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The Recovery of Lithium from Geothermal Water in the Hatchobaru Area of Kyushu, Japan

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The recovery of lithium from geothermal water at Hatchobaru in Kyushu, Japan, was investigated. A coprecipitation method using aluminium salts was employed. The lithium concentration in the geothermal water used in the present study was about 10 ppm. To make our experimental results more applicable for geothermal water, a reference lithium solution (10 ppm) was also studied as a control solution. A perfect recovery of lithium was obtained for the reference lithium solution by choosing appropriate conditions. For geothermal water, the yield of Li was not so good as in the control solution. However, an almost complete recovery of lithium was attained for geothermal water by the removal of calcium ions and polymerized silica. The mechanism of Li recovery was also considered.

The lithium industry was a minor one before World War II. In recent years, however, commercial uses of lithium and its compounds have increased in many fields, such as ceramics, glass, batteries, and metallurgy. In addition to these commercial uses, it is also anticipated that lithium can be used as blanket material in fusion reactors.[1)] Still more, from the point of view of the energy problem,[2)] the most important solution in the next coming century will definitely be the more basic use of lithium in the fusion energy process. A basic deuterium–tritium (D–T) reaction will release a neutron, an alpha particle, and an energy of 17.6 MeV carried by the neutron and alpha particle. Deuterium is available in seawater, but natural tritium is scarce. Bombarded by a neutron, lithium can be used as a breeder for tritium in the fusion reactor. The energy value of one gram of lithium can be increased by adding to the breeding ratio (tritons produced/tritons consumed) or by increasing the amount of energy per fusion. Lee estimated that the effective energy content of natural Li ranges from about 8.5×10^3 kW h (normal) per gram to 2.7×10^4 kW h (thermal) per gram of natural lithium.[3)]

In Japan, there are practically no lithium resources. Although the concentration is very dilute ($\fallingdotseq$0.18 ppm), there is a vast supply of lithium in seawater (estimated to be 2.5×10^{14} kg), probably the most reliable energy resource in the near future. At the present stage, however, the recovery of lithium from seawater in a commercially practical way is very difficult. Possible substitute for petroleum have been investigated recently in Japan. One of them is a geothermal energy. Water from the Hatchobaru power plant (50 MW), for example, gives Li values of about 140 (kg/d), (5.3×10^4 kg/Year) provided that the Li content is 10 ppm, and the fluid velocity of geothermal water, 600 t/h. Though the Li content thus obtained is small, it is equal to about one hundred million private persons' electric demand (as 1 kW·Year/Man·Year). Incidentally, the Li production in the world is about 9000 t (metric)/Year (1977), and most of lithium in the world is produced in the U.S.A. (*ca.* 70%), U.S.S.R(15—20%), Africa and china.[4)] The possible lithium recovery from Hatchobaru geothermal water will contribute only 0.6% to the total world production at present. Within the next 10 years however, the ratio of geothermal energy to the total energy in Japan will become 1%. According to our calculation, lithium products in Japan in the near future will become about 50 times as large as at present. The Li concentration in seawater is about 0.2 ppm, as has been stated above, while the concentration in geothermal water from the Hatchobaru bore is about 10 ppm. Thus, the recovery from geothermal water seems relatively easy and practicable compared with that from seawater. In the present work, the recovery of lithium from geothermal water is aimed at. As techniques to recover lithium from a lithium containing solution, there have been used the inorganic ion-exchange method, the adsorption method using many adsorbents, the solvent-extraction method, the coprecipitation method, and so on. The coprecipitation method seemed to be the simplest among these and so was employed in the present study. Although the lithium recovery from low-concentration solutions has been extensively investigated,[1,5—24)] the details of the mechanism for Li recovery seem not yet to have been clarified. Since the many factors concerning Li recovery are very complicated, the reported results are sometimes in conflict with each other. Thus, in the present work, a basic investigation will be made at first, then it will be applied to geothermal water.

Experimental

Geothermal Water. The geothermal water used in the present study was sampled out from bores at the Hatchobaru Power Station in Kyushu, Japan. The sampling of geothermal water was done from May 10, 1980, to January 22, 1981. Some typical constituents of geothermal water are shown in Table 1.

Reagents. *a) Precipitating Agents*: The $AlCl_3\cdot6H_2O$, $NaAlO_2$, $FeSO_4\cdot7H_2O$, $FeCl_3\cdot6H_2O$, $MgSO_4\cdot7H_2O$, $Ti(SO_4)_2$, and H_fO_2 were commercially obtained from Wako Pure Chemical Industries, Ltd.; the $ZrO\cdot nH_2O$ was from the Shinnippon Kinzoku Kagaku Co. Ltd.; the Ta_2O_5 was from Johnson, Mathey and Co., Ltd., and the $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, from the Ishizu Pharmaceutical Co., Ltd.

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Table 1. Typical compositions (and pHs) of geothermal waters from bores in Ohtake and Hatchobaru areas (in ppm)

Constituents	Ohtake Well Nos.		Hatchobaru Well Nos.	
	No. 9	No. 10	No. 4	No. 7
Na	1050	1030	2250	2140
K	132	124	277	266
Li	4.79	4.73	10.9	10.2
Ca	28.4	29.7	60.2	76.3
Mg	0.01	0.21	1.21	1.21
F	2.95	2.35	4.05	3.80
Cl	1774	1738	1954	1651
HCO_3	57	77	12	11
SO_4	145	193	138	95
HBO_2	84	78	191	170
SiO_2	531	433	679	746
As	2.0	2.1	3.2	3.6
pH	8.57	8.44	6.99	7.04

b) Other Reagents: The LiCl, Na_2CO_3, $(NH_4)_2CO_3$, $CaCl_2 \cdot 2H_2O$, EDTA ($C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$), $CaCO_3$, NH_4Cl, E.B.T (indicator), and NN (indicator) were obtained from Wako Pure Chemical Industries, Ltd. All the reagents used were guaranteed reagents.

Instruments. A Toyo Kagaku Sangyo pH meter, Model Pt-3D, and Denki Kagaku Keiki pH meter, MG-7, were used with a combination electrode, HCE 101C-1T, for the measurement of the (apparent) pH's of the reference lithium solutions (abbreviated as ref. Li solutions hereafter) and geothermal water. A Nippon Jarrell-Ash AA-8200 atomic absorption spectrophotometer and flame emission were used to determine the lithium content in the sample solutions. The X-Ray diffraction patterns were measured with a Rigaku Rotor Flex RU-200 diffractometer. The DTA and TG curves were measured with a Rigaku Denki thermal analysis instrument, No. 802981.

Procedure. To examine the performance of precipitating agents, the procedure shown in Fig. 1 was employed.

Results and Discussion

No precipitating agents employed in this study, except for aluminium salts, exhibited any pronounced effect on lithium recovery. Aluminium salts have previously been employed as reagents for Li extraction,[5] and the efficiencies of Al salts were confirmed in the present investigation. Hereafter, the results will be shown and discussed only for the aluminium salts. The recovery of lithium from geothermal water is the main purpose of the present work. However, the compositions of geothermal water are different from place to place. A ref. Li solution with the same lithium concentration as in geothermal water from Hatchobaru was prepared as a control solution to make the experimental results

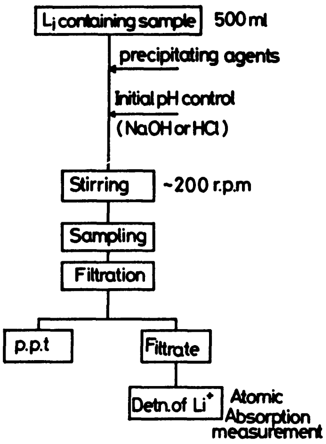

Fig. 1. Flow chart of procedure for the estimation of lithium recorvery.

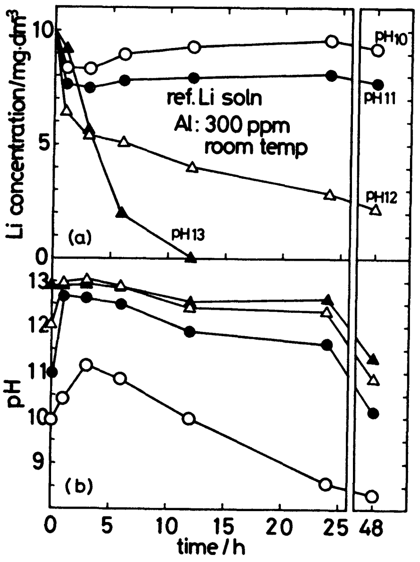

Fig. 2. The plots of residual Li concentration *vs.* time and pH *vs.* time for reference Li solution with various kinds of pH at room temperature.
Initial Li concentration: 10.0 ppm; Al concentration: 300 ppm ($AlCl_3$). (Apparent) initial pH: —○— 10.0; —●— 11.0; —△— 12.0; —▲— 13.0.

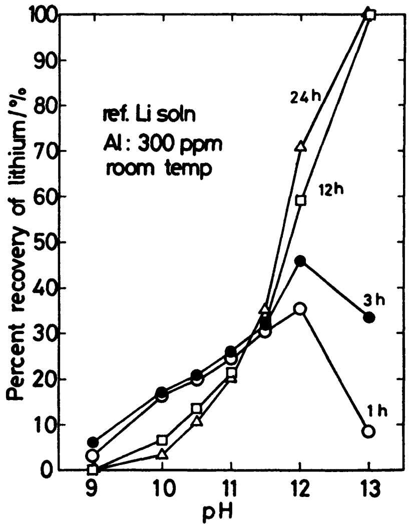

Fig. 3. The relation between percent recovery of lithium and initial pH for reference Li solution at room temperature. Initial Li concentration: 10.0 ppm; Al concentration: 300 ppm ($AlCl_3$), Stirring time: —○— 1 h; —●— 3 h; —□— 12 h; —△— 24 h.

widely applicable. In this study, LiCl was added to distilled water so that the Li concentration became 10 ppm, to be referred to hereafter as the "reference Li solution." Extensive investigations of lithium recovery have been made by many researchers. However, the conditions of Li extraction from a low-Li-content solution are influenced by many factors, such as the Li concentration, the salt constituents and their concentrations in the solution, the concentrations of the precipitating agents, the pH, the temperature, and the stirring time. Thus, the optimum conditions reported cover wide range, depending on the characteristics of the solutions, and are sometimes in conflict with each other. First, the results for the ref. Li solution will be shown. Figure 2 shows the plots of the residual Li consentration *vs.* the time, and the (apparent)pH *vs.* the time for the ref. Li solution at room temperature. The figure shows that the influence of the initial (apparent)pH is great. In this case, the experiment at an initial pH value of 12 gives the best results within about an hour. However, Fig. 2 also shows that, after 24 h, the higher the pH, the better the yield recovered. From this result, the plot of the Li recovery *vs.* pH was made, and it is shown in Fig. 3. The plot of the time dependence of pH shows a tendency, from the beginning to 1—3 h, for the values of the pH's to increase and then to decrease gradually. These changes in the pH and Li recovery with the passage of time seem to be an important key to the mechanism of Li recovery. As long as aluminium salts were used, a high Li recovery was obtained at relatively higher pH regions in this experimental study. This suggests that the use of sodium aluminate needs only a small amount of pH-control agents (acid or base) for the recovery of lithium. In Fig. 4, a pH titration curve for Al salt in an acidic solution is shown. The equilibria of Al^{3+}, $Al(OH)_3$, and AlO_2^-(or $Al(OH)_4^-$) are:

$$\mathrm{Al^{3+}} \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftarrows}} \mathrm{Al(OH)_3} \underset{\mathrm{H^+}}{\overset{\mathrm{OH^-}}{\rightleftarrows}} \mathrm{Al(OH)_4^-}.$$

With this equilibria relation and calibration curve, the Al content in the (Li containing) solution was also determined. That is, the central region of the titration curve was used; it corresponds to the total content of the aluminium in solution. The coexistence of the Li ion did not disturb the Al analysis. At an initial pH of the 13, the Li recovery *vs.* the time, the (apparent)pH *vs.* the time, and the Li recovery *vs.* the Al concentration were examined with various kinds of Al concentrations. The results are shown in Figs. 5 and 6. Except for the Al concentrations of 50 and 1000 ppm, the percentage of the recovery of Li was about 100% after stirring for a long time. There is also a tendency that the higher the Al concentration, the quicker the recovery. For an Al concentration of 50 ppm, almost no effective recovery was observed, and for 1000 ppm, a percentage of the recovery of only 50—60% was obtained, not in accord with our expectation. This might be explained

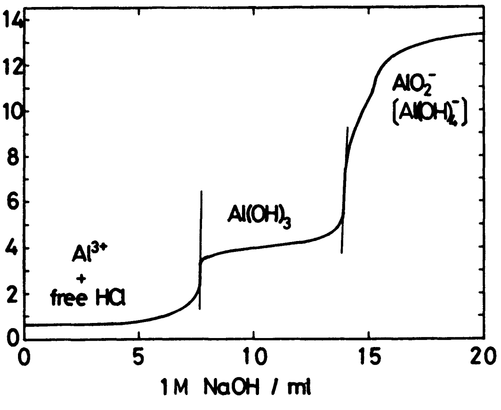

Fig. 4. pH change of aluminium salt solution during alkaline titration. [Al concentration of lithium aluminate is also determined using this potentiometric technique].

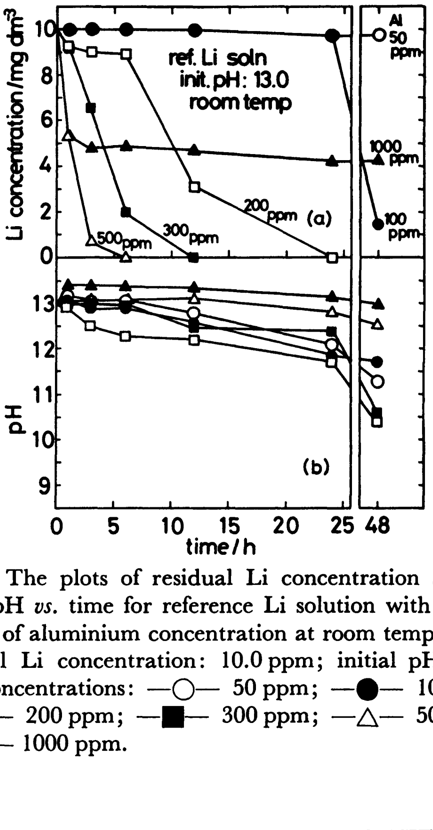

Fig. 5. The plots of residual Li concentration *vs.* time and pH *vs.* time for reference Li solution with various kinds of aluminium concentration at room temperature. Initial Li concentration: 10.0 ppm; initial pH: 13.0; Al concentrations: —○— 50 ppm; —●— 100 ppm; —□— 200 ppm; —■— 300 ppm; —△— 500 ppm; —▲— 1000 ppm.

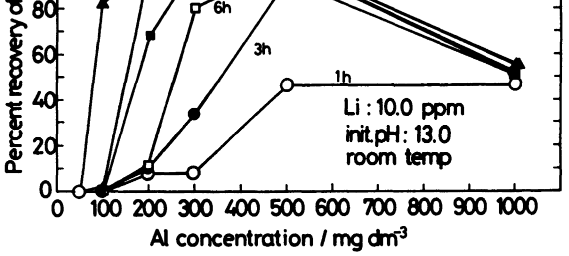

Fig. 6. The relation of percent recovery of lithium and Al concentrations for reference Li solution at room temperature.
Stirring time: —○— 1 h; —●— 3 h; —□— 6 h; —■— 12 h; —△— 24 h; —▲— 48 h.
(Apparent) initially set pH: 13.0. Al salt: $AlCl_3$.

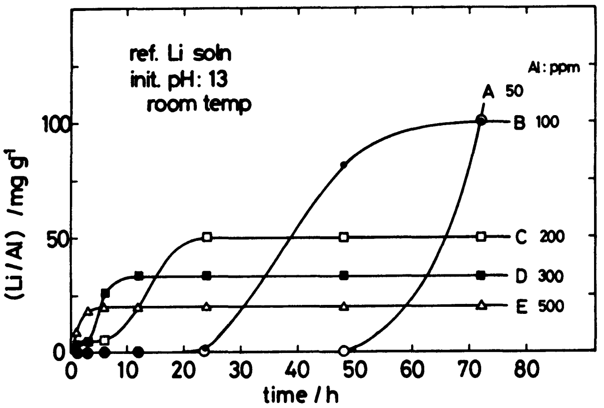

Fig. 7. The relation of (lithium/alminium) and stirring time for reference Li solution at room temperature. Al concentrations and percent recoveries of Li (in parentheses): A —○— 50 ppm (50%); B —●— 100 ppm (100%); C —□— 200 ppm (100%); D —■— 300 ppm (100%); E —△— 500 ppm (100%); [Theoretical maximum = 257 mg(Li)/g(Al), as $LiAlO_2$] (Apparent) initially set pH: 13.0.

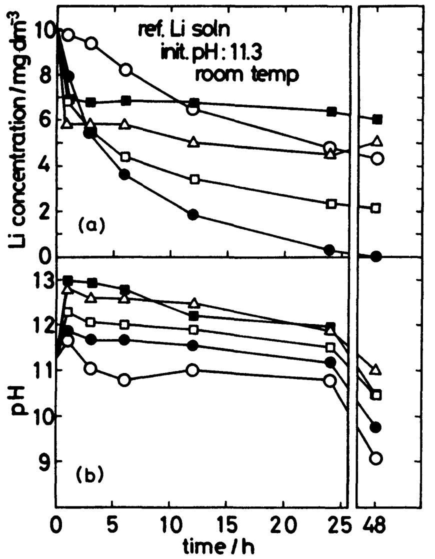

Fig. 8. The plots of residual Li concentration *vs.* time and pH *vs.* time for reference Li solution with various kinds of Al concentrations at room temperature. Al concentrations: —○— 50 ppm; —●— 100 ppm; —□— 200 ppm; —■— 300 ppm; —▲— 500 ppm; initially set (apparent) pH: 11.3.

by the partial crystallization of the aluminium hydroxide coprecipitated. The relation of (Li(mg)/Al(g)) and the time course is shown in Fig. 7. The figure shows that, although a 100% recovery of Li for an Al concentration of 100—500 ppm is achieved after 72 h stirring, the Li yield for 1 g of aluminium decreases with the increase in the Al concentration. However, as the relation between the stirring time and the Al concentration shows, there are several cases of Li recovery [see Fig. 7]. Therefore, the stirring time is also an important factor for Li recovery from the economical point of view. Figure 8 shows the plot of the Li recovery *vs.* time for the respective Al concentration at an initial pH of 11.3.

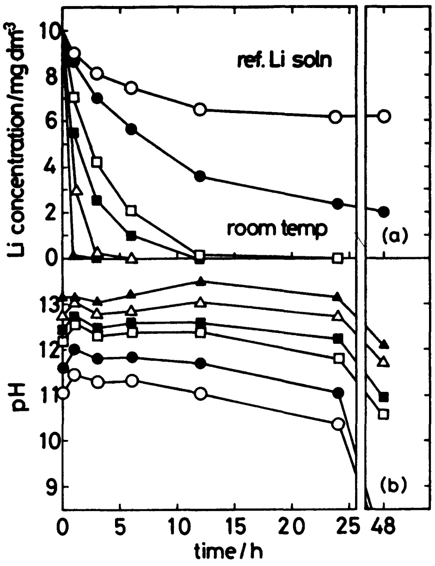

Fig. 9. The plots of residual Li concentration *vs.* time and pH *vs.* time for reference Li solution with various kinds of Al concentrations at room temperature. [Without initial pH controls] Al concentrations ($NaAlO_2$): —○— 50 ppm; —●— 100 ppm; —□— 200 ppm; —■— 300 ppm; —△— 500 ppm; —▲— 1000 ppm.

The effects of Al concentration differ much from the results for the initial pH of 13 and a higher Li recovery is obtained in the region of relatively low Al concentrations. As has been stated above, in this experimental research, the recovery of lithium was achieved in a relatively higher pH region. This result differs considerably from the results of Goodenough *et al.*[5] In a high pH region, Al salt will exist in the state of the aluminate ion ($Al(OH)_4^-$), and the use of water-soluble aluminate might be preferable, as has been mentioned already. In Fig. 9, the results for sodium aluminate instead of aluminium chloride are shown without any pH control. This experimental result could not be compared with those for $AlCl_3$ since the initial pH control was not made. However, from the values of initial pH, the experimental results for the Al concentration of 1000 ppm by the use of $AlCl_3$ at pH 13 and the results for the Al concentration of 50 ppm at pH 11.3 can be compared with those of the corresponding Al concentration by the use of $NaAlO_2$. As far as these high and low Al concentrations are concerned, the use of sodium aluminate seems to be superior to that of aluminium chloride (see Figs. 5, 8, and 9). The difference should be small in principle, but the real difference observed cannot be explained properly at present.

On the Mechanism of Li Recovery. On the Li recovery by the coprecipitation method, two explanations are considered; one is the recovery by adsorption,[17] and the other, that by precipitation by the formation of a water-insoluble aluminate complex.[5–8] However, no satisfactory explanation has yet been given. Therefore, in the present work, attempts will be made to clarify the effects of both adsorption and precipitation by

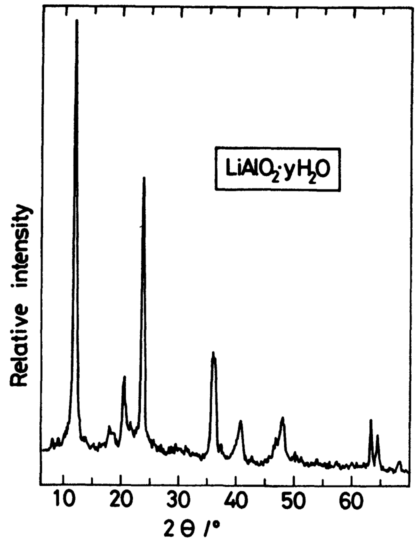

Fig. 10. X-Ray diffraction pattern of lithium alminate, $LiAlO_2 \cdot yH_2O$ (Cu $K\alpha$).

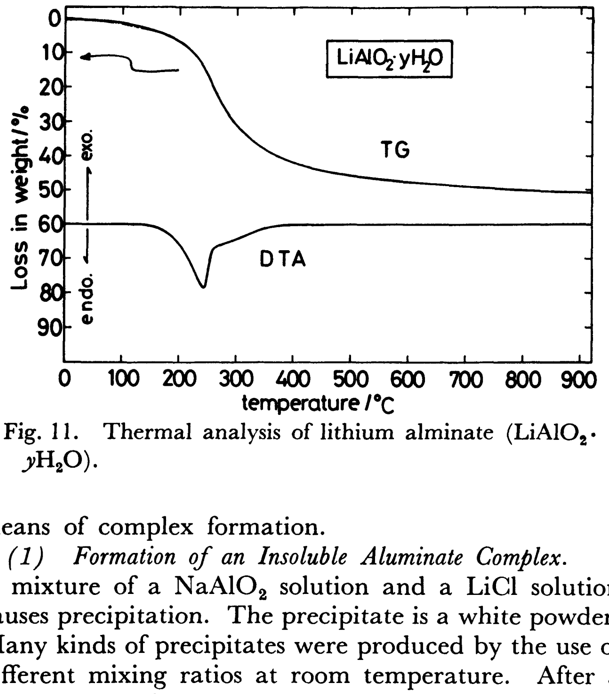

Fig. 11. Thermal analysis of lithium alminate ($LiAlO_2 \cdot yH_2O$).

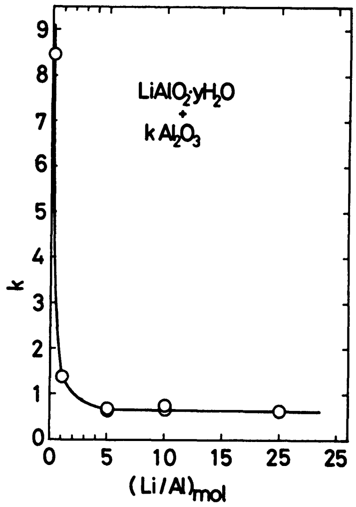

Fig. 12. Relation of $(Li/Al)_{mol}$ vs. k, where k represents the amount of additionally produced aluminium hydroxide.

means of complex formation.

(1) Formation of an Insoluble Aluminate Complex. A mixture of a $NaAlO_2$ solution and a LiCl solution causes precipitation. The precipitate is a white powder. Many kinds of precipitates were produced by the use of different mixing ratios at room temperature. After a certain time of stirring, the precipitates were filtrated with a glass filter (G-4) and then washed with water and acetone until the chloride ion was no longer detectable. Parts of the precipitates were dried in two ways: (A) by vacuum drying at room temperature, and (B) by 105 °C drying. The X-ray diffraction patterns and DTA and TG curves were measured for the A and B samples. A and B gave nearly the same patterns. In Figs. 10 and 11, the pattern and the DTA and TG curves for B (prepared under a Li-rich condition; $(Li/Al)_{mol}=5$) are shown. The X-ray diffraction patterns obtained for B were consistent with the lattice constants of lithium aluminate ($LiAlO_2 \cdot yH_2O$) listed on the ASTM card (20-618). The diffraction patterns for these compounds agreed very closely with each other, irrespective of the mixing ratio of Li to Al, although the relative intensities sometimes differed. It might be noted here that if a stoichiometrically excess amount of aluminium salt for lithium was used, additional peaks of aluminium hydroxide were found. The composition of the lithium aluminate complex has been reported to be $Li_2O \cdot 2Al_2O_3$ or $Li_2O \cdot 2.5Al_2O_3$ or around $Li_2O \cdot 4.7Al_2O_3$;[5,20] this seemed somewhat in conflict with our present results obtained by means of X-ray diffraction analysis. If the aluminium complex is $LiAlO_2 \cdot yH_2O$, the ratio of Li_2O to Al_2O_3 is unity. Therefore, the precipitates obtained in our study were dissolved by hot hydrochloric acid to determine the accurate ratio of aluminium to lithium. For the analysis of aluminium, the titration method was employed (see Fig. 4). The results show that, in the synthesis of the lithium aluminate complex, the reduction of the molar ratio of LiCl to $NaAlO_2$ increases the aluminium content in the lithium aluminate complex. The DTA and TG curves for lithium aluminate complex exhibit simple patterns, as is shown in Fig. 11. However, the increase in the aluminium content in the lithium aluminate complex gives an additional endothermic DTA peak about 230 °C. The TG curve for the lithium aluminate complex (Sample B) in Fig. 11 shows a rapid decrease in weight in the range of about 200 and 300 °C; this might correspond to the dehydration of hydrated water in the lithium aluminate complex. A consideration of several data on the lithium aluminate complex leads to the following formula:

Lithium aluminate complex precipitated in the solution$\equiv LiAlO_2 \cdot yH_2O$(crystal)$+k\ Al_2O_3 \cdot zH_2O$(amorphous).

It seems that, theoretically, in the very high pH region (about pH 13), only the lithium aluminate exsists. However, the real lithium aluminate complex precipitated contains relatively much aluminium. Aluminium hydroxide seems to be very easily formed. Figure 12 shows the relation of the k value and the lithium to aluminium ratio, $R[=(Li/Al)_{mol}]$. k decreases with an increase in R. Even if the R goes beyond 5, however, the k value does not decrease below about

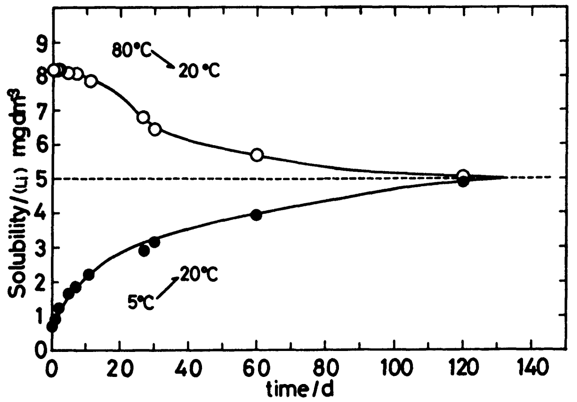

Fig. 13. Solubility of lithium alminate, $LiAlO_2 \cdot yH_2O$, represented by Li concentration (mg dm^{-3}) at 20 °C. —●—: Heated to 80 °C (1 d) and set to 20 °C. —○—: Cooled to 5 °C (1 d) and set to 20 °C.

0.6. From this value, the ratio of $(Li : Al)_{mol} = 1 : 2.2$ is obtained; this value is intermediate between 2.0 and 2.5. To diminish the k values, various conditions were introduced, such as a high pH, a high temperature (90 °C) and low temperature (5 °C) of the solutions, and high and low concentrations of LiCl and Al salts, but the results were all unsatisfactory. The use of solvents such as methanol, ethanol, acetone, and their mixture with water sometimes lowered the k values, but it was difficult to decrease the k to less than the 0.38 in the present work. [By the way, the $LiAlO_2$ listed in the ASTM card on the X-ray diffraction pattern was prepared at room temperature by the hydrolysis of γ-$LiAlO_2$ which is synthesized at a high temperature.[25]]

(2) Adsorption. A $NaAlO_2$ (500—1000 ppm as Al) solution was hydrolyzed to aluminium hydroxide by blowing CO_2 through the solution. Immediately after the $Al(OH)_3$ had been prepared, the Li ion was adsorbed, but the amount of the lithium adsorbed on hydroxide was very small. According to an experimental study by Kitamura *et al.*,[17] the value of 0.36 mg (Li)/g (adsorbent) is obtained under the best conditions. The reason for the difference between their results and ours is not clear, but, as a result of the substle difference in preparation conditions, a partial crystallization of aluminium hydroxide might have occurred in the present work. Kitamura *et al.* reported that amorphous aluminium hydroxide adsorbs much lithium, while crystallized aluminium hydroxides (beyerite, pseud böhmite *etc.*) do not adsorb lithium.

These results show that the success with lithium recovery using the coprecipitation method can not be explained by the adsorp tion only, but can be explained by the formation of a ithium aluminate complex slightly soluble in water. The formation of the lithium aluminate compound was also found in geothermal water after the removal of polymerized silica using much iron(III) hydroxide. That is, after the removal of the silica, Al salt (50—100 ppm as Al) was added to the geothermal water and the compound precipitated was measured by means of an X-ray diffractometer. In the lithium recovery using Al salt, the formation of the lithium aluminate complex is dominant. Therefore, the solubility of the lithium aluminate will be very important. The solubility of the lithium aluminate ($LiAlO_2 + (0.38Al_2O_3)$) obtained in the present study was measured by determining the Li concentration; it is shown in Fig. 13. The figure shows that the solubility of lithium aluminate is 5.0 ppm (as Li) at 20 °C.

Provided the solubility equilibrium of lithium aluminate

$$LiAlO_2 \rightleftarrows Li^+ + AlO_2^-$$

the solubility product is:

$$K_{sp} = [Li^+][AlO_2^-] = 5.2 \times 10^{-7} \text{ (at 20 °C)}.$$

If the detection limit of Li^+ by the atomic-absorption flame method is 0.02—0.05 ppm, the concentration of aluminate ions of 0.072—0.180 M; in other words, an aluminium concentration of 2000—5000 ppm is required to recover the lithium essentially to completion. The same calculation tells us that an Al concentration of about 200 ppm is required to reduce the lithium concentration to 0.5 ppm. However, when a pure LiCl solution ($[Li^+] = 10$ ppm) was used, the Al concentration of 200 ppm was enough to recover the Li completely with the optimum pH and temperature. On the basis of the above results, the following mechanism may be suggested. First, stoichiometrically excess amount of aluminium salt causes the reaction of Li^+ and the aluminate ion (AlO_2^-) to form the lithium aluminate complex, ($LiAlO_2 \cdot yH_2O$). Then, successively or simultaneously the residual Li^+ will be adsorbed by the aluminium hydroxide which is formed by the extra amount of Al salt, although the $Al(OH)_3$ is easily formed even if a stoichiometrical amount of Al salt is used. This simplified two-step mechanism can explain the major part of the lithium recovery by the coprecipitation method. The solubility of $LiAlO_2$ will depend upon the pH, the temperature, and the various kinds of polynuclear aluminium complexes and other kind of salts in solution. Thus, the values cited above may be first approximations.

Influence of Temperature on Li Recovery. It is clear that, when the Li concentration of 10 ppm is used, the formation of the lithium aluminate complex is essential and the solubility may largely depend upon the solution temperature. Geothermal water in the Hatchobaru area has a relatively high temperature (80—90 °C) at the outlet. In view of the effective utilization of the geothermal water, operations at a high temperature will be required. The experimental results on Li recovery at 80 °C are shown in Fig. 14. The figure depicts behavior fairly different from that at room temperature. That is, for all the ref. Li solutions with variously set pH's, minima are found. Within 1 to 6 h, the plot of the residual Li concentration *vs.* the time shows minima, and then shows a linear rise to the Li concentration of 9—10 ppm with the time. This phenomenon might be interpreted as follows. In the first stage, the lithium aluminate complex and aluminium hydroxide which adsorbed Li^+ are precipitated rapidly; then the aluminate dissolves linearly according to the solubility equilibrium and $Al(OH)_3$ releases the

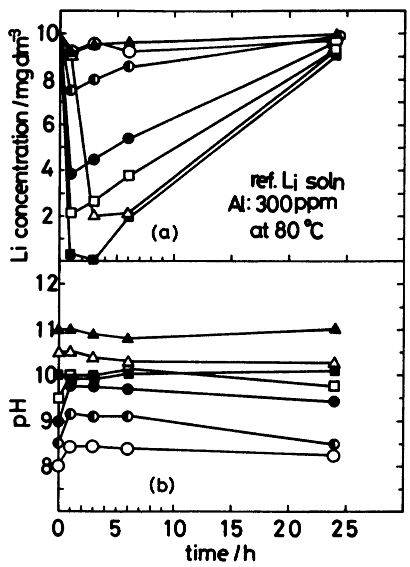

Fig. 14. The plots of residual Li concentration *vs.* time and pH *vs.* time for reference Li solution with various kinds of initially set pHs at 80 °C.
Al concentration: 300 ppm ($AlCl_3$); Apparent initial pHs: —○— 8.0; —◐— 8.5; —●— 9.0; —□— 9.5; —■— 10.0; —△— 10.5; —▲— 11.0.

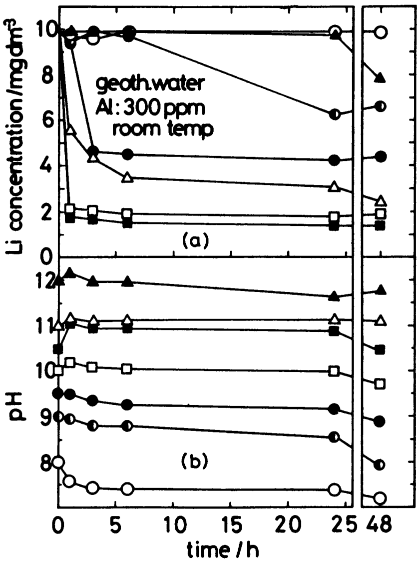

Fig. 15. The plots of residual Li concentration *vs.* time and pH *vs.* time for geothermal water with various kinds of initially set pHs at room temperature. Al concentration: 300 ppm ($AlCl_3$).
(Apparent) initial pHs: —○— 8.0; —◐— 9.0; —●— 9.5; —□— 10.0; —■— 10.5; —△— 11.0; —▲— 12.0.

Li^+ ions. Also, in this case, a high temperature seems to accelerate the precipitating speed, as is shown in Fig. 14. When the Li recovery is made at a high temperature, the pH control must be made accurately and a short recovery time is desirable.

Li Recovery Using Geothermal Water. The basic study of Li recovery has revealed several important facts, and now Li can be recovered from geothermal water.

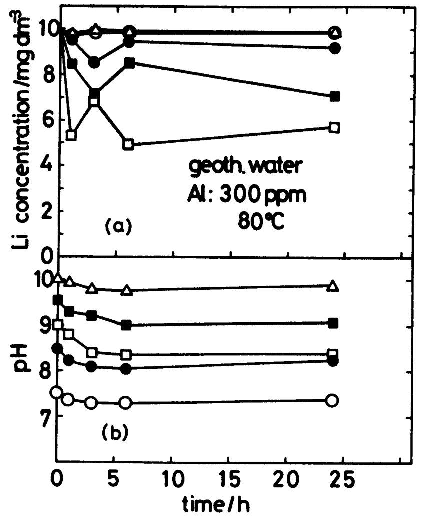

Fig. 16. The plots of residual Li concentration *vs.* time and pH *vs.* time for geothermal water with various kinds of pHs at 80 °C. Al concentration: 300 ppm ($AlCl_3$).
(Apparent) initial pHs: —○— 7.5; —●— 8.5; —□— 9.0; —■— 9.5; —△— 10.0.

Figure 15 shows the results obtained at room temperature. For geothermal water, even under the best conditions, only a recovery of 80 to 85% was attained; the optimum pH was in the range of 10—10.5. For the ref. Li solution, the percentage of recovery was 100% at the optimum pH (about 13). A relatively large difference in the behavior of Li extraction was found between the ref. Li solution and geothermal water. That is, for geothermal water, the pH dependence on the Li recovery was not large as in the case of the ref. Li solution. Geothermal water seems to have a kind of buffering action. The use of an Al concentration of 500 ppm increased the Li recovery, and the optimum pH region became wider (pH 10—11). Figure 16 shows the experimental results at 80 °C using an Al concentration of 300 ppm. The extent of Li recovery is very low, as had been expected, and the optimum pH is around 9, which is lower than that for geothermal water at room temperature. A comparison of Fig. 16 with Fig. 14 shows that, for the ref. Li solution, a high Li recovery is possible within a few hours. For geothermal water, however, no such rapid recovery of lithium is observed. In the case of the ref. Li solution, the yield of Li becomes small (within 10%) after 24 h. For geothermal water, however, the change in the Li recovery with the time is relatively small. From this fact, it can also be recognized that geothermal water has a buffering action even if the temperature rises. Next, the dependence of the Al concentration by the use of $NaAlO_2$ on the Li recovery was studied; it is shown in Figs. 17 and 18 at room temperature and at 80 °C respectively. The addition of $NaAlO_2$ to geothermal water without pH control was done just as in the case of the ref. Li solution. The yield of Li in this case was not so good as in the case of the ref. Li solution using the Al concentration of 100 ppm. In the case of geothermal water, the recovery of lithium was naught

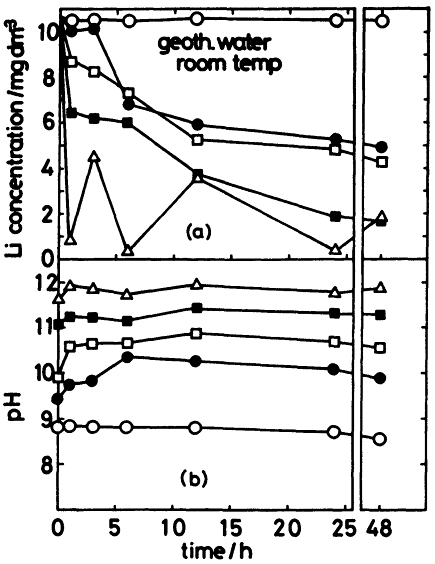

Fig. 17. The plots of residual Li concentration *vs.* time and pH *vs.* time for geothermal water with various kinds of Al concentrations at room temperature.
Al concentrations ($NaAlO_2$): —○— 100 ppm; —●— 200 ppm; —□— 300 ppm; —■— 500 ppm; —△— 1000 ppm.

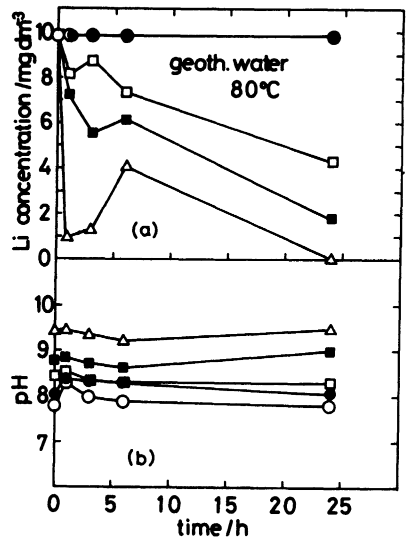

Fig. 18. The plots of residual Li concentration *vs.* time and pH *vs.* time for geothermal water with various kinds of Al concentrations at 80 °C.
Al concentrations ($NaAlO_2$): —○— 100 ppm; —●— 200 ppm; —□— 300 ppm; —■— 500 ppm; —△— 1000 ppm.

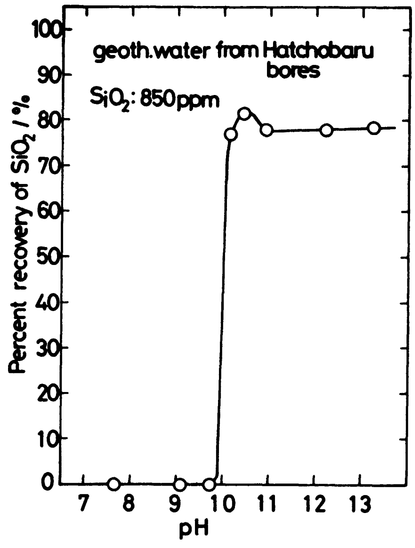

Fig. 19. The relation between precipitation of polymerized colloidal (or suspended) silica in geothermal water and pH. [The values in ordinate were determined from the silica concentrations in filtrates passed through the No. 131 filter papers.]

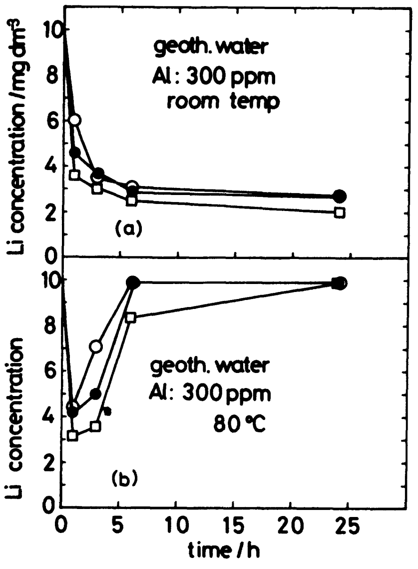

Fig. 20. The plots of Li concentration *vs.* time, for geothermal waters with three kinds of silica concentrations at room temperature (a) and at 80 °C (b).
Al concentration: 300 ppm ($AlCl_3$). [Li^+]: 9.9 ppm.
Silica concentrations: —○— 100% (=stock geothermal water; 850 ppm); —●— 20%; —□— 0%.

using the same concentration of aluminium salt. Even if the Al concentrations of 500 and 1000 ppm are used, a complete recovery is not accomplished. Strangely, the residual lithium concentration changed in a zig-zag fashion with the passage of time for the Al concentration of 1000 ppm. The results at 80 °C for Al concentrations of 300, 500, and 1000 ppm are similar to those at room temperature, although for Al concentrations of 100, or 200 ppm, practically no Li is recovered. The reasons for this are not clear. One reason may be that geothermal water contains various kinds of salts. The most probable constituents which function negatively are high-concentration sodium chloride, polymeric silicic acid, and calcium ions. The addition of much NaCl (10^4—3×10^4 ppm) to a ref. Li solution did not change the effect on the Li recovery. The polymerization of silicic acid and silicate in geothermal water is accelerated by the addition of alkali, and the particle sizes of the colloidal silica are increased. Colloidal and suspended silica in geothermal water was examined by

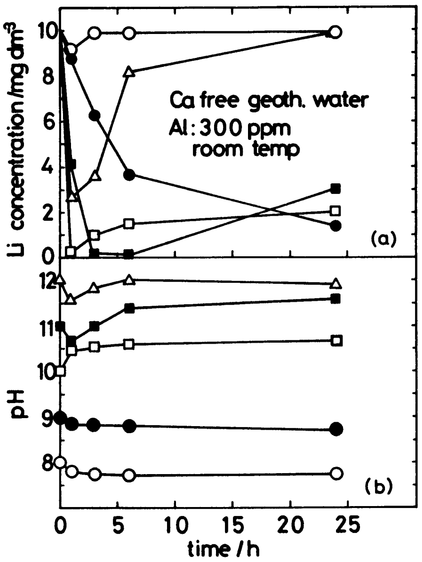

Fig. 21. The plots of residual Li concentration *vs.* time, and pH *vs.* time for Ca free geothermal water with various kinds of pHs at room temperature.
Al concentration: 300 ppm ($AlCl_3$). [Li^+]: 10.0 ppm (Apparent) initial pHs: —○— 8.0; —●— 9.0; —□— 10.0; —■— 11.0; —△— 12.0.

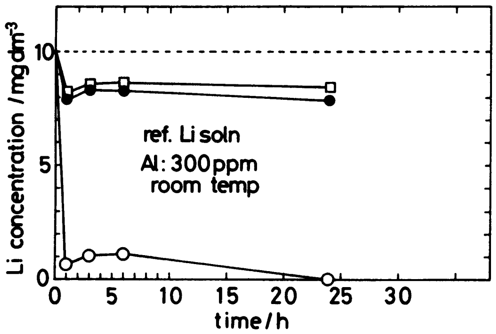

Fig. 22. The plots of residual Li concentration *vs.* time for reference Li solution with three kinds of Ca concentrations at room temperature. Al concentration: 300 ppm ($NaAlO_2$).
Ca concentrations ($CaCl_2$): —○— 0 ppm; —●— 70 ppm; —□— 400 ppm.

the molybdenum yellow method in connection with the percentage of the recovery of silica *vs.* the pH. The results are shown in Fig. 19. As is shown in this figure, a greater part of the silica in geothermal water is recovered at pH 10 or above. A perfect recovery of silica from geothermal water is accomplished by the addition of $FeCl_3$ ([Fe^{3+}] = 1000 ppm), with the pH controlled at 10.5. The influence of silica in geothermal water was examined at room temperature and at 80 °C; the results are shown in Fig. 20. The results show that polymeric silica affects the Li recovery, but to a small extent. The influence of the calcium ions was then examined. The calcium ions (about 20 ppm) in the geothermal were eliminated in the form of calcium oxalate. The results are shown in Fig. 21. A comparison of Fig. 21 with Fig. 15 (with Ca^{2+}) shows that the Li recovery rises remarkably and that the short-time percent-recovery is relatively high in the case of calcium-free geothermal water. Experiments were also made for ref. Li solutions to which calcium chloride had been added so that the Ca concentrations were 70 and 400 ppm respectively. The effects of calcium ions are prominent, as is shown in Fig. 22.

It may be concluded, from the results obtained, that geothermal water has a kind of buffering action and that the buffer capacity may be attributed mainly to the polymeric silicic acid and/or silicate ions. The existence of polymeric silica and calcium ions leads to remarkably negative effects on the recovery of lithium from geothermal water at the Hatchobaru bores. The mechanism of lithium recovery by the coprecipitation method can be explained by the formation of lithium aluminate complex, followed by the adsorption of residual lithium by the aluminium hydroxide (amorphous) coprecipitated.

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