too large and has too low a charge to be effectively adsorbed. Very strong adsorption of  $\text{Eu}^{3+}$  from neutral solutions seems to be affected by  $\text{Ca}^{2+}$  only at very high concentration (Fig. 3). The decrease in the adsorption of  $\text{Eu}^{3+}$  and  $\text{Am}^{3+}$  with increasing pH is probably due to the hydrolysis of these trivalent cations, more pronounced than that of  $\text{Sr}^{2+}$ , which leads to formation of less charged and even anionic species of  $\text{Eu}^{3+}$  and  $\text{Am}^{3+}$  [1].

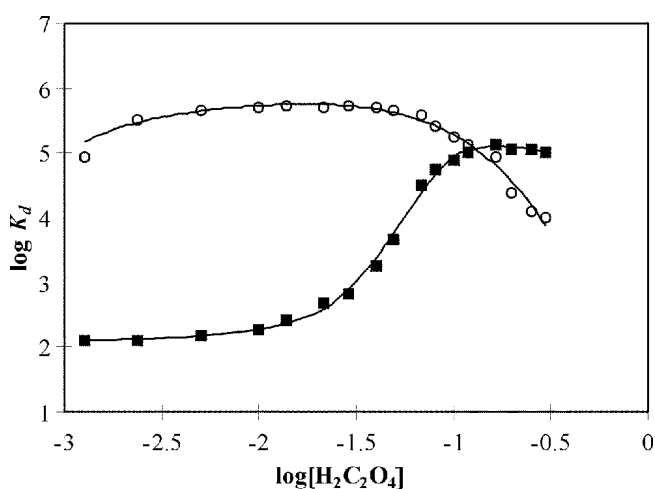
Adsorption of  $\text{Sr}^{2+}$  on Apatite II can be enhanced strongly if  $\text{Ca}^{2+}$  ions are removed from solution by precipitation with oxalic acid, followed by filtration of the resultant precipitate (Fig. 4). Again, this effect must be due to the  $\text{Sr}^{2+}$ – $\text{Ca}^{2+}$  competition for the adsorbent sites. On the other hand, adsorption of  $\text{Eu}^{3+}$  ions (which probably coprecipitate with  $\text{CaC}_2\text{O}_4$ ) is only slightly affected in this case, consistent with the negligible effect of  $\text{Ca}^{2+}$  on adsorption of  $\text{Eu}^{3+}$  (Fig. 3). However, a large excess of oxalic acid,



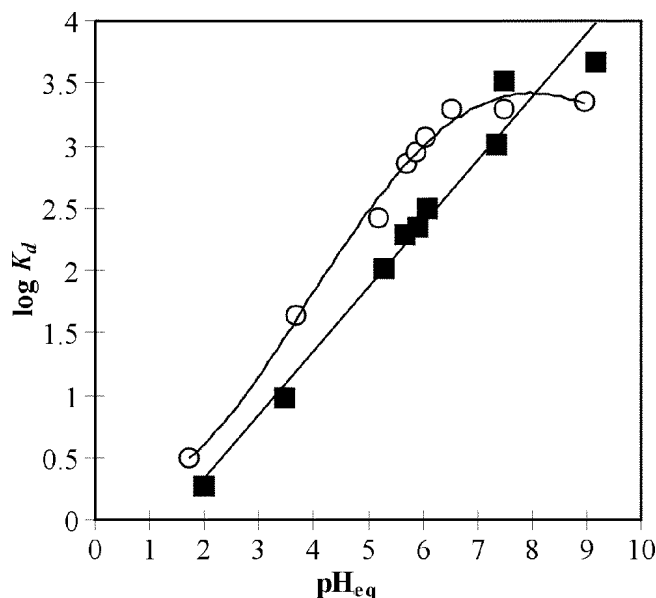
**Fig. 3.** The effect of  $\text{CaCl}_2$  (concentration in  $\text{mol dm}^{-3}$ ) on the adsorption of  $\text{Sr}^{2+}$  ( $\blacksquare$ ) and  $\text{Eu}^{3+}$  ( $\circ$ ) ions on Apatite II from neutral (pH 7) aqueous solutions.

which significantly decreases the adsorption of  $\text{Eu}^{3+}$ , deteriorates the mechanical properties of the adsorbent. This can be explained as a result of both complexing the  $\text{Eu}^{3+}$  ions by oxalate and removing the  $\text{Ca}^{2+}$  ions not only from the solution, but also (to some extent) from the solid phase of Apatite II.

Other chelating agents, EDTA and citric acid, significantly reduce the adsorption of  $\text{Eu}^{3+}$  but only slightly influence that of  $\text{Sr}^{2+}$ . As a result, the adsorption of both ions on Apatite II becomes similar (Figs. 5 and 6 vs. Fig. 1). Nevertheless, the adsorption of both  $\text{Sr}^{2+}$  and  $\text{Eu}^{3+}$  from neutral solutions containing these chelating species at moderate concentration is still satisfactory for practical purposes. This means that Apatite II appears to be a promising material for the secondary engineered barrier in a nuclear waste repository, which restrains migration of the most troublesome long-lived radionuclides (except radiocaesium) from nuclear waste repositories. It should also



**Fig. 4.** Adsorption of  $\text{Sr}^{2+}$  ( $\blacksquare$ ) and  $\text{Eu}^{3+}$  ( $\circ$ ) ions on Apatite II from  $0.01 \text{ mol dm}^{-3}$   $\text{CaCl}_2$  aqueous solution at pH 7, after  $\text{Ca}^{2+}$  ions were precipitated with an equal volume of oxalic acid of varying concentration.

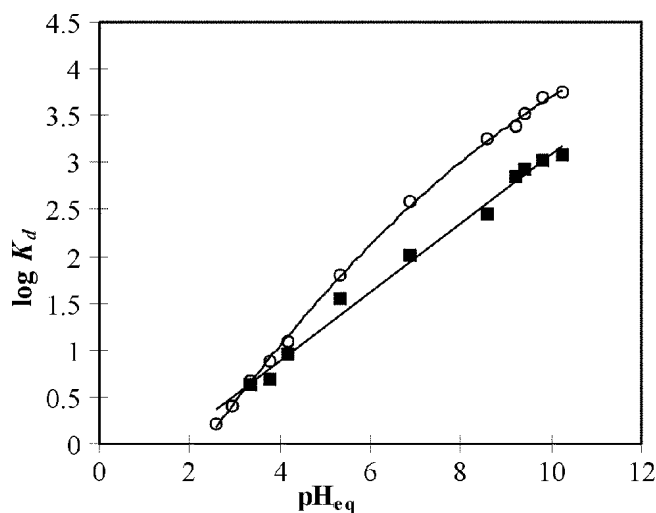


**Fig. 5.** The effect of pH on the distribution of Sr<sup>2+</sup> (■) and Eu<sup>3+</sup> (○) ions between Apatite II and aqueous solution:  $5 \times 10^{-3}$  mol dm<sup>-3</sup> EDTA + 0.01 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>.

be noted that the strong pH buffering effect of Apatite II to pH 6.5 to 7 in aqueous solutions [5], means that a large mass of Apatite II, as used in a barrier, would buffer the solution moving through it, creating a spatial gradient in chemical effects, and ensuring that most sorption will occur at pH 7 prior to the solutions exiting the barrier. Batch tests do not generally reflect such spatial effects.

#### Leaching studies on the loaded adsorbent encapsulated in a Portland cement matrix

Another study was carried out in order to learn whether radionuclide-loaded Apatite II grains can act as a primary engineered barrier in a nuclear waste repository after encapsulating the grains into a matrix of Portland cement. Therefore, the <sup>85</sup>Sr-loaded adsorbent samples encapsulated



**Fig. 6.** The effect of pH on the distribution of Sr<sup>2+</sup> (■) and Eu<sup>3+</sup> (○) ions between Apatite II and aqueous solution: 0.1 mol dm<sup>-3</sup> citric acid + 0.01 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>.

in the cement matrix were leached with distilled water, according to the procedure described elsewhere [2]. Unfortunately, leaching of radiostrontium from such the matrix (containing 30% Apatite II) appeared rather high (ca. 8% <sup>85</sup>Sr leached after 112 days). This result is comparable to the value observed for the Portland cement matrix containing the mixture of various salts and no adsorbent (a model for evaporator bottoms), and it is much greater than leaching from matrices containing other strontium adsorbents, i.e.  $\alpha$ -crystalline polyantimonic acid or barium sulphate [2]. The presence of the CaC<sub>2</sub>O<sub>4</sub> precipitate in the cemented sample of Apatite II makes the leaching somewhat lower. The high leaching rate of Sr<sup>2+</sup> ions from the matrix is probably due to the high calcium content in the cement. That is, a great extent of Ca<sup>2+</sup> ions are exchanging the Sr<sup>2+</sup> ions in the loaded adsorbent. We may, however, expect that matrices made of materials containing no calcium, e.g. bitumen, sulphur cement, etc., would encapsulate Apatite II much more effectively from the point of view of leaching radiostrontium. Further studies in this direction are, therefore, desired.

#### Conclusions

A novel adsorbent, Apatite II, with high affinities for strontium, europium and trivalent actinides, and with relatively fast rate of their adsorption, effectively removes these radionuclides from neutral aqueous solutions containing moderate amounts of chelating agents and inorganic salts commonly present in liquid nuclear wastes. Poor leaching properties in relation to radiostrontium preclude the use of Apatite II as the primary barrier material encapsulated in Portland cement blocks, and therefore, the search for other matrices is required. Nevertheless, this inexpensive material, obtained in large amounts from natural sources, seems to be a promising backfill for at least secondary engineered barriers in nuclear waste repositories.

**Acknowledgments** The authors thank Dr. James Conca (Los Alamos National Laboratory, USA) and Dr. Judith Wright (UFA Ventures, Inc., Carlsbad, NM 88220, USA) for kind supplying the sample of Apatite II, and for discussion. We also thank Mrs. Wanda Dalecka and Mrs. Krystyna Żuchowska for skilful technical assistance.

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