

《Original》

Chemical Treatment of Low-Level Radioactive Liquid Wastes(II)

(The Determination of Cation Exchange Capacity on
various Clay Minerals)

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(Received May 25 1977)

Abstract

This experiment has been carried out to determine the pH dependent cation exchange capacity concerning the sorption phenomenon of long-lived radionuclides contained in low-level liquid radioactive waste on various clay minerals.

The pH dependent cation exchange capacity determined by Sawhney's method are used to the analysis of sorption phenomenon.

About 70 percent of the total cation exchange capacity is contributed by the pH dependent CEC due to the negative charge originated naturally in clays in case of clinoptilolite, vermiculite and sodalite.

It is suggested in this test that the high neutral salt CEC, that is, highly charged clays would show good fixation yield. The removal of radionuclides at the pH range more than pH 9 is considered the hydroxide precipitation of metal ion rather than the cation exchange.

The Na-clay prepared by the method of successive isomorphic substitution with electrolyte showed a considerable improvement in removal efficiency for the decontamination.

요 약

원자력 발전소에서 나오는 방사성 핵종이 clay 속에 고정되는 반응기구를 분석하기 위해서 clay의 양이온 교환능을 Sawhney 방법으로 측정했다.

Clinoptilolite, vermiculite 및 sodalite들의 pH dependent CEC를 측정한 결과 총 양이온 교환능의 약 70% 정도가 영구 고정되어진다고 생각되는 neutral salt CEC에 의해 일어나고 나머지는 가역과정인 clay 속의 유기물질과 다른 금속(Al, Mg)의 치환에 의해 일어난다는 결론을 얻었으며, pH 9 이상에서 clay에 의한 방사성 핵종의 제거는 이온 교환 기구에 의한 고정보다 오히려 중금속 이온의 침전에 의해서 더 많이 일어난다는 것도 밝혀냈다.

그리고 연속 치환에 의해서 처리된 Na-clay는 방사성 핵종제거에 상당히 향상된 제거 효율을 나타내고 있다.

I. Introduction

Many attempts to decontaminate the low-level radioactive liquid waste discharged from nuclear power station have been carried out with respect to the sorption capability of clay minerals.

In review of the sorption test of radioactive elements and stable elements, S. J. Rimshaw¹⁾ showed the removal efficiency of series of minerals considering exchangeable capacity of nuclides on various minerals such as Marble Chips, pebble phosphate and natural soils.

But using only the radiosotopes for the test, this test didn't show the genuine sorption mechanism.

Kay Payne²⁾ studied Cu(II) species are removed from aqueous solution by Kaolinite clay suspensions with various solution pH. Calvin H. Delegard³⁾ et al showed that radionuclides were entrapped in crystalline sodium alumino silicate, cancrinite and nepheline. These attempts were based on the gross sorption phenomenon of clay and soils.

The removal of radionuclides contained in liquid radioactive waste using clay minerals has been considered of sorption mechanism on surface of clay mineral.

According to McLaren and Crawford,⁴⁾ the sorption mechanisms in clays are classified by four components; namely

- (1) available and exchangeable,
- (2) weakly bound to specific sites,
- (3) organically bound,
- (4) occluded oxides and residual.

However, sorption mechanism is mainly occurred by ion exchange. The mechanism phenomenon occurring on the available and exchangeable sites has been assumed to the cation exchange.

Various approaches have been conducted to determine the cation exchange capacity (CEC). The influence of cation hydration, ionic size, charge and polarizability has been studied in regard to the strength of the bonding forces with clays.

An approach to determine the pH dependent CEC with extraction method and various pH solution was initiated by Coleman and Thomas⁵⁾.

They indicate that pH dependent CEC has two components; one, weakly dissociated acid groups of soil organic matter and two, partially neutralized complexes of Al and Mg ions in the interlayers of 2:1 layer silicate.

However, separation of the total pH dependent CEC into two components is less certain.

Sawhney⁶⁾ developed a procedure for direct determination of the two components CEC.

The purpose of the present paper is to clarify the conditions of clay in relation to the sorption of radioactive nuclides in clays by the estimation of pH dependent CEC of clays using Sawhney's method.

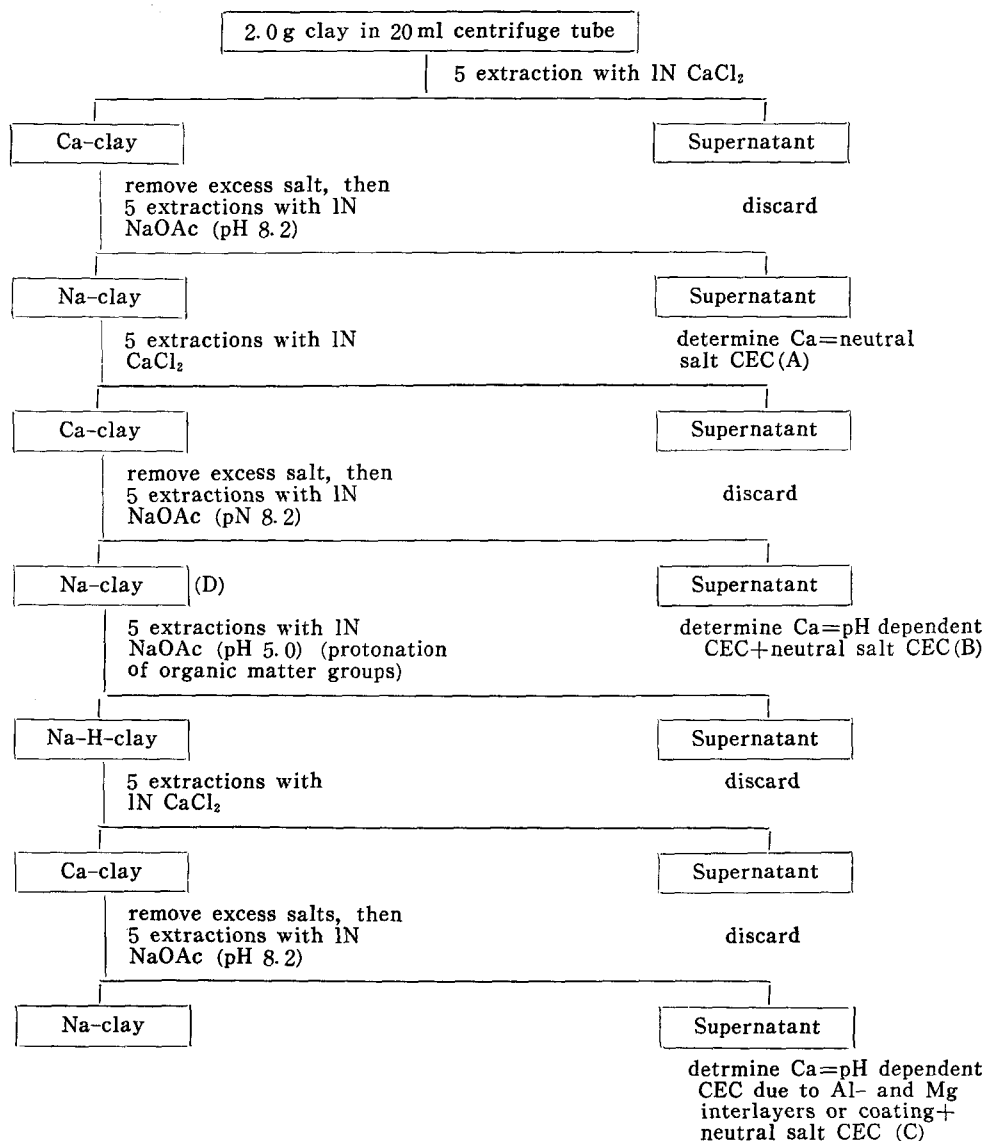
The Na-clay prepared in this experiment will be applied to the radioactive waste solution and the removal efficiency of Sr and Cs will be compared with the Na-clay prepared by saturation with NaCl solution carried out in previous report⁷⁾.

II. Material and Method

The clay minerals used in the experiment were obtained from Ward's National Science Establishment, Rochester, New York.

The clay minerals were ground and sized to 100 mesh. It was not pretreated to remove the organic matter and metal oxides.

A known quantity of minerals was mixed



B-A=pH dependent CEC

B-C=pH dependent CEC due to weakly dissociated acid groups in organic matter

C-A=pH dependent CEC due to Al-and Mg interlayers or coatings

Fig. 1. Flow diagram for the determination of neutral salt CEC, pH dependent CEC and the components of pH dependent CEC of clays.

with the electrolytes and stirred to equilibrium for 30 minutes at a temperature of 40 to 45°.

Centrifuge washing of a clay minerals and Vensene titration of Ca for CEC should be made accurately.

Eriochrome Black T. was used as an indi-

cator. The cation exchange capacity for Ca is calculated as following; milliequivalent exchange capacity per 100 gr= $m1$ Versene x

$$N \times \frac{100}{\text{sample wt.}}$$

(Versene solution: disodium dihydrogen EDTA)

III. Experiment

Continuous determination of CEC procedure for the determination of neutral salt CEC, pH dependent CEC and componts of pH dependent CEC are illustrated in Fig. 1. Although this experiment was carried twice for each samples to determine the CEC correctly, the numerical value less than 3 to 4 meq per 100 g of clay may not be authentic as data, because the error in the successive determination of CEC is accompanied with increasing manipulation of the sample.

IV. Result and Discussion

The magnitude of cation exchange capacity of clay minerals depends on the type of clay minerals, the extraction method with electrolyte and various pH range of electrolyte.

The successive CEC determination illustrate the exchange sites that were not available for saturation with Ca ions at the pH of the neutral salt became available on extraction with NaOAc of pH 8.2 increasing the CEC significantly.

Extraction with acid NaOAc of pH 5.0 rendered unaviable a major portion of the exchangeable sites, showing that the hydrogen ion (H^+) could compete with the cations for the active sites.

Considering the data in Table 1, sodalite, clinoptilolite, vermiculite and montmorillonite show the high CEC (B column in table 1).

The contribution by the pH dependent CEC due to organic matter to the total CEC is turned into about 27 to 30 percent in case of vermiculite and montmorillonite.

Clinoptilolite and sodalite also show about 26 to 30 percent of the total CEC is caused

Table 1. Neutral salt CEC, pH dependent CEC and components of pH dependent CEC of clay minerals

Clay	A	B	C	B	B	C
				A	C	A
Bentotite	50-54	78-83	52-56	28	26	2
Vermiculite	100-105	135-140	103-108	35	32	3
Montmorillonite	85-90	115-120	88-93	30	27	3
Sodalite	93-98	125-130	97-102	32	28	4
Clinoptilolite	110-115	160-165	104-109	50	46	4
Natriolite	42-47	68-73	45-50	26	23	3
Cancrinite	40-45	70-75	42-47	30	27	2
Activated Clay	63-68	80-85	64-69	17	16	1
Soil	1-1.5	6-7	1-1.5	5	5	—

A : neutral salt CEC

B : pH dependent CEC + neutral salt CEC

C : pH dependent CEC due to Al and Mg + neutral salt CEC

B-A : pH dependent CEC

B-C : pH dependent CEC due to organic matter

C-A : pH dependent CEC due to Al and Mg

by the pH dependent CEC due to organic matter.

Bentotite, activated clay, natriolite and cancrinite show the low CEC. The CEC of soil is disregarded comparing with the clay minerals. It is proved that the cation exchange is occurred almost in the aluminosilicate structure.

An increase of CEC due to the organic matter is indicated after treatment with NaOAc of pH 8.2.

The increase was, however, completely reversible on the treatment with acid NaOAc, indicating that the pH dependent CEC is primarily due to weakly dissociated organic groups. These results also point out that the reversibility between cations and hydrogen ions at low pH makes the CEC decreased. At pH 5, hydrogen ions successfully compete for active sites and at pH 3.5 al-

most no cation uptake occurs.

The hydrogen ion attacks the clay lattice, freeing aluminium and magnesium ions which may be taken up by the exchange sites; that is, some of the exchange attributed to hydrogen ion could be caused by metal ions dissolved from clay.

A. S. R. Juo and Barber⁸⁾ proposed that hydrogen ion is apparently preferred over some divalent cation in ion exchange on montmorillonite and clay minerals and over cesium on vermiculite and clinoptilolite.

It is resulted from that the reversible portion of the CEC is considered to be inadequate for the fixation of radioactive elements in liquid waste owing to its dependence of pH.

In this experiment, the contribution of hydroxy Al and Mg complexes to pH dependent CEC is negligible for the total CEC.

Extraction with pH range 5 is not sufficient to replace Al and Mg. The pH dependent CEC due to Al and Mg interlayers has been suggested irreversible because Al and Mg ion are believed to precipitate as hydroxide from in alkaline solution.

The neutral salt CEC due to negative charge occurring in clay minerals significantly contributes the total CEC of clinoptilolite, vermiculite, sodalite and montmorillonite. The neutral salt CEC is originated in alumino-silicate structure naturally.

S. Lee Swartzen -Allen⁹⁾ indicate that at all pH value, clay particles carry a net negative charge which is compensated by the presence of positive counterions.

Van Olphon¹⁰⁾ suggest that the principal source of the observed negative source charged on the clay particles is isomorphic substitution. The latter implies that the constituent metal ions of the lattices are

replaced isomorphically by cations of lower charge. For relatively highly charged clays such as montmorillonite, vermiculite, sodalite and clinoptilolite reveal high neutral CEC. Bentotite, cancrinite and natriolite show relatively low charge. From these facts, the sorption of radionuclides in clay minerals due to the neutral salt CEC has been suggested to be genuine fixation. Vermiculite, clinoptilolite, montmorillonite and sodalite are considered to be applied for the fixation of radionuclides considering the high neutral CEC. Clinoptilolite was demonstrated early for the cesium removal from solution containing high concentrations of competing cations by L. L. Ames¹¹⁾.

The CEC due to organic matter is not considered of permanent fixation because its sorption mechanism is reversible.

The application of this neutral salt CEC to real radioactive waste shows some problems.

The cations such as calcium and sodium used for this test are different from the fission product on their physical properties.

However, the mechanism demonstrated so far will not be deviated significantly in the application for real radioactive waste. Especially, the application for commonly occurring zeolites minerals such as clinoptilolite and sodalite which have relatively higher negative charge can be used for the removal of radioactive ions in liquid radioactive waste. The further test with Na-clay prepared through Fig. 1 procedure was carried out.

The Na-clay prepared from D in Fig. 1 and the two kinds of radioactive solutions having radioactivity ranged $10^{-3}\mu\text{Ci/ml}$ spiked independently by Cs^{137} and by Sr^{90} were mixed with each clay minerals for 2 hr. The radioactive solution was adjusted to pH

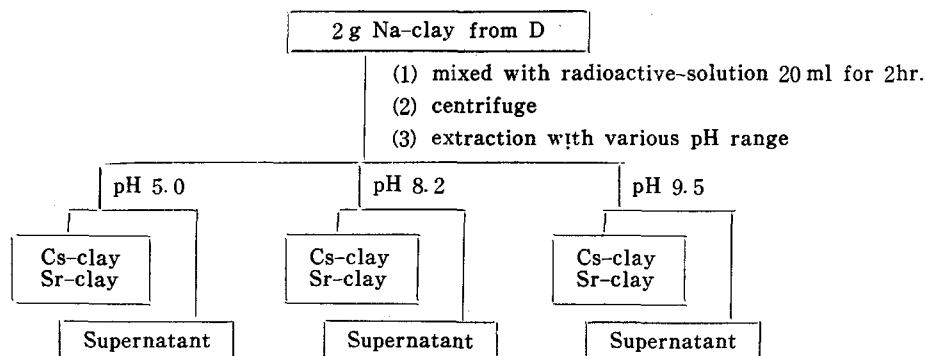


Fig. 2. Flow diagram for the removal efficiency of the Na-clay with various pH range

5, 8.2 and 9.5 separately.

After centrifuge, the supernatant was used to counting with scintillation counter. The procedure and result are outlined in Fig. 2 and Table 2 and 3.

The resulted data shows that the removal efficiencies of Cs^{137} and Sr^{90} with various clay minerals at pH 9.5 are almost same.

But the values of the total CEC tabulated in Table 1 are different for each clay minerals. This fact is explained that the removal of Cs^{137} and Sr^{90} ions at high pH range would rather be performed by the precipitation of metal hydroxide mechanism than by the cation exchange phenomenon in the available and exchangeable sites.

At pH 8.2, considering the removal efficiency, its result is similar to the result in version of CEC in table 1. It is important to adjust the pH range for the fixation of radionuclide in real liquid radioactive waste system.

Na-clinoptilolite and Na-vermiculite show prominent removal efficiency for both Cs and Sr in table 2 and 3.

The Na-montmorillonite prepared by successive substitution with electrolyte shows better removal efficiency than that of Na-montmorillonite prepared in the previous paper.

Table 2. Removal efficiency of cesium (10^{-3} $\mu\text{Ci/ml}$) by serial treatment of Na-clay

Clay	pH	pH 5.0	pH 8.2	pH 9.5
Vermiculite		62%	88%	98%
Montmorillonite		65%	85%	98%
Clinoptilolite		72%	92%	98%
Bentotite		68%	78%	95%

Removal Efficiency (%)

$$= \left(1 - \frac{\text{Counts After Treatment}}{\text{Counts Before Treatment}} \right) \times 100$$

Table 3. Removal efficiency of strontium (10^{-3} $\mu\text{Ci/ml}$) by serial treatment of Na-clay

Clay	pH	pH 5.0	pH 8.2	pH 9.5
Vermiculite		62%	88%	98%
Montmorillonite		60%	88%	97%
Clinoptilolite		70%	92%	98%
Bentotite		52%	63%	93%

V. Conclusion

The determination of the pH dependent CEC by Sawhney's method helped us to study the sorption process of cations in clay minerals.

(1) Considering the two components of the pH dependent CEC, the pH dependent CEC

due to organic matter is proved to be the major contribution for the total CEC, and the pH dependent CEC due to Al and Mg is negligible for that.

(2) the pH dependent CEC due to organic matter has been considered of reversible character, so that the fixation occurring in clay minerals structure due to neutral salt CEC is believed to be the genuine fixation of radioactive nuclides.

The amount of fixation due to neutral salt CEC become to 70 percent of the total CEC.

(4) Searching the highly charged clay existing in Korea is important for the treatment of heavy metal ions discharged from industry and radionuclides from nuclear power plant. The Na-clinoptilolite, sodalite, vermiculite, montmorillonite prepared in the test show good removal efficiency to remove the radioactive elements such as strontium and cesium compared with the Na-clay prepared

in previous report.

VI. References

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