Sorption of Strontium on Zirconia Modified Vermiculite

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Zirconia-modified vermiculite (ZrMV) was prepared by mixing of zirconium oxycation with vermiculite followed by calcination at 523 K for two hours. Vermiculite and ZrMV were characterized by surface area and X-ray diffraction patterns. Sorption of strontium as a function of pH, strontium ion concentration, time, and temperature was studied on ZrMV, and the results were compared with those of vermiculite. The percentage sorption of strontium on vermiculite and ZrMV increased with increase in pH and lowering concentration of Sr\(^{2+}\). The rate of uptake of strontium by ZrMV was found to be much faster than that for vermiculite. The distribution coefficient of strontium on ZrMV is of the order of 10\(^4\) mL/g at pH 3, and the amount of strontium sorbed on ZrMV was always found to be much higher than that on the parent clay. The sorption data were fitted to Langmuir adsorption model for obtaining the sorption capacity of the sorbent. Increase of temperature increases the distribution coefficient of strontium on both ZrMV and vermiculite. Distribution of strontium on ZrMV was also determined from the groundwater samples obtained from the waste disposal site at Kalpakkam.

1. Introduction

Naturally occurring swelling clays (e.g. montmorillonite, vermiculite) are regarded as the backfill material in the engineered barriers of high-level radioactive waste forms.\(^1\)\(^,\)\(^2\) Huge deposits of this clay material are abundant all over India, especially in the states of Andhra Pradesh and Tamil Nadu.\(^3\) The swelling clays act as a barrier between the waste form and the biosphere.\(^2\)\(^,\)\(^4\) The characteristic properties of these swelling clays, such as high cation-exchange ability, low hydraulic permeability, adequate thermal conductivity, etc., ensure that the long-lived radioactive fission products are retained in the clay for more than 10\(^3\) years, such that the radioactivity of the long-lived radioactive fission products decays to very low levels.

Vermiculites are structurally similar to montmorillonite, except that they have higher cation-exchange capacity.\(^5\) It consists of octahedral (aluminum oxide) and tetrahedral (silicon oxide) sheets, which are bonded together by sharing a common oxygen atom as illustrated in Figure 1. Isomorphous substitution by lower valent metal ion for Si\(^{4+}\) and Al\(^{3+}\) results in the generation of net negative charge to the layer, which is normally compensated by cations such as Na\(^+\), Ca\(^{2+}\), or Mg\(^{2+}\). These cations are situated between the layers and can be exchanged with any desired cations by simple ion exchange. Vermiculites have higher cation-exchange capacity than smectite clays (e.g. montmorillonite) due to greater isomorphous substitution by lower valence metal ions for Si\(^{4+}\) and Al\(^{3+}\) ions present in the lattice. Thus, it is expected for the vermiculite to sorb metal ions more efficiently than montmorillonite.

For the rapid sorption and enhancement of catalytic activity, swelling clays (bentonite and montmorillonite) were intercalated with polymeric oxocations such as [Al\(_{13}\)O\(_4\)(OH)\(_{24}\)(H\(_2\)O)\(_{12}\)]\(^{7+}\), an Al\(_{13}\)\(^{7+}\) Keggin ion,12 a tetrameric [Zr\(_4\)(OH)\(_8\)(H\(_2\)O)\(_{16}\)]\(^{8+}\) ion,7 or a trimeric chromium oxyformate [Cr\(_3\)(HCO\(_2\))\(_6\)(H\(_2\)O)\(_6\)]\(^{+}\) ion etc. into the lamella of swelling clay\(^1\)\(^-\)\(^13\) that results in propping of oxide link acting as pillars between the interlayer. However, no reports were available for pillaring of vermiculites by classical intercalation procedures, and it has been reported\(^9\) that it is relatively easy to pillar with Al\(_{13}\)\(^{7+}\) Keggin ion or zirconium oligomers in smectites rather than vermiculites. It was also reported, even in some cases of smectite clays, that pillaring can also be resulting from oligomeric aluminum species other than Al\(_{13}\)\(^{7+}\) Keggin ion.12 This has resulted in a decrease in lattice distance rather than the increase normally observed due to pillaring. Nevertheless, these pillared smectite type clays, especially montmorillonite, were shown to exhibit good selectivity and rapid kinetics of sorption of fission products such as \(^{137}\)Cs and \(^{90}\)Sr.\(^14\)\(^\text{-}^17\)

In the present study, we have adopted the classical method of pillaring of clays, that is, we have attempted\(^17\) to intercalate with smaller Zr\(_4\)\(^{8+}\) tetramer rather than bigger Al\(_{13}\)\(^{7+}\) polymer in the lamella of vermiculite to observe if pillaring is possible. This zirconia modified vermiculite (ZrMV) was prepared by mixing partially hydrolyzed zirconium oxychloride (results in

\(\text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}\)

Figure 1. The idealized structure of swelling phyllosilicate minerals. The elements shown in square brackets are isomorphous substituted ions.

\[\text{Tetrahedra (Si [Al], O, OH)}\]

\[\text{Octahedral (Al[Mg, Li, Fe], O, OH)}\]

\[\text{M = hydrated Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+}\]

\[\text{Tetrahedra (Si [Al], O, OH)}\]

\[\text{Octahedral (Al[Mg, Li, Fe], O, OH)}\]

\[\text{Tetrahedra (Si [Al], O, OH)}\]
tetrameric $[\text{Zr}_4\text{(OH)}_8\text{(H}_2\text{O})_4]^{8+}$ ion) with vermiculite followed by calcination. Sorption behavior of strontium on ZrMV and the parent clay, vermiculite, was reported in this paper. Sorption of strontium on ZrMV and vermiculite was studied as a function of pH, time, temperature, and the concentration of strontium. The suitability of ZrMV as a potential backfill material was also ascertained by obtaining the basic distribution data for the sorption of $^{85+89}$Sr on ZrMV from the groundwater samples procured from the radioactive waste-disposal site at Kalpakkam.

2. Experimental

Materials. All the reagents used were of Analytical AR grade. Vermiculite (CEC 0.9 meq/g) was procured from M/s Sigma Enterprises, Chennai, India and it is composed of SiO$_2$ 53.3%, Al$_2$O$_3$ 9.2%, TiO$_2$ 2.5%, FeO 3.0%, Fe$_2$O$_3$ 5.3%, MnO 0.14%, NaO 1.16%, K$_2$O 1.53%, CuO 0.07%, MgO 2.6%, and rest H$_2$O. The vermiculite was ground and sieved to particles of diameter 400–500 μm. This fraction was used for intercalation and subsequent sorption studies. Radioactive isotope $^{85+89}$Sr was obtained from the Board of Radiation and Isotope Technology (BRIT), Mumbai, India.

Preparation of zirconia modified vermiculite (ZrMV). ZrMV was prepared by an analogous method$^6$ used for pillaring of zirconium oxide in montmorillonite. Initially, vermiculite was converted to the sodium form by stirring 50 g of vermiculite in 500 mL of 1 M NaCl for 12 hours. This procedure was repeated twice. One litre of 0.1 M zirconium oxychloride was adjusted to pH 4 and added to 37 g of Na-vermiculite. The mixture was stirred for 24 hours at 303 K. The product obtained was filtered and washed with distilled water until the filtrate was free from chloride ion. The modified vermiculite was dried at 373 K for 24 hours and further calcined at 523 K for two hours to obtain ZrMV. This final product and the parent vermiculite were used for the subsequent sorption studies.

Characterization. X-ray diffraction pattern of vermiculite and ZrMV were obtained using a Philips 1011 X-ray diffractometer with Cu Kα radiation. Surface area of the vermiculite and ZrMV was determined by the BET method using a Micromerities Pulse Chemisorb 2700 System.

Sorption of strontium on vermiculite and ZrMV.

Effect of pH. Sorption of strontium as a function of equilibrium pH was studied by equilibrating 10 mL of solution containing $^{85+89}$Sr tracer with 0.05 g of the sorbent at 301 K. The pH of the solution was adjusted, using dilute nitric acid, to the pH range 1–6. After six hours of equilibration, the solution was centrifuged and the radioactivity of the supernatant was measured using a well-type NaI(Tl) scintillation counter. The distribution coefficient ($K_d$) and percentage sorption of strontium (%Sorb) on the sorbent were calculated using the following eq

$$K_d (\text{mL/g}) = \frac{A_i - A_f}{V} \times 100,$$

$$\% \text{Sorb} = \left(\frac{A_i - A_f}{A_i}\right) \times 100, \quad (1)$$

where $A_i$ and $A_f$ are the initial and final activities of the solution phase, respectively. $V$ and $m$ are the volume of the solution (mL) and the mass of the sorbent (g), respectively, taken for equilibration.

Kinetics of sorption. Sorption of strontium as a function of time was studied at 301 K by equilibrating 0.05 g of the sorbent with 10 mL of the solution containing 0.001 M nitric acid and $1.14 \times 10^{-4}$ M Sr$^{2+}$ ions added in the form of strontium nitrate spiked with $^{85+89}$Sr. The equilibration was stopped at various intervals of time and the percentage of strontium sorbed by the sorbent was calculated from the radioactivity measurements. A similar experiment was also performed with the initial strontium concentration of $1.14 \times 10^{-3}$ M.

Effect of Sr$^{2+}$ ion concentration. Effect of strontium ion concentration on the sorption of strontium was studied by equi-

librating 0.05 g of the sorbent with 10 mL of the solution containing 0.001M nitric acid spiked with $^{85+89}$Sr tracer and varied concentrations of strontium ion at 301 K for six hours. The strontium ion concentration in the solution was varied from $5.7 \times 10^{-8}$ M to $1.14 \times 10^{-4}$ M. The amount of strontium sorbed by the sorbent was calculated from the radioactivity measurements.

Effect of Na$^+$ and Ca$^{2+}$ ion concentration. The effect of sodium and calcium ions on $K_d$ of strontium was studied at 301 K by equilibrating 0.05 g of the sorbent with 10 mL of the solution containing 0.001 M nitric acid, $1.14 \times 10^{-4}$ M Sr$^{2+}$ spiked with $^{85+89}$Sr tracer, and varied concentration of additives for six hours. The concentration of additives (Na$^+$ and Ca$^{2+}$) was varied from 0.001 M to 0.1 M and they were added as nitrate salts.

Effect of temperature. The influence of temperature on the distribution coefficient was studied by equilibrating 0.05 g of the sorbent with 10 mL of the solution containing 0.001 M nitric acid and $1.14 \times 10^{-4}$ M strontium ion spiked with $^{85+89}$Sr tracer at 301 K. The value of $K_d$ was calculated using eq 1 and similar experiments were also performed at 307 and 313 K.

Sorption of strontium from groundwater (Kalpakkam). Groundwater samples were obtained from three different locations of shallow land radioactive waste-disposal sites at Kalpakkam. The water sample was spiked with $^{85+89}$Sr tracer, and 10 mL of the solution was equilibrated with 0.05 g of vermiculite and ZrMV for 24 hours. $K_d$ was calculated from the radioactivity measurements.

3. Results and Discussion

X-ray diffraction patterns of vermiculite (as obtained and sodium form) and zirconia modified vermiculite (ZrMV) are shown in Figure 2. Vermiculite exhibited several reflections in the 20 range 7.3°–5.9° indicative of the presence of various hydrated monovalent and divalent cations in the interlayer. Conversion of vermiculite into the sodium form shifts the d$_{001}$ peak of vermiculite from 14 Å (2θ = 6.3) to 12.6 Å (2θ = 7.0) as shown in Figure 2. Further this peak position gets shifted to 14.5 Å (2θ = 6.0) after zirconia modification. The shift of d$_{001}$ from 12.6 Å to 14.5 Å is the indication that vermiculite was swollen by the presence of zirconium oxide in the interlayer. However, pillaring in smectite clays e.g. montmorillonite or bentonite, normally results in propping of interlayer distance from 4 to 14 Å depending upon the method of preparation. Even though, vermiculites belong to swelling clays, structurally similar to smectites, however, did not prop apart to the anticipated expansion by the current procedure adopted for pillaring which can be attributed to the higher basal charge of vermiculites than smectites. It was estimated by ICP-MS that nearly 3.8 mg of zirconium is present per gram of ZrMV. Further, very marginal increase of surface area from 11 m$^2$/g for vermi-

![Figure 2. XRD pattern of ZrMV and vermiculite.](image-url)
cullite to 49 m²/g for ZrMV was observed indicating that it was difficult to intercalate or provide pillars in vermiculites than in smectites by classical procedures. However, the presence of minimal amount of zirconia in the interlayer have created more room for the diffusion of strontium ion in ZrMV that seems to be adequate for the rapid sorption of strontium as it can be seen from the following results.

Figure 3 shows the amount of strontium sorbed as a function of time. It can be seen that there is a rapid sorption of strontium in the initial stages of equilibration followed by saturation. In all the cases, equilibrium was established within 5 hours and the rate of sorption of strontium on ZrMV was always higher than that on the parent vermiculite. This could be due to the partial propping of vermiculite by zirconia that facilitates the diffusion of strontium at a much faster rate compared to vermiculite. In vermiculites, the negatively charged lamella are attracted towards each other by the presence of positively charged ions in the interlayer. Diffusion of Sr²⁺ ion towards the sorption site is hindered in this case, and it occurs by pushing the lamella apart while moving towards the sorption site. However, the presence of zirconia in the interlayer, propped the interlayer apart and created more room for the diffusion of Sr²⁺. Sorption of strontium that emanates from zirconia can be ruled out by the fact that zirconium oxide sorbs Sr²⁺ only above pH 9. Thus, the enhancement in the rate of sorption can only be attributed to the increase in the diffusion of metal ions such that it reaches the interior sorption sites in a short time.

The percentage of strontium sorbed by the sorbent as a function of pH is presented in Table 1. Sorption of strontium increased with increase in pH in both the sorbents, and the sorption was always found to be higher in the case of ZrMV. More than 99% of strontium was sorbed by ZrMV when the equilibrium pH was 3, but only 70% was sorbed by vermiculite at this pH. Kᵢ values of strontium ion in the presence of sodium and calcium ion are shown in Table 2. The distribution coefficient of strontium decreased with increase in the concentration of additive (Na⁺ or Ca²⁺), and sorption was negligible when the concentration of the additive exceeded 0.1 M in all the cases.

The classical Langmuir equation relating the strontium ion concentration in sorbent and in solution is given by

\[
\frac{C_i}{C_s} = \frac{1}{Kb} + \frac{C_s}{b},
\]

where \(C_i\) is the equilibrium concentration of Sr²⁺ (mg/L), \(C_s\) is the amount of strontium sorbed on the sorbent (mg/g), \(K\) is the Langmuir adsorption constant (L/mg), and \(b\) (mg/g) is the maximum amount of strontium that can be sorbed. The magnitudes of \(K\) and \(b\) are obtained from the slope and intercept of the plot shown in Figure 4, as given in the same figure. The

### Table 1: Variation of Percentage Sorption of Strontium Tracer on Vermiculite and ZrMV as a Function of pH

<table>
<thead>
<tr>
<th>pH₀</th>
<th>Percentage sorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vermiculite</td>
</tr>
<tr>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2.00</td>
<td>20.2</td>
</tr>
<tr>
<td>3.00</td>
<td>70.6</td>
</tr>
<tr>
<td>4.00</td>
<td>87.5</td>
</tr>
<tr>
<td>4.95</td>
<td>87.5</td>
</tr>
<tr>
<td>5.86</td>
<td>88.0</td>
</tr>
<tr>
<td>6.67</td>
<td>89.1</td>
</tr>
</tbody>
</table>

### Table 2: Variation of Distribution Coefficient (\(Kᵢ\)) of Strontium in the Presence of Sodium and Calcium Ion

<table>
<thead>
<tr>
<th>[M⁺]</th>
<th>(Kᵢ) of strontium, mL/g, in the presence of Na⁺ ion</th>
<th>Ca²⁺ ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vermiculite</td>
<td>ZrMV</td>
</tr>
<tr>
<td>0.1</td>
<td>42</td>
<td>55</td>
</tr>
<tr>
<td>0.05</td>
<td>120</td>
<td>225</td>
</tr>
<tr>
<td>0.01</td>
<td>411</td>
<td>2896</td>
</tr>
<tr>
<td>0.001</td>
<td>566</td>
<td>22178</td>
</tr>
</tbody>
</table>

\[\text{[Sr}^{2+}] = 1.14 \times 10^{-3} \text{ M}, \ V/m = 200 \text{ mL/g}, \ T = 301 \text{ K}, \ \text{equilibrium time} = 6 \text{ h}, \ \text{[Sr}^{2+}] = \text{ trace}.\]

### Table 3: Variation of Distribution Coefficient of Strontium from 0.001 M Nitric Acid on Vermiculite and ZrMV

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>(Kᵢ) of strontium, mL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vermiculite</td>
</tr>
<tr>
<td>298</td>
<td>230</td>
</tr>
<tr>
<td>307</td>
<td>243</td>
</tr>
<tr>
<td>313</td>
<td>250</td>
</tr>
</tbody>
</table>

\[\text{[Sr}^{2+}] = 1.14 \times 10^{-3} \text{ M}, \ V/m = 200 \text{ mL/g}, \ \text{equilibrium time} = 6 \text{ h}.\]

The sorption capacity of strontium on vermiculite and ZrMV was found to be 32.5 and 31.5 mg/g, respectively. It is interesting to note that, though the sorption capacities are almost the same, the rate of sorption of strontium on ZrMV was always higher than that on vermiculite as shown in Figure 3. This could be possible only when the sorption sites that were hindered in vermiculite can be accessed without much difficulty while the strontium ion was diffusing in modified vermiculite. Table 3 shows the distribution coefficient of strontium from 0.001 M nitric acid on ZrMV and vermiculite at three.

![Figure 3](image-url)  
*Figure 3.* Variation of percentage sorption of strontium from 0.001 M nitric acid as a function of time.

![Figure 4](image-url)  
*Figure 4.* Langmuir plot for the sorption of strontium on vermiculite and ZrMV.
different temperatures. It is seen that $K_d$ values increases with increase of temperature indicating that sorption process is endothermic.\textsuperscript{18, 20, 21}

The mobility of groundwater at the radioactive waste disposal sites is the mode of transport for the migration of radionuclides from the waste form to the geosphere. To avoid the contamination of the environment and the hazards to human beings, it was proposed to use the naturally occurring swelling clays (e.g. montmorillonite, vermiculite) as the backfill material in the engineered barriers of high-level waste forms.\textsuperscript{1, 2, 22} To study the retention ability of strontium on both ZrMV and vermiculites, equilibration was performed with the groundwater samples obtained from three different locations of waste-disposal sites at Kalpakkam. The samples were spiked with $^{85+89}$Sr tracer and the distribution coefficients of strontium obtained on both sorbents are shown in Table 4. The data reveal that the modified vermiculite is a superior candidate than vermiculite as a backfill material for retaining strontium for a sufficiently long time and thus can avoid the migration and contamination of the environment.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Constituents</th>
<th>$K_d$, mL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vermiculite</td>
<td>ZrMV</td>
</tr>
<tr>
<td>1</td>
<td>pH = 6.32, Na$^+$ = 48 mg/L, K$^+$ = 6 mg/L, Ca$^{2+}$ = 9.62 mg/L, Mg$^{2+}$ = 2.92 mg/L, dissolved solids = 110 mg/L</td>
<td>1119</td>
</tr>
<tr>
<td>2</td>
<td>pH = 7.70, Na$^+$ = 36 mg/L, K$^+$ = 12 mg/L, Ca$^{2+}$ = 6 mg/L, Mg$^{2+}$ = 3.8 mg/L, dissolved solids = 154 mg/L</td>
<td>1523</td>
</tr>
<tr>
<td>3</td>
<td>pH = 7.32, Na$^+$ = 9 mg/L, K$^+$ = 3.7 mg/L, Ca$^{2+}$ = 26.5 mg/L, Mg$^{2+}$ = 5.5 mg/L, dissolved solids = 80.3 mg/L</td>
<td>1022</td>
</tr>
</tbody>
</table>

$T$ = 301 K, $V/m$ = 200 mL/g, equilibrium time = 24 h.

4. Conclusions

In this study, we have shown that it is difficult to place pillars completely in the interlayer of vermiculites by classical methods. However, it is possible to partially swell or prop apart the lamella of vermiculite to some extent by the tetrameric $[\text{Zr}_4\text{(OH)}_8\text{(H}_2\text{O})_{16}]^{8+}$ ion that results in a zirconia modified product, ZrMV, which seems to be adequate for the rapid sorption and the percentage of the sorption ($= K_d > 10^4$ mL/g at pH 3) of strontium in modified vermiculite were much higher. The sorption of strontium was favored by an increase in temperature. ZrMV can be considered as a superior candidate over vermiculite as a backfill material, and it can ensure the retention of radioactive strontium leached out from the waste forms.

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References