

## Cesium Ion Exchange on Synthetic Birnessite ( $\text{Na}_{0.35}\text{MnO}_2 \cdot 0.6\text{H}_2\text{O}$ )

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Uptake of  $\text{Cs}^+$  on poorly crystalline layered manganese oxide (Na birnessite) is reported. Distribution coefficients ( $K_d$ ) showed significant uptake of  $\text{Cs}^+$  under acidic (pH 2.4) or basic conditions (pH 10.2). The uptake of  $\text{Cs}^+$  takes place with release of  $\text{Na}^+$  into the solution confirming ion exchange. The maximum uptake of  $\text{Cs}^+$  was  $2.0 \text{ mmol g}^{-1}$  at pH 10.2.

The principal long-term problem caused by nuclear accidents is the contamination of the environment with radioactive  $^{137}\text{Cs}$ , because cesium is very volatile and can be carried long distances.<sup>1</sup> Decontamination of the environment, humans, and animals is possible with the use of cesium-selective materials either by dispersion, for example, in water or soil, or by ingestion by humans and animals.<sup>1</sup> Different methods such as ion exchange, precipitation, solidification, and stabilization can be applied for remediation or treatment of soil and groundwater contaminated by  $^{137}\text{Cs}$ .<sup>2</sup> Among them, ion exchange using different materials is the most studied.<sup>2</sup> Much attention has been focused toward the uptake of  $\text{Cs}^+$  on zeolites,<sup>3–6</sup> clay minerals,<sup>1,2,7–10</sup> adsorbents based on copper ferrocyanide,<sup>11</sup> and ammonium molybdophosphate–calcium alginate.<sup>5,12</sup> Titanosilicate  $[(\text{Na},\text{K})_2\text{Si}_5\text{TiO}_{13} \cdot n\text{H}_2\text{O}]^{13}$  and layered metal sulfide  $(\text{K}_{2-x}\text{Mn}_x\text{Sn}_{3-x}\text{S}_6)^{14}$  had also been studied for uptake of  $\text{Cs}^+$  from aqueous solutions.

Manganese oxides with layered and tunnel structures, consisting of  $\text{MnO}_6$  octahedral units shared by corners or edges, exhibit excellent cation-exchange properties.<sup>15–17</sup> Synthetic crystalline Na- and K-birnessites (layered structure) were more highly efficient for removal of trace radiocobalt than radiocesium from aqueous solutions.<sup>16</sup> Synthetic hollandite ( $2 \times 2$ ) and todorokite ( $3 \times 3$ ) materials were also effective for uptake of trace radiocesium.<sup>17</sup> Since the syntheses of hollandite and todorokite are usually complicated and difficult, this limits inexpensive production on a large scale. Na birnessite is a precursor, which is easily synthesized at low cost. If Na birnessite shows selectivity for  $\text{Cs}^+$ , it will be a potential candidate for  $\text{Cs}^+$  sequestration. Inorganic materials selective for  $\text{Cs}^+$  are particularly desirable, because the materials can be used for remediation of nuclear wastes and groundwater contaminated by  $^{137}\text{Cs}$ .<sup>14</sup>

Na birnessite with a crystallite size of less than 100 nm calculated using Scherrer's equation from powder X-ray diffraction exists as a poorly crystalline phase.<sup>18</sup> The aim of this study is to investigate the uptake of  $\text{Cs}^+$  from aqueous solutions on poorly crystalline synthetic Na birnessite.

Na birnessite was synthesized as described in the literature.<sup>19</sup> A  $300 \text{ cm}^3$  of  $\text{MnCl}_2$  solution was prepared by dissolving reagent grade  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (19.8 g, 0.10 mol Mn) in a  $2\text{-dm}^3$  beaker. A solution ( $660 \text{ cm}^3$ ) containing 16.0 g of NaOH (0.40 mol) and  $60 \text{ cm}^3$  of  $\text{H}_2\text{O}_2$  (30%) was quickly poured into the

$\text{MnCl}_2$  solution under vigorous stirring at room temperature. The reaction was complete with effervescence, and a black-brown suspension was obtained. After stirring for 1 h, the suspension was filtered, washed with water several times, and air-dried at room temperature. The resultant material is abbreviated as Na birnessite.

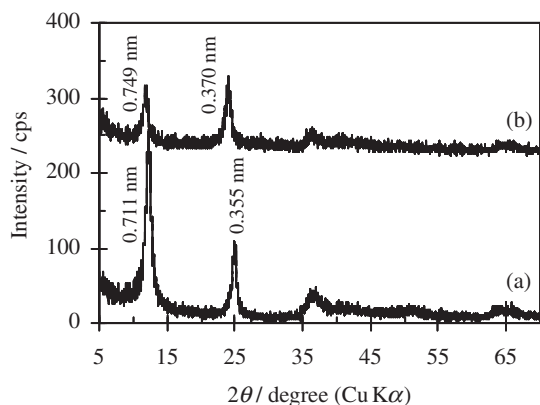
Powder X-ray diffraction (XRD) patterns of the material were collected using an X-ray diffractometer (RINT 2100; Rigaku Corp.), operating at 40 kV voltage and 24 mA current, with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54052 \text{ \AA}$ ). Thermal decomposition of the material was carried out in a TG-DTA (TG DTA 2000; MAC Science Co., Ltd.) in a flowing air atmosphere ( $100 \text{ cm}^3 \text{ min}^{-1}$ ). For chemical analysis of Na and Mn, material (50 mg) was dissolved in  $5 \text{ mol dm}^{-3}$  HCl ( $5 \text{ cm}^3$ ) containing few drops of  $\text{H}_2\text{O}_2$ . The solution was analyzed by atomic absorption spectrometry (AAAnalyst 300; Perkin-Elmer). The mean oxidation state of manganese in the material was determined by oxalic acid method as described.<sup>19</sup>

Distribution coefficients ( $K_d$ ) of  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  were determined by a batch method using a mixed solution of LiCl, KCl, RbCl, and CsCl (0.1 or  $1.0 \text{ mmol dm}^{-3}$  each). Material (0.25 g) was dispersed in a solution ( $25 \text{ cm}^3$ ) with frequent shaking for 2 d at room temperature. The concentration of each cation in the solution before and after uptake of cations was determined by atomic absorption spectrometry. The  $K_d$  value was calculated as follows:  $K_d (\text{cm}^3 \text{ g}^{-1}) = \text{cation uptake} (\text{mmol g}^{-1}) / \text{equilibrium cation concentration} (\text{mmol dm}^{-3})$ .

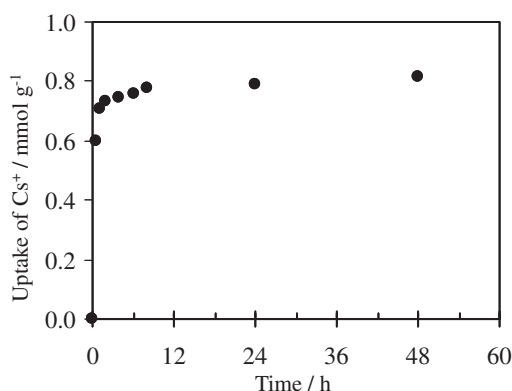
The effect of time on uptake of  $\text{Cs}^+$  was determined by dispersing the material (0.50 g) in  $1 \text{ mmol dm}^{-3}$  CsCl solution ( $500 \text{ cm}^3$ ) with stirring using a magnetic stirrer, and aliquots ( $5 \text{ cm}^3$ ) were sampled at different intervals of time (final pH 10.1). To elucidate effects of pH, material (0.10 g) was dispersed in  $2.0 \text{ mmol dm}^{-3}$  CsCl ( $100 \text{ cm}^3$ ) at different pH values 2.5–10.7. The solution pH was adjusted using  $1 \text{ mmol dm}^{-3}$  HCl or NaOH. For uptake isotherms, material (0.10 g) was dispersed in  $100 \text{ cm}^3$  of CsCl solution at different concentration (0.25– $20.0 \text{ mmol dm}^{-3}$ ). The final pH was 10.0–10.2. For desorption of  $\text{Cs}^+$  from  $\text{Cs}^+$ -exchanged material, material (0.10 g) was dispersed in  $0.10 \text{ mol dm}^{-3}$  HCl, KCl, KOH,  $\text{NH}_4\text{Cl}$ , or  $\text{NH}_4\text{OH}$  solution ( $100 \text{ cm}^3$ ).

The compositional formula of Na birnessite can be written as  $\text{Na}_{0.35}\text{MnO}_2 \cdot 0.6\text{H}_2\text{O}$  based on the chemical analysis data (Na = 7.4 wt %, Mn = 50.1 wt %, and  $\text{H}_2\text{O}$  = 10.1 wt %). The water content was evaluated from the mass loss of TG curve at  $200^\circ\text{C}$ . The mean oxidation state of manganese in Na birnessite was determined to be +3.67.

The powder XRD pattern of Na birnessite showed poorly crystalline material (Figure 1a). The material exhibited two major diffraction peaks with  $d$  values of 0.711 and  $0.355 \text{ nm}$ , indicating the formation of birnessite with a basal spacing of  $0.711 \text{ nm}$  along the  $c$  axis, similar to that reported for the layered



**Figure 1.** XRD patterns of Na birnessite (a) and after uptake of  $\text{Cs}^+$  (b).



**Figure 2.** Effect of time on uptake of  $\text{Cs}^+$  with Na birnessite.

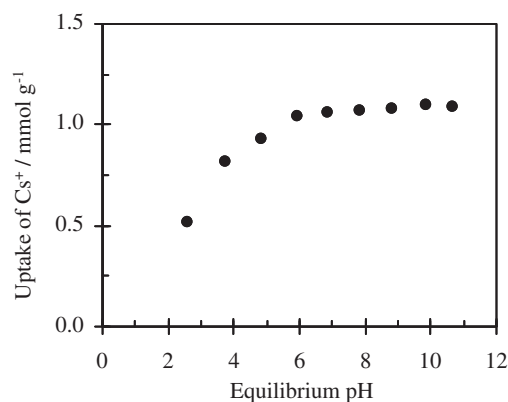
structure of birnessite previously.<sup>19</sup> The crystallite size of Na-birnessite calculated from Scherrer's equation was 12.8 nm. The uptake of  $\text{Cs}^+$  on the Na birnessite was performed by stirring 0.10 g of the material in 100  $\text{cm}^3$  of 20  $\text{mmol dm}^{-3}$  CsCl solution for 1 d; uptake of  $\text{Cs}^+$  (2.0  $\text{mmol g}^{-1}$ ) was followed by the release of  $\text{Na}^+$  (2.1  $\text{mmol g}^{-1}$ ) into the solution. The XRD pattern showed that the basal spacing of the product increased from 0.711 to 0.749 nm after  $\text{Na}^+$  (ionic radius 0.10 nm) located in the interlayer space was replaced by  $\text{Cs}^+$  (ionic radius 0.17 nm) (Figure 1b).

The uptake rate of  $\text{Cs}^+$  was studied to assess the time required for the system to attain equilibrium. The results from 1  $\text{mmol dm}^{-3}$  CsCl solution at volume to mass ratio ( $V/m$ ) of 1  $\text{dm}^3 \text{g}^{-1}$  is shown in Figure 2. Initial uptake rate of  $\text{Cs}^+$  was rapid with 0.70  $\text{mmol g}^{-1}$  within 1 h (88% uptake). It was apparent that equilibrium was almost achieved within 24 h. Prolonged standing up to 48 h resulted in a little change in the uptake of  $\text{Cs}^+$ . The  $\text{Cs}^+$  replaced  $\text{Na}^+$  after contact of Na birnessite with the solution. The higher affinity of the Na birnessite for  $\text{Cs}^+$  over the  $\text{Na}^+$  can be considered the main reason for the uptake of  $\text{Cs}^+$ . The XRD patterns of the products after ion exchange during 1, 4, and 24 h reactions were similar to Figure 1b. The  $\text{K}_{2x}\text{Mn}_x\text{Sn}_{3-x}\text{S}_6$ , which is a layered material with  $\text{K}^+$  as exchangeable cation, exhibited an extremely fast uptake of  $\text{Cs}^+$  from relatively low concentration (1  $\text{mg dm}^{-3}$ ) at  $V/m$  ratio of 1  $\text{dm}^3 \text{g}^{-1}$  in 5 min.<sup>14</sup> Ammonium molybdophosphate

**Table 1.**  $K_d$  values of cations in solution<sup>a</sup>

Solution <sup>a</sup> / $\text{mmol dm}^{-3}$	$K_d/\text{cm}^3 \text{g}^{-1}$				pH
	$\text{Li}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$	
0.10	na	980	4100	4300	2.4
0.10	$>10^5$	$>10^5$	$>10^5$	$>10^5$	10.2
1.0	na	150	600	600	2.4
1.0	440	4150	3350	1900	10.1

<sup>a</sup>(LiCl, NaCl, KCl, RbCl, and CsCl), na: no adsorption.

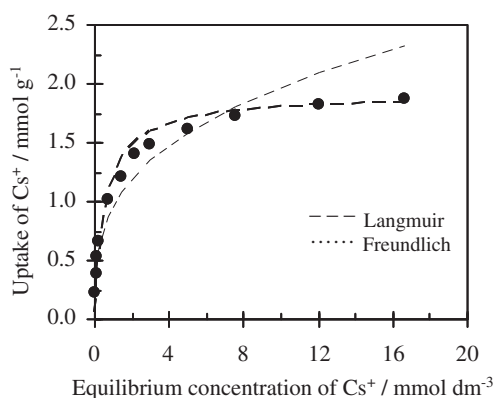


**Figure 3.** Effect of pH on uptake of  $\text{Cs}^+$  with Na birnessite.

(AMP)-calcium alginate composites were also effective for uptake of  $\text{Cs}^+$  from 10  $\text{mg dm}^{-3}$  solution at  $V/m$  ratio of 100  $\text{cm}^3 \text{g}^{-1}$  attaining equilibrium in 3 h.<sup>5</sup>

The affinity of a material for a cation is usually defined in terms of distribution coefficient,  $K_d$  ( $\text{cm}^3 \text{g}^{-1}$ ), which is a mass-normalized partition coefficient between the solid phase and solution phase. The  $K_d$  is an experimental value obtained through cation concentration measurements before and after uptake of cation occurs. The  $K_d$  values of cations on Na birnessite are summarized in Table 1. A high  $K_d$  value of 4300  $\text{cm}^3 \text{g}^{-1}$  (98% uptake) for  $\text{Cs}^+$  was obtained in 0.10  $\text{mmol dm}^{-3}$  mixed solution under acidic conditions (pH 2.4), and subsequently the uptake of  $\text{Cs}^+$  increased to nearly 100% under basic conditions (pH 10.2). The  $K_d$  value of  $\text{Cs}^+$  decreased as the concentration of cations in mixed solution was increased. A  $K_d$  value of 600  $\text{cm}^3 \text{g}^{-1}$  (80% uptake) for  $\text{Cs}^+$  was obtained in 1.0  $\text{mmol dm}^{-3}$  solution at pH 2.4. At higher pH 10.1, the uptake of  $\text{Cs}^+$  was found to be higher with a  $K_d$  value of 1900  $\text{cm}^3 \text{g}^{-1}$  (95% uptake). Dyer et al.<sup>16</sup> determined the  $K_d$  of  $^{137}\text{Cs}$  in the concentration range of  $2.0 \times 10^{-8}$ – $3.7 \times 10^{-7}$   $\text{mol dm}^{-3}$  with crystalline sodium birnessite and found that the uptake decreased with an increase in solution pH. Their sodium birnessite was a well crystalline material synthesized by using  $\text{MnCl}_2$ ,  $\text{NaOH}$ , and  $\text{Mg}(\text{MnO}_4)_2 \cdot 6\text{H}_2\text{O}$ .<sup>16</sup>

The effect of pH on uptake of  $\text{Cs}^+$  with Na birnessite using 2  $\text{mmol dm}^{-3}$  CsCl solutions at different pH values of 2.5–10.5 was conducted (Figure 3). The uptake increased with an increase of solution pH, becoming almost constant at pH 6.0–10.5. The material displayed  $\text{Cs}^+$  uptakes of 0.5 and 1.1  $\text{mmol g}^{-1}$  at pH values of 2.5 and 10.5, respectively. The uptake of  $\text{Cs}^+$  under acidic conditions can be attributed to a two-step process involving the initial formation of the  $\text{H}^+$ -form birnessite and the subsequent uptake of  $\text{H}^+$  by  $\text{Cs}^+$  ions.<sup>16</sup> The  $d$  values



**Figure 4.** Uptake isotherm of  $\text{Cs}^+$  with Na birnessite.

calculated from the XRD patterns of the products at pH 2.5, 6.9, and 10.0 were 0.732, 0.743, and 0.745 nm, respectively. Layered metal sulfide ( $\text{K}_{2x}\text{Mn}_x\text{Sn}_{3-x}\text{S}_6$ ) also showed good performance for the uptake of  $\text{Cs}^+$  from acid and alkaline solutions with a maximum uptake of  $1.7 \text{ mmol g}^{-1}$  at pH 7.<sup>14</sup> The maximum uptake of  $\text{Cs}^+$  from  $0.1 \text{ mol dm}^{-3}$  solution ( $\text{CsCl} + \text{CsOH}$ ) with  $\text{H}^+$ -form birnessite was found to be  $2.0 \text{ mmol g}^{-1}$  at pH 11.0.<sup>15</sup>

The uptake isotherm is important to describe the uptake behavior of  $\text{Cs}^+$  on the Na birnessite. The relation between the uptake of  $\text{Cs}^+$  on the material and the equilibrium concentration in the solution is usually described by the Langmuir and the Freundlich models. The isotherm for uptake of  $\text{Cs}^+$  was determined at equilibrium pH 10.1, and the experimental data are presented in Figure 4 with their fittings to the Langmuir and the Freundlich models. The data could not be fitted by the Freundlich model (correlation coefficient,  $R^2 = 0.962$ ) but was fitted by the Langmuir model ( $R^2 = 0.998$ ):  $q = (q_m b C_e) / (1 + b C_e)$ , where  $q$  ( $\text{mmol g}^{-1}$ ) is the uptake amount of  $\text{Cs}^+$  at the equilibrium concentration  $C_e$  ( $\text{mmol dm}^{-3}$ ),  $q_m$  ( $\text{mmol g}^{-1}$ ) is the maximum uptake capacity of the material,  $b$  ( $\text{dm}^3 \text{ mmol}^{-1}$ ) is the Langmuir constant related to the free energy of the uptake. The results indicated that the material was very efficient for  $\text{Cs}^+$  uptake from the low initial concentration of  $0.25 \text{ mmol dm}^{-3}$ , showing uptake of 93%. The basic assumptions of the Langmuir model are (a) the maximum uptake corresponds to a saturated monolayer of a cation, (b) all the surface sites are equivalent and the energy of the uptake is constant over all the sites (i.e., surface is homogeneous), and (c) the uptake of cations occurs at definite sites.<sup>14</sup> It is apparent that  $\text{Cs}^+$  ions are arranged in the interlayer space between the manganese oxide layers as evidenced from the expansion of the basal spacing (Figure 1b). The exchange capacity of Na birnessite  $q_m$  calculated from the Langmuir model was  $1.9 \text{ mmol g}^{-1}$ , which was nearly equal to the experimental value of 2.0. This uptake capacity ( $2.0 \text{ mmol g}^{-1}$ ) compares well with that of the most  $\text{Cs}^+$ -selective materials (layered metal sulfides, zeolites, and ammonium molybdophosphate–calcium alginate exhibiting  $1.7$ – $3.3 \text{ mmol g}^{-1}$ ).<sup>4,5,14</sup> Very recently, a maximum uptake of  $\text{Cs}^+$  ( $5.5 \text{ mmol g}^{-1}$ ) from aqueous solution on microporous titanosilicate had been reported.<sup>13</sup>

The desorption of  $\text{Cs}^+$  was studied by reacting  $\text{Cs}^+$ -exchanged birnessite with large excess of different solutions

( $0.10 \text{ mol dm}^{-3}$ ); the desorption of  $\text{Cs}^+$  was 46, 94, 97, 76, or 43% from HCl, KCl, KOH,  $\text{NH}_4\text{Cl}$ , or  $\text{NH}_4\text{OH}$  solution, respectively. The low desorption of  $\text{Cs}^+$  in HCl solution can be related to the high affinity of the material toward  $\text{Cs}^+$  in the acidic conditions. In contrast, the high desorption of  $\text{Cs}^+$  from KCl or KOH solution can be related to the high affinity of the material toward  $\text{K}^+$  at high concentration, since the  $K_d$  value of  $\text{K}^+$  was higher than  $\text{Cs}^+$  from  $1.0 \text{ mmol dm}^{-3}$  mixed solution at pH 10.1.

The above results suggest that the uptake of  $\text{Cs}^+$  proceeds by an ion-exchange mechanism, replacing the exchangeable  $\text{Na}^+$  present in the Na birnessite.

In conclusion, the poorly crystalline synthetic Na birnessite exhibited ion-exchange properties with  $\text{Cs}^+$ . The  $K_d$  values of  $\text{Cs}^+$  increased with increase in solution pH. This is in contrast to the crystalline Na birnessite being efficient only under acidic solution. Initial uptake rate of  $\text{Cs}^+$  on the Na birnessite was rapid with  $0.70 \text{ mmol g}^{-1}$  within 1 h (88% uptake) at  $V/m$  ratio of  $1.0 \text{ dm}^3 \text{ g}^{-1}$  from  $1.0 \text{ mmol dm}^{-3}$  solution. The maximum uptake capacity was  $2.0 \text{ mmol g}^{-1}$ . The material was very efficient for uptake of  $\text{Cs}^+$  at a wide pH range of 2.5–10.5. The Na birnessite, which is an inexpensive material with high selectivity for  $\text{Cs}^+$  at low concentration, may be considered as cost-effective material for the uptake of  $\text{Cs}^+$  from contaminated waters.

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