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On the Uranium Exchange of Clay Minerals

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Abstract

The total exchange capacities of representative clay minerals are determined as follows: kaolinite 9.1 m.e./100 g, illite 22.0 m.e./100 g and montmorillonite 65.1 m.e./100 g respectively.

Regarding the cation exchange ability, U^{IV} shows the maximum ability in montmorillonite, but in other clay minerals it is not always so. Nevertheless, the total mass of U^{IV} content in each clay is always of the greatest value succeeding to Th^{III} .

X-ray investigations of uranium-calys indicate that the dimension of layer spacing was reduced by about 16.5% in montmorillonite, 4% in illite and negligibly in kaolinite. This fact seems to afford a key to clarify the structural mechanism of cation exchange.

Extraction of uranium from uraniferous clay by digesting with dilute acid and alkali-carbonate or -bicarbonate solution is discussed from the stand-point of cation replacement.

Introduction

It is well known that the clay minerals have ion-exchange property, and this problem has been studied not only from the theoretical point but also for practical purposes by researchers in agriculture, ceramics, industry etc.

In mineralogy, the characteristic behaviour of ion-exchange has an intimate relationship with the crystal structure, and also with combined water of clay minerals.

The present authors have studied the uranium exchange of clay minerals in order to illustrate several geochemical problems of uranium concerning the process of sedimentation, from this study has been introduced some efficient extraction method of uranium from these materials of which uranium content is even of a low grade.

Measurement of the total exchange capacity

At first, we measured the total exchange capacity of the representative clay minerals: kaolinite, illite and montmorillonite according to the following process.

Sample clay was added to 1 N. CH_3COONH_4 aq. to convert it into NH_4 -clay. Next, 10% NaCl aq. was added to NH_4 -clay. By measuring the nitrogen in free NH_4 , isolated from NH_4 -clay, we regarded the amount of nitrogen as the total

exchange capacity of clay mineral. The values determined by the above method are as follows:

Kaolinite from Naegi	9.1 m.e./100 g
Illite from Matsushiro	22.0 m.e./100 g
Montmorillonite from Hojun	65.1 m.e./100 g

Measurement of cation exchange ability

In order to investigate the cation exchange ability of these clays, sample clays were converted into K-clay, and various dilute salt solutions including cations equivalent to total exchange capacity of each clay were added to above K-clay. After a week, the amount of isolated potassium was quantitatively determined by means of flame photometre, and we regarded the value of potassium as the cation exchange capacity and calculated the percentage of the cation exchange capacity to the total exchange capacity as the cation exchange ability.

The results were listed in next Table (1).

Table (1) Exchange abilities of various cations

	Montmorillonite				Illite				Kaolinite			
	chloride		sulphate		chloride		sulphate		chloride		sulphate	
	exchange ability in %	mass %	exchange ability in %	mass %	exchange ability in %	mass %	exchange ability in %	mass %	exchange ability in %	mass %	exchange ability in %	mass %
Na ⁺	48.7	0.73	47.5	0.71			37.8	0.19	30.0	0.06	28.9	0.06
Ca ⁺⁺	66.6	0.87	66.6	0.87	72.7	0.32	72.7	0.32	42.2	0.08	41.1	0.07
Zn ⁺⁺	61.5	1.31	65.0	1.38	65.9	0.47	72.7	0.52	44.4	0.13	43.3	0.13
Fe ⁺⁺⁺	72.0	0.87	65.0	1.18	63.6	0.26	63.6	0.39	45.5	0.08	45.5	0.12
U ⁺⁺⁺⁺	84.8	2.19	68.2	1.76	70.4	0.61	61.4	0.54	42.2	0.15	42.2	0.15
Th ⁺⁺⁺	70.1	2.65	66.1	2.49	77.3	0.99	61.4	0.78	47.8	0.25	44.4	0.23

Judging from the above results, the total exchange capacity of montmorillonite is largest and that of kaolinite is smallest. Regarding the cation exchange ability, there was no identical relationship between each clay mineral, as the mechanism of cation exchange differs according to the variety of clay minerals. Seen from the above results, U⁺⁺⁺⁺ showed the maximum value of exchange in montmorillonite, but in the other minerals U⁺⁺⁺⁺ was not always maximum. Especially in kaolinite, Th⁺⁺⁺ showed a rather large value. But these values indicate the proportion of cations to total exchange capacity of each clay, and do not show the total mass of cation retained in each clay. When the total mass of various cations was recalculated, as is shown in the above Table, U⁺⁺⁺⁺ content was of the largest value succeeding to Th⁺⁺⁺ in each clay.

X-ray investigation

Now, if these cations enter into the crystal structure of clay mineral by ion-exchange, the dimension of layer spacing of layer lattice must undergo some deviation. If there is no change, it is not a cation exchange in crystal structure but the surface phenomena due to broken bonds which are not the inner crystal structure of clay minerals. Therefore, in order to investigate these relations in details, we measured the dimension of lattice spacing along C-axis by using Norelco with original clay, K-clay and U-clay.

The above data showed that the change of layer spacing by cation exchange was largest in montmorillonite and was rather small in illite, was negligible in kaolinite. These facts indicated a good agreement with above experiments concerning the exchange capacity and exchange ability.

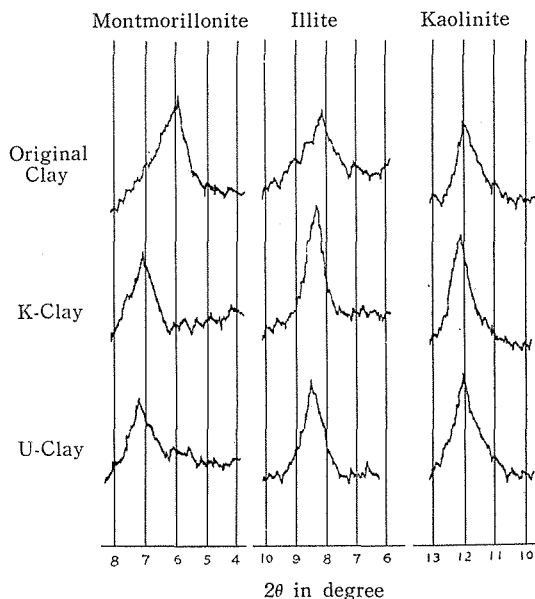


Fig. 1. Strip charts of various clays
Cu $K\alpha$, 4-1-8, $\frac{1}{2}^\circ/1M$

Table (2) Lattice constants of (001)

Clay mineral	2θ	d(A)
original kaolinite	12.02	7.357
K-exchanged kaolinite	12.04	7.344
U-exchanged kaolinite	12.03	7.351
original illite	8.16	10.826
K-exchanged illite	8.37	10.554
U-exchanged illite	8.50	10.394
original montmorillonite	5.93	14.941
K-exchanged montmorillonite	7.03	12.563
U-exchanged montmorillonite	7.08	12.475

Extraction of uranium from uraniferous clay

Uranium of uraniferous clay must be replaced by dilute solution of other cation,

even if its exchange ability is weaker than uranium. Therefore we attempted to extract uranium from uraniferous clay by altering it into hydrogen-clay or alkali-clay by treating with dilute hydrochloric acid, sulphuric acid, sodium carbonate and sodium bicarbonate.

Experimental method

Various normality solutions, 100 c.c. of HCl, H₂SO₄, Na₂CO₃ and NaHCO₃ were added to 1 g sample powder obtained from the Ningyo Pass.* After a week, each solution was filtered and 20 c.c. portion of filtrate was evaporated completely in platinum crucible. The residue in crucible was fused with 3 g. flux† for twenty minutes in electric furnace adjusted at 650±10°C. The intensity of fluorescence under the ultra-violet ray was determined by means of sensitive fluorimetric apparatus equipped with photomultiplier tube. Thus the extraction percentages determined are shown in Table 3.

Table (3) Extraction percentage of uranium

	1 N	0.1 N	0.01 N	0.001 N
HCl	18.97	25.29	22.13	3.16
H ₂ SO ₄	25.29	31.61	25.29	0.95
Na ₂ CO ₃	6.32	9.48	6.32	0.95
NaHCO ₃	6.32	9.48	6.32	0.63

The tendency of the extraction percentage of uranium to decline as its normality decreases was identical in all the experiments. The extraction percentage digested in 1 N solution shows a rather lower value, therefore, the value of 0.1 N solution is always maximum.

Judging from the above experimental results, there are still too many unsolved problems to relate directly the extraction of uranium with cation exchange. Close investigations of cation exchange ability and mechanism in various environments such as effects of oxidation, reduction, and common salts will raise the extraction efficiency to a large extent.

* Uranium deposit of the Ningyo Pass in Okayama and Tottori prefecture is one of the most important uranium mines in Japan. The specimen under consideration is -200 mesh fine powder of silt and clay sediments bedded on the basal conglomerate upon the Chugoku granite. Its uranium content is 0.087% U₃O₈.

† Flux is preliminarily prepared by mixing NaF 9 g., Na₂CO₃ 45.5 g. and K₂CO₃ 45.5 g.

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