Adsorption of Cesium by Japanese Acid Clay

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We have already reported[1] the separation of uranium from fission products by the adsorption of the latter to Japanese acid clay in an organic solution. We pointed out the strong preference for adsorbing cesium to other fission product nuclides. This phenomenon was found also in aqueous solutions, so we extended the survey to aqueous systems, especially in regard to the effect of the heat treatment of the clay on adsorption.

Experimental

Sample Description.—Japanese acid clay, from Ōmi, Niigata prefecture, was obtained from the Koso Chemicals Co. The clay was used without pretreatment or was used after heating it at different temperatures up to 1200°C for 1.5~2 hr., followed by gradual cooling.

The ion exchange capacities were determined by using the barium-saturation-acid titration technique described by Suto[2].

The Measuring of the K_d Values of Cesium.—About 10 ml. of an aqueous solution, containing 1~2μC. of carrier free cesium-137, was placed in a graduated glass cylinder with a stopper, and 30~50 mg. of the clay were added. After equilibrium was reached with intermittent shaking, the solution was centrifuged. One milliliter of aliquot was counted in a well-type scintillation counter with a NaI (Tl) crystal, after the mixture had been left standing for 20 min. to ensure radioactive equilibrium with ^{137m}Ba. The K_d values were then calculated by the following equation:

$$K_d = \frac{\begin{array}{c}\text{[Cs concn. of the sample soln. before adding} \\ \text{the clay (c. p. m./ml.)} - \text{Cs concn. after} \\ \text{equilibration (c.p.m./ml.)]} \times \\ \text{[Vol. of the soln. (ml.)]}\end{array}}{\begin{array}{c}\text{[Weight of the clay (g.)]} \times \text{[Cs concn. after} \\ \text{equilibration(c. p. m./ml.)]}\end{array}}$$

The time of equilibration was almost the same in various solutions, either carrier free, with carrier, or containing a salt such as sodium nitrate: this time was found to be 0.5~1.0 hr.

Compared with the data of montmorillonite[3] and kaolinite[4], where the times of equilibration for the cesium adsorption in aqueous systems were 16~696 hr. and 40 days, the adsorption by Japanese acid clay is rapid. Presumably this is due to the ease of defloculation of this clay; a larger proportion of sites is soon made available for exchange. It was also noticed that the adsorption of cesium was better at a lower temperature; for example the K_d values of cesium from aqueous solution were 6430, 6450, 5570, 5470, 4270 and 3980 at 0, 10, 20, 30, 40 and 50°C respectively.

Results and Discussion

The Meaning of the K_d Values.—Many surveys have been made of the ion-exchange properties of clay minerals. Almost all of them, however, treated the results of the experiments by hold-up volume or by the percentage of adsorption at various concentrations and various pH values. This seems due to a lack of information as to whether the phase equilibrium really exists, even in the case of clay minerals. We confirmed this point by the following two methods and discussed all the data using K_d values.

(1) In some K_d value measurements, the volume of the solution and the amounts of the clay to be added were changed, only to find that the calculated K_d values were changed only a little with varying these two factors.

(2) Cesium was adsorbed to the clay from a 0.2 M nitric acid aqueous solution, and the supernatant solution was rejected. This clay was next brought in contact with 0.2 M nitric acid, the K_d value of the desorption being measured. The same experiments were repeated, and the changes in the K_d values of desorption were observed. The results are shown in Table I. The gradual increase in K_d

TABLE I. DESORPTION OF CESIUM-137 WHICH WAS ADSORBED ON JAPANESE ACID CLAY

No.	Total activity (c.p.m.)	Desorbed activity (c.p.m.)	K_d
1	1246000	109140	2080
2	1137640	91400	2280
3	1046240	77660	2500
4	968580	65270	2760
5	903310	238150*	3160

Desorption: 0.2 M. nitric acid, 10 ml. (*50 ml.) Japanese acid clay, 50 mg. Time of equilibration, 1.5 hr.

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[1] N. Oi and T. Kamada, Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

[2] T. Suto, "Clay minerals", Iwanami, Tokyo (1958), p. 146.

[3] T. Tamura and D. G. Jacobs, *Health Physics*, **2**, 391 (1960).

[4] M. A. Tamers and H. C. Thomas, *J. Phys. Chem.*, **64**, 29 (1960).

values seems to show the existence of some irreversible adsorption, but on the whole we can probably assume a phase equilibrium.

The Influence of the Concentration of Acid, Alkali and Salt.—The K_d values of cesium-137 at various concentrations of nitric acid, hydrochloric acid, ammonia, sodium chloride, sodium nitrate, aluminum nitrate and cesium nitrate in an aqueous solution were measured; they are shown in Figs. 1 and 2. Here it must be pointed out that the adsorption of cesium by this clay is much more highly specific than that of these ions: H^+, Na^+, NH_4^+ and Al^{3+}. It was also shown that the cesium adsorption was at its maximum in water (pH=7), the K_d value then being 7000. When the concentration of the solute in the solution increased except in the case of ammonia, which is one of the weak electrolytes, the K_d values decreased rapidly, and to almost the same value; the K_d value was below 1000 above 0.2 M. This indicates, on the contrary, the possibility of cesium desorption by a solution of a higher concentration.

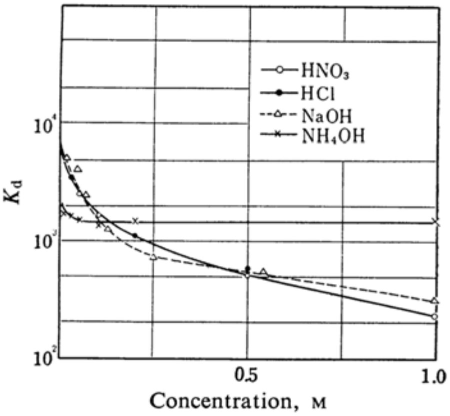

Fig. 1. Influence of acids and alkalis on the K_d values of cesium.

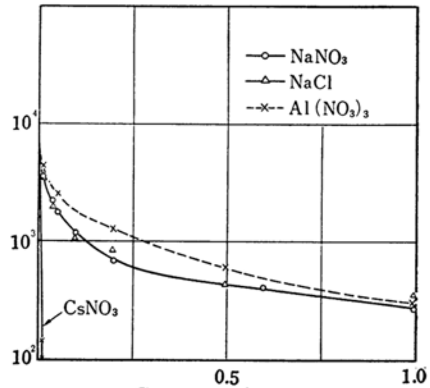

Fig. 2. Influence of salts on the K_d values of cesium.

Above all, it seems to indicate that the adsorption is a cationic exchange in nature and that the decrease in K_d values is due to the competition between cesium and other ionic species at the higher concentrations.

Influences of the Heat Treatment of Japanese Acid Clay.—It is known that the adsorbability for cesium of clay minerals, especially montmorillionite, is enhanced by heat treatment. In this case, the basal diffraction of the X-ray diffraction pattern changes from 15~17 Å to about 10 Å. Tamura et al.[3-5] suggested the importance of this 10 Å c-axis spacing for the adsorption of cesium; they also pointed out the affinity for cesium of illite and synthetic micas, which have a 10 Å c-axis spacing.

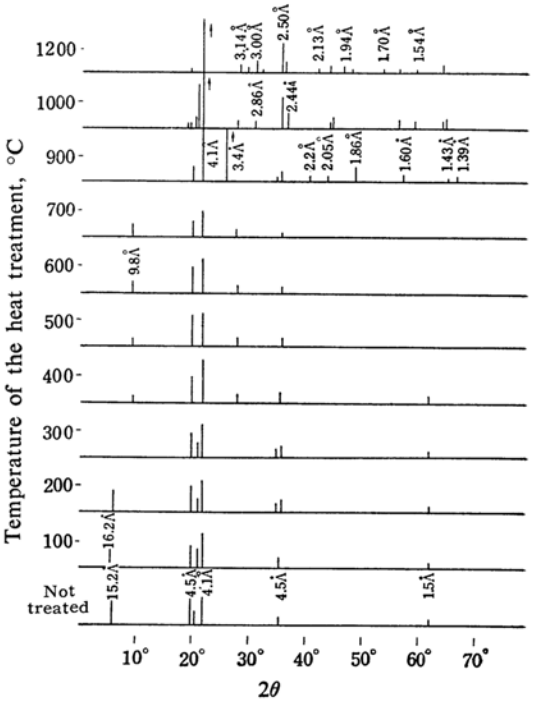

Fig. 3. X-Ray diffraction patterns of the heat treated Japanese acid clay.

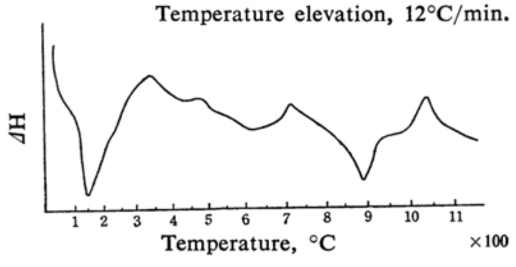

Fig. 4. Curve obtained by the differential thermal analysis of the Japanese acid clay.

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[5] T. Tamura and D. G. Jacobs, *Health Physics*, 5, 149 (1961).

We carried out the experiment with heat-treated clay and considered our results using X-ray diffraction patterns (Fig. 3) and differential thermal analysis (Fig. 4). The changes in the K_d values of some systems are shown in Fig. 5. It is shown that the selectivity for cesium was most improved by heating it to a temperature in the 400～500°C range. By comparing these results, the following conclusions⁶⁾ were reached:

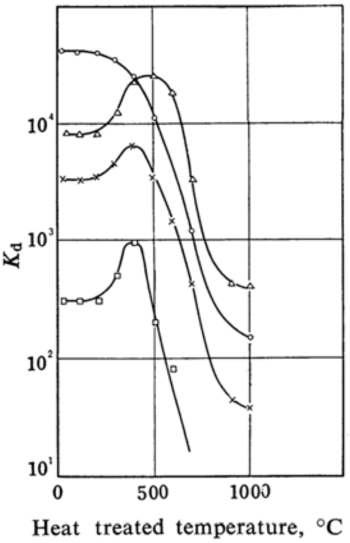

Fig. 5. Changes of the K_d values of cesium by using heat treated Japanese acid clay.
—○— *n*-Butylacetate, uranyl nitrate 0.1 M
—×— 0.1 M uranyl nitrate aqueous solution
—△— Water
—□— 1 M Nitric acid

(1) Japanese acid clay loses about 10%. of its weight at 100～150°C by the removal of its absorbed water. This process, however, does not work positively but rather somewhat negatively in cesium adsorption.

(2) Up to 700°C, the patterns of X-ray diffraction show little change except in their basal reflection. This changes from 15～16 Å at 100～200°C to about 10 Å at 400～700°C, while its intensity also increased. The process of the formation of the 10 Å axis corresponds to the maximum point of the adsorption.

(3) The endothermic peak of 350～650°C is due to the removal of the structural water (or –OH), and in this process the c-axis changes to 10 Å. After the complete dispersion of the structural water, the K_d values drop. The pattern of differential thermal analysis indicates two stage changes within this temperature range, one rather moderate in the range of 350～450°C and the other slightly steep up to 500°C. The clay of the first stage showed the maximum K_d values.

(4) The endothermic-exothermic peak of the 850～1100°C range corresponds to the change in colloidal silica, which is one of the components of this clay, to α-crystobalite via α-quartz. This is clear from the X-ray patterns. Here the K_d values decreased to a minimum.

Thus, the K_d maximum corresponds to the process of 10 Å c-axis formation and also to the removal of the structural water. These results qualitatively agree with Tamura et al's data³⁾.

Fripiat et al.⁷⁾ studied the relation of the dehydration of montmorillonite to its infrared spectroscopy. They pointed out the increase in the stretching vibration frequency of the hydroxyls as the dehydration progressed. We also took infrared spectra of the untreated and heat treated clays, but we could not clearly determine the relation between the increase in OH stretching and the maximum K_d value. This is presumably because the K_d maximum is due to the structural factor and not to the ion exchange character.

In Fig. 5. a curve showing the K_d changes in *n*-butylacetate is also included. This shows no maximum value. This seems to indicate that the mechanism of the adsorption in an organic solution is mainly molecular and is different from that in an aqueous solution, ion exchange adsorption.

On the other hand, when cesium was adsorbed by this clay and was heated for half an hour at about 1000°C, it was fixed to the clay and was not eluted even when boiled with large amounts of water.

The Cesium Concentration and the Change in K_d Values.—The experiment above was carried out using carrier-free (about 10^{-7} mol./l.) cesium-137. However, as much as 10^{-4} mol./l. of cesium is handled in high-level waste. Besides, the behavior of cesium at a higher concentration also seems interesting with regard to the adsorption mechanism: therefore, we carried out experiments up to 0.1 mol./l., using both untreated and heat-treated clays at 400°C. The results are shown in Fig. 6. In the cesium concentration range of below 10^{-6} mol./l. heat-treated clay showed higher K_d values, but at a higher cesium concentration untreated clay showed better adsorption. The adsorption isotherms of both clays at a higher cesium concentration indicated a maximum adsorption, the amounts of adsorption being almost the same as their ion exchange capacities, 0.45 and

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6) Cf. G. W. Brindley, "X-Ray Identification and Crystal Structures of Clay Minerals", The Mineralogical Society, London, (1951), p. 118.

7) J. J. Fripiat, J. Chaussidon and R. Touillaux, *J. Phys. Chem.*, **64**, 1234 (1960).

0.14 meq./g. and 59 and 17 mg. of cesium adsorption per gram of the clay for untreated and for treated clays respectively. These results show that ion exchange plays a major role in the adsorption of cesium, but that at a lower cesium concentration a somewhat specific, perhaps structural adsorption takes place and causes an increase in the K_d values.

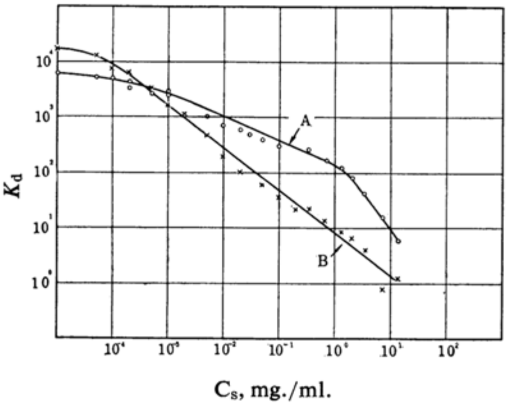

Fig. 6. Changes of the K_d values of cesium by increasing cesium nitrate concentration in water.
A, Untreated clay
B, Heat treated clay at 400°C

Adsorption of Cesium-137 from Fission Products Mixture.—A simple survey of cesium adsorption from the fission products of this clay showed that cerium, zirconium and niobium were adsorbed at about 1% of the K_d value of cesium. Ruthenium was eliminated more efficiently. The behavior of nuclides was altered by the heat treatment of the clay; for example, in the case of 200 day-cooled fission products, the gross K_d values of total γ-activities in water were 460 and 16, by the untreated clay and the clay treated at 500°C respectively.

Summary

Japanese acid clay, a montmorillonite-type one, exhibited a special affinity for cesium-137 from an aqueous solution. The phase epuilibrium of the adsorption was confirmed, and the K_d values were used to analyze the data.

The K_d value of cesium was highest in pure water, but it was decreased by increasing the aqueous acid, alkali and salt concentration.

When clay which had been treated at 400~500°C was used, the K_d value increased two- or three-fold. This phenomenon corresponds to the formation of 10 Å c-axis spacing and the dispersion of the structural water of the clay. This peculiarity, however, appears only at a low cesium concenration, below 10^{-6} mol./l. At a higher cesium concentration, the adsorption of cesium depends simply on the cation exchange capacity of the clay; heat-treated clay showed a poorer adsorption.

The adsorption of cesium from a fission products mixture was also simply examined.

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