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Basic Study on Lithium Recovery from Lithium Containing Solution

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Basic study of Li recovery using high purity sodium aluminate solution as coprecipitating agent has been made. Al concentration, pH and temperature greatly affect the Li recovery, and in this study the temperature was maintained constant (25 °C). For reference lithium solution, the optimum (initial) pH obtained increased with an increase in Al concentration. Optimum pH=11.0—12.5 for [Al]=50—1000 mg dm^{-3}. The optimum pH values obtained were lower than those in the previous work by about one pH unit. The following relationship was found between the Al concentration C_{Al} (mg dm^{-3}) and the optimum pH; Opt. $pH^{exp}=8.23+1.5\log C_{Al}$. Furthermore, these experimental pH values were in fair agreement with the pH values calculated from the solubility product of aluminium hydroxide, $K_{sp}(HAlO_2)=[H^+][AlO_2^-]=10^{-13.2}$, i.e., $pH^{calcd}=9.5+\log C_{Al}$. Effects of coexistent ions on Li recovery were examined. Sodium and potassium ions did not interfere, while calcium, magnesium, and monosilicate ions did. However, the interference from Ba^{2+} ions was small. Especially, interference by calcium and monosilicate ions were significant. Bubbling of CO_2 gas into the Li solution with proper Al concentration made a remarkable improvement on Li recovery. Accordingly, the influence of water soluble carbonates on Li recovery was investigated. The carbonates (Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$) used were found to be very effective for Li recovery. The addition of sodium aluminate solution (500 mg dm^{-3}) to untreated geothermal water showed around 70% of Li recovery at the best. This incomplete recovery of lithium is due to the matrix effect of geothermal water. For reference Li solution with Al concentration of 500 mg dm^{-3}, optimum pH was 12.5, while for Ca, SiO_2-free geothermal water the same pH gave very low Li recovery. However, when a pH value of 11.5 is chosen, a remarkable increase in Li recovery was obtained (98—99%). The silica component in geothermal water interfered with the Li recovery, but the influence was relatively small. The silica in the geothermal water in this case, was polymerized and showed some buffering action, such as prevention of interference from calcium ions. This is the significant difference between poly and monosilicate ions which do not show any buffering action. The addition of sodium carbonate to the Ca,SiO_2-free geothermal water caused a remarkable acceleration of the Li recovery, similar to that for the reference Li solution.

Lithium has been widely used in recent years in batteries, glass, ceramics, aluminium refinning and other industries. A world wide increase in demand is expected in future. In addition to these commercial uses, lithium is also anticipated to be the fuel for nuclear fusion and a blanket material in fusion reactors[1] in the 21 century. The estimated lithium resources are not enough when the increase in future demand is taken into account. Lithium recovery from geothermal water using a coprecipitation method has been studied as a part of the basic investigation of lithium extraction from brines.[2] The results have taught us that among the coprecipitating agents used in the previous work, aluminium salts showed the best performance. The appropriate pH for Li recovery is in the high pH region of 10—13. Thus, from the operational point of view, the use of $NaAlO_2$ seemed better than that of $AlCl_3$. In the previous work, the $NaAlO_2$ addition method was partly applied. However, the salt was added in a powdered form and the data obtained showed some scatter, although the trends were probably real. Commercially obtained $NaAlO_2$ was used as the coprecipitating agent in the form of a highly alkaline solution.[3] Provided the same lot number of $NaAlO_2$ is used, the data showed relatively good reproducibility, but the data obtained from different lots showed large discrepancies. The reason could be: (1) a difference in the ratio of Al to NaOH, for example Al/NaOH=0.76—0.82, (2) the presence of impurities. In this study, a $NaAlO_2$ solution of high purity, except for NaOH, was prepared as coprecipitating agent for lithium recovery.

Experimental

Reagents. The special grade LiCl, NaCl, KCl, $CaCl_2\cdot 2H_2O$, $MgCl_2\cdot 6H_2O$, $BaCl_2\cdot 2H_2O$, Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$ were obtained from Wako Pure Chemical Industries, Ltd. Al plates (99.99%) and $Na_2SiO_3\cdot 9H_2O$ were obtained from Wako pure Chemical Industries, Ltd. All other reagents used were also obtained from Wako Pure Chemical Industries, Ltd.

Measurements and Apparatus. The concentration of lithium, sodium, potassium, calcium and magnesium were measured on a Japan-Jarrel Ash AA-8200 atomic absorption spectrophotometer. Silica was measured on a Shimadzu UV-200 double beam spectrophotometer, according to the JIS method.[4] pHs of solutions containing lithium were measured with an Instrument Co.Ltd., digital pH meter, DP-1400. An Ikeda Rika six-series magnetic stirrer was used to stir solutions.

Sample Solutions. a) Li Solution: The proper amount of LiCl was dissolved in distilled water, and adjusted to a Li concentration of 10 mg dm^{-3} ($[Li^+]_0=10$ mg dm^{-3}).

b) Geothermal Water: Geothermal water was sampled from a reservoir pond at mixed wells at the Hatchobaru power plant in Ohita prefecture, in January, 1983. Geothermal water was used in the laboratory six months after sampling.

Coprecipitating Agent. Prior to the preparation of the

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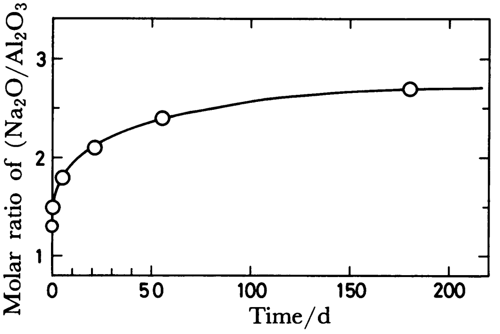

Fig. 1. Spontaneous decomposition of sodium aluminate solution with various (Na_2O/Al_2O_3) molar ratios at room temperature. [Na_2O]: 150 (g dm^{-3}).

$NaAlO_2$ coprecipitating agent, a preliminary test was made to examine the stability of the $NaAlO_2$ solution. The $NaAlO_2$ solution is said to be unstable at an Na_2O concentration of less than 90 g dm^{-3} and molar ratio of Na_2O to Al_2O_3 less than 1.3 at 25—50 °C, but when the ratio of $(Na_2O/Al_2O_3)_{mol}$ is set between 1.5—2.5, it is relatively stable at room temperature.[5] In the present work, the Na_2O concentration was fixed at 150 g dm^{-3}, and the value of $(Na_2O/Al_2O_3)_{mol}$ was changed between 1.3—2.7 taking into account the results obtained by Shimizu et al.[5] The stability of the sodium aluminate solution prepared as described above was examined at room temperature (around 25 °C) as shown in Fig. 1. It was found that the relationship between the spontaneous decomposition time, t (in day) and the molar ratio, $R[=(Na_2O/Al_2O_3)_{mol}]$ was given by:

$$\log t = 1.78 R - 2.504$$

Thus, the $NaAlO_2$ stock solution was adjusted to be; [NaOH]=200 g dm^{-3}, [Al]=50 g dm^{-3} and $(Na_2O/Al_2O_3)_{mol}$=2.7.

High grade Al plates were washed with acetone and water, dipped in alkaline solution(1 M*-NaOH), washed with water, dipped in acidic solution (1M-HCl), washed with water, and finally washed with acetone and/or ether. The plates were then stored in a desiccator. Al (25g) was taken into the solution in which 100 g of NaOH was dissolved with 400 ml of distilled water, and the solution was stirred. After the complete dissolution of the aluminium plates, the solution was filtrated with a sintered-glass filter (G-4), washed and transfered to a 500 ml volumetric flask to be diluted to the mark.

Procedure. The similar experimental procedure on Li recovery was used as was described in the previous work.[2] In the present study, the Li containing solutions were placed in a thermostat (25 °C) to be free from temperature effect. The initial pH was adjusted using 1 M-HCl solution. Carbonates were added after the addition of coprecipitating agents to examine their effects. The pHs were then adjusted. When the influence of coexistent ions was being examined, the ions were just added to the Li solution. Subsequently the same procedure was followed as for the solution which were free from coexistent ions.

Treatment of Geothermal Water. Geothermal water was treated in the same way as that described above.[2] Ca-free geothermal water was prepared as follows; 30 ml of saturated $Na_2C_2O_4$ solution was added to the 1 liter of geothermal water, stirred for 2 h; the CaC_2O_4 precipitate that formed was filtrated with a glass filter (G-4). Silicate-free geothermal water was prepared as follows; $FeCl_3$ was added to be Fe concentration of 1000 mg dm^{-3}, and pH was adjusted (pH=9.5) with 5 M-NaOH solution. After being stirred for 2 h, the precipitate formed was filtered with filter paper (No. 131). Ca,SiO_2-free geothermal water was prepared by combining the above procedures, that is, by first removing calcium ions, and then silicate ions. The main components of the geothermal water are shown in Table 1.

Table 1. Li, Ca, and SiO_2 Concentrations in Hatchobaru Geothermal Water (Nontreated and Treated) in (mg dm^{-3})

Geoth. Water	Li	Ca	Total SiO_2
Nontreated G.W.	10.56	12.9	870
G4-filtreated G.W.[a]	10.56	12.9	434
Ca free-G.W.	10.21	0.2	788
SiO_2 free-G.W.	9.63	6.2	4
Ca, SiO_2 free-G.W.	9.33	0.2	4

a) G4: Glass filter G4, G.W.: Geothermal Water.

Results and Discussion

The Relationship betweem Al Concentration and Optimum pH on Li Recovery for Li Solution. pH dependence on Li recovery at various Al concentrations (50—1000 mg dm^{-3}) was examined. Figure 2 (1) shows the data for Al concentration of 300 mg dm^{-3} as an example. In the upper half of the left side of the figure(a) are given the residual Li concentrations as a function of time elapsed at various pHs. In the lower half of the left side of the figure(b) are given the time traces of pHs for the Li containing solutions with six initial pHs. Those solutions with initial pHs of 10—11.5 show rapid increase in pHs at the beginning, while those with initial pHs of 12—12.5 change slowly. The relationship between the initial pH and the percent recovery of lithium is shown in the right side of the figure(c). After 3 h, the curve with initial pH of 12 shows the maximum percent recovery of lithium among those with several pHs. At pH 12, around 86% of lithium was recovered after 6 h, while after 24 h, 100% was recovered. The data for other Al concentrations are shown in Fig.2 (2). The relationship between the Al concentration and the optimum pH for Li recovery thus obtained are shown as a solid line in Fig. 3, where at the appropriate pH if maximum recovery of lithium is obtained we designate that the optimum pH. For a Li solution, as the figure shows, the optimum initial pH obtained increases continuously with increase in Al concentration, where the optimum pH is 11.0—12.5 for [Al]= 50—1000 mg dm^{-3}. The optimum pH values obtained were lower than those obtained in the previous work[2] by about one pH unit. The following empirical formula

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* 1 M=1 mol dm^{-3}.

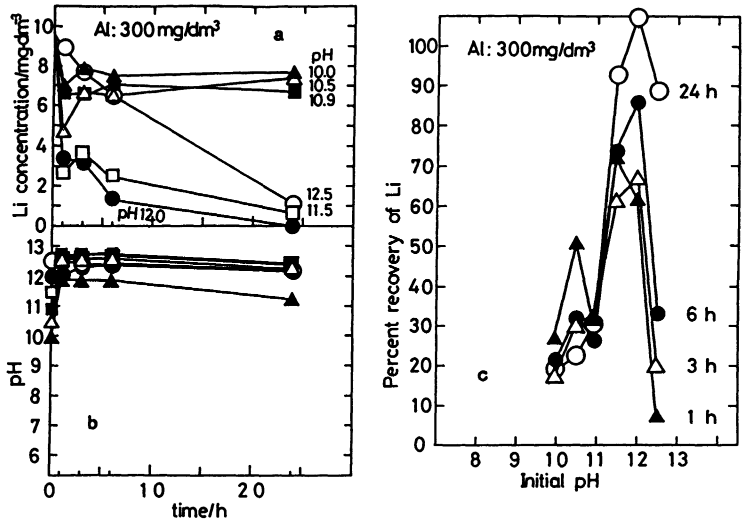

Fig. 2.(1) Initial pH dependence on Li recovery at Al concentration of 300 mg dm^{-3} at 25 °C. a) Time course of [Li$^+$], b) Time course of pH, c) The relation of initial pH and percent recovery of lithium.

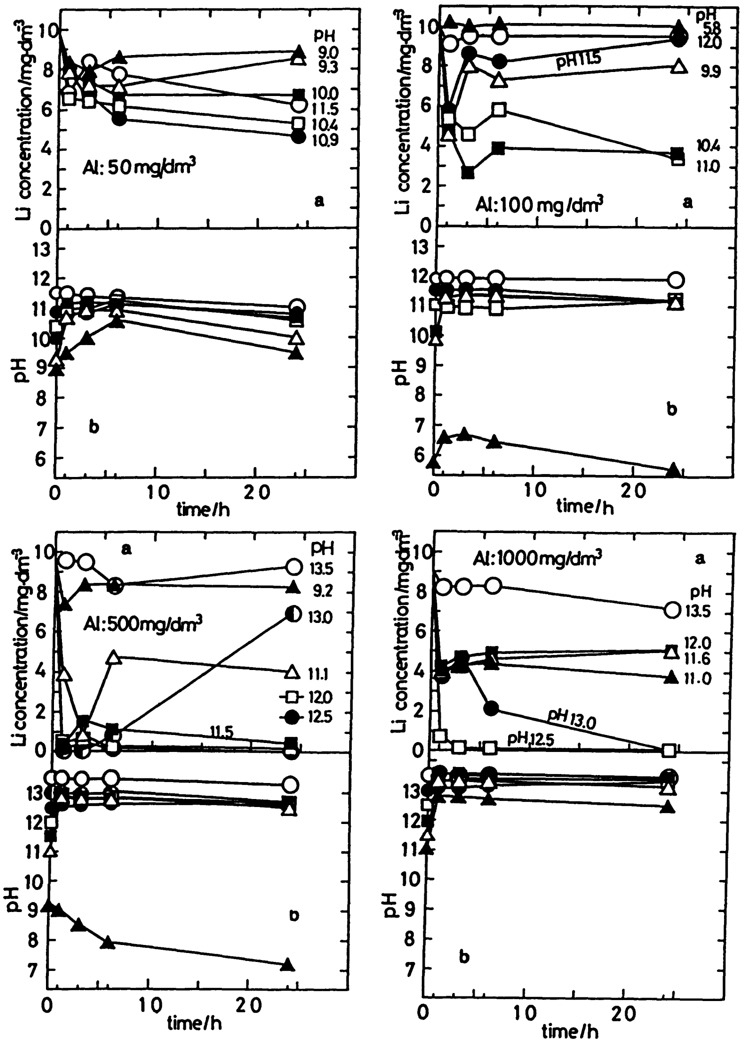

Fig. 2.(2) Initial pH dependence on Li recovery at various Al concentrations at 25 °C.

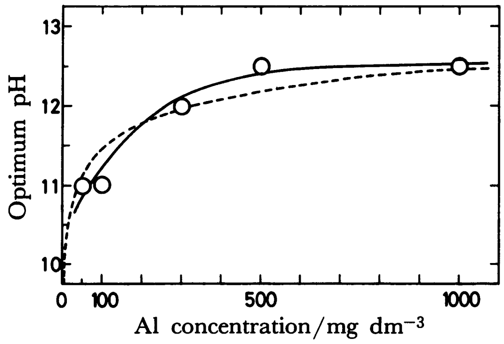

Fig. 3. The relationship between Al concentration and optimum initial pH for Li concentration of 10 (mg dm^{-3}) solution at 25 °C. ——: Experimental curve, -----: Theoretical curve obtained using solubility product of aluminium hydroxide {$K_{sp}(HAlO_2)=[H^+][AlO_2^-]=10^{-13.2}$}.

was found between the Al concentration C_{Al}(mg dm^{-3}) and the optimum pH;

$$pH^{exp}_{opt}([Li]_0 = 10\ \mathrm{mg\ dm^{-3}}:25°C) = 8.23 + 1.5 \log C_{Al}$$

These experimental optimum pH values were in fair agreement with the pH values calculated from the solubility product of aluminium hydroxide, $K_{sp}(HAlO_2)=[H^+][AlO_2^-]=10^{-13.2}$ that is, $pH^{calcd}=9.5+\log C_{Al}$. The broken line in Fig. 3 was plotted using these calculated values. This characteristic correspondence suggests that the optimum pH for Li recovery using the coprecipitation method will have some relation to the solubility product of aluminium hydroxide.

Influence of Coexistent Ions. Ca^{2+} and Mg^{2+} ions were known to interfere with the precipitation of lithium ions as aluminate.[6] The influence of Na^+, (K^+), Ca^{2+}, Mg^{2+}, (Ba^{2+}), and monosilicate ions on the Li recovery was investigated using freshly prepared high purity $NaAlO_2$ solution. The results are shown in Fig. 4. Sodium ions seem to behave differently in comparison with the Li solution. However, after 24 h, nearly the same percent recovery was obtained. Potassium ions seemed not to have any influence on Li recovery although its concentration is low, about two orders comparing with sodium ions. Alkaline earth metal ions, Ca^{2+} and Mg^{2+} ions interfere

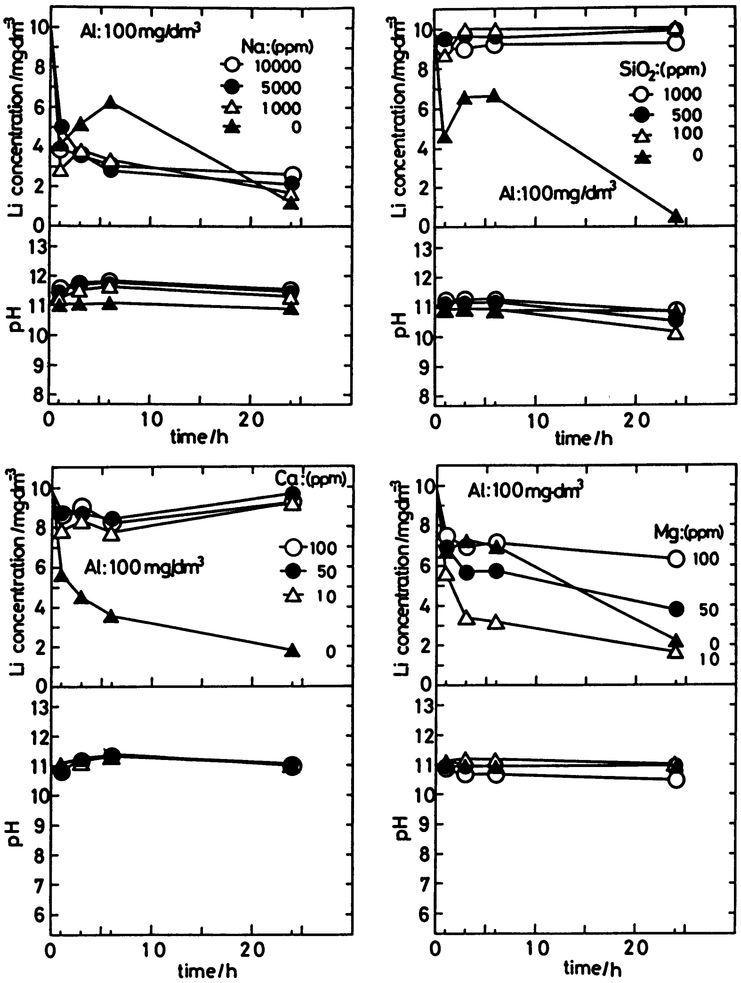

Fig. 4. Influence of coexistent ions on Li recovery at 25 °C. Interference ions illustrated were; [Na^+], [Ca^{2+}], [Mg^{2+}], [SiO_3^{2-}]. Counter ions used were Cl^- for cations, Na^+ for anions.

with the Li recovery as is shown in the figure. Especially, Ca^{2+} ions give large interference. Even a Ca concentration as low as 10 mg dm^{-3}, prevented the recovery of lithium. To examine the uptake of Ca ions into aluminate precipitates in detail, the residual Ca concentration in the Li containing solutions was measured. Figure 5 shows the results. For the solution with an initial Ca concentration of 10 mg dm^{-3}, the maximal uptake was 99%, while for Ca concentrations of 50 and 100 mg dm^{-3}, it was 94 and 70%, respectively. If Ca^{2+} ions were taken up into the precipitate in the form of $Ca(AlO_2)_2$, the total calcium content which corresponds to 74 mg Ca dm^{-3} will be incorporated into the precipitates, assuming that the calcium aluminate is completely insoluble. Considering these results, when a Ca salt is added to a Ca concentration of 10 mg dm^{-3}, there should remain enough room for the aluminate ions to react with lithium ions. In practice, however, very little lithium was recovered. The reason is not clear at present. But one possible explanation is that the calcium aluminate precipitated accelerates the formation of aluminium hydroxide, and the aluminate covers the surface of hydroxide. Interference from Mg^{2+} ions is not so large as is easily recognized in Fig. 4. Even for a Mg concentration of 50 mg dm^{-3}, a Li recovery of 60% (24 h) was obtained, and for 100 mg dm^{-3}, 36% (24 h). If Mg^{2+} ions were precipitated completely as $Mg(AlO_2)_2$, magnesium corresponding to a Mg concentration of up to 45 mg dm^{-3} would be taken up completely for 100 mg dm^{-3} of Al. Therefore, it seems that Ca $(AlO_2)_2$ is only slightly soluble in water, while $Mg(AlO_2)_2$ is more soluble than Ca $(AlO_2)_2$. Nevertheless, the residual Mg concentration in the solution became zero within 1 h at any initial Mg concentration. This phenomenon might be interpreted by the occulusion of magnesium ions into magnesium and/or lithium aluminate precipitates and by adsorption on aluminium hydroxide. Interference from Ba^{2+} ions was also studied but no meaningful influence was found. The influence of addition of monosilicate ions is also shown in Fig. 4. Monosilicate ions differ greatly from the polysilicate ions in geothermal water as is described later. This difference will be attributed to the reactivities of silicate ions with aluminate ions.

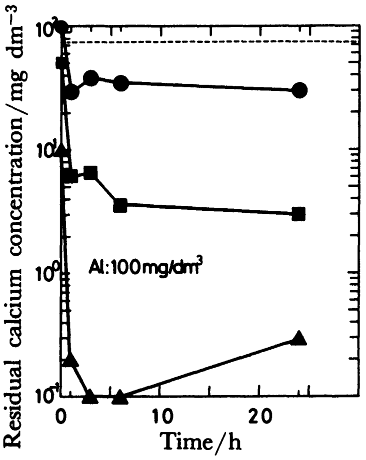

Fig. 5. Uptake of calcium ions into aluminate precipitates at 25 °C. $[Al]_0$=100(mg dm^{-3}), $[Li]_0$=10(mg dm^{-3}).
—▲—: $[Ca]_0$=10(mg dm^{-3}), —■—: $[Ca]_0$=50(mg dm^{-3}), —●—: $[Ca]_0$=100(mg dm^{-3}).

Effects of Carbonate Ions. We found that the blowing of CO_2 gas into the Li solution with appropriate Al concentration raised the Li recovery remarkably. Thus, three kind of water soluble carbonates were used to examine whether carbonate ions are effective or not on Li recovery. Concentrations of carbonates were chosen to be 0.2, 0.6, 1.0, and 2.0 g dm^{-3}. Figure 6 illustrates the effects of carbonates. The figure evidently shows the effectiveness of carbonate addition; the more carbonate, the better the Li recovery. The effects of potassium and ammonium salts seems to be superior to sodium salt although the

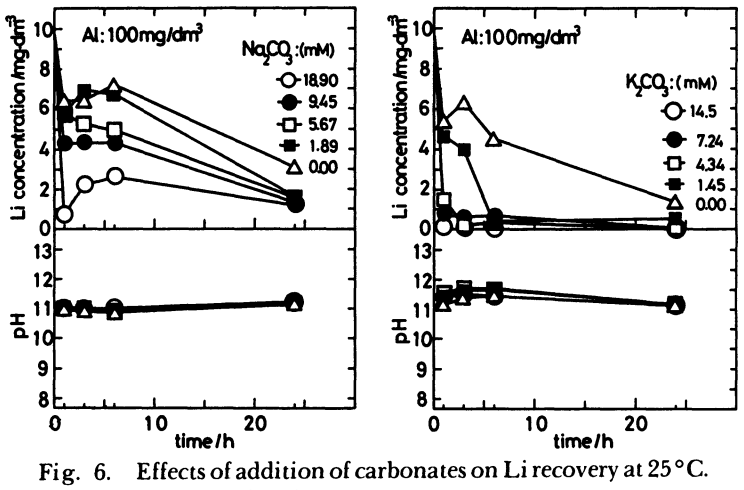

Fig. 6. Effects of addition of carbonates on Li recovery at 25 °C.
Concentrations of carbonates:
—△—: 0.0 (g dm^{-3}), —■—: 0.2 (g dm^{-3}), —□—: 0.6 (g dm^{-3}), —●—: 1.0 (g dm^{-3}), —○—: 2.0 (g dm^{-3}).

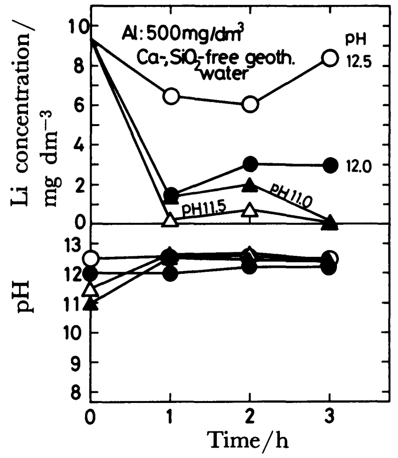

Fig. 7. pH dependence on Li recovery for Ca,SiO$_2$-free geothermal water at 25 °C. $[Al]_0=300$ (mg dm^{-3}). —▲—: pH 11.0, —△—: pH 11.5, —●—: pH 12.0, —○—: pH 12.5.

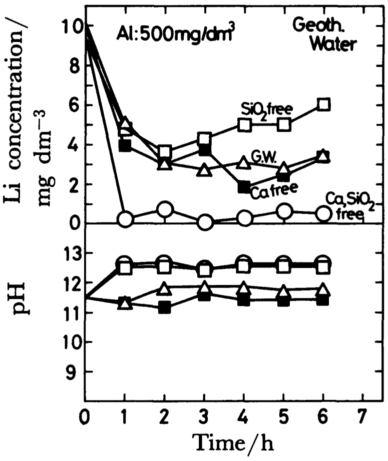

Fig. 8. Time courses of Li recovery for non-treated, Ca-free, SiO$_2$-free, and Ca,SiO$_2$-free geothermal waters at pH 11.5 at 25 °C. $[Al]_0=500$ (mg dm^{-3}). —△—: Non-treated geothermal water, —■—: Ca-free geothermal water, —□—: SiO$_2$-free geothermal water, —○—: Ca,SiO$_2$-free geothermal water.

results of ammonium salt was not shown here. However, the difference in univalent (alkaline) cations seems not to have any appreciable influence on Li recovery, as is already stated above. The effects of carbonate addition on Li recovery is significant but the reason is not clear. Three reasons are considered as follows: First, carbonate ions affect the surface conditions of aluminium hydroxide which is simultaneously formed with lithium aluminate to raise the adsorption capacity for lithium uptake (i.e., amorphous aluminium hydroxide which is very effective on Li adsorption[7] will be stably maintained). Second, the addition of carbonates lowers the solubility of the lithium aluminate formed. Thirdly, the optimum pH might be maintained by a pH buffer action due to the carbonate ions.

Mechanism. A mechanism for the Li recovery using the coprecipitation method was proposed in the previous paper.[2] That is, lithium is recovered by the formation of lithium aluminate and by adsorption on aluminium hydroxide. However, it seems that all the properties found in the study will not be explained satisfactorily by this mechanism. More detail discussion will be made in the following paper.

Lithium Recovery from Geothermal Water. The results of pH dependence on Li recovery from geothermal waters (nontreated and treated) is shown in Fig. 7. For an Li solution, optimum pH value for an Al concentration of 500 mg dm^{-3} was 12.5. However, for Ca,SiO$_2$-free geothermal water, the same pH gave only low recovery of 32—12% after 1—3 h from the beginning of Al salt addition. In this Ca,SiO$_2$-free geothermal water, the optimum pH was 11.5 which is lower than that of Li solution by one pH unit, and a high percent recovery of 98—99% was obtained after 1—3 h. The results for Ca-free, SiO$_2$-free, Ca,SiO$_2$-free and nontreated geothermal waters at an initial pH of 11.5 are shown in Fig. 8. The figure shows that there is little difference between nontreated and Ca-free geothermal waters. That is to say, the influence of polymerized silica is not large on Li recovery. However, for SiO$_2$-free geothermal water, the percent recovery of lithium is poorer compared with nontreated geothermal water because of the presence of calcium ions. The reason is that as the polysilicate ions have a buffer action, silicate ions prevent the interference from Ca ions to form calcium silicate although the polymerized silica itself exhibits some interference on Li recovery.

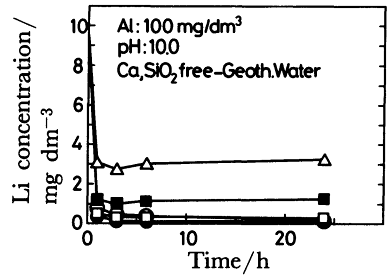

Fig. 9. Effects of Na$_2$CO$_3$ addition on Li recovery for Ca,SiO$_2$-free geothermal water at pH 10.0 at 25 °C.
—△—: $[Na_2CO_3]=0.0$ (g dm^{-3}), —■—: $[Na_2CO_3]=0.25$(g dm^{-3}) ($=2.36\times10^{-3}$ M), —□—: $[Na_2CO_3]=0.50$ (g dm^{-3}) ($=4.72\times10^{-3}$ M), —●—: $[Na_2CO_3]=1.0$ (g dm^{-3}) ($=9.44\times10^{-3}$ M), —○—: $[Na_2CO_3]=2.0$ (g dm^{-3}) ($=18.9\times10^{-3}$ M).

Effects of Carbonate Addition on Ca,SiO$_2$-free Geothermal Water. Sodium aluminate was added to generate an Al concentration of 100 mg dm^{-3} in Ca,SiO$_2$-free geothermal water in order to examine the effectiveness of Na$_2$CO$_3$ addition on Li recovery. As the optimum pH for the Li solution with an Al concentration of 100 mg dm^{-3} is 11.0, an initial pH of 10.0 was chosen for this solution. As Fig. 9 shows, the effect of the Na_2CO_3 addition is clearly recognized. The reason for the improvement in Li recovery found on Ca,SiO_2-free geothermal water will be the same as that for the Li solution.

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