ADSORPTION BEHAVIOUR OF CESIUM ON MARL

R. M. CORNELL

ETHZ Zürich Laboratorium für anorganische Chemie, CH-8092 Zürich, Switzerland

(Received 6 January 1992; revised 18 February 1992)

ABSTRACT: Adsorption of Cs on two samples of marl with different calcite, quartz and clay contents and surface areas of ~10 m²/g was followed using the batch sorption technique. The experiments were carried out in an atmosphere of N₂/1% CO₂ using a synthetic groundwater of pH 7.3 and an ionic strength of 0.1 m. The initial Cs concentration ranged from 10⁻⁸ to 10⁻⁴ M. Sorption of Cs was non-linear, fast and reversible. At equilibrium Cs concentrations <10⁻⁸ M, an isotope exchange mechanism appeared to operate, whereas at higher concentrations, sorption involved ion exchange. The distribution coefficients ranged from 23-995 ml/g. They varied markedly with rock/water ratio; this variation could be explained in terms of the non-linear isotherm displayed by Cs. Although the two samples of marl differed in composition, uptake of Cs on both samples was very similar because the content of the principal sorbing component (illite) was the same in both samples.

Cesium is a radionuclide that has been introduced into the environment by both nuclear accidents (e.g. Chernobyl) and by fall-out from nuclear testing. It is also of concern in safety assessment programmes for nuclear waste repositories owing to the large inventories, the long half-lives of the isotopes and the high solubility of the element. The mobility of Cs may be considerably reduced by interactions with clay minerals in soils, sediments and rocks (Tamura & Jacobs, 1960; Komarneni & Roy, 1980; Brouwers et al., 1983; Cremers et al., 1988; Lieser & Steinkopf, 1989a; Yanagi et al., 1989). This behaviour is particularly important in waste repository safety analysis where an essential characteristic of the host rock must be its ability to retard radionuclide migration.

In Switzerland, one particular rock for a nuclear waste repository is marl, a carbonaceous, sedimentary rock. The present report describes the interaction of Cs with marl. The studies reported had the principal aim of considering the effect of Cs concentration, marl composition and rock/water ratio on the extent of adsorption of Cs. A further objective was to compare the adsorption behaviour of Cs on marl with that found previously for a crystalline rock (Aksoyoglu, 1990), which is also under consideration as a host rock for nuclear waste repository.

MATERIALS AND METHODS

Samples of marl were collected from a region in the vicinity of Wellenberg in central Switzerland; this area is under consideration as a potential repository site. A feature of marl is its extreme inhomogeneity; the composition can vary markedly over a distance of even a few metres. The present experiments were carried out on two samples, H4 and F4 with small and large calcite contents, respectively. The mineralogical and chemical compositions of the two samples are shown in Table 1. The amount of iron oxide present was found by a dithionite/citrate analysis (Holmgren, 1967) and the amount of organic matter was
R. M. Cornell

TABLE 1. Composition (wt%), CEC (mEq/100 g) and surface area (m²/g) of marl samples.

<table>
<thead>
<tr>
<th>Components</th>
<th>F4</th>
<th>H4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>42</td>
<td>24</td>
</tr>
<tr>
<td>Quartz</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Ankerite</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Chlorite</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>* Illite + illite-smectite</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0-3</td>
<td>0-3</td>
</tr>
<tr>
<td>Fe(III) hydroxide</td>
<td>1-2</td>
<td>0-6</td>
</tr>
<tr>
<td>Organics</td>
<td>0-50</td>
<td>0-65</td>
</tr>
<tr>
<td>CEC</td>
<td>9-0</td>
<td>9-2</td>
</tr>
<tr>
<td>BET surface area</td>
<td>9-9</td>
<td>11-4</td>
</tr>
</tbody>
</table>

* Illite-smectite mixed-layer: illite = 1:2-5.

determined by treating the marl with 3-5% H₂O₂ for 24 h and weighing the residue. The carbonate, quartz and clay contents of the marl were found by X-ray diffraction and the amount of pyrite by coulometric sulphur analysis. The cation exchange capacity (CEC) was measured by the ethylenediamine method (Cornell & Aksoyoglu, 1991), and the surface area was determined by the BET method.

The samples were briefly crushed and then ground (30 s and 1 min, respectively) in a tungsten carbide coated jaw crusher and grinder. Characterization and adsorption experiments were carried out with the <63 µm size-fraction of rock obtained by dry sieving (mineral separation was avoided by briefly grinding the sample until all particles passed through the sieve). The grinding treatment increased the surface area of the sample and hence the number of potential adsorption sites; the distribution coefficients obtained will, therefore, be different from those of the intact rock. The aim of this study, however, was to determine how certain parameters influence Cs uptake and a good estimation of this can be obtained using the crushed material.

A synthetic groundwater of composition 7·9 × 10⁻² M Na⁺, 1·2 × 10⁻³ M K⁺, 2·7 × 10⁻³ M Mg²⁺, 3·3 × 10⁻³ M Ca²⁺, 4·4 × 10⁻⁴ M Sr²⁺, 2·6 × 10⁻⁴ M Si⁴⁺, 1·4 × 10⁻⁴ M F⁻, 8·1 × 10⁻² M Cl⁻, 4·5 × 10⁻³ M SO₄²⁻, 4·4 × 10⁻³ M alkalinity and pH 7·3, was used for the adsorption experiments. This composition is considered to be typical of that of the marl water found in situ. Before carrying out adsorption experiments, the marl and the marl water were equilibrated until a constant composition of marl water was reached. This was done by holding suspensions of marl/marl water in dialysis tubing (pore size 2-4 nm) in containers of marl water and renewing the water on a daily basis until chemical analysis of the water outside the bag showed no further change in composition; analysis at this stage showed that the composition of the filtered (0-22 µm nucleopore filter) water inside the bag was the same as that of the water outside the bag. The equilibrated marl water was then used for the adsorption and desorption experiments. All equilibrations were carried out, with shaking, in a glove box in an atmosphere of N₂/1% CO₂; this atmosphere is considered to be the best approximation to that found in situ. A series of rock/water (r/w) ratios (1/2, 1/5, 1/10, 1/100) was used. The number of water renewals depended on the r/w ratio and ranged
from 3 (r/w = 1/100) to 7 (r/w = 1/2). After equilibration, the composition of the water was close to that of the original synthetic water for all r/w ratios.

The cations in solution were analysed using inductively coupled plasma spectroscopy (ICP), F⁻ and SO₄²⁻ by ion chromatography, Cl⁻ by potentiometric titration and alkalinity by acid titration. The concentration of natural Cs was determined by inductively coupled plasma mass spectrometry (ICP-MS). In the original synthetic marl water, the concentration of natural Cs was below the detection limit of ICP-MS (<8 × 10⁻¹⁰ M). After equilibration of the marl with the synthetic water, however, the Cs concentration in solution increased to 1·8 × 10⁻⁸ M indicating that some leaching of natural Cs from marl during the conditioning period had occurred.

All adsorption/desorption experiments were carried out in duplicate, in an atmosphere of N₂/1% CO₂ in a glove box. A complete series of experiments, with initial Cs concentration ranging from 5 × 10⁻⁸ M to 3 × 10⁻⁴ M, was carried out with a r/w ratio of 1/10. Cesium solutions were labelled with ¹³⁷Cs tracer and measurements were carried out using an intrinsic germanium detector. The marl suspensions were held in dialysis bags suspended in polyethylene flasks of spiked, equilibrated water and agitated gently on an end-over-end shaker. Dialysis bags were used to facilitate phase separation. Blanks (without marl) indicated that loss of Cs due to adsorption on the dialysis bags or on the walls of the vessels was <5%. Acid leaching tests at the end of the adsorption experiments showed that in the presence of marl, uptake on the vessel walls and bags was <1% and hence could be neglected. The effect of r/w ratio (1/2, 1/5, 1/10, 1/100) was checked in triplicate with one Cs concentration (3·2 × 10⁻⁶ M Cs).

The kinetics of adsorption were followed using a bulk suspension (20 g/200 ml) and a Cs concentration of 3 × 10⁻⁷ M. The suspension was sampled at intervals, the total volume of all aliquots taken during the experiments being <3% of the initial volume. Adsorption coefficients (Kₐ values) were calculated from the difference between the count rates of the initial and final solutions. Once the adsorption coefficients from the kinetic experiments reached the steady state, all other suspensions were sampled and measured.

For the desorption step, the original solution was replaced by tracer-free, equilibrated, synthetic marl water. The kinetics of desorption from the bulk sample were followed until a steady state was reached after which all other samples were measured.

RESULTS AND DISCUSSION

Adsorption/desorption of Cs on marl

Uptake of Cs on marl was rapid with more than 80% adsorption taking place in the first 60 min. The adsorption coefficient (Kₐ) reached a constant value for sample H4 in approximately seven days and desorption took the same time (Fig. 1). For F4 marl, the kinetics were faster with adsorption and desorption both being completed within 24 h.

The changes in sorption/desorption coefficients as a function of equilibrium Cs concentration in solution are shown in Fig. 2 (r/w = 1/10). Over the concentration range considered, sorption of Cs on marl was reversible. The Kₐ values decreased significantly (from 915 ml/g to 22·7 ml/g for F4) as the Cs loading on the solid increased (i.e. non linear adsorption) suggesting that as Cs uptake on marl increased, energetically less favourable sites became involved in sorption (cf. Lieser & Steinkopf, 1989a). The maximum uptake of Cs in these experiments corresponded to 1% of the total CEC of the marl.
The rapid and reversible adsorption of Cs on marl suggests that a simple ion exchange sorption mechanism operates. It has been reported that trace amounts of Cs may be very strongly held on minerals such as illites and micas on high-energy sites termed frayed-edge sites (Sawhney, 1964; Brouwers et al., 1983; Cremers et al., 1988). These sites, which are located at the outer edges of the interlayers of the clays, contribute to ~0.1% of the total sites available for Cs adsorption (Brouwers et al., 1983; Cremers et al., 1988). Adsorption on these sites is thermodynamically reversible, but because the Cs is strongly held, its release is slow (Brouwers et al., 1983). In the present work, Cs sorption was readily reversible over the entire concentration range considered which suggests that the number of high-energy frayed-edged sites on marl is negligible. A possible explanation for this is that
Cs adsorption on marl

the marl was taken from an underground site and hence not exposed to the weathering effects which can lead to the formation of frayed edges.

The concentration of natural, stable Cs (coming from the marl) in the equilibrated marl water is $1.8 \times 10^{-8}$ M. It would be expected that, when the concentration of the Cs tracer is well below the total Cs concentration, an isotope exchange mechanism would operate. This is supported by observations that over the equilibrium Cs concentration range of $5 \times 10^{-10}$ to $4 \times 10^{-9}$ M, (i) sorption was linear, (ii) the sorption/desorption coefficients were approximately constant, and (iii) adsorption was reversible.

**Sorption isotherms**

The sorption/desorption data for the non-linear part of the curve were fitted to a linearized Freundlich equation,

$$\log[Cs]_s = \log K + N\log[Cs]_t$$

where $[Cs]_s =$ the concentration of Cs adsorbed on the solid (mol, kg$^{-1}$), $[Cs]_t =$ the equilibrium solution concentration (M), and $K, N =$ the Freundlich constants.

Sorption/desorption isotherms for F4 and H4 marls are shown in Fig. 3. The isotherms are very similar for both marls. The Freundlich exponents ($N$) of 0.63 are in line with the non-linearity of adsorption and are comparable with values found in studies on similar rocks (Torstenfelt et al., 1982).

**Effect of marl composition on Cs adsorption**

An interesting feature of Fig. 2 is that, although F4 and H4 differ considerably in composition (Table 1), the sorption/desorption coefficients for both marls are very similar ($K_a F4/K_a H4 = 0.8$). Preliminary adsorption experiments and also data from the literature (Torstenfelt et al., 1982), indicated that Cs adsorption on calcite and quartz is negligible, as would be expected in view of the low CEC of these components. In addition to marked

Fig. 3. Sorption/desorption isotherms of Cs on marl. ▲ = F4 sorption, △ = F4 desorption, ● = H4 sorption, ○ = H4 desorption. Lines correspond to the Freundlich fittings.
differences between samples in the levels of these non-sorbing components, there were also differences in the levels of the different clays present in the two marls; H4 contained twice as much chlorite and seven times more kaolinite than F4. Owing, however, to their small CEC (Grim, 1968), these clays contribute less to sorption by ion exchange than do the other clays in marl, i.e. the illites and the illite-smectite mixed-layer clay (Sawhney, 1964).

The illites and mixed-layer clays which do adsorb Cs to a large extent are present in H4 and F4 in similar amounts (Table 1). This appears to be the reason for the very similar uptake of Cs by these two marls. It can be concluded that, for ions that adsorb only by simple ion exchange, sample heterogeneity only influences the extent of adsorption when it concerns variations in the level of the illitic clays. However, it should be emphasized that, for nuclides which can be expected to adsorb by other mechanisms, and hence may adsorb on all components of marl, differences in adsorption behaviour from one sample to the next may be significant.

Sample heterogeneity appears to influence the kinetics of sorption to some extent. Adsorption on both marls initially involves rapid uptake on the outer accessible sites followed by, for H4, slower diffusion towards sites in the interior of the aggregates. The aggregates in both samples of marl consist of a mixture of quartz, calcite and clays with far more calcite being present in F4 than in H4. Differences in the amounts of the different components probably alter the physical structure of the aggregates and the accessibility of a proportion of the sorption sites; this may be responsible for differences in the rates of sorption in the later stages of the reaction.

The effect of rock/water ratio on sorption coefficient

It has been reported that experiments in which the initial Cs concentration was the same, but in which the r/w ratios varied, produced sorption coefficients which differed by up to one or two orders of magnitude (Meier et al., 1987; Lieser & Steinkopf, 1989b). The relationship between sorption coefficient and r/w ratio can be formulated as follows:

\[
K_d = \frac{C^0 - C_i}{C_i} \times \frac{V}{m}
\]

where \(K_d\) = sorption coefficient (ml/g), \(C^0\) = initial solution concentration (m) \(C_i\) = equilibrium concentration (m), \(V\) = volume of solution (ml) and \(m\) = mass of solid (g). Equation (1) can be rearranged to give,

\[
K_d \times \frac{m}{V} + 1 = \frac{C^0}{C_i}
\]

If \(K_d(m/V) \ll 1\), the shift in concentration of Cs from \(C^0\) to \(C_i\) is negligible. On the other hand, if \(K_d(m/V) \gg 1\), eqn. (2) becomes,

\[
K_d \times \frac{m}{V} = \frac{C^0}{C_i}
\]

This means that as the r/w ratio is varied from, for example, 1/2 to 1/100, then despite using the same initial Cs concentration, the equilibrium Cs concentration will vary over the r/w ratio range because uptake will depend on the surface area of rock available. If sorption is linear over the concentration range considered, the r/w ratio should not influence \(K_d\), but if sorption is non-linear, \(K_d\) will depend on the equilibrium Cs concentration and will,
Cs adsorption on marl

therefore, be affected by variations in the \( r/w \) ratio; at any particular \( r/w \), \( K_d \) should fit on the adsorption isotherm.

To test this expectation, sorption experiments were carried out with F4 marl with \( r/w \) ratios of 1/2, 1/5, 1/10 and 1/100 and an initial Cs concentration \( = 3.2 \times 10^{-6} \text{ M} \) (i.e. on the non-linear part of the curve in Fig. 2). The \( K_d \) values obtained are listed in Table 2: clearly \( K_d \) varies markedly with the \( r/w \) ratio. The data in Table 2 were fitted to the curve for \( r/w = 1/10 \) shown earlier in Fig. 2 (Fig. 4). It is apparent that the sorption coefficients obtained for different \( r/w \) ratios with the one initial Cs concentration, fall on the same line as that obtained for the \( r/w \) ratio = 1/10 with a series of initial Cs concentrations; the equilibrium Cs concentration is, of course, different for different \( r/w \) ratios. It can be concluded that the dependence of \( K_d \) on \( r/w \) ratio is simply the result of non-linearity of sorption, i.e. the fact that uptake depends on the concentration of Cs in solution. If sorption were linear, \( K_d \) would be independent of \( r/w \) ratio; this is, in fact, the case for Ni adsorption on marl (Cornell & Aksoyoglu, 1992).

Comparison of Cs adsorption on crystalline and sedimentary rocks

In Switzerland, both crystalline and sedimentary rock formations are under consideration as host rocks for a nuclear waste repository. Previous investigations of sorption of Cs on crystalline, granitic rock (mylonite) showed that uptake involved ion exchange and took place predominantly on the mica-type minerals (biotite and muscovite) present in mylonite (Aksoyoglu, 1990).

Cesium adsorption on both marl and mylonite was reversible and also non-linear. The kinetics of sorption on mylonite were slower (four weeks to reach equilibrium) than on marl of the same size fraction (\(<63 \mu\text{m}\)). Slow sorption on the granitic rock can be attributed to diffusion into aggregates. A striking difference between the sorption behaviour of the two rocks is in the maximum \( K_d \) obtained over the same Cs concentration range. For mylonite, \( K_d \) ranged from 21–3800 ml/g, whereas for marl, the maximum \( K_d \) was only 995 ml/g.

Micas and illites have similar, non-expanding, three layer structures (Van Olphen, 1977), hence the extent of Cs sorption per unit area of the two types of mineral is expected to be similar. In addition to illite, marl contains other clays which make some contribution to sorption. Furthermore, the surface area of marl is tenfold greater than that of mylonite (10 and 1 m\(^2\)/g, respectively). It was, therefore, expected that maximum Cs adsorption on marl

\[
\text{Table 2. Sorption coefficients obtained with various rock/water ratios using F4 marl (initial [Cs] = 3.2 \times 10^{-6} \text{ M}).}
\]

<table>
<thead>
<tr>
<th>Rock/water ratio (g/ml)</th>
<th>Equilibrium [Cs] M</th>
<th>( K_d ) (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>( 1.09 \times 10^{-8} )</td>
<td>594 (6)</td>
</tr>
<tr>
<td>1/5</td>
<td>( 2.80 \times 10^{-8} )</td>
<td>572 (6)</td>
</tr>
<tr>
<td>1/10</td>
<td>( 8.15 \times 10^{-8} )</td>
<td>385 (2)</td>
</tr>
<tr>
<td>1/100</td>
<td>( 1.75 \times 10^{-6} )</td>
<td>92.3 (4)</td>
</tr>
</tbody>
</table>

Experimental errors in sorption coefficients were \( \sim 8\% \). The \( K_d \) values are the means of triplicates and the relative standard deviations as percentages are given in parentheses.
R. M. Cornell and S. Aksoyoglu

CONCLUSIONS

Sorption of Cs on marl was fast and reversible and involved simple ion exchange. At equilibrium Cs concentrations lower than that of the concentration of natural, stable Cs \((10^{-8} \text{ M})\), the isotherm was linear which is in accord with an isotope exchange mechanism. At higher Cs concentrations, sorption was non-linear.

As a result of the non-linearity of the sorption isotherm, sorption coefficients were strongly dependent on the \(r/w\) ratio.

Although the two samples of marl investigated contained different amounts of quartz, calcite, kaolinite and chlorite, the extent of uptake of Cs on both samples was similar because the amount of the main sorbing component of the marl (illites) was the same in the two samples. For the extent of Cs sorption on marl, sample inhomogeneity appears to be important only in so far as it involves the illitic component. The kinetics of sorption, however, appear to be dependent on the proportions of non-sorbing components such as calcite, most probably because variations in the amounts of these components in the aggregates led to variations in the accessibility of some of the sorption sites.

Sorption of Cs on both sedimentary (marl) and crystalline (mylonite) rock was reversible and non-linear and involved ion exchange. The main factor governing the \(K_d\) values for the two rocks was the ionic strength of the system; for marl with a groundwater with ionic strength \(0.1 \text{ M}\), \(K_d\) was noticeably smaller than for mylonite which had a groundwater with ionic strength two orders of magnitude less. These results indicate that the composition of

---

**Fig. 4.** Change in \(K_d\) with equilibrium \([Cs]\) for various rock/water \((r/w)\) ratios (F4 marl). Note that \(K_d\) for the 1/10 \(r/w\) ratio was determined for a range of initial \([Cs]\), whereas for the other \(r/w\) ratios, only one initial \([Cs]\) was used: \(\bullet = 1/2, \quad \Delta = 1/5, \quad \square = 1/10, \quad \blacksquare = 1/100.\)
Cs adsorption on marl

the groundwater can be as important as the composition of the rock in influencing sorption and hence must be taken into account when choosing a site for a nuclear waste repository.

ACKNOWLEDGMENTS

We are indebted to M. Mantovani and R. Keil for experimental assistance and to Professor P. W. Schindler and Professor H. von Gunten for valuable discussions. The work described was carried out at the Paul Scherrer Institute, Switzerland. Partial financial support from NAGRA is acknowledged.

REFERENCES


