doi:10.1246/cl.2011.867

Capture of Radioactive Nuclear Wastes from Sea Water by Use of Clay Minerals

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The use of smectite-type clay minerals is proposed for capturing radioactive nuclear wastes from sea water. Iodine molecules dissolved in a 3 wt % aqueous NaCl solution were completely taken up by a column packed with Ag-modified synthetic saponite. Cs^+ and Sr^{2+} ions in a 3 wt % aqueous NaCl solution were adsorbed efficiently on a column packed with magnesium vermiculite under appropriate conditions.

Japan has now been confronted with an urgent problem to eliminate radioactive wastes such as molecular iodine (I_2), cesium ions (Cs^+), and strontium ions (Sr^{2+}) from sea water or water containing a large amount of sodium chloride.[1] A number of methods have been reported to immobilize I_2 or Cs^+ by use of inorganic adsorbents.[2–5] For example, Ag^+-exchanged zeolites, which are treated with hydrogen gas, react with iodine vapor to form solid AgI.[2,6] For capturing Cs^+ ions, the use of zeolite or Prussian blue is proposed. It is still uncertain, however, whether these materials are applicable to radioactive wastes dissolved in the sea water, in which a large amount of Na^+ ions might replace Ag^+ or Cs^+ ions in host compounds.

Clay minerals, ubiquitous materials in nature, attract a great deal of attention due to large surface area and high cation-exchange capacity.[7] We studied the absorption of cationic metal complexes by clay minerals.[8–12] A synthetic hectorite ion-exchanged with chiral metal complexes, for example, is proven to be applicable as a stereoselective adsorbent for a wide range of organic and inorganic substances. In this communication, we propose an effective method to take up radioactive nuclear wastes, $^{131}I_2$, ^{129}I, $^{137}Cs^+$, and $^{90}Sr^{2+}$, from an aqueous NaCl solution by use of clay minerals.

The adsorption of I_2 was studied by three kinds of clay minerals, sodium montmorillonite (Kunipia F, Kunimine Ind. Co.) (denoted by MON), magnesium vermiculite (the product in South Africa) (VER),[13] and synthetic saponite (Smecton, Kunimine Ind. Co.) (SAP). Their elemental compositions are given in Supporting Information (SI).[16] A 2 mL portion of colloidal suspension containing 10 mg of a clay mineral was mixed with 2 mL of 3 wt % aqueous NaCl solution containing 2×10^{-6} mol of I_2. Here NaCl was added as a model of sea water containing 3.1 wt % of NaCl. The suspension was stood for 5 min and centrifuged. The supernatant was analyzed by measuring UV–visible spectra. The results are shown by the dotted curves in Figure 1. From the absorbance at 440 nm ($\varepsilon_{440} = 740$), the amount of unbound I_2 in a supernatant was determined to be 38% (MON), 38% (VER), and 24% (SAP), respectively. Thus clay minerals acted as an adsorbent of I_2 but failed in eliminating I_2 completely. Furthermore, some unabsorbed products that showed the electronic absorbance in the UV region (<400 nm) were produced. These were thought to be anionic species containing iodine atoms such as I_3^- (the peaks at 290 and 360 nm) or IO_3^- (the increased absorbance in the region of 200–240 nm).[14]

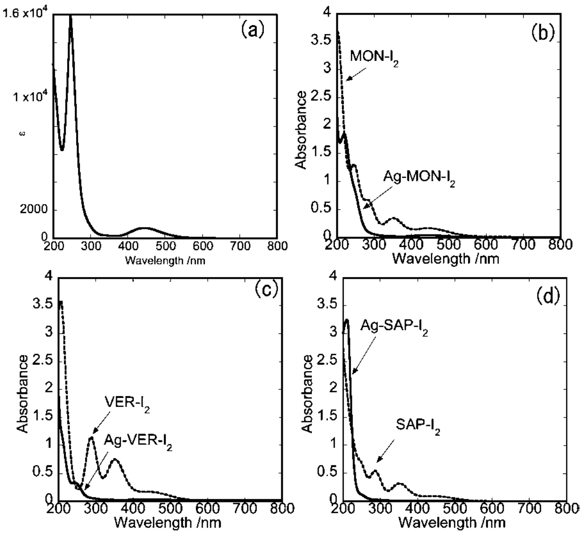

Figure 1. The UV–vis spectra of supernatants after an aqueous I_2 solution was mixed with a colloidal clay suspension and centrifuged: (a) an aqueous I_2 solution, (b) MON, (c) VER, and (d) SAP. Dotted and solid lines show the results for clays and Ag^+-modified clays, respectively.

In order to improve the capturing efficiency, clays exchanged with Ag^+ ions were used as an adsorbent. 7×10^{-6} mol of $AgNO_3$ was added to 2 mL of aqueous suspension containing 10 mg of a clay mineral. The suspension was stood for 1 h and centrifuged. The supernatant was decanted and the precipitate was mixed with 4 mL of aqueous solution containing 3 wt % NaCl and 1×10^{-6} mol of I_2. After 5 min, the suspension was centrifuged and the supernant was analyzed by UV–visible spectra. As shown by the solid curves in Figure 1, the amount of I_2 in the supernatant was reduced to less than 1×10^{-7} mol for all clay minerals. Moreover, the production of anionic species such as I_3^- and IO_3^- was suppressed as deduced from the UV spectra. One possibility for the role of Ag^+ ions was that a portion of adsorbed Ag^+ ions was photoreduced to Ag and reacted with I_2 to produce AgI. Since AgI was insoluble in water, it was eliminated from solution. In fact, SAP exchanged with Ag^+ ions turned dark violet after 10 h under sunlight. Such coloration indicative of Ag clusters was even more accelerated by illuminating Ag^+-modified SAP with a Xe lamp.

The above results motivated us to eliminate I_2 more thoroughly by means of liquid chromatography on a column packed with Ag-modified SAP. SAP itself is unsuitable as a packing material since it consists of particles too small (ca. 20 nm). Thus, SAP was attached to silica particles with the help of organic polymers.[12] The packing material was prepared by mixing SAP, poly(vinyl alcohol), and silica gel (Neopre Gel) at a ratio of 1:0.4:20 as a slurry and dried under gentle heating (<60 °C). 3 g of the produced material (denoted by SAP/PVA/SiO_2) was soaked in an aqueous solution containing 3×10^{-5} mol of $AgNO_3$. SAP/PVA/SiO_2 was colored dark brown when it was left under sunlight for 10 h. The material (denoted by Ag-SAP/PVA/SiO_2) was washed with water and packed into a glass tube to make a column (0.8 cm (i.d.) × 3 cm). 2 mL of water containing 4×10^{-6} mol of I_2 and 3 wt % NaCl was mounted and eluted with 3 wt % aqueous NaCl solution at a flow rate of 1.0 mL min^{-1}. The eluent was collected at every 1 mL and analyzed by UV–vis spectra. As a result, the eluent was transparent up to 210 nm, when 10 mL of the eluent was flowed. It indicated that the column took up mounted I_2 completely with no elution of I_3^- and IO_3^- ions. At this stage, the upper part of the column changed from dark brown to pale yellow (SI).[16] It might reflect the conversion of Ag clusters on a column to insoluble AgI. The same results were obtained when the mounting of I_2 was repeated two more times. At the fourth elution, about 5% of mounted I_2 was eluted through the column (SI).[16] Based on the results, the column was capable of taking up at least 1.2×10^{-5} mol of I_2, which was estimated to be 10% of initially attached Ag^+ ions.

The valence state of Ag on the column was examined by XPS measurements. As shown in Table 1, the presence of Ag was confirmed by the appearance of peaks due to Ag atoms ($3d_{3/2}$ and $3d_{5/2}$) for both Ag-SAP/PVA/SiO_2 and I_2-treated Ag-SAP/PVA/SiO_2 (SI).[16] No such peaks were observed for SAP/PVA/SiO_2. In order to compare the binding energy (E_b) among the samples, the E_b of C(1s) was taken to be a common reference. The E_b values for Ag $3d_{5/2}$ corrected on this assumption are given in the parentheses in the table. E_b for Ag-SAP/PVA/SiO_2 was close to that for Ag wire, while E_b for I_2-treated Ag-SAP/PVA/SiO_2 was about 2 eV higher than that for Ag-SAP/PVA/SiO_2. The reported E_b values for Ag and AgI are 368.2 and 368.0 eV, respectively.[15] Thus, the observed increase of E_b (ca. 2 eV) on treating with iodine did not agree with the expected view that AgI crystals were formed by the reaction of Ag with I_2 in a clay.[15] The interaction of AgI with a clay silicate surface might be one possibility for the observed large increase of E_b.

Table 1. The results of the binding energy (eV) of Ag as determined by XPS measurements.

Sample	C 1s	Ag $3d_{5/2}$
SAP/PVA/SiO_2	289.6	—
Ag-SAP/PVA/SiO_2	290.1	372.7 (367.3)[a]
I_2-treated Ag-SAP/PVA/SiO_2	289.1	373.6 (369.2)[a]
Ag wire	284.7	367.8

[a] The values corrected as a reference of the binding energy of C(1s) in Ag wire.

As for the uptake of Cs^+ ions, vermiculite is known to adsorb strongly Cs^+ ions.[4,5] Thus, first adsorption was compared between Cs^+ and Na^+ ions for VER. 2 mL of water suspension containing 50 mg of VER was mixed with 2 mL of aqueous solution containing 1.0×10^{-5} mol of either $CsNO_3$ or NaCl. The suspension was stirred for 30 min and centrifuged. The amount of unbound Cs^+ or Na^+ ions in a supernatant was determined by means of ICP measurements. As a result, the fraction of uptaken cations (β) was calculated to be 80% and 13% for Cs^+ and Na^+ ions, respectively. Thus, Cs^+ ions were bound to vermiculite stronger than Na^+ by a factor of 6. Next the adsorption of Cs^+ ions was studied in the presence of a large amount of Na^+ ions. 2 mL of water suspension containing 100–500 mg of VER was mixed with 2 mL of 6 wt % aqueous NaCl solution containing 1.0×10^{-5} mol of $CsNO_3$. The suspension was stirred for 15 min and centrifuged. From the amount of unbound Cs^+ ions in a supernatant, the degree of uptake was obtained to be $\beta = 55\%$, 76%, 83%, 85%, and 87% for 0.10, 0.20, 0.30, 0.40, and 0.50 g of VER, respectively. It was deduced that, in spite of the presence of a large amount of Na^+ ions, VER could take up more than 80% of Cs^+ ions. Moreover, the bound fraction increased with the increase of the adsorbent (VER). The tendency was rationalized in terms of the competitive adsorption between Cs^+ and Na^+ onto the vacant site as described in SI.[16] Thus, complete capture would be realized at a very high ratio of [VER] to [Cs^+].

In order to confirm the above expectation, the uptake of Cs^+ ions was performed chromatographically on a column packed with VER. A slurry of 1.0 g of VER was poured into a glass tube to form a column of 0.8 cm (i.d.) × 1 cm (SI).[16] A 3 wt % aqueous NaCl solution containing 1.0×10^{-3} M of $CsNO_3$ was eluted at a rate of 1.0 mL min^{-1}. An eluent was collected at every 1.0 mL and analyzed by ICP. As shown in Figure 2, no Cs^+ ion was detected in the eluent up to 10 mL, indicating the complete uptake by VER. The same figure includes the elution curve of Mg^{2+} ions. In the initial stage (<2 mL of eluted volume), the concentration of dissociated Mg^{2+} ions was 16 times as high as that of Cs^+ ions in an eluent. It decreased on further elution until the amount of dissociated Mg^{2+} ions was lower than that of adsorbed Cs^+ ions. The results were rationalized in terms of the mechanism that Mg^{2+} ions in a clay were replaced with both Na^+ and Cs^+ ions at the initial stage and that thereafter bound

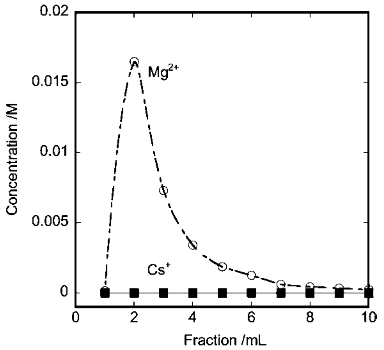

Figure 2. The elution of Cs^+ and Mg^{2+} ions when a 3 wt % aqueous NaCl solution containing 1.0×10^{-3} M of $CsNO_3$ was flowed at a rate of 1.0 mL min^{-1}. The column was packed with 1 g of VER.

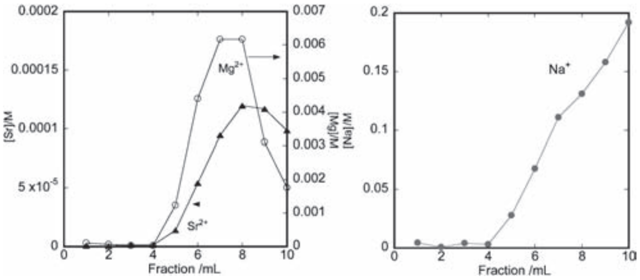

Figure 3. The elution of Sr^{2+} and Mg^{2+} ions when a 3 wt% aqueous NaCl solution containing 6.0×10^{-5} M of $Sr(NO_3)_2$ was flowed at a flow rate of $1.0\,mL\,min^{-1}$. The column was packed with 10 g of $N(C_2H_5)_4{}^+$-exchanged resin as an upper part and 1 g of VER as a lower part.

Na^+ ions were replaced with Cs^+ ions at the later stage. The column (1 g of VER) could adsorb at least 1.0×10^{-5} mol of Cs^+ ions, which was estimated to be 0.7% of the whole cation-exchange capacity of VER.

The above chromatographic experiments were extended to the uptake of Sr^{2+} ions by the VER column. A 3 wt% aqueous NaCl solution containing 6.0×10^{-5} M of $Sr(NO_3)_2$ was eluted on a column packed with 1 g of VER (0.8 cm (i.d.) × 1 cm) at a flow rate of $1\,mL\,min^{-1}$. No uptake of Sr^{2+} ions was achieved because of the presence of a large amount of Na^+ ions (about 8.5×10^3 excess). We noticed, however, that nearly the complete capture of Sr^{2+} ions was achieved in the presence of the same molar concentration (0.51 M) of tetraethylammonium perchlorate ($N(C_2H_5)_4ClO_4$) (SI).[16] This implied that $N(C_2H_5)_4{}^+$ ions with a large ionic radius were a much weaker adsorbate than Sr^{2+} ions so that their presence did not interfere the absorption of Sr^{2+} ions. Thus, if Na^+ ions were replaced by $N(C_2H_5)_4{}^+$ ions, Sr^{2+} ions would be captured on the clay column. Based on this expectation, we prepared a dual column which consisted of 0.8 cm (i.d.) × 10 cm of $N(C_2H_5)_4{}^+$-exchanged resin (prepared from Na-type HCR-S, Muromachi Technos Co., Ltd.) as an upper part and 0.8 cm (i.d.) × 2.0 cm of VER as a lower part (SI).[16] A 3 wt% aqueous NaCl solution containing 6.0×10^{-5} M of $Sr(NO_3)_2$ was eluted on the column at a rate of $1.0\,mL\,min^{-1}$. As shown in Figure 3, more than 98% of Sr^{2+} ions were captured up to the elution volume of 4 mL. When the elution volume exceeded 4 mL, Sr^{2+} ions were not adsorbed on the column due to the increase of Na^+ ions in an eluent. Thus, more complete uptake of Sr^{2+} ions would be possible if a longer column of $N(C_2H_5)_4{}^+$-exchanged resin was used. The significance of the present results is thought to lie in the fact that the uptake of Sr^{2+} ions from sea water is possible if a large amount of Na^+ ions are not eliminated but are replaced by other kinds of cations. Such cation-exchange would be easier than cation-elimination in the case of hundreds of tons of sea water.

In conclusion, the rapid and complete uptake of molecular I_2 and Cs^+ ions from a 3 wt% aqueous NaCl solution was achieved by using a clay mineral column. If Na^+ ions were replaced with $N(C_2H_5)_4{}^+$ ions, Sr^{2+} ions were also taken up by the column. Let the present results be scaled up to the three sequentially connected columns (a), (b), and (c), which are packed with (a) 1 kg of SAP/PVA/SiO_2 (80 cm (i.d.) × 10 cm), (b) 10 kg of cation-exchange resin (80 cm (i.d.) × 10 cm), and (c) 1 kg of VER (80 cm (i.d.) × 10 cm). The flow rate could attain 0.6 ton per hour. If sea water contained 0.1 ppm of I_2 (4×10^{-7} M), 0.1 ppm of Cs^+ ions (7.5×10^{-7} M), and 0.01 ppm of Sr^{2+} ions (1.1×10^{-7} M), these columns are estimated to be capable of purifying ca. 10 ton of sea water in 17 h.

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