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Application of the Radioactive Multitracer Technique to a Study of Adsorption of Metal Ions on α-Fe_2O_3

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The radioactive multitracer technique was applied to a study of adsorption of metal ions on α-Fe_2O_3 from aqueous solutions. The pH dependence of the adsorption of the elements, Sc, Ga, As(V), Se(IV), Rb, Sr, Y, Zr, Nb, and Mo(VI), was simultaneously determined using a multitracer solution separated from an Ag target irradiated by a 135 MeV/nucleon ^{12}C beam available from the RIKEN Ring Cyclotron. Characteristic adsorption behavior of each element was determined under strictly identical experimental conditions.

We established convenient and reliable radiochemical procedures by which radioactive multitracer solutions free from carriers are prepared from Au, Ag, and Cu targets irradiated with a high-energy heavy-ion beam accelerated by the RIKEN Ring Cyclotron.1,2) Use of the multitracer solutions enables us to determine the characteristic behavior of different elements under strictly identical experimental conditions and to make a precise comparison among them.

The adsorption-desorption process of metal ions on solid surfaces from aqueous solutions plays an important role in the transport of elements in the natural environment. Acid rain, which has become an increasingly serious problem in recent years, is sure to disturb the adsorption equilibrium of elements in the soil. From such a point of view, a systematic study on the adsorption of different elements is considered to be urgent. Although extensive studies were conducted on the adsorption behavior of some of the individual elements,3-6) no versatile investigation appears to have been reported yet concerning precise comparison of the adsorption of a number of elements under identical experimental conditions.

Here, the multitracer technique was applied to the study of the adsorption of elements on a model compound, α-Fe_2O_3, from aqueous solutions. The pH dependence of the adsorption of the elements, Sc, Ga, As(V), Se(IV), Rb, Sr, Y, Zr, Nb, and Mo(VI), was simultaneously determined using a multitracer solution separated from an Ag target irradiated by a 135 MeV/nucleon ^{12}C beam.

Three sheets of Ag foil (24 mmø × 100 μm) were stacked in a 40-mmø aluminum ball with a 20-mmø piercing hole and were irradiated by a 135 MeV/nucleon ^{12}C beam in the falling-ball irradiation system1) installed in a beam course of the RIKEN Ring Cyclotron. The beam intensity was about 100 nA and the

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irradiation time was several hours. The beam profile was roughly 10 mm × 10 mm.

The irradiated Ag foils (about 1.5 g in total) were dissolved in 19 cm^3 of conc. HNO_3. After dilution with an equal volume of distilled water, 14 cm^3 of a 4 mol dm^{-3} NaCl solution was added. After removal of AgCl precipitate by filtration, the solution was diluted with distilled water and adjusted to pH 2 with a dil. NaOH solution. Thus, a carrier-free multitracer solution was yielded, which was 1.0 mol dm^{-3} in $NaNO_3$ and 0.1 mol dm^{-3} in NaCl.2)

Ten milligrams of α-Fe_2O_3 (surface area: 27 m^2 g^{-1}) were added to 10 cm^3 of the multitracer solution at pH 2. The pH of the resulting suspension was adjusted to different values with a small amount of a dilute NaOH solution (less than 50 mm^3). The suspension was shaken at room temperature for 1 h. After centrifugation of the suspension, 5 cm^3 of the supernatant solution was withdrawn for measurement of γ-ray spectra.

The γ-rays of radioactive nuclides in the solution before adsorption and of those in the supernatant solution after that were measured with pure Ge detectors. The peak areas of the spectra were computed with the BOB 76 code7) on a FACOM M780 computer at the Institute. Assignment of the γ–rays was performed on programs developed by us. The percentage of adsorption for each nuclide was calculated by comparing the peak areas at the given γ–ray energy for the solutions before and after adsorption with correction for decay.

Figure 1 shows the pH dependence of adsorption of 10 elements obtained simultaneously in an experimental run. The patterns of adsorption can be classified into the following five groups: A) Sc, Y, and Zr, whose percentage of adsorption increases with increase of pH, attaining complete adsorption in the alkaline region, B) Se(IV) and Mo(VI), which are adsorbed almost completely in the acid pH range, but whose adsorption decreases with increase in pH, C) Ga, which is adsorbed completely in the neutral region, but whose adsorption decreases in both acid and alkaline pH ranges, D) Rb and Sr, which show little or low adsorption within the entire pH range studied, and E) As(V) and Nb, which give high adsorption yield within the entire pH range.

The adsorption of elements in Group A is a typical one observed for a number of metal cations.3-6) On the other hand, the adsorption pattern of Group B elements is similar to those observed for SeO_4^{2-}, CrO_4^{2-}, and SO_4^{2-} on amorphous iron oxyhydroxide,8-10) as well as for $[Sb(OH)_6]^-$ on α-Fe_2O_3.11) The observation indicates that carrier-free Se(IV) and Mo(VI) exist as oxyanions in the multitracer solution employed, as is expected from their ordinary solution chemistry. The adsorption behavior of the Group C element, Ga, is compatible with its amphoteric nature. The results of Rb and Sr (Group D) are typical of elements not hydrolyzable except for in strongly alkaline solutions, while that of Nb in Group E is representative of strongly hydrolyzed elements within the entire pH range.12) It is interesting to note that strong adsorption throughout the entire pH range was observed for As(V), which is considered to be the oxyanions in the solution.

The results described above demonstrate the usefulness of the multitracer technique in studying the behavior of a number of elements under identical experimental conditions. The adsorption characteristics of the elements revealed in the present work provide a basis for understanding their behavior in natural environments. The results are also useful in the separation of different elements. It is seen from Fig. 1 that the pairs, Se - As, Sr - Y, and Zr - Nb can be separated using adsorption on α-Fe_2O_3 at pH 11, 8, and 2, respectively. This is applicable in radiochemistry for separation of daughter nuclides from their parents.

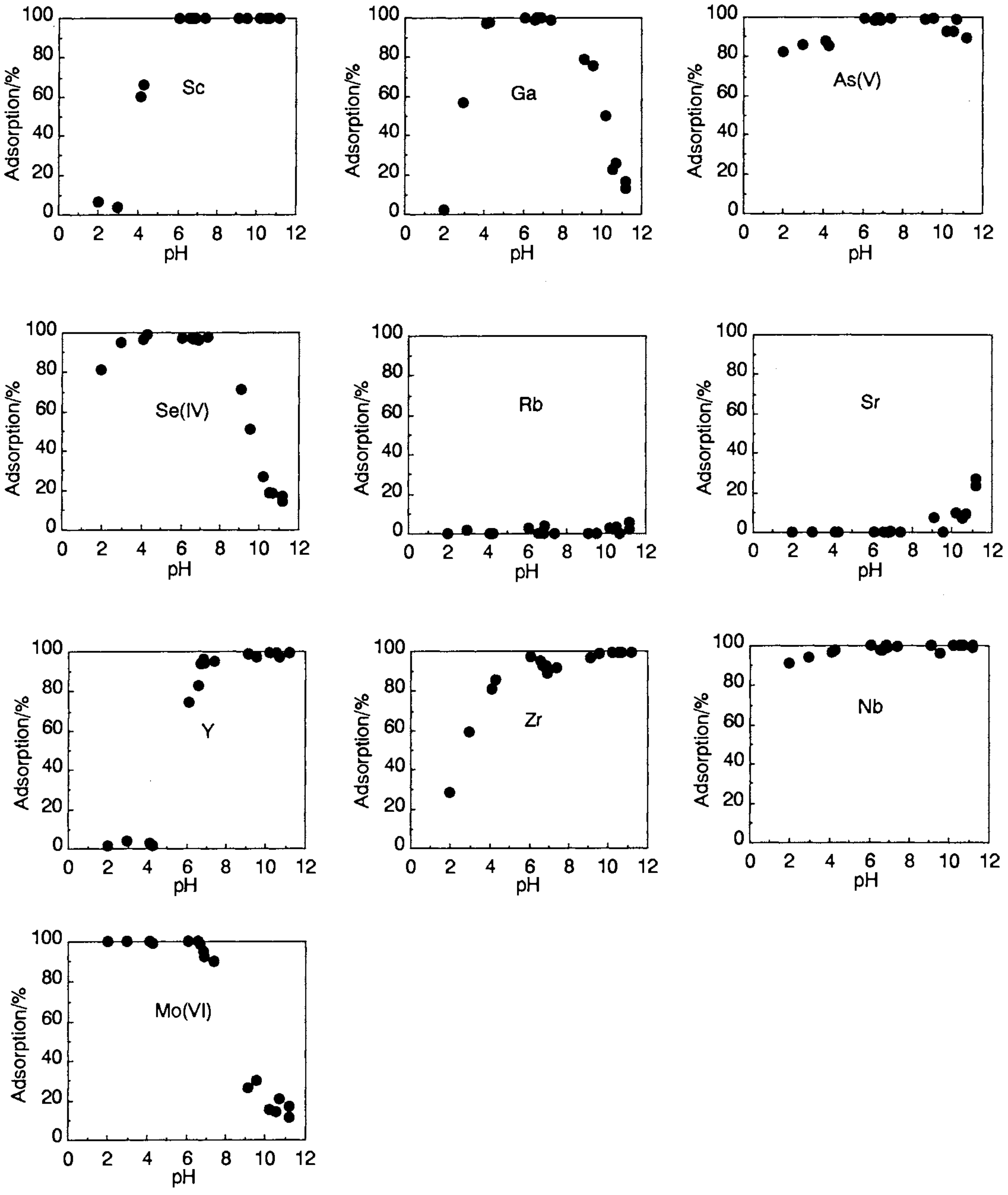

Fig. 1. The pH dependence of adsorption of the elements, Sc, Ga, As(V), Se(IV), Rb, Sr, Y, Zr, Nb, and Mo(VI), determined simultaneously under strictly identical experimental conditions using the multitracer technique.

Detailed discussion on the mechanisms of the adsorption in terms of the surface charge of α-Fe_2O_3 and chemical species of the elements in the multitracer solution will be described elsewhere, along with experimental data on other elements and those on kinetic aspects of adsorption. Similar work on different adsorbates is also in progress.[13)]

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References

1) S. Ambe, S. Y. Chen, Y. Ohkubo, Y. Kobayashi, M. Iwamoto, M. Yanokura, and F. Ambe, Chem. Lett., 1991, 149.
2) S. Ambe, S. Y. Chen, Y. Ohkubo, Y. Kobayashi, M. Iwamoto, M. Yanokura, and F. Ambe, Anal. Sci., 7, Suppl. 317 (1991).
3) E. A. Jenne, "Chemical Modeling in Aqueous Systems," ACS Symp. Ser. 93, Am. Chem. Soc., Washington, D. C. (1979).
4) P. H. Tewari, "Adsorption from Aqueous Solutions," Plenum, New York (1981).
5) M. A. Anderson and A. J. Rubin, "Adsorption of Inorganics at Solid-Liquid Interfaces," Ann Arbor Science, Michigan (1981).
6) J. A. Davis and K. F. Hayes, "Geochemical Processes at Mineral Surfaces," ACS Symp. Ser. 323, Am. Chem. Soc., Washington, D. C. (1986).
7) H. Baba, H. Okashita, S. Baba, T. Suzuki, H. Umezawa, and H. Natsume, J. Nucl. Sci. Technol., 8, 1227 (1972).
8) J. A. Davis and J. O. Leckie, "Chemical Modeling in Aqueous Systems," ACS Symp. Ser. 93, Am. Chem. Soc., ed by E. A. Jenne, Washington, D. C. (1979), p. 299.
9) J. A. Davis and J. O. Leckie, J. Colloid Interface Sci., 74, 32 (1980).
10) M. M. Benjamin and N. S. Bloom, "Adsorption from Aqueous Solutions," ed by P. H. Tewari, Plenum, New York (1981), p. 41.
11) S. Ambe, Langmuir, 3, 489 (1987).
12) C. F. Baes, Jr. and R. E. Mesmer, "The Hydrolysis of Cations," R. E. Krieger, Florida (1986).
13) S. Y. Chen, S. Ambe, Y. Ohkubo, M. Iwamoto, Y. Kobayashi, N. Takematsu, and F. Ambe, Anal. Sci., 7, Suppl. 1105 (1991).

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