Synthetic clay excels in ⁹⁰Sr removal

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Tests with actual ground water from Hanford site, and fundamental studies of $2Na^+ \rightarrow Sr^{2+}$ exchange equilibria revealed that a synthetic clay is extremely selective for ${}^{90}Sr$ with a high capacity for uptake. Comparative studies with existing Sr selective ion exchangers clearly revealed that the present synthetic clay exhibited the best performance for ${}^{90}Sr$ removal from actual ground water collected from three different locations at Hanford. This novel Sr ion sieve is expected to be useful for the decontamination of the environment after accidental release and contamination with ${}^{90}Sr$.

Naturally occurring cation exchangers such as clays and zeolites have been used to decontaminate and dispose of the radioactive species.^{1–4} There has been a great deal of effort to develop high performance synthetic cation exchangers for the uptake of Sr and Cs⁵⁻¹⁰ and their immobilization. A need exists for high performance cation exchangers to separate Sr, Cs, and other species from high-level alkaline tank wastes and remediation of process and ground water at the Hanford nuclear site, the latter to prevent contamination of the Columbia River.¹¹ Here we report the discovery of a new synthetic clay, $Na_2Si_6Al_2Mg_6O_{20}F_4 \cdot xH_2O$ (nominal composition), which excels in ⁹⁰Sr removal from contaminated ground waters. This phase will also be useful in ⁹⁰Sr immobilization in the interlayers by modest heating after the Sr ion uptake.

The starting precursor for the synthesis method was derived by a sol-gel process and is briefly described here. A single phase or monophasic gel was prepared by dissolving $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ separately in absolute ethanol and then combining and mixing the two solutions by stirring for 1 h before adding tetraethoxysilane, $Si(OC_2H_5)_4$. The stoichiometric composition of the three components on an oxide basis was 6MgO-Al₂O₃-6SiO₂. The above mixed sol of the three components was stirred for three hours to achieve homogeneity. The container was then covered with a plastic film and placed in an oven at 60 °C to form a gel through hydrolysis, condensation, and polymerization reactions for three days. This monophasic gel was then dried in an oven at 100 °C, calcined at 475 °C for 12 h, and ground to a powder to pass through a -325 mesh screen. This gel

powder was then mixed with an equal weight of -325 mesh NaF crystalline powder in a platinum crucible and sintered for 18 h at 890 °C in a programmed furnace. These sintering conditions were found to be ideal for synthesis of this type of fluorinated clay as had been reported previously.⁹ After cooling the crucible to room temperature, the reaction products were repeatedly washed with de-ionized water to remove all the soluble components including NaF. The reaction products were then washed with saturated boric acid to remove any impurities of water insoluble fluorides. Finally, the sample was washed with NaCl solution to completely saturate all the exchange sites with Na, and washed with deionized water to remove excess Na before gently drying to obtain a dry powder.

This powder was characterized by x-ray diffraction (XRD) that revealed a phase pure swelling mica (figure not shown) with an analyzed composition close to the expected ideal composition of $Na_2Si_6Al_2Mg_6O_{20}F_4 \cdot xH_2O$. This phase is hereafter referred to as Na-2-mica because it contains two Na ions per unit cell. The Na-2-mica was further characterized by scanning electron microscopy (SEM) that revealed flakes of about $2-3 \mu m$. ²⁷Al and ²⁹Si magic angle spinning nuclear magnetic resonance (MASNMR) spectroscopy was used to determine the coordination and nearest neighbor environments of Al and Si. The ²⁷Al results revealed that almost all Al was present in the tetrahedral coordination, as expected. The ²⁹Si MASNMR revealed Q_3 resonances of Si (3Al) at -78.8 ppm, Si (2Al) at -82.7 ppm, Si (1Al) at -86.7 ppm, and Si (0Al) at -93.6 ppm, and these indicate that the negative charge is distributed nonuniformly

1254 JOURNALS

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on the layer. The approximate intensities of Si (3Al), Si (2Al), Si (1Al), and Si (0Al) are 21%, 30%, 32%, and 17%, respectively, which is what is expected based on the chemical composition.

The Na-2-mica (hydrated form) was used in all the following Sr²⁺ exchange experiments. A Sr²⁺ exchange isotherm was determined using 25 mg (anhydrous basis) of the Na-2-mica, and equilibrating while shaking with 25 cm³ of mixed solutions having different mol ratios of Na⁺/Sr²⁺ at 25 °C for 4 weeks. Two different total normalities (Sr + Na) of 0.00247 and 0.00468 were used in the equilibria experiments. After equilibration, the solid and solution phases were separated by centrifugation and the solutions were analyzed for Sr²⁺ and Na⁺ by atomic emission spectroscopy and also inductively coupled plasma spectroscopy for some Sr^{2+} analyses. The amounts of Sr²⁺ ions exchanged and Na⁺ ions released by Na-2-mica were determined from the difference in the concentration between the equilibrated solution and the starting reference. The theoretical cation exchange capacity [247 meq/100 g on anhydrous basis] was used for plotting the ion exchange isotherms. Selective strontium uptake in the presence of a large excess concentration of Na⁺ was also determined by equilibrating 25 mg of Na-2-mica sample for 24 h in 25.0 cm³ of 0.50N NaCl solution containing 0.0002N SrCl₂. We also used a 0.50N NaCl solution containing 0.0004N SrCl₂. These two solutions have [Na⁺]/[Sr²⁺] equivalent ratios of 2500:1 and 1250:1, respectively. The solid and solution phases were separated by centrifugation and solutions were analyzed as described above. The selective uptake of Sr from 0.5N NaCl is expressed as distribution coefficient, K_{d} which is defined as the ratio of the amount of strontium sorbed per gram of solid to the amount of strontium remaining per cm³ of solution. All of the data points in the isotherms and K_d values represent the average of triplicate measurements. The three measurements for each data point agreed within 5%.

Figure 1 shows the exchange isotherms of sodium/ strontium equilibria with two different total normalities. From these isotherms, one can see that almost all Sr^{2+} was taken up from solution until an equivalent fraction in the solid of 0.6 to 0.7 was reached. These isotherms clearly show that the Na-2-mica phase is extremely selective for Sr²⁺ in the presence of Na⁺ at low concentrations of Sr. These isotherms are steeper than those reported previously for Na-4-mica,9 a different synthetic clay, suggesting that this Na-2-mica phase is superior to Na-4-mica in Sr^{2+} uptake. Figure 2 shows the Kielland plot which is calculated from equilibrium data with 0.00468 total normality using standard procedures.¹² This plot is linear within experimental errors and suggests that the strontium exchange proceeds mainly on one kind of site in Na-2-mica, i.e., the interlayer Na⁺ site. At $x_{Sr} < 0.9$, the Kielland plots fall above the dotted line.

The dotted line indicates that the corrected selectivity coefficient is equal to unity. Any points that fall above this line indicate selectivity for Sr^{2+} uptake. Only one point at high Sr concentration falls on the dotted line indicating little or no preference. From the equilibrium study using 0.00468N (Fig. 2), total Sr^{2+} exchange capacity was determined to be 231 meq/100 g, which is



Equivalent Fraction in Solution, X_{Sr}

FIG. 1. Selective ion exchange isotherms for Na-2-mica with two different total normalities of NaCl/SrCl₂ solutions.



FIG. 2. Kielland plot for $2Na^+ \rightarrow Sr^{2+}$ exchange on Na-2-mica.

Ion-exchange material	Liquid-solid ratio	K _d (ml/g)	Total Sr loading (mmol/g)	⁹⁰ Sr loading (mmol/g)	DF^{b}
IONSIV IE- 911. UOP	4000	$1.62 imes 10^4$	$6.56 imes 10^{-3}$	9.91×10^{-10}	4.68
Sr-Treat, Selion, Inc.	4000	$1.13 imes 10^4$	5.83×10^{-3}	8.80×10^{-10}	3.63
PSU Na-2-Mica	4000	$7.32 imes 10^4$	7.62×10^{-3}	1.15×10^{-9}	$1.89 imes 10^1$

TABLE I. Strontium removal data from groundwater sample 199-N-106A^a (high strontium-90 concentration).

^aThe composition of 199-N-106A ground water is as follows: Li, 3; Be, <0.5; Na, 6350; Mg, 6800; K, 1960; Ca, 39400; Cr, 2.76; Mn, <0.5; Rb, 1.28; Sr, 183; Cs, <0.5; Ba, 23.2, and ⁹⁰Sr., 3.92. All the values are in ng/ml except ⁹⁰Sr, which is in units of pCi/ml.

 ${}^{b}DF$ = Decontamination factor is the ratio of the initial ${}^{90}Sr$ activity in solution to that of the final activity in solution.

higher than that reported previously for Na-4-mica.⁹ The extremely high preference for strontium over sodium was also indicated by the K_d measurements, which showed distribution coefficients of 6484 ± 458 (ml/g) and 2020 ± 134 (ml/g) with 0.0002N and 0.0004N SrCl₂ concentrations, respectively, in the presence of 0.5N NaCl.

Further tests of this material were conducted with actual N-area ground water containing 90Sr from the Hanford site. Water from three different wells were treated and compared with the performance of the best available ion exchangers. This Na-2-mica performed better than all the exchangers tested with the water from the three different wells. For example, Table I lists the distribution coefficients, loading and decontamination factors using ground water sample 199-N-106 A with high 90Sr concentration. The results clearly show that the Penn State University (PSU) Na-2-mica gave the best ⁹⁰Sr removal as determined by $K_{\rm d}$, highest ⁹⁰Sr loading, and highest decontamination factor (Table I). The high selectivity of the PSU Na-2-mica phase can be explained based on the high charge density of the layers, narrow interlayer spacing and low hydration energy of Sr^{2+} ions. The high charge density leads to easy dehydration of the less hydrated Sr²⁺ ions compared to hydrated Mg, Ca, Na, etc., ions in the ground water, and thus the narrow interlayer spacing is ideal for the uptake of dehydrated Sr ions. All

the above results clearly show that a highly selective ⁹⁰Sr ion-sieve with a very high capacity has been developed, which is expected to find applications in the decontamination of the environment after accidental releases.

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