

Sorption Behavior of Cesium-137, Cerium-144 and Cobalt-60 on Zeolites

Seok-Chul Kim, Byung-Hun Lee

Hanyang University

= Abstract =

The sorption behavior of some typical fission products such as Cs-137, long-lived radionuclide; Ce-144, rare-earth element; and Co-60, corrosion product on zeolite A, zeolite F-9 (faujasite) and amorphous zeolite was determined with the salt concentrations, 0.01M- to 2.0 M- nitric acid and ammonium nitrate, and the shaking time, 15 minutes interval from 15 minute to 90 minute. Kd values were obtained through the batch experiment.

In conclusion, the optimal conditions for isolation and removal of the typical radionuclides are as following: zeolite, amorphous zeolite; concentration, 0.01M- HNO₃ and 0.1 M-NH₄NO₃; pH4; shaking time, one hour; the most effective species, Cs-137.

1. INTRODUCTION

Although nuclear reactors produce large amounts of fission products, under normal working condition only small fractions of all the fission products find their way into waste entering the environment.

Activated corrosion products, such as iron, chromium, manganese, cobalt and nickel, arise from corrosion of piping and inreactor components.

Much attention have given to appropriate treatment of the liquid waste produced at nuclear power plants in various ways, that is, the radionuclides desolved by various inorganic sorbents,^{1~3)} but relative little attention has

been given to zeolite inorganic ion-exchanger.

Zeolites, of natural as well as synthetic origins, have good adsorption properties, strong affinity for alkaline metal and high stability under radiation and high temperature. These properties have been utilized for selective isolation and removal of long-lived radionuclides or troublesome fission products in radioactive liquid waste from nuclear power plants^{4~7)}.

The aim of present work is to determine, under the identical condition, the sorption behaviors of some typical fission products such as ¹³⁷Cs, long-lived radionuclides; ¹⁴⁴Ce, representative rare-earth element and ⁶⁰Co corrosion product, on various zeolites, zeolite

A-3, zeolite F-9, zeolite mixture, and find sorbents which are best suit for the separation of some troublesome radionuclides from liquid radioactive wastes.

2. EXPERIMENTAL

2.1 Materials

The tracers used in procedure are as follows: Cs-137 ($t_{1/2}=30.1y$) in cesium chloride, Ce-144 ($t_{1/2}=284d$) in cerous chloride, and Co-60 ($t_{1/2}=5.3y$) in cobalt chloride were obtained from the Radiochemical Centre, Amersham, England.

The synthetic zeolites used for this study are shown in Table 1. Zeolite A-3 and F-9 were obtained from Wako Chemical Co., in Japan, and zeolite mixture were obtained from Sigma Chemical Co. in U.S.A. The zeolites were ground down as 200 mesh fineness.

All reagents used in procedure were of A.R. quality and therefore were used without further purification.

Table 1. Zeolites used.

Name	Composition	Type
zeolite A-3	$Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 4.5HO$	A type
zeolite F-9	$(Na_2, Ca, Mg, K^2) O \cdot Al_2O_3 \cdot 4.5SiO_2 \cdot 7HO$	Faujasite
zeolite mixture	Unknown	amorphous

2.2 Procedure

2.2.1 X-ray crystallography

X-ray diffraction test was carried out by Shimadzu Vd-1 system with following opera-

tional condition in the Research Institute of Industrial Science, Hanyang University.

The diffraction conditions are as follows; Cu, KaNi, filter; 30 kV-10mA; 1000 c/s full scale; $2^\circ/\text{min}$ scanning speed; 20 mm/min chart speed; record slit-0.5; scattering slit-1; time constant-1.

2.2.2 Separation Procedure

Kd value with change of shaking time was inspected for the purpose of determining optimal shaking period according to different tracer and solution. For the simplification of experiment single condition was selected; time interval 15 min; 0.1 M Nitric acid and 0.1 M ammonium nitrate; zeolite A-3, F-9 and zeolite mixture.

A radioactive tracer was added to 4 ml of nitric acid or ammonium nitrate solution of different concentrations. One milliliter of resulting solution was pipetted out as a sample of the original solution. 0.1g zeolite inorganic ion-exchanger was added to the remaining 3 ml of solution, and shaken during a fixed period by the wrist action shaker. After shaking, 1 ml of supernatant solution was sampled. Radioactivity of the original and supernatant solutions was measured by the well type γ -scintillation spectrometer, BAIRD Model-810.

The concentration of the aqueous phase was adjusted to 0.01M-, 0.02M-, 0.05M-, 0.1M-, 0.2M-, 1.0M-, 2.0M-, nitric acid and that of ammonium salts to 0.01M-, 0.02M-, 0.05 M-, 0.1M-, 0.2M-, 0.5M-, 1.0M-, 2.0M-, amonimum nitrate. After completing separa-

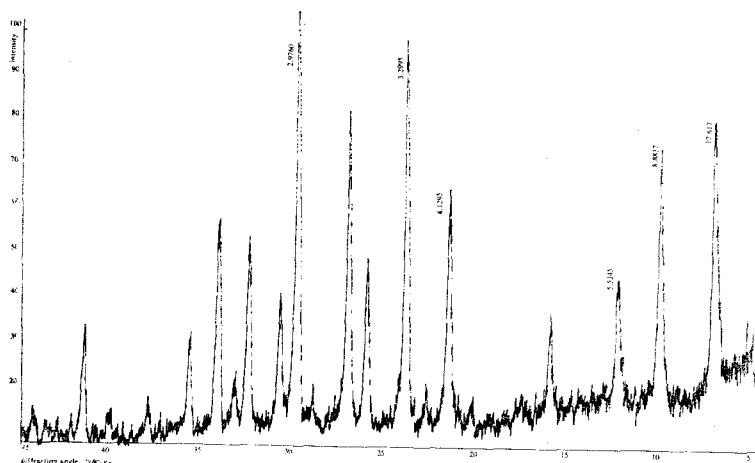


Fig. 1. X-ray diffraction diagram of zeolite A-3.

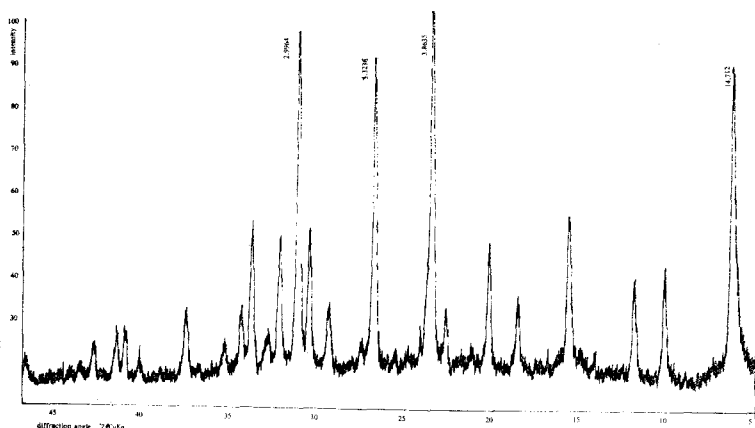


Fig. 2. X-ray diffraction diagram of zeolite F-9.

tion procedure, the Kd value was calculated by the formula:

$$Kd = \left(\frac{\text{Counting rate of original solution}}{\text{Counting rate of supernatant solution}} - 1 \right) \times \frac{\text{ml of the aqueous phase}}{\text{g of zeolite used}} \text{ ml/g}$$

3. RESULTS AND DISCUSSION

3.1 X-ray Crystallography

The X-ray diffraction pattern of zeolite examined are shown in Figs. 1-3. The pattern of zeolite A-3 and F-9 is similar to that of

zeolite A and faujasite respectively. The pattern of zeolite A-3 provided strong reflection 65(100) at about 12.6A and 100(311) at about 3.7A. The pattern of faujasite provided the strong reflection 100(111) at about 14.7 A and 100(310) at about 3.78A. But, zeolite mixture pattern is not shown strong reflection through whole angles. And it is identified as amorphous zeolite. Zeolite A and faujasite have three dimensional aluminosilicate framework with the supercages linked by hexagonal

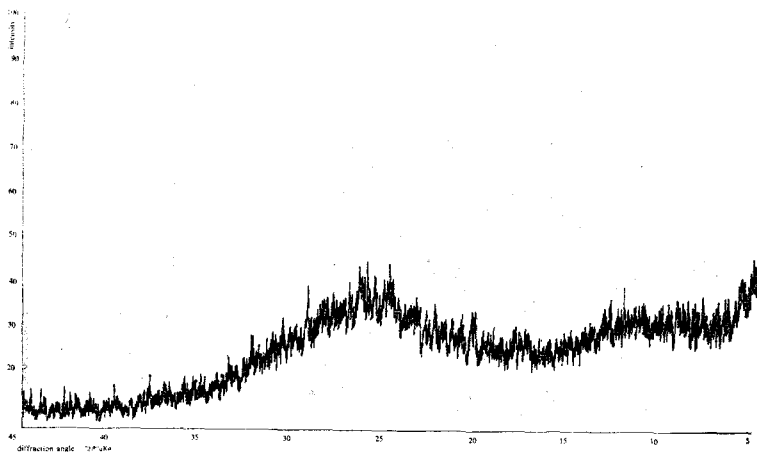


Fig. 3. X-ray diffraction diagram of amorphous zeolite.

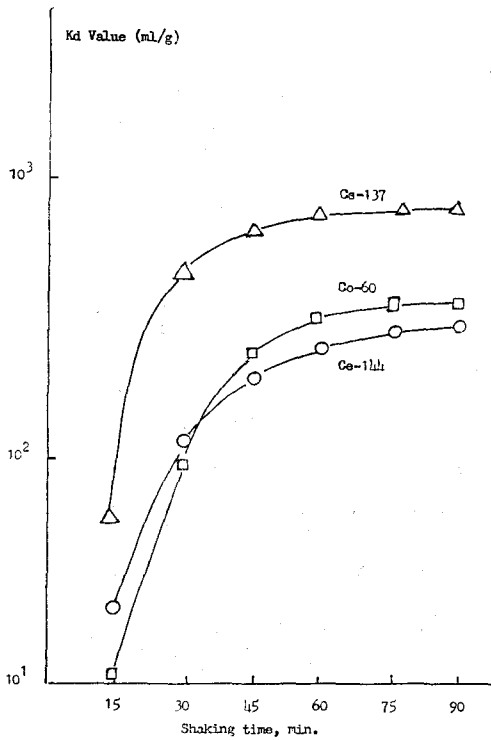


Fig. 4. Change of Kd value with shaking time in HNO_3 -zeolite A-3 system.

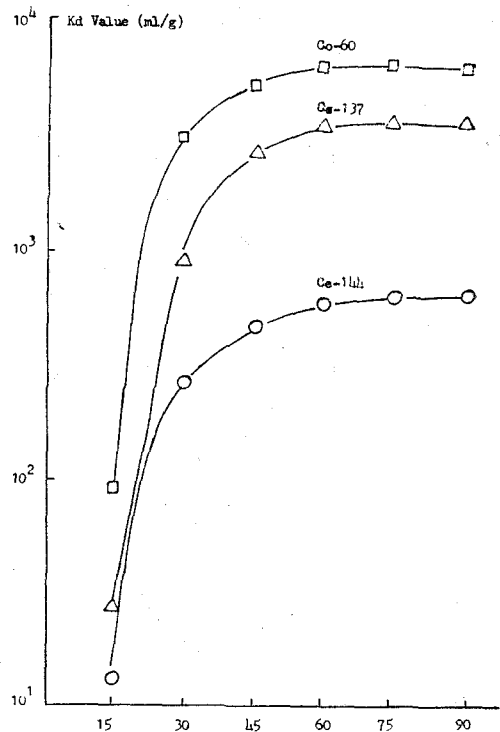


Fig. 5. Change of Kd value with shaking time in NH_4NO_3 -zeolite A-3 system.

prisms. Also, zeolite A and faujasite have three exchange sites; Site I is located within the supercage cavities, Site II adjacent to the single 6-rings and Site III within the hexagonal prisms.

3.2 Determination of Kd value

The Kd value changes with the shaking time are shown in Figs. 4-9. Optimal shaking period of all the radionuclides is around one hour with all types of zeolite. The Kd values

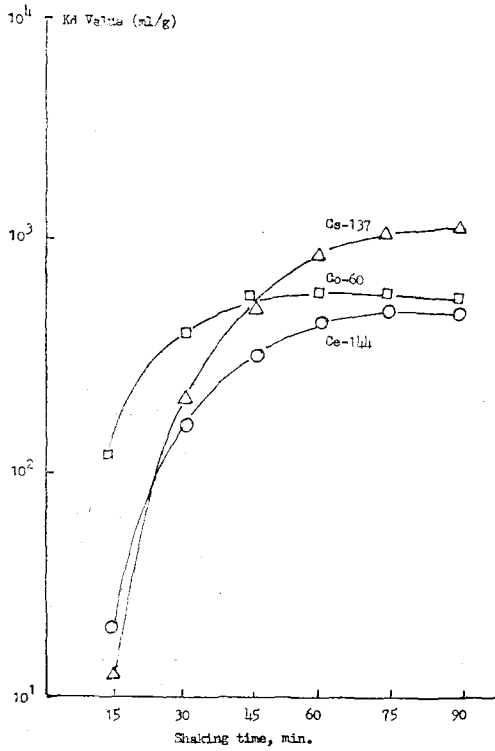


Fig. 6. Change of Kd value with shaking time in HNO_3 -zeolite F-9 system.

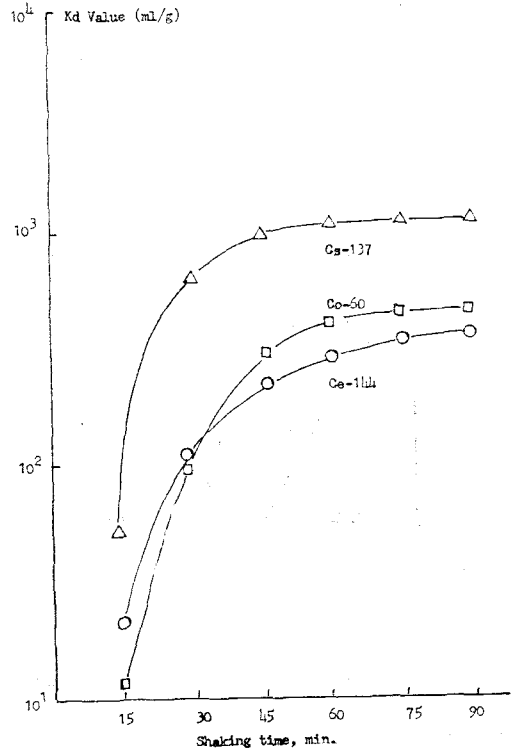


Fig. 8. Change of Kd value with shaking time in HNO_3 -amorphous zeolite system.

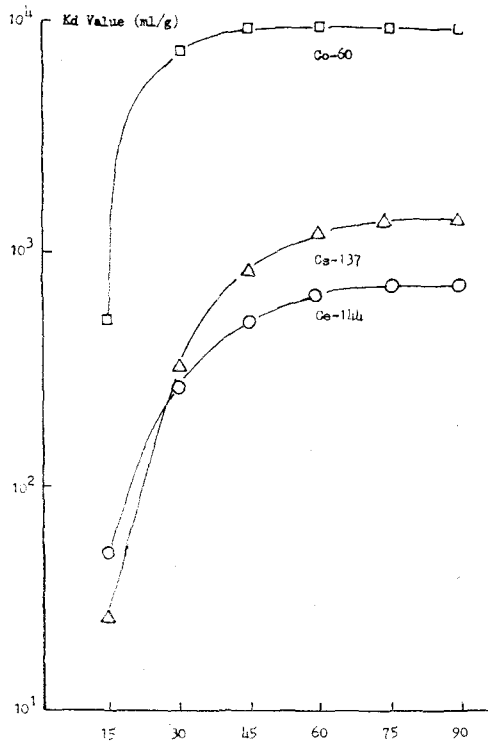


Fig. 7. Change of Kd value with shaking time in NH_4NO_3 -zeolite F-9 system.

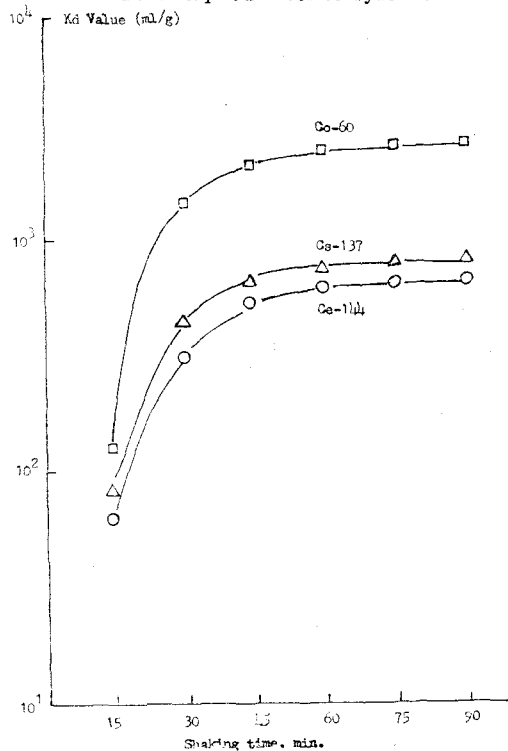


Fig. 9. Change of Kd value with shaking time in NH_4NO_3 -amorphous zeolite system.

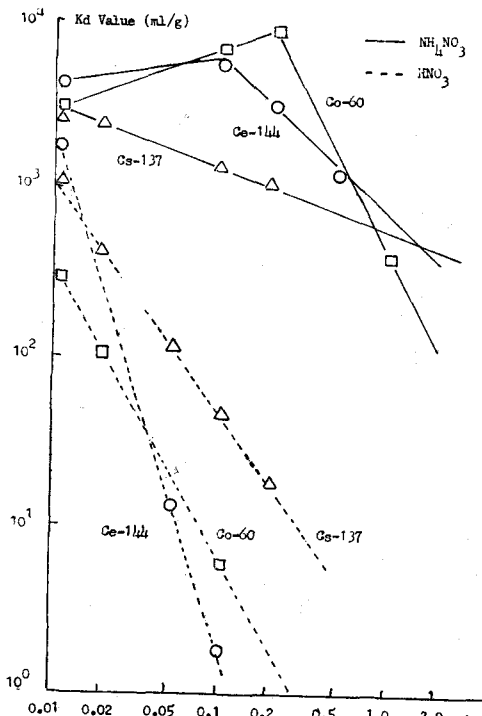


Fig. 10. Change of concentration of nitric acid and ammonium nitrate in aqueous phase with zeolite A-3.

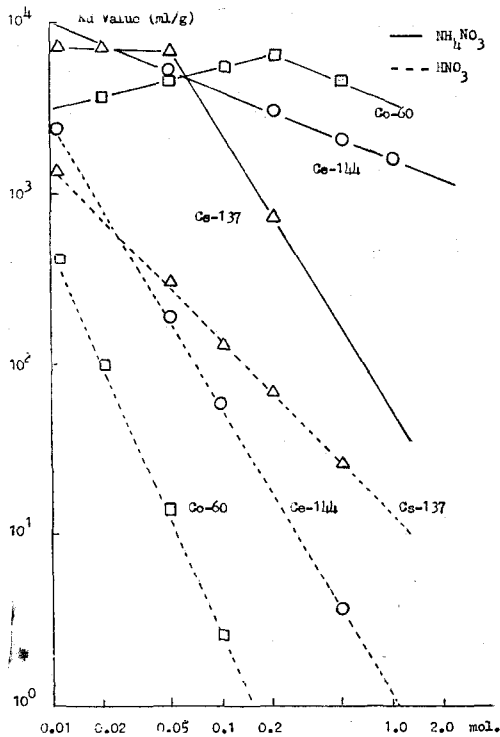


Fig. 11. Change of concentration of nitric acid and ammonium nitrate in aqueous phase with zeolite F-9.

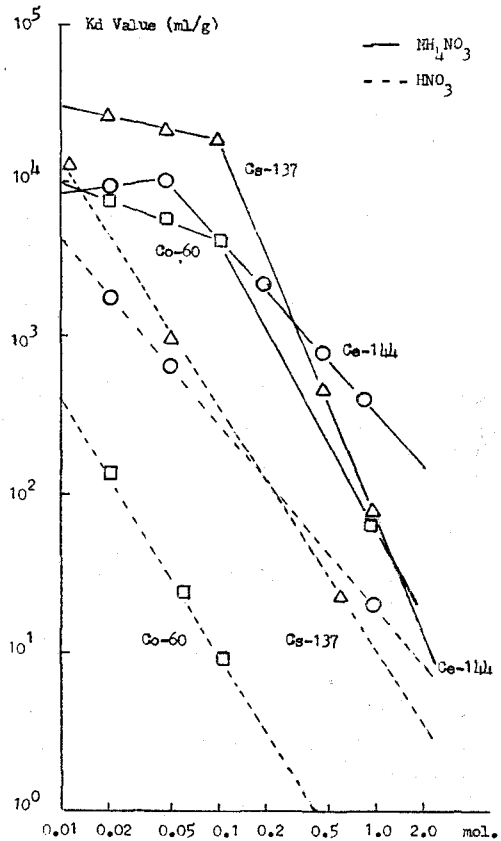


Fig. 12. Change of concentration of nitric acid and ammonium nitrate in aqueous phase with amorphous zeolite.

change with single tracers in nitric acid and ammonium nitrate are shown in Figs. 10-12. From the results, the most suitable concentration of solutions are identified 0.01 M HNO_3 and 0.1 M NH_4NO_3 . And, Kd value changes with mixture tracer in nitric acid and ammonium nitrate solution are shown in Figs. 13-18. Amorphous zeolite is most effective zeolite.

3.2.1 Effect of concentration

The dependence of distribution coefficients of the radionuclides upon the concentration

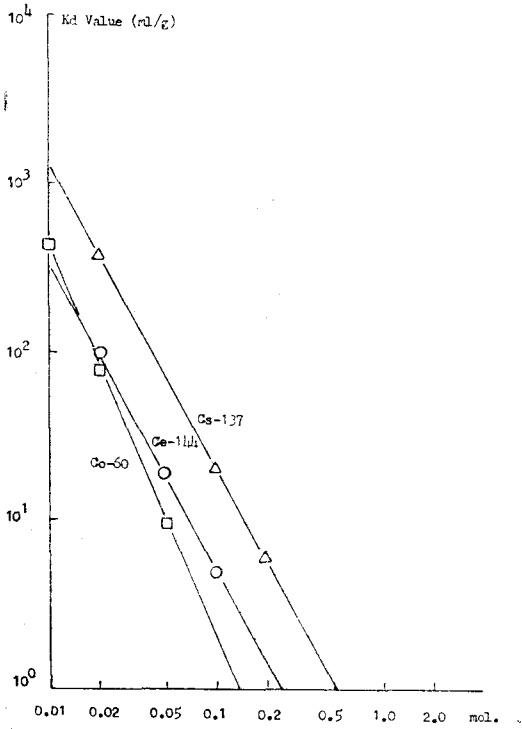


Fig. 13. Change of HNO₃ concentration in aqueous phase with zeolite A-3.

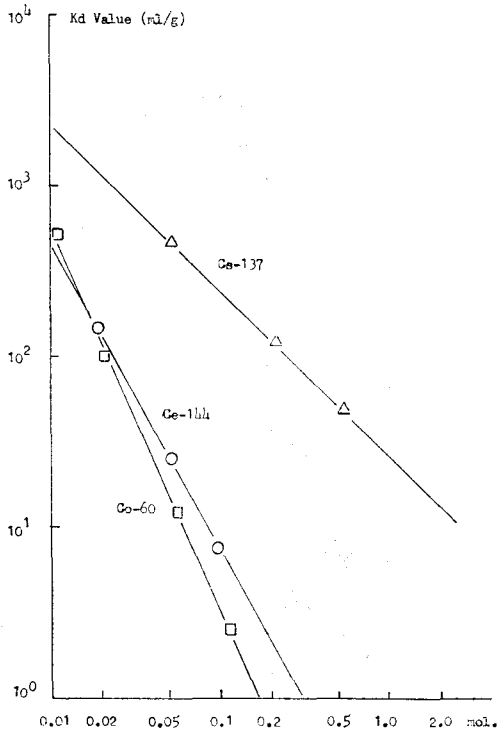


Fig. 15. Change of HNO₃ concentration in aqueous phase with zeolite F-9.

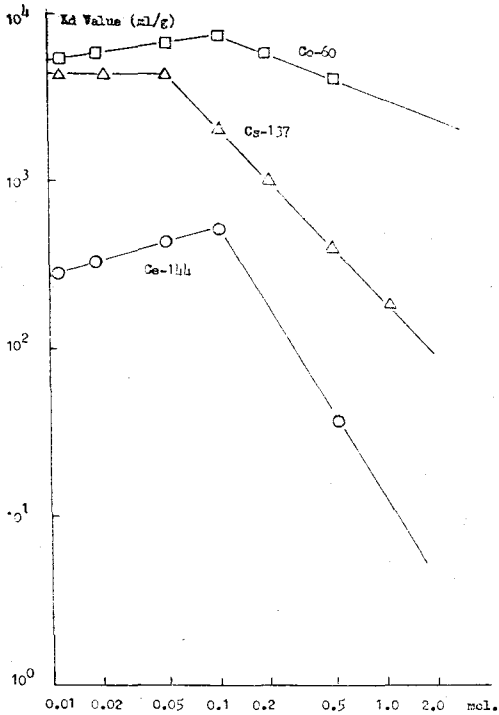


Fig. 14. Change of concentration of NH₄NO₃ in aqueous phase with zeolite A-3.

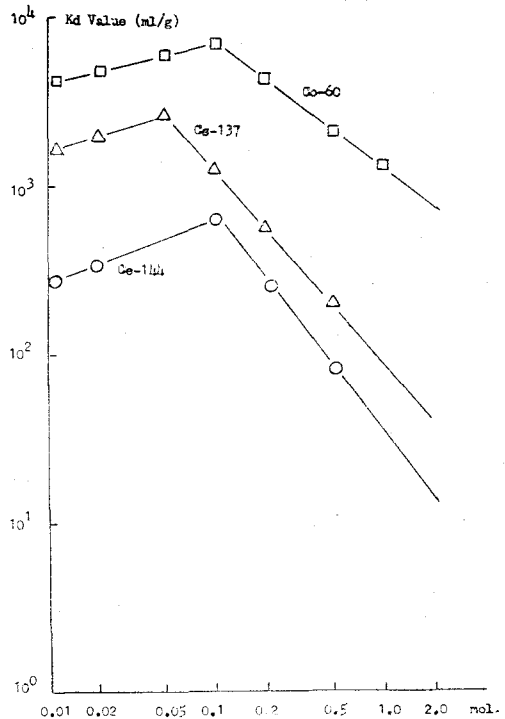


Fig. 16. Change of NH₄NO₃ concentration in aqueous phase with zeolite F-9.

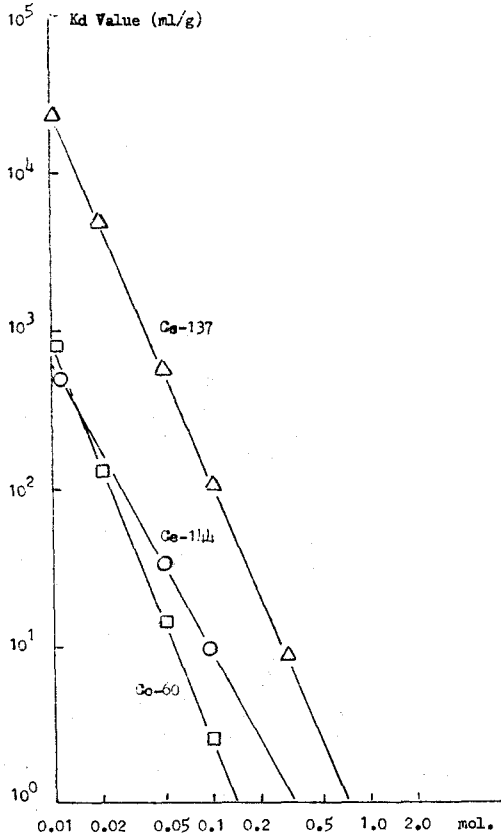


Fig. 17. Change of HNO₃ concentration in aqueous phase with amorphous zeolite.

of nitric acid and ammonium nitrate is shown in Figs. 10-18.

In 0.01M to 0.1M nitric acid and 0.01M to 0.1 M ammonium nitrate, relatively high Kd values were obtained for each zeolites. Zeolite inorganic ion-exchangers have strong affinity for cesium ion. Each zeolites have similar Kd value trends such that the value is high at 0.01 M-HNO₃ and 0.1 M-NH₄NO₃, decreasing with increasing concentration of both solutions. The above phenomena can be stated that the solution reacted with exchanging cations, such as H⁺ or NH₄, to form anion complex which greatly reduced the Kd values.

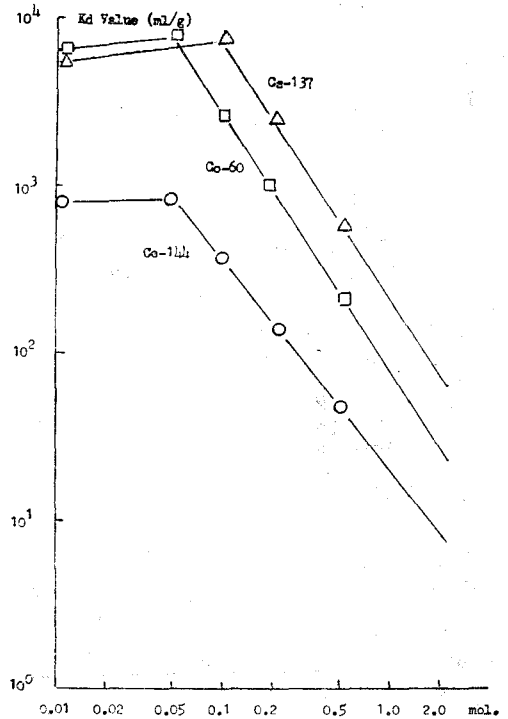


Fig. 18. Change of NH₄NO₃ concentration in aqueous phase with amorphous zeolite.

3.2.2 Effect of pH

The Kd values of ammonium nitrate in the concentration of 0.01M to 2.0 M are considerably higher than those of nitric acid.

In the identical concentration, both solutions show different pH value; 0.1 M HNO₃ and NH₄NO₃ shows pH 1.2 and 5.9 respectively. Reported results of natural zeolite²⁾ show that their Kd values did not vary with change of pH, which is not the case with any of three synthetic zeolite. Thus, synthetic zeolite requires pH adjustment in practical use. And it confirmed that around pH 4 is suitable to zeolite treatment in the nitric acid and ammonium nitrate solution.

3.3 Separation Mechanism

3.3.1 Exchangeable ions of zeolite

The reason that Kd value trends show three reactivities can be assumed that zeolite structural properties affect on it. Sodium ions of zeolite A and faujasite are known to be positioned in three types of site in the zeolite frame work structure. Cs and Co ions are considered to occupy similar site as sodium ions. Three steps of the Kd value trends, fast, slow, and no change, would be explained by a difference of the reactivities of these sodium ions. The sodium ions in the Site III would be the least reactive and would explain the unexchanged.

The ultimate base exchange capacity of zeolite depends upon the chemical composition; a higher exchange capacity is observed with zeolite of low $\text{SiO}_2/\text{Al}_2\text{O}_3$. In aqueous solution, exchange capacities of hydrated zeolite vary with the exchange cation. Zeolite A and faujasite have indicated a Si/Al ratio of slightly less than 1 and 2.2 respectively.

Figs. 10-18 show that univalent ion Cs-137 has higher Kd value than those of the divalent Co-60 and trivalent Ce-144 in connection with zeolite's exchangeable ions in both zeolite structures. It is not always possible to displace the 12 sodium ions in zeolite A, and 43 sodium and 29 calcium ions in faujasite, present in α -cage, with those of Cs-137, Co-60 and Ce-144⁸⁾.

In case of cesium complete replacement is

prevented by steric consideration, but in the cobalt electrostatic forces also involved, since introduction of divalent cation into a single-charged cage necessitates the presence of an empty cage in the structure; this leads to charge separation, and become energetically unfavorable. Ion exchange equilibria in zeolite A and faujasite have involved mostly univalent and divalent counter ions. It was reported that D.W. Breck's⁹⁾ attempt to exchange zeolites with trivalent cerium ions were unsuccessful. This is assured that displaced to heavy metal ion by other mechanisms such as ionic sieve effect.

3.3.2 Cation sieve effect

Partial sieving effect of zeolites toward various cations has been attributed to one or more of three possible mechanisms; (1) the cation may be too large to enter smaller channels and cavities within the Zeolite, (2) the distribution of charge on the zeolite structure may be unfavorable for the cations, (3) the size of the hydrated cation in aqueous solution may influence and retard exchange of the cation.

The trivalent cerium is involved in second type ion sieve effect in Zeolite A and Faujasite⁹⁾.

3.3.3 Adsorption

The nature of this mechanism is conjectured from the manner in which sodium ion is desorbed by zeolite during the period of heavy

metal adsorption. But ion-exchange alone will not suffice to explain the following points: variation of K_d value for different ions as reported in results; Among cobalt, cerium and cesium, the K_d value of cesium is two times of that of cerium and cobalt.

These phenomena would not occur under a system governed only by ion-exchange but different mechanism must be conjectured to arise the exchange reaction. Therefore, ion-exchange of heavy metal ions by Zeolite cannot be attributed to a simple mechanism of ion-exchange or physical adsorption.

3.4 Optimal condition for isolating and removing

The optimum condition isolating and removing troublesome radionuclides Co-60, Cs-137 and Ce-144 with zeolite A, faujasite and amorphous zeolite is determined in Figs. 4-18. The K_d value of Cs-137, in 0.01M HNO_3 , was about two times of Ce-144 and Co-60, which evidences a strong affinity for cesium even in the presence of other co-present ions. But K_d value of Co-60, in 0.1M NH_4NO_3 was about two times of cesium and cerium, which evidence a strong affinity for cobalt with the presence of co-present ions. Among zeolite A, faujasite and amorphous zeolite, amorphous zeolite exhibited a greater difference K_d value with their structural properties. This results indicate that the rate determining step of the ion-exchange reaction in zeoli-

tes is diffusion of metal ions within the zeolite, so that smaller particles which would possess a large relative surface area should have a greater ion-exchange velocity. In view of structural property, amorphous zeolite has large surface area compared with zeolite A and faujasite having frame work⁸⁾. The reason what amorphous zeolite is shown the most high K_d value, is due to the adsorption behavior rather than ion-exchange mechanism.

In conclusion, the optimal condition for isolation and removal of cesium, cerium and cobalt is: zeolite, amorphous zeolite, concentration 0.01 M HNO_3 and 0.1 M NH_4NO_3 ; pH, 4; shaking time, one hour; the most effective species, Cs-137 in 0.01 M HNO_3 .

REFERENCES

- 1) F. Kawamura and K. Motojima, Nucl. Tech., 58, 242 (1982).
- 2) M. Suss and G. Pfrepper, Radiochim. Acta, 29, 33 (1981).
- 3) E. Akatsu and R. Ono, J. Nucl. Sci. Tech., 2(4), 141 (1965).
- 4) R.M. Barrer and J.D. Falconer, Proc. Roy. Soc., 236A, 227 (1965).
- 5) H.L. Rothbart, H.W. Weymouth and W. Rieinan, Talanta, 11, 43 (1964).
- 6) B. Chu, D.C. Whitney and R.M. Diamond, J. Inorg. Nucl. Chem., 24, 1405 (1962).
- 7) T. Sakurai, Y. Komaki, A. Takashi and N. Izuno, J. Nucl. Sci. Tech., 21(11), 862 (1984).
- 8) W. Breck, "Zeolite molecular sieve", John Wiley (1974).
- 9) D.W. Breck, W.G. Eversole, R.M. Milton, T.B. Reed and T.L. Thomas, J. Amer. Chem. Soc., 78, 5963(1956).

제올라이트에 대한 세슘-137, 세륨-144 및 코발트-60 흡착거동

한양대학교

김 석 철 · 이 병 현

=요 지=

주요 핵분열 생성물인 세슘-137, 장수명 핵종과 세륨-144, 희토류원소 그리고 부식 생성물인 코발트-60 등의 제올라이트 A, 제올라이트 F-9(Faujasite) 그리고 비정형 제올라이트에 대한 흡착거동을 염농도 0.01 M 부터 2.0 M 질산과 질산암모늄 그리고 교반시간 15분부터 90분까지 15분 간격으로 검토하였다. Kd 값은 Batch 실험방법으로 구했다.

결론으로 주요핵종의 분리 제거의 최적조건은 비정질 제올라이트, 0.01 M-질산과 0.1 M-질산암모늄, pH 4, 교반시간 한시간 그리고 가장 효율높은 핵종은 세슘 -137이다.