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## Investigation of the utility of some synthetic magnesium silicates in radioactive waste treatment

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### Abstract

Three products of 'stevensite' type of clay minerals have been synthesised using different  $\text{SiO}_2/\text{MgO}$  molecular ratios at atmospheric pressure and boiling water temperature. Ion exchange studies have been carried out on these synthetic products with a view to utilise them in the treatment of low and intermediate levels of radioactive liquid wastes.

**Key words :** Stevensite, ion exchange, radio active wastes, sorption, phylitic minerals, decontamination.

### 1. Introduction

As a followup of our earlier work on the use of various naturally occurring clay minerals<sup>1,2</sup> and transformation of vermiculites of Indian origin<sup>3,4</sup>, preliminary investigations carried out by Caillère and Brat<sup>5</sup> have indicated promising exchange capacities of the phylitic minerals in the sorption of cesium. Though a lot of work has been reported on the synthesis of clay minerals using silica and alumina gels<sup>6-9</sup>, most of the workers have synthesised the clay minerals in very small quantities, due to which even evaluation of the physico-chemical properties became difficult.

An attempt has been made to synthesise larger quantities of phylitic minerals so that their use in the radioactive liquid waste management could be made.

### 2. Materials and methods

#### 2.1. Materials

Reagents and chemicals used were of A.R. grade. Silica gel was prepared by the action of dilute hydrochloric acid on sodium silicate.



## 2.2. *Methods*

Using silica gel containing 65 per cent  $\text{SiO}_2$ , three different experiments with  $\text{SiO}_2/\text{MgO}$  molecular ratios as 0.66, 0.88 and 1.33 were carried out. The products obtained were termed as 1, 2 and 3 respectively. Silica gels were continuously boiled with magnesium acetate solution at atmospheric pressure in 2-litre round bottomed pyrex glass flasks. Regular samples were withdrawn from the flasks and were subjected to X-ray analysis to evaluate the formation of crystalline products. As the products obtained at the end of 45 days of boiling showed good crystallinity the experiments were stopped at this stage. Products were separated free from magnesium acetate solution by repeated washings with distilled water and dried in an oven at  $315^\circ\text{K}$  and weighed. The products were evaluated for their physico-chemical and sorptive behaviour. Chemical analyses were carried out, following the standard methods adopted earlier by Riley<sup>10</sup>. X-ray analyses were carried out using Philips X-ray machine PW 1010, using  $\text{CuK}_\alpha$  radiations (34 K.V., 18 m.a.) and Ni filter. Theoretical structural formulae for half-unit cell structure were calculated using the method adopted earlier by Caillère and Hénin<sup>11</sup>.

Ion exchange studies were made by batch method using Boyd, Schubert and Adamson<sup>12</sup> model of ion exchange equilibria, with radioactive tracer Cs-134.

## 3. Results and discussion

### 3.1. *X-ray analysis*

Products 1, 2 and 3 show most of the prominent lines (Table I) corresponding to Stevensite<sup>13</sup> group of clay minerals. Presence of 0.152 nm value indicates the formation of trioctahedric mineral.

### 3.2. *Equilibrium uptake capacities, weights obtained, % yield and densities*

1M NaCl solution was equilibrated at  $\text{pH} \simeq 6.8$ . The amount of  $\text{Mg}^{++}$  exchanged is given as meq/100 g. It is seen from Table II that equilibrium uptake capacities, % yield and the densities of the products synthesised go on increasing as  $\text{SiO}_2/\text{MgO}$  molecular ratio in the initial reactants is increased from 0.66 to 1.33. Equilibrium uptake capacity of Stevensite group of minerals is generally around 38 meq/100 g<sup>14</sup>. Stevensite group of minerals have density values between 2.15 and 2.20<sup>15</sup>. These values further confirm our earlier conclusion that these three products correspond to stevensite.

### 3.3. *Chemical analysis*

$\text{SiO}_2/\text{MgO}$  molecular ratio in the case of Stevensite<sup>16</sup> is approximately equal to 1.39. Synthetic products (Table III) fall in close proximity to this value.

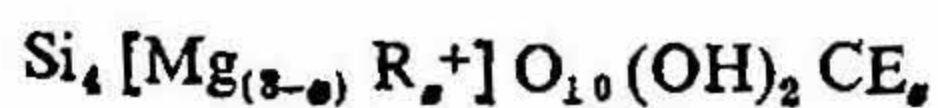
**Table I**
**X-ray analysis data : SiO<sub>2</sub>-MgO reaction products**

| Product 1 |                  | Product 2 |                  | Product 3 |                  | Stevensite (13)                      |                  |
|-----------|------------------|-----------|------------------|-----------|------------------|--------------------------------------|------------------|
| dnm       | I/I <sub>0</sub> | dnm       | I/I <sub>0</sub> | dnm       | I/I <sub>0</sub> | dnm                                  | I/I <sub>0</sub> |
| 1.22      | 10               | 1.18      | 10               | 1.219     | 10               | 1.24 }<br>1.12 }<br>0.50 }<br>0.49 } | 10<br><br>2      |
| 0.45      | 5                | 0.455     | 8                | 0.450     | 5                | 0.454                                | 10               |
| 0.418     | 5                |           |                  | 0.413     | 4                |                                      |                  |
|           |                  |           |                  | 0.360     | 3                | 0.350 }<br>0.300 }                   | 5                |
| 0.258     | 6                | 0.260     | 8                | 0.260     | 3                | 0.262                                | 9                |
| 0.223     | 2                |           |                  |           |                  | 0.228                                | 2                |
| 0.189     | 8                |           |                  |           |                  |                                      |                  |
| 0.175     | 7                | 0.171     | 1                |           |                  | 0.173                                | 4                |
| 0.164     | 6                |           |                  | 0.168     | 1                |                                      |                  |
| 0.152     | 6                | 0.152     | 10               | 0.152     | 8                | 0.152                                | 9                |
|           |                  | 0.137     | 7                |           |                  | 0.131                                | 7                |

**Table II**
**Equilibrium uptake capacities, weights obtained, % yield and densities**

| Product No. | Uptake capacities using NaCl (meq/100 g) | Weights obtained (g) | Yield (%) | Densities (g/cc) |             |
|-------------|--|----------------------|-----------|------------------|-------------|
|             |  |                      |           | Crystallographic | Pycnometric |
| 1.          | 42.0                                     | 7.66                 | 79.9      | 1.89             | 1.95        |
| 2.          | 46.0                                     | 8.03                 | 81.5      | 2.11             | 2.15        |
| 3.          | 50.0                                     | 9.01                 | 95.1      | 2.15             | 2.20        |

**3.4. Theoretical structural formulae**

 Structural formulae of Stevensite<sup>17</sup> is represented as:




Where R is a monovalent cation or vacant cation lattice site, in the latter case CE is generally equal to  $2x$  and  $x \approx 0.1$ . Structural formulae of the synthetic products 1, 2 and 3 (Table IV) agree well with the above mentioned formula of Stevensite.

Table III

Chemical analysis : SiO<sub>2</sub>-MgO reaction products

| Product No. | SiO <sub>2</sub> | MgO   | Total H <sub>2</sub> O (at 1,370° K) | Total  | SiO <sub>2</sub> /MgO (Molecular ratio) |
|-------------|------------------|-------|--------------------------------------|--------|---|
| 1.          | 48.41            | 24.20 | 28.06                                | 100.67 | 1.33                                    |
| 2.          | 46.93            | 22.90 | 30.48                                | 100.31 | 1.37                                    |
| 3.          | 49.60            | 23.14 | 27.12                                | 99.86  | 1.43                                    |

### 3.5. Estimation of sorption capacities and selectivity coefficients

These were estimated by batch method using Cs-134 + Cs<sup>+</sup> Conc. 10<sup>-2</sup> M. Results of sorption capacities ( $F_{cs}$ , given in terms of meq/100 g) and selectivity coefficients ( $K_{Mg}^{Cs}$ ) towards Cs<sup>+</sup> are given in Table V and Fig. 1. It is seen that the sorption capacity of the synthetic products 1, 2 and 3 towards Cs<sup>+</sup> ion goes on increasing and the selectivity coefficient goes on decreasing with the increase in SiO<sub>2</sub>/MgO molecular ratio from 0.66 to 1.33 in the initial reactants. Thus, product 3, with SiO<sub>2</sub>/MgO molecular ratio = 1.33 in the initial reactants, with higher sorption capacity and decreased selectivity coefficient is better suited for the decontamination of radioactive effluents containing Cs<sup>+</sup> ions.

## 4. Potential application in radioactive waste treatment

Tailor-made synthetic products with high sorption capacity and better yield can be effectively used in the treatment/disposal of radioactive liquid wastes containing radio-cesium. Further, these tailor-made minerals will find an important role after a decade or so, when the natural vermiculite resources get depleted by their continuous use in radioactive liquid waste management.

## 5. Conclusion

The investigations on the yield of the products 1, 2 and 3 suggest that the product 3 obtained from SiO<sub>2</sub>/MgO molecular ratio = 1.33 (in the initial reactants) gives the best yield (95 per cent). The equilibrium uptake values and the sorption capacity towards

Table IV

Theoretical structural formula : Product 1

| Chemical analysis        | No. of molecules | No. of oxygens | No. of cations | No. of ions in half lattice structure |
|--------------------------|------------------|----------------|----------------|---------------------------------------|
| SiO <sub>2</sub> = 48.41 | 0.8068           | 1.6136         | 0.8068         | 4.00                                  |
| MgO = 24.20              | 0.6050           | 0.6050         | 0.6050         | 3.00                                  |

$$N = 2.2186.$$

Taking  $n = 11$  (i.e., No. of oxygens in half lattice structure of the dehydrated mineral).

$$\text{We have } n/N = 11/2.2186 = 4.9581.$$

∴ Theoretical structural formula: Si<sub>4.0</sub> Mg<sub>3.0</sub> O<sub>10</sub> (OH)<sub>2</sub>.

Using these calculations, structural formulae of products 2 and 3 have been found to be:

Product 2 : Si<sub>4.02</sub> Mg<sub>2.95</sub> O<sub>10</sub> (OH)<sub>2</sub>

Product 3 : Si<sub>4.07</sub> Mg<sub>2.85</sub> O<sub>10</sub> (OH)<sub>2</sub>.

Table V

Sorption capacities and selectivity coefficients

(Using Cs-134 + Cs<sup>+</sup> Conc. = 10<sup>-2</sup> M)

| Product No. | F <sub>Cs</sub> (meq/100 g) | K <sub>Mg</sub> <sup>Cs</sup> |
|-------------|-----------------------------|-------------------------------|
| 1.          | 23.3                        | 7.5                           |
| 2.          | 28.6                        | 6.5                           |
| 3.          | 34.4                        | 2.0                           |

Cs<sup>+</sup> ions indicate that these values increase with the increase in SiO<sub>2</sub>/MgO molecular ratio in the initial reactants.

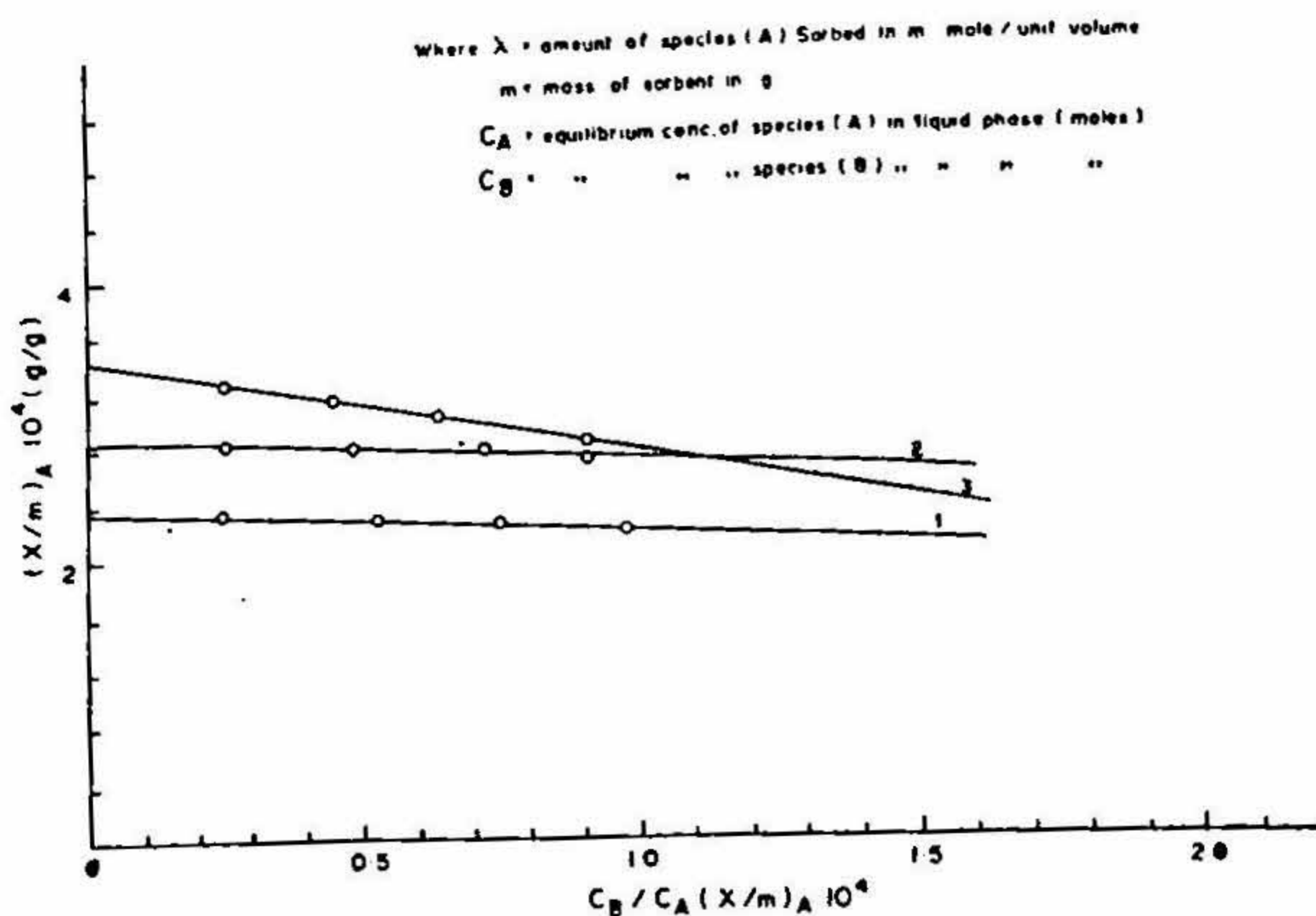


FIG. 1. Relation between  $(X/m)_A$  and  $(X/m)_A C_B/C_A$  with  $Cs^+$  conc.  $10^{-2}$  M.

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