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A ^{133}Cs, ^{29}Si, AND ^{27}Al MAS NMR SPECTROSCOPIC STUDY OF Cs ADSORPTION BY CLAY MINERALS: IMPLICATIONS FOR THE DISPOSAL OF NUCLEAR WASTES

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Abstract

A deep geological repository in stable plutonic rock is being considered for the long-term storage of spent nuclear fuel in Canada. In this study, we examine the adsorption of Cs^+ on clay minerals that may be used as engineered barriers in a repository or that are associated with fracture zones in the host rock. Ion-exchange experiments show that montmorillonite adsorbs more Cs than vermiculite, both 2:1 layer clay minerals. In the disordered structure of vermiculite, Cs was found to adsorb preferentially close to tetrahedral sites, where Al substitution for Si produced a local charge imbalance. Kaolinite, a 1:1 clay mineral, adsorbs very little cesium on its external surfaces. Elevated temperature and pressure, similar to those that would occur in an underground repository, do not affect the amount of Cs^+ adsorbed by montmorillonite. Cesium-133 MAS NMR spectroscopy indicates that Cs^+ is adsorbed in the interlayer of montmorillonite in two stages and in two environments: the layer of H_2O molecules, where Cs^+ is surrounded by H_2O molecules, and the layer closer to the clay surface, where Cs^+ is more tightly bonded to the basal oxygen atoms of the tetrahedra. The first stage of cesium adsorption is a rapid uptake in both the basal oxygen layer and the H_2O molecule layer, in a ratio of 2:1. The H_2O molecule layer reached its capacity immediately, and the amount of cesium adsorbed remains constant up to seven days. However, the adsorption in the basal oxygen layer increases after one hour to a ratio of 5:1 with respect to the H_2O molecule layer, and remains at that level for the rest of the adsorption time.

Keywords: nuclear waste containment, montmorillonite, ^{133}Cs, ^{29}Si, ^{27}Al MAS NMR spectroscopy, cesium adsorption, ion exchange.

Sommaire

On considère présentement un reposoir géologique profond dans une roche plutonique stable pour l'enfouissement à long terme de déchets nucléaires au Canada. Dans cette étude, nous examinons l'adsorption du Cs^+ sur des minéraux argileux qui pourraient être utilisés comme barrières planifiées autour du reposoir ou bien qui se trouvent le long de fractures dans la roche hôte. Les expériences sur l'échange ionique montrent que la montmorillonite adsorbe plus de Cs que la vermiculite, tous deux des argiles à couches 2:1. Dans la structure désordonnée de la vermiculite, le Cs devient adsorbé de préférence près de sites tétraédriques, où l'aluminium peut substituer au Si pour produire un écart local à l'électroneutralité. La kaolinite, un argile de type 1:1, adsorbe très peu de césium sur ses surfaces externes. Une température et une pression élevées, semblables aux conditions anticipées dans un reposoir souterrain, n'ont aucun effet sur le taux d'adsorption du Cs^+ sur la montmorillonite. La spectroscopie MAS NMR du césium-133 indique que le Cs^+ est adsorbé dans l'interfeuillet de la montmorillonite en deux stades et deux milieux: la couche de molécules d'H_2O, dans laquelle le Cs^+ est entouré de molécules de H_2O, et la couche plus près de la surface de l'argile, où le Cs^+ serait plus fortement lié aux atomes d'oxygène formant la base des tétraèdres. Le premier stade de l'adsorption du césium est rapide, et implique à la fois la couche d'atomes d'oxygène et la couche de molécules d'H_2O, dans une proportion de 2:1. La couche de molécules d'H_2O atteint sa capacité immédiatement, et la quantité de césium adsorbée demeure constante pour jusqu'à sept jours. Toutefois, l'adsorption dans la couche d'atomes d'oxygène à la base des tétraèdres augmente après une heure dans un rapport de 5:1 par rapport au taux dans la couche de molécules de H_2O, et demeure inchangée pour le reste de la période d'adsorption.

(Traduit par la Rédaction)

Mots-clés: isolation de déchets nucléaires, montmorillonite, spectroscopie MAS NMR, isotopes ^{133}Cs, ^{29}Si, ^{27}Al, adsorption de césium, échange ionique.

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INTRODUCTION

CANada Deuterium Uranium (CANDU) nuclear reactors have generated approximately 15% of all electricity produced in Canada over the last fifty years, and almost half of the electricity in Ontario currently is being produced by nuclear energy. A number of radioactive elements, including Cs, are produced, either by nuclear fission inside the uranium oxide fuel pellets, or by neutron activation of metals and impurities in the fuel assembly. Most radioactive isotopes of Cs have short half-lives, so that within 10 years, Cs represents less than 1% of the radioactive waste products (Johnson *et al*. 1994). However, ^{135}Cs produced by the fission of ^{235}U has a half-life of 2.3 million years. This is a problem for long-term waste disposal, as Cs is soluble and hence mobile in water (Comans *et al*. 1991, Maiti *et al*. 1989).

At present, spent fuel is stored at sites of nuclear power generation in water-filled pools for at least ten years, before being transferred to reinforced concrete dry-storage containers at the reactor sites, where it can be monitored (AECL 1994). Disposal in a deep geological repository is being considered for long-term storage of high-level nuclear waste in Canada. Spent nuclear fuel, sealed in durable metal containers, would be placed in a network of tunnels and emplacement rooms 500 to 1000 m deep in stable plutonic rock of the Canadian Shield (AECL 1994, Simmons & Baumgartner 1994, Davison *et al*. 1994a, b). Backfill comprised of glacial clay and bentonite surrounding the metal container would buffer and slow the movement of groundwater. Bentonite is a sedimentary rock that contains montmorillonite, and has hydrophilic and swelling properties. Clays minerals in permeable fracture zones in the host plutonic rock that resulted from alteration of the wall rock could adsorb radionuclides, thereby retarding their migration to the surface and hence into the food chain. These clay minerals include kaolinite, vermiculite and montmorillonite (McMurry & Ejeckam 2002).

In this study, the processes controlling the adsorption of Cs onto individual clay minerals were investigated by means of ion-exchange experiments. Changes in the chemical environment of the sorption sites were observed with magic angle spinning – nuclear magnetic resonance spectroscopy (MAS NMR). Ion-exchange was also done at elevated temperatures and pressure to simulate conditions similar to those present at depth in the repository. Radionuclides may also adsorb on biofilms, which are slimy polymers produced by bacteria. Biofilms with negative surface charges can become sorption sites for positively charged ions (Brown & Sherriff 1999) such as Cs^+. In the presence of iron oxides, biofilms may grow rapidly, clogging open pore-spaces and preventing the free movement of groundwater while acting as a sorptive "sponge" or storage site for radionuclides (Stroes-Gascoyne & West 1997).

REVIEW OF RELEVANT WORK

Phyllosilicates have been studied by solid-state NMR (Weiss *et al*. 1990a, b, Kim *et al*. 1996a, b, Kim & Kirkpatrick 1998, Sullivan *et al*. 1998), and sorption isotherms have been found for Cs^+, Sr^{2+} and Ba^{2+} (an analog for Ra^{2+}) onto kaolinite and smectite clays (Westrich *et al*. 1998) at 25°, 50° and 70°C over pH values from 2 to 12. Kim *et al*. (1996b) and Weiss *et al*. (1990a) showed that Cs^+ adsorption in expandable clay minerals occurs at two sites, with Cs^+ being relatively tightly bound to the basal oxygen atoms or loosely bonded to H_2O molecules. In other NMR studies, Kim *et al*. (1996b) concluded that Cs^+ is adsorbed on the basal surfaces and on broken edges of kaolinite clay. Weiss *et al*. (1990b) used variable temperatures to study the motion of Cs adsorbed on clay mineral, and found that there was a motional averaging of Cs between the sites when the samples were saturated to 100% relative humidity (RH). However, after complete dehydration, there was no motional averaging. In addition, a general trend of deshielding of Cs^+ occurred with increased Al^{3+} substitution for Si^{4+} (Weiss *et al*. 1990b), as there are fewer electrons to shield the ^{133}Cs nucleus, giving a more strongly positive position of the peak.

MATERIALS AND METHODS

Materials

Montmorillonite (STx–1), kaolinite (KGa–1) and vermiculite (VTx–1) were obtained from the Source Clay Repository of the Clay Mineral Society (CMS), Missouri, USA. X-ray-diffraction (XRD) results indicate that the bulk sample labeled vermiculite (VTx–1) is not pure and contains a number of other minerals. In order to avoid contamination from the other minerals, grain aggregates of vermiculite were separated from the bulk sample by handpicking, after which the vermiculite aggregates were ground with a mortar and pestle. The XRD pattern of the handpicked grains is consistent with pure vermiculite (Brindley 1980). The kaolinite sample (KGa–1) gave an XRD pattern that is consistent with pure kaolinite (Brindley 1980). Montmorillonite sample STx–1 was found to contain a trace amount of a silica phase, identified by Liang & Sherriff (1993) as cristobalite, which is intergrown and could not be separated.

Ion-exchange experiments

In the initial ion-exchange experiments, 6 g montmorillonite, kaolinite, and vermiculite were each weighed into 500 mL beakers, to which 50 mL of 0.1

M aqueous CsCl solution was added. These were left on a mechanical rocker for six hours, and then the residues were washed and oven-dried at 80°C for 6 hours.

For exchange experiments at higher temperature and pressure, 6 g montmorillonite (STx–1) were weighed into three 500 mL glass beakers and 50 mL of 0.1 M aqueous CsCl solution added and mixed to form a slurry. For the 80°C adsorption experiment, 200 mL of solution were used to compensate for evaporation from the open beakers in the oven. After 6 hours, the beakers were removed from the oven, allowed to cool for 30 minutes, and the clear liquid decanted. The clay residues were washed three times with 50 mL of distilled water and oven-dried at 80°C for 6 hours. In the higher pressure and higher temperature experiment, 150 mL of 0.1 M aqueous CsCl solution was mixed with 6 g montmorillonite and heated in a pressure cooker. The temperature and pressure were recorded each hour for 6 hours before the pressure cooker was allowed to cool for one hour, and the samples washed and dried in the oven. To investigate the adsorption of cesium in the presence of an active bacteria consortium, ion-exchange experiments were conducted by addition of an active bacteria culture in the cesium ion-exchange experiment with montmorillonite using the same weight of cesium plus clay and experimental conditions.

To measure the rate of adsorption of Cs, 1.2 g of montmorillonite (STx–1) were weighed into glass vials and 10 mL of 0.1 M CsCl was added. The first set of triplicate samples (M1–1, M2–1 and M3–1) were shaken to mix and were then filtered immediately (within one minute) using a Buchner filter system with 10-μm filter paper. The vials and filters were washed with 10 mL of distilled water. The clay residues were air-dried for 20 minutes before being oven-dried at 80°C for 6 hours. The second set of the triplicate samples (M1–2, M2–2 and M3–2) were washed after 10 minute of adsorption time, then dried as above. Subsequent triplicate sets were washed after additional 10-minute intervals for the first hour, then after each hour for the next six hours, and then each day for the next seven days.

The oven-drying process is believed to have no effect on the clay mineral structure or the adsorption process. Clay minerals, montmorillonite in particular, have two sources of H_2O; adsorbed water and hydroxyl H_2O. Adsorbed water is lost at about 110°C during heating, and its release is also dependent on the hydration energy. Hydroxyl H_2O is lost from the clay structure when two hydroxyl groups combine to form a H_2O molecule. This occurs at even higher temperature. Dehydroxylation of smectite occurs between 500 and 700°C (Borchardt 1977), although Grim (1968) observed that Ca-dominant montmorillonite showed a gradual loss of cation-exchange capacity on heating to 300°C, and loses its lattice H_2O at 700°C. These temperatures are much higher than the drying temperatures used in our experiment. Therefore, the 80°C drying temperature should not affect the clay-mineral structure or its cation-exchange capacity.

Analytical techniques

Inductively coupled plasma (ICP) – optical emission spectrometry (OES) and atomic absorption (AA) were used to analyze the clay minerals before and after ion exchange. The clays were dried at 110°C overnight, before 0.1 g samples were weighed into 50 mL centrifuge tubes with 8.5 mL HNO_3 and 1.5 mL HF to digest the sample. After mixing, the samples were heated in a CEM model MDS 2100 microwave oven for one hour. Twenty mL of distilled water was added to the cooled acid solution before being heated in the microwave oven for another hour. This solution was then diluted 500-fold with distilled water. Aliquots of each sample were analyzed for Cs using a Varian AA spectrometer, model 300 and for major elements with a Varian Liberty 200 ICP–OES. Structural formulae were calculated with the program FORMULA.

Nuclear magnetic resonance spectroscopy

The MAS NMR spectra were collected using a Bruker AMX500 spectrometer with a 11.7 Tesla magnet. Powdered samples, packed in zirconia rotors, were spun at 5 to 8 kHz in a Doty Scientific MAS probe. The ^{27}Al spectra were obtained at a frequency of 130.3 MHz, with a 15° pulse angle, a relaxation delay of 0.5 s, and from 900 to 6000 scans. The ^{29}Si spectra were obtained at a frequency of 99.3 MHz, a pulse width of 4 μs, relaxation delays of 5 s, and from 150 to 7000 scans. Peak positions for ^{27}Al were measured relative to 1.0 M aqueous solution of aluminum chloride ($AlCl_3$) and for ^{29}Si to tetramethylsilane (TMS). For ^{133}Cs, spectra were obtained at a frequency of 65.6 MHz, and a pulse width of 1 μs, with a relaxation delay of 1 s, and between 700 and 8000 scans. Relative intensities of ^{133}Cs peaks were obtained by physically cutting out and weighing the peaks areas and associated sidebands using hard copies of the spectra. This technique gave more consistent results for the broad overlapping ^{133}Cs peaks than computer simulations of the spectra. These values were converted to weight percent Cs using the results of the chemical analyses.

RESULTS AND DISCUSSION

Kaolinite, of ideal formula $Al_2[Si_2O_5](OH)_4$, is a 1:1 type of clay mineral with a low cation-exchange capacity (CEC) owing to the lack of exchangeable interlayer cations. Montmorillonite, of ideal formula $(Ca,Na)_x(Al,Mg,Fe)_2[(Si,Al)_4O_{10}](OH)_2 \bullet nH_2O$, and vermiculite, of ideal formula $(Mg,Ca)_x(Mg,Al,Fe)_3[(Si,Al)_4O_{10}](OH)_2 \bullet n(H_2O)$ are 2:1 clay minerals. In each group of the 2:1 layer minerals, the clays can be dioctahedral, with two trivalent cations in the octahedral layer, or trioctahedral, with three divalent cations. Tetrahedrally coordinated Al^{3+} may partially replace Si^{4+}, creating an excess negative charge that can be neutralized by adsorption of cations such as Ca^{2+}, Na^+, and Mg^{2+}. The adsorbed cations for montmorillonite may provide insufficient positive charge to completely neutralize the negative charge, leaving it susceptible to partial or a complete ion-exchange (Faure 1998). Vermiculite has a higher negative charge in the layer of tetrahedra owing to a higher concentration of Al^{3+}; Mg^{2+} is the dominant exchangeable cation in the interlayer (Deer *et al.* 1998).

These differences in cation-exchange capacity were reflected in the adsorption of Cs shown by the clays (Table 1). Montmorillonite adsorbed about 6% Cs, and increases in temperature and pressure had no significant effect. This result allows the sorption experiments at room temperature and pressure to be used for the prediction of the processes occurring under the temperature and pressure conditions expected in an underground repository. A microbial community, which would be present in the repository, slightly enhanced the adsorption of Cs to a total of 7.5 wt% owing to the formation of a polysaccharide biofilm (Ejeckam & Sherriff 2003, Stroes-Gascoyne *et al.* 2000).

In the ion-exchange experiment designed to measure the rate of adsorption, the amount of Cs adsorbed by montmorillonite in the first minute was about 4 wt%, and it remained at this level for the first hour. At the end of one hour, the amount of cesium adsorbed increased to about 6 wt% and remained at this level for the remaining seven days of the experiment (Fig. 1).

Vermiculite (VTx–1), with only 0.04 atoms per formula unit (*apfu*) of Ca^{2+}, compensated for 0.33 *apfu* Cs^+ adsorbed with losses of Na^+ (0.11 *apfu*) and Mg^{2+} (1.1 *apfu*). Insufficient Cs^+ was adsorbed on vermiculite to compensate for the Mg^{2+} lost (Table 2, columns 1A and B). Kaolinite adsorbed very little Cs^+ (0.04 *apfu*), with little accompanying change in composition (Table 2, columns 2A and B). In contrast, montmorillonite, which adsorbed the highest amount of Cs (0.39 *apfu*), showed reductions in Ca^{2+} from 0.23 to 0.02 *apfu*, Mg^{2+} from 0.54 to 0.45 *apfu*, and Na^+ from 0.11 to 0.03 *apfu*. Montmorillonite lost 91% and 75% of its initial Ca^{2+} and Na^+ concentration respectively, which are replaced by Cs^+ (Table 2, columns 3A and B).

TABLE 1. AMOUNT OF Cs ADSORBED BY CLAY MINERALS

Mineral	Conditions	Cesium (wt%)
Montmorillonite (STx-1)	RT, P	6.1 ± 0.2
Montmorillonite (STx-1)	80°C	6.6 ± 0.03
Montmorillonite (STx-1)	107°C, 1.5 bars	6.2 ± 0.2
Montmorillonite (STx-1) + active bacteria*	RT, P	7.5 ± 0.4
Vermiculite (VTx-1)	RT, P	3.8 ± 0.0
Kaolinite (KGa-1)	RT, P	0.8 ± 0.0

* Ejeckam & Sherriff (2003).

The ^{27}Al and ^{29}Si spectra of montmorillonite, vermiculite and kaolinite can be related to their chemical compositions. The ^{27}Al spectrum of montmorillonite consists of a single peak due to octahedral Al at 2.3 ppm. The expected peak due to the small amount of Al calculated to be in the tetrahedral site could be hidden by the broad spinning sidebands at about 60 ppm (Table 3, Fig. 2). The single ^{29}Si peak at –93.5 ppm (Table 4, Fig. 3) shows that there was insufficient Al in the tetrahedral site to produce disorder (Table 2). A broad peak at –111 ppm is attributed to the presence of cristobalite (Liang & Sherriff 1993) or amorphous silica. Both the ^{27}Al and ^{29}Si peaks shifted to lower frequency with Cs adsorption, indicating increased shielding. The change in ^{29}Si peak position increased from 0.2 ppm to 0.5 ppm with adsorption at 80°C, and to 0.6 ppm for the higher pressure and temperature adsorption (Table 4, Fig. 3).

The ^{27}Al MAS NMR spectrum of vermiculite consists of a large peak at 66.4 ppm due to Al in tetrahedral configuration, and a small peak at 8.8 ppm due to Al in octahedral coordination (Table 3, Fig. 4). This spectrum does not agree with the calculated formula for vermiculite, in which all Al is in tetrahedral coordination (Table 2). The ^{VI}Al peak shows a decrease of 0.6 ppm in

TABLE 2. CHEMICAL COMPOSITION AND STRUCTURAL FORMULA OF CLAY MINERALS (A) BEFORE AND (B) AFTER Cs ADSORPTION

	1A	1B	2A	2B	3A	3B
SiO_2 wt%	35.59	40.29	34.28	35.87	51.38	50.71
Al_2O_3	5.80	5.37	42.61	43.45	15.75	15.03
TiO_2	0.89	0.91	n.d.	n.d.	n.d.	n.d.
Fe_2O_3	5.77	5.58	0.04	0.05	0.53	0.41
MnO	0.04	0.03	0.00	0.00	n.d.	n.d.
MgO	21.01	17.09	0.02	0.0	2.46	1.99
CaO	0.22	0.42	0.02	0.01	1.49	0.11
Na_2O	0.36	0.01	0.09	0.07	0.37	0.11
K_2O	5.43	5.22	0.04	0.03	0.10	0.08
CsO_2	0.00	4.87	0.00	0.81	0.00	6.10
Total	76.11	80.51	81.05	80.28	72.09	74.53
Si *apfu*	5.79	6.37	3.81	3.86	7.52	7.64
^{IV}Al	1.11	1.00	0.19	0.14	0.48	0.37
^{VI}Al	-		5.39	5.36	2.24	2.30
Ti	0.11	0.11	0.00	0.00	n.d.	n.d.
Fe^{3+}	0.78	0.74	0.00	0.00	0.05	0.05
Mg	5.09	4.03	0.00	0.00	0.54	0.45
Mn^{2+}	0.01	0.00	0.00	0.00	n.d.	n.d.
Cs	0.00	0.33	0.00	0.04	0.00	0.39
Ca	0.04	0.07	0.00	0.00	0.23	0.02
Na	0.11	0.00	0.02	0.02	0.11	0.03
K^+	1.13	1.05	0.01	0.00	0.02	0.02
H^+	4.00	4.00	4.00	4.00	4.00	4.00
CATSUM	14.17	13.71	9.42	9.42	11.18	11.25
O	22.00	22.00	18.00	18.00	22.00	22.00

Note: 1 vermiculite, 2 kaolinite, 3 montmorillonite.

peak position with Cs adsorption, indicating an increase in the nuclear shielding by electrons, whereas the ^{IV}Al peak remains constant within the error of the measurement. Vermiculite has three ^{29}Si MAS NMR peaks, at –84.4, –88.4 and –92.8 ppm, which shift to –85.6, –88.7 and –92.8 ppm after Cs adsorption (Table 4, Fig. 5). The three peaks, assigned to Q^3(2Al), Q^3(1Al) and Q^3(0Al) respectively (the superscript refers to the number of adjacent tetrahedrally coordinated atoms), have been previously interpreted to be due to disorder caused by 16% of the tetrahedral sites containing Al (Thompson 1984). There was a decrease in the extent of peak shift due to increased shielding, with Cs adsorption from 1.2 ppm for the Si(2Al 1Si) site to 0.3 ppm for the Si(1Al 2Si) site. The peaks due to the Si(3Si) do not shift with Cs adsorption. This difference in shift indicates that Cs^+ is preferentially adsorbed to the oxygen atoms of the SiO_4 sites adjacent to Al, which have the highest local charge-imbalance.

The single peaks due to octahedral ^{27}Al and tetrahedral ^{29}Si of kaolinite agree with the calculated formula that there is less than 5% Al in the tetrahedral sites. Both ^{27}Al and ^{29}Si NMR peaks exhibit the opposite effect on Cs^+ adsorption to montmorillonite and vermiculite, with both ^{27}Al and ^{29}Si peaks becoming slightly less shielded (Table 3, 4). As only 0.04 *apfu* Cs was adsorbed by kaolinite (Table 2), this deshielding may be due to expansion of the clay as a result of the adsorption of H_2O molecules during the experiments.

Cesium-133 has a natural abundance of 100%, a spin number (I) of 7/2, but a very small electric quadrupole moment (Q). Chemical shifts range from +100 to –500

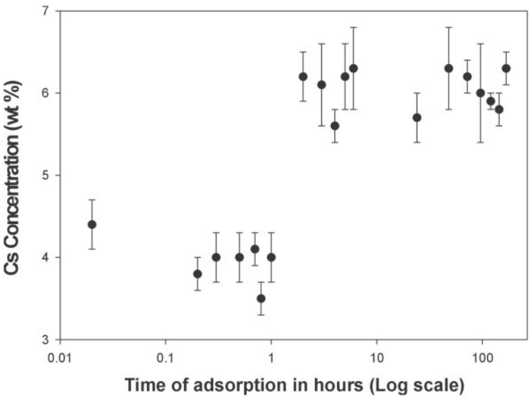

FIG. 1. Rate of Cs adsorption by montmorillonite.

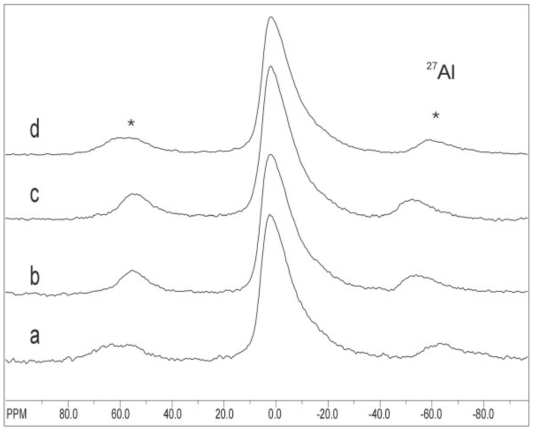

FIG. 2. ^{27}Al spectra of montmorillonite, (a) before Cs adsorption, and after Cs adsorption at (b) ambient conditions, (c) 80°C, and (d) 107°C, 1.5 bar. * Indicates spinning sidebands.

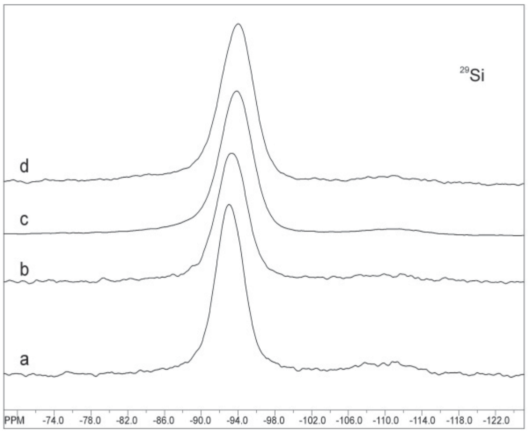

FIG. 3. ^{29}Si spectra of montmorillonite (a) before Cs adsorption, and after Cs adsorption at (b) ambient conditions, (c) 80°C, and (d) 107°C, 1.5 bar.

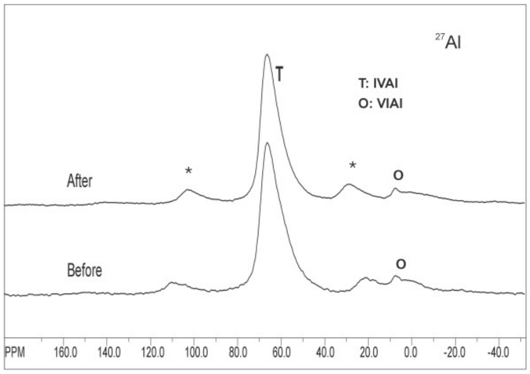

FIG. 4. ^{27}Al spectra of vermiculite before and after Cs adsorption. * Indicates spinning sidebands.

ppm relative to a 0.1M aqueous solution of CsCl, although Hartman *et al.* (1998) found values outside this range owing to unpaired electrons. The peak positions of ^{133}Cs adsorbed in clays are dependent on the absolute humidity or water content of the air in the NMR laboratory (Kim *et al.* 1996b). Variation in humidity is a major problem in Winnipeg, with completely different spectra being obtained in the –30°C winter with extremely low absolute humidity, even in the laboratory at 25°C, compared to +30°C summer temperatures with higher absolute humidity (Fig. 6). At –30°C, 1 kg of air can only hold 0.3 g of water vapor, whereas at +30°C it can hold 26.5 g (Tarbuck & Lutgens 2000). The ^{133}Cs MAS NMR spectrum of montmorillonite obtained in March, when winter conditions still prevailed, gave a noisy and unresolved spectrum. However, when the same sample was run in July, it gave a much better resolved spectrum, with two distinguishable peaks (Fig. 6). The ^{133}Cs spectra used here were obtained in the summer, but the peak positions should not be treated as absolute values, as there is rarely high absolute humidity in Winnipeg.

The initial ^{133}Cs MAS NMR spectrum of kaolinite consists of three small peaks at 213 ppm, –21.4 ppm and –50.7 ppm, which all disappear after the sample is washed for a second time, indicating a weak surficial adsorption. The peak at 213 ppm is due to solid CsCl.

The ^{133}Cs spectrum of vermiculite has one broad peak at 42.5 ppm, with large spinning sidebands. This is similar to the peak found by Weiss *et al.* (1990a) at 55.1 ppm, which they assigned to dehydrated Cs in the interlayer sites, tightly bound to the basal oxygen atoms because of the large negative charge on the layer of tetrahedra.

The ^{133}Cs MAS NMR spectrum of montmorillonite after ion exchange at room temperature and pressure has two peaks (Fig. 7), the largest at –28.4 ppm (Peak 1), with a peak width of about 800 Hz, and a smaller one at 23.5 ppm (Peak 2), with a peak width of about 1300 Hz. The frequency of Peak 1 was –26.5 ppm for the sample exchanged at 80°C and –24.5 ppm after higher temperature and pressure exchange. Peak 2 was at a constant frequency. The amount of Cs represented by each peak was calculated from the relative intensity of the peaks and the chemical composition (Fig. 8). The amount of Cs represented by Peak 2 remains constant at about 1 wt%, whereas the amount shown by Peak 1 increased after 1 hour of adsorption time from 2.5 to 5.5 wt% (Fig. 8).

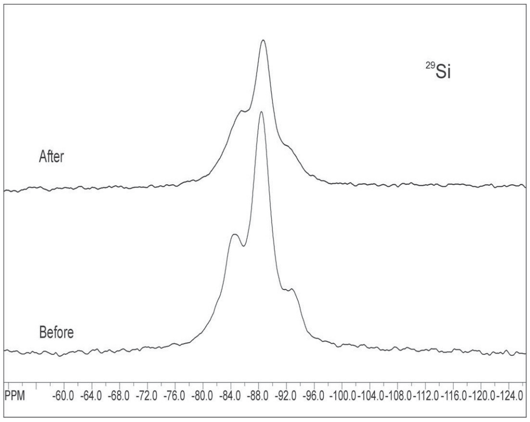

FIG. 5. ^{29}Si spectra of vermiculite before and after Cs adsorption.

Sullivan *et al.* (1998) and Weiss *et al.* (1990a, b) proposed that when montmorillonite is hydrated, cations adsorbed in the interlayer are separated from the clay surfaces by H_2O molecules and able to move freely throughout the interlayer. They may exchange rapidly between a surface-bonded and hydrated species. Kim *et al.* (1996b) reported that Cs^+ adsorption in illite occurs at two locations, CS1 and CS2, which are equivalent to the basal oxygen layer and the layer of H_2O molecules, respectively. The chemical shift of Cs in the CS1, but not CS2, changed with composition of the clay

TABLE 3. ^{27}Al MAS NMR PEAK POSITIONS BEFORE AND AFTER ION EXCHANGE

Mineral	Before	After	^{27}Al site coordination
Kaolinite (KGa-1)	2.9 ppm	3.1 ppm	Octahedral
Montmorillonite (STx-1)	2.3 ppm	1.5 ppm	Octahedral
Montmorillonite (STx-1) at 80°C	2.3 ppm	1.9 ppm	Octahedral
Montmorillonite (STX-1) at 107°C, 1.5 bar	2.3 ppm	1.9 ppm	Octahedral
Vermiculite (VTx-1)	66.4 ppm	66.6 ppm	Tetrahedral
	8.6 ppm	8.0 ppm	Octahedral

± 0.1 ppm.

TABLE 4. ^{29}Si MAS NMR CHEMICAL SHIFTS BEFORE AND AFTER ION EXCHANGE

Mineral	^{29}Si chemical shift (ppm)			
	Before	After	Change	Assignment
Montmorillonite (STx-1)	-93.5	-93.7	-0.2	Q^3(0Al)
Montmorillonite (STx-1) at 80°C	-93.5	-94.0	-0.5	Q^3(0Al)
Montmorillonite (STx-1) 107°C, 1.5 bars	-93.5	-94.1	-0.6	Q^3(0Al)
Kaolinite (KGa-1)	-91.4	-91.1	+0.3	Q^3(0Al)
Vermiculite (VTx-1)	-84.4	-85.6	-1.2	Q^3(2Al)
	-88.4	-88.7	-0.3	Q^3(1Al)
	-92.8	-92.8	0.0	Q^3(0Al)

± 0.1 ppm.

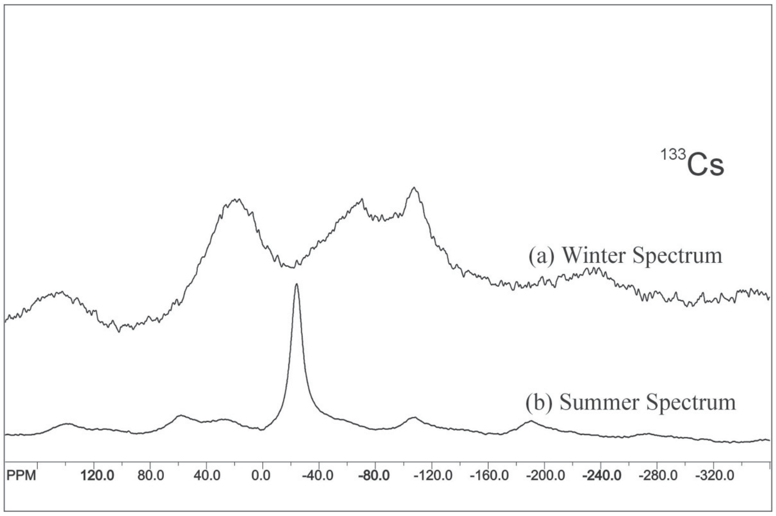

FIG. 6. ^{133}Cs spectra of the same montmorillonite sample obtained in (a) winter and (b) summer.

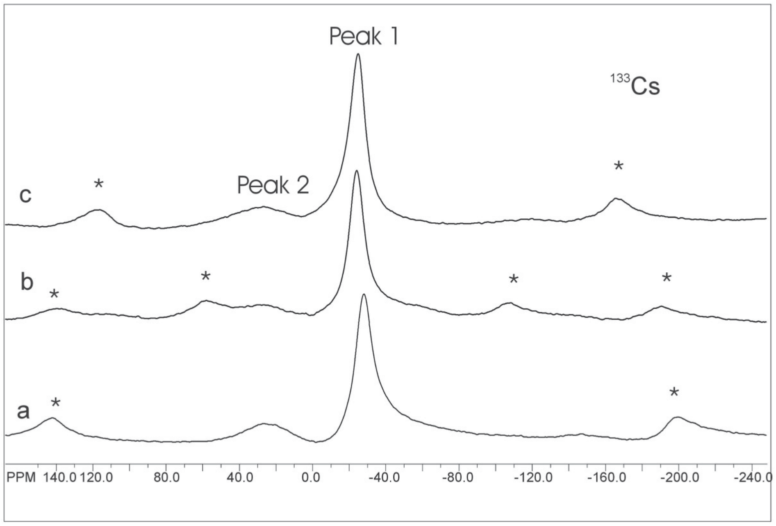

FIG. 7. ^{133}Cs MAS NMR spectrum of montmorillonite after Cs absorption at (a) RTP, (b) 80°C, and (c) 107°C and 1.5 bars. * Indicates spinning sidebands.

minerals, becoming more shielded with increasing Si:Al ratio (Kim *et al.* 1996b). The CS1 peaks were more negative and narrower than those from the CS2 sites, showing Cs^+ to be more tightly bonded (Kim *et al.* 1996b). In this study, Peak 1 is the more shielded of the two peaks, and so was assigned to sites bonded to the basal oxygen atoms of the layer of tetrahedra. As Peak 2 is less shielded, it was assigned to the diffuse Cs^+ atoms surrounded by H_2O molecules. During initial adsorption on montmorillonite, Cs^+ enters the basal oxygen bonded and hydrated sites in a ratio of about 2:1. After about one hour, this ratio increases to 5:1, which represents the final stable configuration (Fig. 8). This multisite adsorption model, also proposed by Comans *et al.* (1991), could explain the variable rate of adsorption of Cs in montmorillonite.

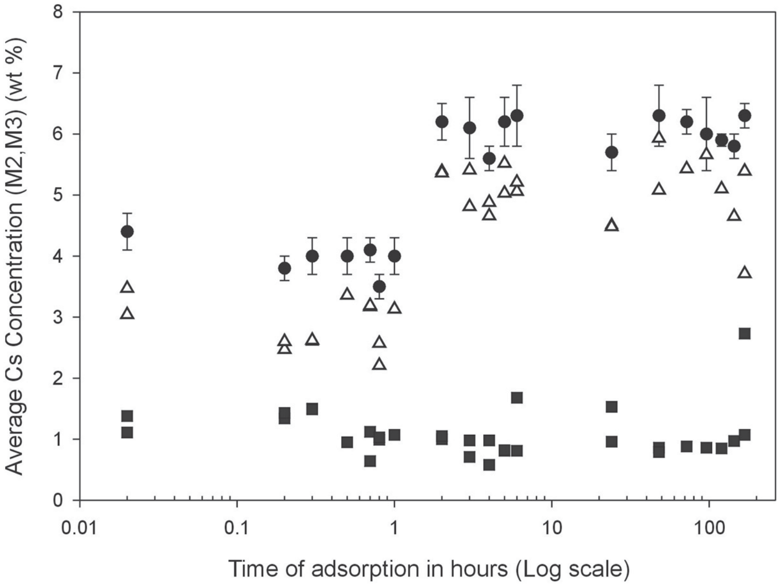

FIG. 8. Amount of Cs adsorbed at two sites in the interlayer of montmorillonite, as calculated from the ^{133}Cs MAS NMR, Peak 1 at the layer of basal oxygen atoms (open triangles) and Peak 2 at the layer of H_2O molecule (solid squares). Solid circles with error bars show total amounts.

Implications for nuclear waste

This study is important to the long-term storage of radioactive waste in a deep geological repository because clay minerals are an important component of materials in the design of the repository. Clay minerals are also products of alteration, either from hydrothermal alteration or from the long-term interaction of groundwater with the granitic host-rock. The waste in a metal container will be placed in storage room cut in the granite, and backfilled with bentonite and crushed granite. Should the metal container be breached, the radionuclides could escape from the vault, and be transported by the groundwater through the permeable fractures to the surface. In this study, montmorillonite clay present in the engineered barrier and the fractures has been shown to be able to adsorb and remove radioactive cesium from solution. This study shows that the majority of Cs^+ adsorbed by montmorillonite (a major component of bentonite) becomes strongly bonded rapidly to the basal oxygen atoms of the silicate tetrahedra. This finding is important because it indicates that Cs^+ will be strongly held. Further research would be necessary to measure the rate of desorption of cesium.

CONCLUSIONS

Cesium is adsorbed at several sites of the clay minerals, on the surface of kaolinite and in the interlayer of 2:1 clay minerals, with kaolinite adsorbing less Cs^+ than vermiculite and montmorillonite. Adsorption is rapid on all clay minerals, and takes less than one minute. The adsorption of Cs^+ on montmorillonite occurs in two stages. The first stage involves the rapid uptake of Cs by attachment to the oxygen atoms of the H_2O molecules in the interlayer, and the second stage involves the slower process that continues as Cs^+ attaches to the basal atoms of oxygen of the aluminosilicate tetrahedra. Elevated temperature and pressure do not affect the amount of Cs adsorbed.

Cesium adsorption caused the environment of adjacent Si and Al atoms to become more shielded, causing negative shifts in ^{27}Al and ^{29}Si MAS NMR spectra of adjacent nuclei. Only Si sites with adjacent Al atoms were affected for vermiculite.

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