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Adsorption Characteristics of Lithium in Sea Water with Coprecipitated Alumina-Magnesia Gel

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Alumina-magnesia mixed-oxide gel exhibited adsorptive ability for lithium in sea water attributed to weak acidic sites and micropores of diameter 20-30 Å. The adsorption of lithium proceeded predominantly by the mechanism of ion-exchange, on which the facility was shown in the order of $Na^+ > H^+ > NH_4^+$. The elution of lithium adsorbed on the gel was complete with dilute hydrochloric acid.

There is a big demand for lithium having various uses such as dry cell, high performance grease, heat-resistant ceramics, flux for welding, etc. Further, a nuclear fusion furnace will require lithium for the production of tritium as fuel. The collection of lithium in sea water is an attempt of great significance in Japan. It is well known that the concentration of lithium in sea water is as low as about 0.17 $mg\,dm^{-3}$ but the total amount 240 billion tons. The collection of lithium in sea water seems to be very difficult because of the coexistence of other alkali and alkaline earth metals having similar chemical properties. The adsorption processes are probably the most feasible among diverse techniques1) for this collection tested so far. For this to be practical, however, good adsorbents from functional and economical standpoints are essential.2-6) We found here that alumina-magnesia gel prepared through a wet process exhibited the good adsorptive ability for lithium in sea water. Then, we undertook to discuss the preparation method and composition of gel, to improve the ability by means of the pretreatment with proper chemicals, and to elucidate the relationship between surface properties and ability of gel.

Alumina-magnesia gel was precipitated from the mixed solution of aluminum and magnesium chlorides by adding sodium hydroxide solution until pH 9 at room temperature. After aging for 10 h, the resultant precipitate was filtered by suction, thoroughly washed with deionized water, and then dried in an oven at 110 °C overnight. An adsorbent was obtained by grinding the dried gel once, followed by sieving to 20-42 mesh size. The pretreatment of adsorbent was carried out by soaking into sodium chloride, ammonium chloride, or hydrochloric acid solution. The adsorption isotherm on gel was determined using nitrogen at 77 K from which the surface area was calculated from the BET equation and the pore-size distribution by applying the Clanston-Inkley method.7) The solid acidity of gel was measured by titration with n-butylamine using 4-benzeneazo-1-naphthylamine ($pK_a \leqq +4.0$) as an indicator. The adsorption of lithium in sea water was examined in terms of a batchwise operation by shaking 200 mg of adsorbent with 100 cm^3 of sea water at 20 °C for 24 h. Lithium in sea water was determined by flame spectrophotometry. Sea water containing 0.17 mg dm^{-3} of lithium was sampled at the Cape Omaezaki, Shizuoka Prefecture.

The batchwise operation for adsorption test made it clear that alumina-magnesia gel showed better ability for lithium in sea water among various metal oxides and mixed oxides prepared in a similar way. Further, the mixing of alumina and magnesia gels was effective and alumina-magnesia gel of molar ratio 1:1 (AM5050) best, as shown in Fig. 1. This tendency was in fair agreement with the solid acidity (Fig. 2), suggesting the participation of acid sites on the surface of gel to the adsorption just as the adsorption of uranium in sea water with silica-titania gel.[8)] The physical properties on the surface of gel, e.g., specific surface area, mean pore diameter, and micropore volume were all in the intermediate between those of alumina and magnesia gels. The structure of this binary gel may be regarded as the intimate mixture of alumina and magnesia gels in which the framework of alumina gel precipitated from the mixed chloride solution earlier than magnesia is partly stuffed by widely dispersed magnesia. It seems probable that the occurrence of the bond, Al-O-Mg, around the interface of alumina and magnesia particles caused the mixed oxide gel to have a large number of weak acidic sites. Figure 3 shows the micropores of diameter 20-30 Å effective to the adsorption of lithium in sea water because the pore volume of diameter 20-30 Å of alumina-magnesia gel is much larger than that of alumina (A100) or magnesia (M100).

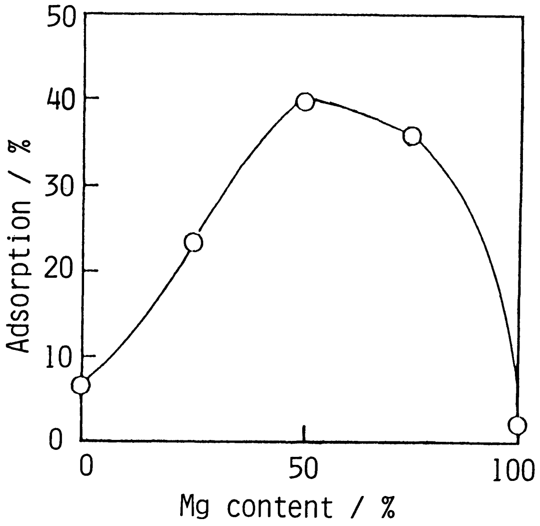

Fig. 1. Effect of the composition of alumina-magnesia gel on the adsorption of lithium in sea water.

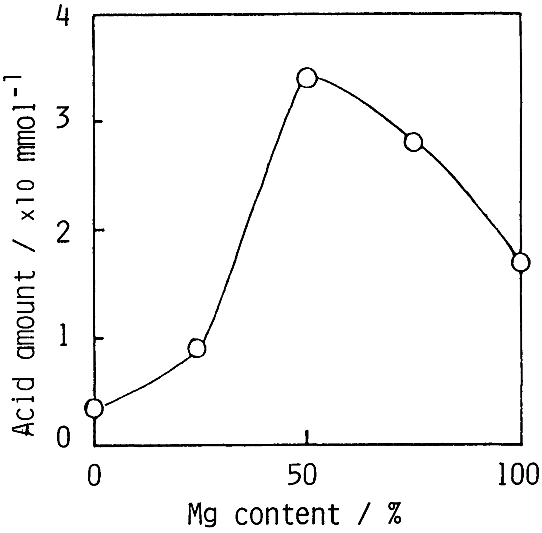

Fig. 2. Relationship between the acid amount and composition of alumina-magnesia gel. ($pK_a \leqq +4.0$)

While, the micropores of diameter 20-30 Å diminished largely through both the adsorption test in sea water and the mixed solution of lithium chloride and lithium hydroxide at the same lithium concentration and pH as sea water (Fig. 4), which implied the participation of the above-mentioned micropores to the adsorption of lithium. It has further been proved that this adsorption was relatively affected by the grain size of adsorbent. The rate determining step of this adsorption seemed to be the internal diffusion of lithium ion into the micropores of diameter 20-30 Å, because the adsorption of lithium ion on the gel occurred mainly at the surface of micropores, which was not so affected by the grain size, and the diffusion of lithium ion through liquid boundary film proceeds easily as well as the adsorption reaction. This adsorption obeyed the Langmuir-type adsorption isotherm; the apparent activation energy was determined to be 45.5 kJ mol^{-1} so that it was attributed to chemical adsorption rather than physical adsorption.

The stoichiometric relations relevant to ion-exchange reaction were satisfied between proton on alumina-magnesia gel pretreated with dilute hydrochloric acid and lithium ion in sea water: the slope of straight line in the plot of log K_d (distribution coefficient) versus equilibrium pH of sea water adjusted the initial pH was closely equal to unity.[9] It can, therefore, be speculated that the adsorption of lithium here proceeds predominantly by the mechanism of ion-exchange.

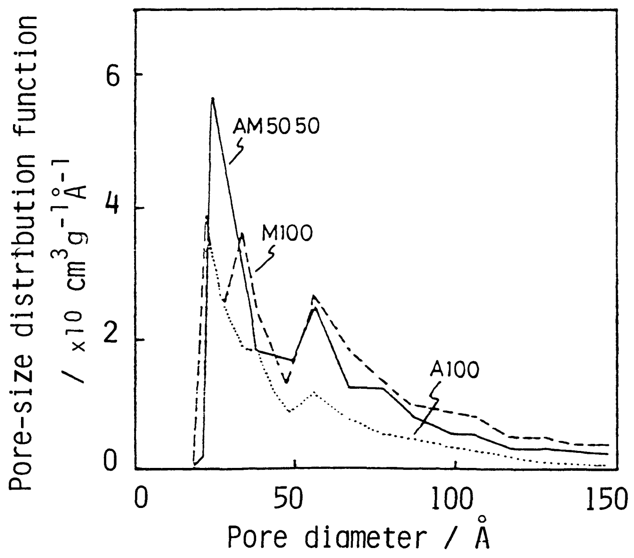

Fig. 3. Pore-size distribution curves of alumina-magnesia (AM5050), alumina (A100), and magnesia (M100) gels.

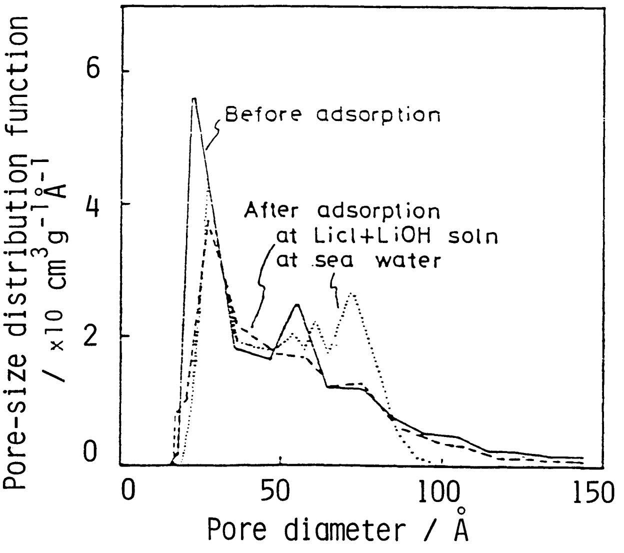

Fig. 4. The variation of pore-size distribution curve of alumina-magnesia [AM5050(Na)] gel after the adsorption.

Alumina-magnesia gel was also precipitated with aqueous ammonia [AM5050(NH_3)] or urea [AM5050(H)]. However, the adsorption ability of either gel was lower than that of the gel precipitated with sodium hydroxide [AM5050(Na)], as shown in Table 1. The comparison of pore volume from 20 Å to 30 Å of each as-prepared gel, which was assumed to contribute largely to the adsorption of lithium, gave a proper interpretation of the difference among the adsorption abilities of these three gels. After the pretreatment of gels with sodium chloride, ammonium chloride, or

Table 1. Effect of preparation method and pretreatment of alumina-magnesia gel[a)]

Precipitant	Adsorption / %			
		Treatment agent		
	as-prepd	NaCl	NH_4Cl	HCl
NaOH	40	50	20	31
aq.NH_3	28	52	27	30
$(NH_2)CO_2$	13	20	11	14

a) AM5050(Na)

hydrochloric acid, the adsorption abilities of gels all were changed; only the pretreatment with sodium chloride made the ability increase remarkably [particularly in AM5050(NH_3)], but no effect of other two pretreatment was recognized. The facility of ion-exchange of lithium was shown in the order of $Na^+ > H^+ > NH_4^+$, because the difference in the pore-size distribution curves of the as-prepared three gels was not so much observed. The adsorption rate also was improved by the pretreatment of both alumina-magnesia gels, AM5050(Na) and AM5050(NH_3) with sodium chloride, together with the adsorption amount.

The Freundlich-type adsorption isotherm related the amount of lithium adsorbed to the equilibrium concentration of lithium in sea water. Then, the adsorption amount of lithium on AM5050(Na) and AM5050(NH_3) pretreated with sodium chloride were evaluated to be 70 $\mu g\, g^{-1}$ and 100 $\mu g\, g^{-1}$ at the lithium concentration in sea water (0.17 $mg\, dm^{-3}$), respectively. Taking account of both the adsorption test using genuine sea water and adsorbent of relatively large size (average diameter about 0.5 mm), these adsorption amounts should be noted. Lithium adsorbed on alumina-magnesia gel of highest ability was completely eluted with 0.05 M hydrochloric acid, and then the lithium was possibly concentrated up to 7 times compared with its original concentration in sea water.

References

1) M. Kanno, Nippon Kaisui Gakkaishi, 39, 240 (1985).
2) H. Izawa, J. Solid State Chem., 60, 264 (1985).
3) Y. Inoue, H. Yamazaki, and Y. Kimura, Bull. Chem. Soc. Jpn., 58, 2481 (1985).
4) M. Abe, Y. Kanzaki, and R. Chitraker, J. Phys. Chem., 91, 2997 (1987).
5) F. J. Seeley and W. H. Baldwin, J. Inorg. Nucl. Chem., 38, 1049 (1976).
6) H. Wada, T. Kitamura, A. Fujii, and S. Kato, Nippon Kagaku Kaishi, 1982, 1152.
7) R. W. Cranston and F. A. Inkley, Adv. Catal., 9, 143 (1957).
8) S. Kaneko, S. Okuda, M. Nakamura, and Y. Kubo, Chem. Lett., 1980, 1621.
9) Y. Fujiki, Y. Komatsu, and T. Sasaki, Nippon Kagaku Kaishi, 1981, 1656.

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