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Preliminary test for reprocessing technology development of tritium breeders

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ABSTRACT

In order to develop the reprocessing technology of lithium ceramics (Li_2TiO_3, CaO-doped Li_2TiO_3, Li_4SiO_4 and Li_2O) as tritium breeder materials for fusion reactors, the dissolution methods of lithium ceramics to recover ^{6}Li resource and the purification method of their lithium solutions to remove irradiated impurities (^{60}Co) were investigated. In the present work, the dissolving rates of lithium from each lithium ceramic powder using chemical aqueous reagents such as HNO_3, H_2O_2 and citric acid ($C_6H_8O_7 \cdot H_2O$) were higher than 90%. Further the decontamination rate of ^{60}Co added into the solutions dissolving lithium ceramics was higher than 97% using the activated carbon impregnated with 8-hydroxyquinolinol as chelate agent.

1. Introduction

Lithium ceramics such as Li_2TiO_3, Li_4SiO_4 and Li_2O are candidates for tritium breeding materials in the fusion reactors [1,2]. In the Japanese blanket design, Li_2TiO_3 has been evaluated as a candidate material in the breeding blanket concept because tritium is able to be recovered at low temperature. On the other hand in EU blanket design, Li_4SiO_4 is considered to be more reliable in terms of lithium mass transfer and compatibility with other blanket materials, such as the neutron multiplier and structural materials. Although it has not been decided yet which is the best breeder material among them, lithium is the important resource in any case.

Development of reprocessing technology for used ceramic tritium breeders has been proposed to recover lithium as the essential resource [3]. In order to develop an advanced Li reprocessing technology on the system to dissolve the ceramics and remove irradiated radioactive isotopes such as ^{60}Co from the above-mentioned, three potential ceramic breeders (Li_2TiO_3, Li_4SiO_4 and Li_2O) as used were investigated to evaluate the dissolution and purification properties of lithium in this study. Figs. 1 and 2 show the conceptual reprocessing process of lithium ceramics as tritium breeding materials in this study.

The advanced reprocessing process for tritium breeding materials consists of four steps as shown in Fig. 2. Step-1 is the dissolving process for lithium recovery from used tritium breeding materials dissolved by chemical aqueous solutions, e.g. diluted nitric acid, organic acid and hydrogen peroxide. Next, Step-2 is the purification process by removing radioactive impurities (e.g. ^{60}Co) generated from structural materials with the neutron irradiation, using chemical adsorbent; a unique and highly effective chemical adsorbent was developed as described later. This purification process is a necessary process for step-3. Step-3 is the process for the control of main elements in aqueous solution dissolving lithium by the addition with lithium-6 depleted by tritium breeding reaction and with titanium lost by the dissolving process. Finally, Step-4 is the fabrication process of lithium ceramics pebbles. Through four steps lithium resource including valuable lithium-6 can be recovered and lithium ceramics pebbles can be reproduced and reused in the nuclear fusion blanket module.

In the present study, Step-1 (dissolving process) and Step-2 (purification process) were mainly investigated.

2. Experimental

Starting powders of Li_2TiO_3, CaO-doped Li_2TiO_3 (CaO-Li_2TiO_3) [4], Li_4SiO_4 and Li_2O were prepared with the purities of 99.9% above as unused. The powders were dissolved by chemical aqueous reagents such as HNO_3, H_2O_2 and citric acid ($C_6H_8O_7 \cdot H_2O$). After chemical dissolving each powder, the recovery rates of lithium dissolved from each lithium ceramic powders were evaluated by measuring the content of lithium in the solution using Inductively Coupled Plasma atomic emission spectrometry (ICP-AES). Further, the decontamination of radioactive impurities such as typical ^{60}Co by addition in the solutions was carried out based on the chemical absorption method using the activated carbon impregnated with 8-hydroxyquinolinol as the chemical chelate agent,

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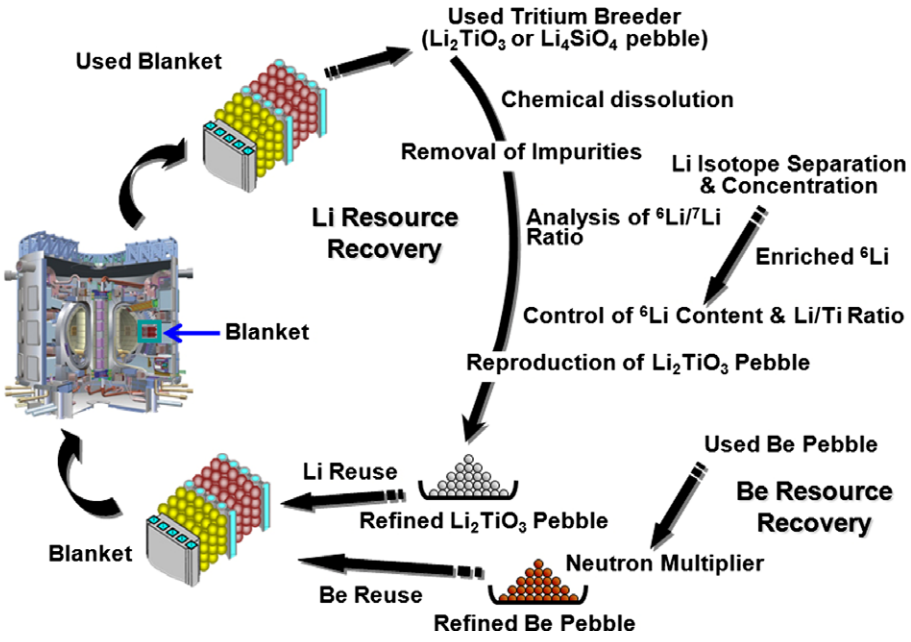


Fig. 1. Li reprocessing system.

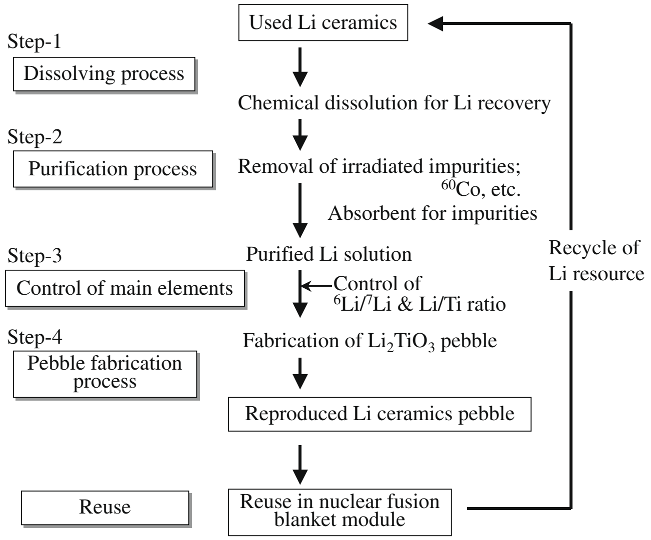


Fig. 2. Conceptual reprocessing process for tritium breeding materials.

and the decontamination rate of ^{60}Co was measured by gamma-ray spectrometry using a Ge semiconductor detector.

Dissolving reactions of the four kinds of lithium ceramics are shown in Eqs. (1)–(5).

- Li_2O

$$Li_2O + HNO_3 \rightarrow LiOH < soluble > + H_2O. \tag{1}$$

- Li_2TiO_3

Solvent: $H_2O_2 + HNO_3$

$$2Li_2TiO_3 + H_2O_2 + 4HNO_3 \rightarrow 4LiNO_3 < soluble > + TiO_2 < insoluble > + H_2TiO_3 < soluble > + xH_2O. \tag{2}$$

Solvent: $H_2O_2 + C_6H_8O_7 \cdot H_2O$ [5]

$$2Li_2TiO_3 + 2H_2O_2 + 2C_6H_8O_7 \cdot H_2O \rightarrow Li_4[Ti_2O_5(C_6H_4O_7)_2] + yH_2O \rightarrow 4Li^+ < soluble > + [Ti_2O_5(C_6H_4O_7)_2 \bullet yOH]^{4-y} < soluble > + yH^+. \tag{3}$$

- $CaO\text{-}Li_2TiO_3$

$$2CaO\text{-}Li_2TiO_3 + H_2O_2 + 4HNO_3 \rightarrow 4LiNO_3 < soluble > + 2Ca(OH)_2 < soluble > + TiO_2 < insoluble > + H_2TiO_3 < soluble > + zH_2O. \tag{4}$$

- Li_4SiO_4

$$Li_4SiO_4 + 4HNO_3 \rightarrow 4LiNO_3 < soluble > + H_2SiO_3 < soluble > + wH_2O.$$

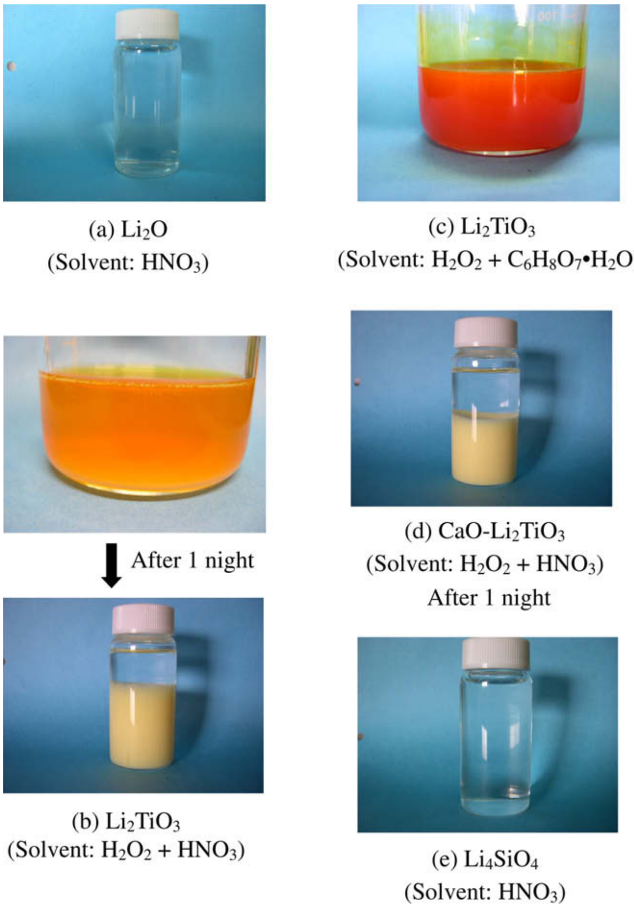
In order to remove the impurities in the lithium-dissolved solutions, a new chemical adsorbent as the activated carbon impregnated with a superior chelating agent, 8-hydroxyquinolinol, was adopted, and the decontamination efficiency of ^{60}Co was evaluated by addition in the dissolved solutions of lithium ceramics.

3. Results and discussion

3.1. Dissolution characteristic

Concerning the dissolution tests, the mixture of 0.44–0.52 mol peroxide hydrogen (H_2O_2) and 0.02 mol nitric acid (HNO_3) was selected as the solvent of Li_2TiO_3 and $CaO\text{-}Li_2TiO_3$ for each 1 g; 0.44 mol H_2O_2 and 0.33 mol citric acid ($C_6H_8O_7 \cdot H_2O$) as the solvent of Li_2TiO_3 for 1 g; and 0.033–0.067 mol HNO_3 as the solvent of Li_4SiO_4 and Li_2O for each 1 g.

Fig. 3 shows the dissolution characteristic of lithium ceramics dissolved by the mixture of HNO_3, H_2O_2 and $C_6H_8O_7 \cdot H_2O$. Li_2O and Li_4SiO_4 were dissolved completely by HNO_3. In case of the solvent of $HNO_3 + H_2O_2$, the solution of Li_2TiO_2 and CaO-Li_2TiO_3 was colored orange soon after the dissolving treatment, and after one night a lot of creamy white precipitates (presumably titanium oxide) were observed. On the other hand, when the solvent was $H_2O_2 + C_6H_8O_7 \cdot H_2O$, Li_2TiO_2 was changed to soil suspension.


(a) Li_2O (Solvent: HNO_3)

(c) Li_2TiO_3 (Solvent: $H_2O_2 + C_6H_8O_7 \bullet H_2O$)

After 1 night

(b) Li_2TiO_3 (Solvent: $H_2O_2 + HNO_3$)

(d) CaO-Li_2TiO_3 (Solvent: $H_2O_2 + HNO_3$) After 1 night

(e) Li_4SiO_4 (Solvent: HNO_3)

Fig. 3. Dissolution of lithium ceramics.

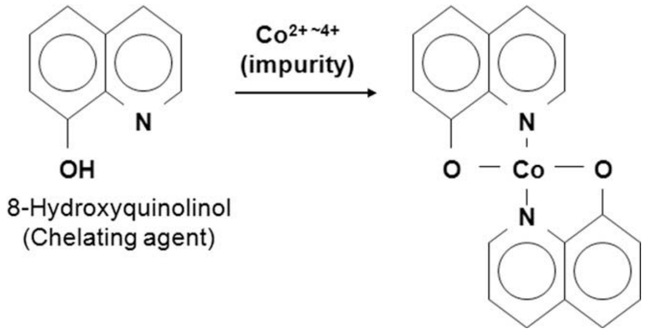


Fig. 4. Removal principle for impurities in Li-dissolved solution using newly developed absorbent impregnated with 8-hydoroxyquinolinol.

Table 1
Experimental results of dissolution of Li ceramics and removal efficiency of impurity (^{60}Co).

Li ceramics	Dissolving condition[a]	Dissolving yields of Li, Ti, Si	Removal efficiency of impurity; ^{60}Co[d]
Li_2O	HNO_3 (66.8 mM) with US[b] at RT[c]	Li: 96–100%	ChAC[e]: 99.8% [DF 199][f]
Li_2TiO_3	H_2O_2 (0.52 M) + HNO_3 (18.4 mM) with US[b] at RT[c]	Li: 91 ± 3%	ChAC[e]: 99.9% [DF 1535][f]
	H_2O_2 (0.44 M) + citric acid (0.33 M) at 80 °C	Li: 96 ± 2% Ti: 2.2–100%	ChAC[e]: 36% [DF 2][f]
CaO-	Li_2TiO_3	H_2O_2	(0.52 M) + HNO_3 (20 mM) with US[b] at RT[c]
Li:	91 ± 3%	No data	
Li_4SiO_4	HNO_3 (33.4 mM) in boiling	Li: 93 ± 4% Si: 7.8–8.4%	ChAC[e]: 97.6% [DF 41][f]

[a] Chemical reagents (HNO_3, H_2O_2, citric acid); added amount to Li ceramics of 1 g each.

[b] Ultra sonic vibrating treatment.

[c] Room temperature.

[d] ^{60}Co added in Li dissolving solution; (1.0–1.3) * E5 Bq.

[e] Adsorbent for radioactive impurities as active-carbon impregnated with cheating agents (8-hydoxyquilolinol).

[f] Decontamination factor.

3.2. Impurity removal characteristic

As shown in Table 1, the dissolving rates of lithium from each lithium ceramic powders were higher than 90%. Then, the decontamination rate of ^{60}Co added into the solutions dissolving lithium ceramics was higher than 97% using the activated carbon impregnated with 8-hydroxyquinolinol. Larger decontamination factors of radioactive cobalt in the lithium solutions were obtained except the case using citric acid for Li_2TiO_3; it is presumed that ^{60}Co in the solution cannot combine with adsorbent by the coexistence with citric acid.

The removal principle is shown in Fig. 4. The impurities in lithium-dissolved solution such as Co ions of trace amounts can be removed with high efficiency by the formation of a strong pentagonal binding with 8-hydroxyquinolinol impregnated with solid-phase (activated carbon).

4. Conclusions

In order to develop an advanced lithium reprocessing technology, the investigation of dissolving process and purification process was performed using four kinds of lithium ceramics; Li_2TiO_3, CaO-doped Li_2TiO_3, Li_4SiO_4 and Li_2O, and the following can be concluded;

(1) Regarding Li_2TiO_3, CaO-doped Li_2TiO_3, Li_4SiO_4 and Li_2O, lithium resources of 90% above were recovered by the aqueous dissolving methods using HNO_3, H_2O_2 and citric acid.
(2) The decontamination efficiencies of ^{60}Co by the addition in the dissolved solutions of lithium ceramics were 97–99.9% above using the new chemical adsorbent; activated carbon impregnated with 8-hydroxyquinolinol. However, in the case of lithium-dissolved solution using citric acid for Li_2TiO_3, the decontamination factor was very low.

Based on this study, more detailed investigations should be conducted including the control of the ratios of lithium-7 to lithium-6 and lithium to titanium, and the fabrication method of lithium ceramics pebbles. It is desirable to realize in a future an ecologically clean and low-cost reprocessing technology for tritium breeding materials.

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