



Pyrochemical reduction of uranium dioxide and plutonium dioxide by lithium metal

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Abstract

The lithium reduction process has been developed to apply a pyrochemical recycle process for oxide fuels. This process uses lithium metal as a reductant to convert oxides of actinide elements to metal. Lithium oxide generated in the reduction would be dissolved in a molten lithium chloride bath to enhance reduction. In this work, the solubility of Li₂O in LiCl was measured to be 8.8 wt% at 650 °C. Uranium dioxide was reduced by Li with no intermediate products and formed porous metal. Plutonium dioxide including 3% of americium dioxide was also reduced and formed molten metal. Reduction of PuO₂ to metal also occurred even when the concentration of lithium oxide was just under saturation. This result indicates that the reduction proceeds more easily than the prediction based on the Gibbs free energy of formation. Americium dioxide was also reduced at 1.8 wt% lithium oxide, but was hardly reduced at 8.8 wt%. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

A pyrometallurgical process, mainly with electrorefining of metal and molten salt-liquid metal extraction, has been developed to apply for nuclear fuel reprocessing [1–5]. As a part of the process, a pyrochemical reduction of spent oxide fuel to metal is being developed to introduce it into the electrorefiner. The technology named the ‘Lithium reduction process’ employs lithium (Li) metal as a reductant and lithium chloride (LiCl) as a solvent [6–9]. A schematic diagram of the Li reduction process is shown in Fig. 1. The main features of this process are:

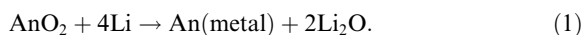
(i) Chopped oxide fuel is contacted with molten LiCl at 650 °C.

(ii) Actinide oxides are reduced to metals by additions of Li metal.

(iii) Reduced metals are washed with fresh LiCl to remove Li₂O and then introduced into electrorefining step of pyrometallurgical reprocessing.

(iv) Li metal is recovered from the LiCl bath used in the reduction step by electrowinning.

In the reduction step (ii), Li dissolves in LiCl up to its solubility limit. The dissolved Li reduces actinide oxides by the following reaction.



The Li₂O generated by the reduction is removed by dissolving in LiCl. This enhances the reaction. The reacted Li is made up by dissolution of floating Li, which has not reacted or dissolved. In this paper, the floating Li is referred to as ‘excess Li’ even if it is necessary to complete the reduction. In the reduction step, alkali and alkali-earth fission products (FPs) would be converted

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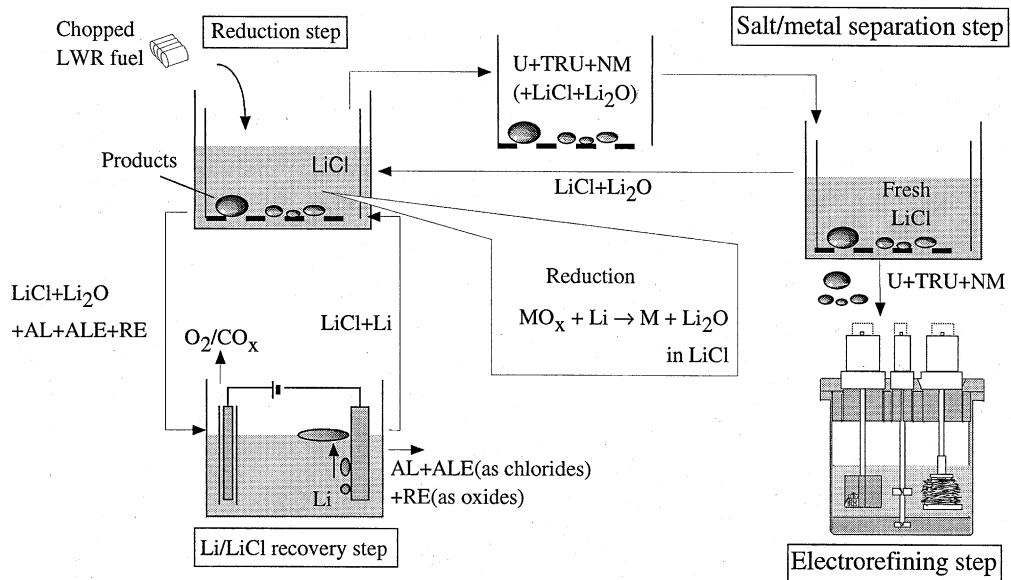


Fig. 1. Schematic diagram of Li reduction process.

to chloride whereas rare earth FPs would remain as oxides including complex oxides, oxychlorides and so on. Eu and Sm may form divalent chlorides.

The lithium reduction process has significant advantages over other technologies which employ other reductants, such as calcium and magnesium, because:

- (i) it does not require ceramic container,
- (ii) it would require a lower temperature process,
- (iii) recycle of the reductant would be easier than other processes.

However, the free energy of formation (ΔG) of lithium oxide and actinide oxides are so close [10] that it is hard to predict the applicability of the Li reduction process to actinides using thermodynamic data alone, and therefore reduction experiments with reliable chemical analysis are necessary to determine the reduction efficiency. The small difference of ΔG also means that the progress of the reduction may depend on the concentration of Li_2O in LiCl , i.e., the chemical activity of Li_2O . It is important to measure the solubility of Li_2O in LiCl where the activity of Li_2O gets to unity and to determine the upper limit of the Li_2O concentration, below which actinides can be reduced to metal. The solubility of Li_2O also decides the requirement of the minimum amount of LiCl solvent against oxide fuel because solid Li_2O adheres to the metal product and takes oxygen into the electrorefiner when exceeding the solubility.

The experiments reported in this article were carried out to measure

- (i) the solubility of Li_2O in LiCl ,
- (ii) the reduction behaviour of granular UO_2 ,
- (iii) whether complete reduction of PuO_2 by lithium is achievable,
- (iv) the upper limit of Li_2O concentration in LiCl , below which PuO_2 can be reduced to metal by Li , and
- (v) the behaviour of americium contained in PuO_2 .

2. Experiments

All experiments were carried out in two argon atmosphere glove boxes to treat chemically reactive materials. One of the glove boxes was equipped with a furnace well and used for reduction tests. The argon atmosphere in this box had 5–10 ppm oxygen and approximately 20 ppm H_2O . The nitrogen concentration was estimated to be four times larger than oxygen, as seen in the air. The atmosphere in the other box used for chemical analysis was assumed to have more impurities because water and acids were used in it. It is O_2 concentration was $< 0.1\%$. The crucibles and stirring rod used in the reduction tests were made from tungsten to avoid possible reaction with plutonium metal. The temperature variation in the crucible with 20 mm diameter and 150 mm height was less than 5°C .

2.1. Solubility measurement of Li_2O in LiCl

The solubility of Li_2O in LiCl was measured in the following manner. In two sets of experiments, 42 and 50

Table 1
Initial weights of materials

Run	AnO ₂	Amount of AnO ₂ (g)	Amount of LiCl (g)	Amount of Li ₂ O (g)
UO ₂ -1	UO ₂	2.322	22.867	–
PuO ₂ -1	PuO ₂	1.931	28.462	–
PuO ₂ -2	PuO ₂	2.019	15.000	1.010

g of LiCl were mixed with 7.4 g of Li₂O in an Inconel crucible. The mixture was heated up to 750 °C and stirred for half a day. After taking a fraction of the mixture as a sample through an Inconel filter, the temperature was lowered by 50 °C. The temperature change, stirring and sampling were repeated until the temperature reached 600 °C. The concentration of Li₂O in each sample was measured as described in Section 2.3.

2.2. Reduction of UO₂ and PuO₂

One reduction experiment with UO₂ (UO₂-1) and two experiments with PuO₂ (PuO₂-1 and -2) were carried out. The materials initially loaded into the crucible in each experiment were listed in Table 1. The uranium dioxide used for UO₂-1 had been produced in an experimental sol-gel process from natural uranium. The sintered spheres were therefore uniform ones of about 200 μm diameter. The feedstock PuO₂ used for PuO₂-1 and -2 was produced by thermal decomposition of plutonium oxalate. The particles were irregularly sized and varied between 2 and 60 μm, and larger particles in the range were predominating. LiCl used in the experiments was purchased from Anderson Physics Laboratory. Since the amount of Li₂O generated by reducing 2 g of PuO₂ had not stopped the reduction in PuO₂-1 (see Section 3.3), it was necessary to increase the Li₂O concentration in PuO₂-2 aiming to determine the upper limit of Li₂O concentration for reduction. Extra Li₂O was therefore loaded at the beginning of PuO₂-2. The Li₂O had been calcined at 1000 °C in the air to remove possible impurities before use.

Table 2 shows the isotopic abundance of PuO₂ which contains 3 wt% of AmO₂. The amount of Pu and Am in

Table 2
Isotopic abundance of PuO₂

Isotope name	Abundance in sample (%)	Abundance in cation (%)
Am241	2.660	3.019
Pu238	0.100	0.114
Pu239	65.091	73.875
Pu240	18.591	21.099
Pu241	1.052	1.194
Pu242	0.616	0.699
Oxide	11.520	13.075
Other	0.370	0.420

each sample were determined from the 129 keV gamma of Pu-239 and 59 keV gamma of Am-241. The crucible containing these materials was heated up to 650 °C over several hours and then stirring started at 100 rpm. After several more hours, reduction was started by addition of approximately 20 mg of lithium metal. The Li was incrementally added 10–20 times in each experiment for following objectives:

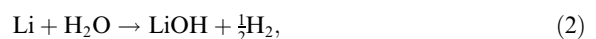
- (i) To follow the progress of reaction by analyzing the variation in Li₂O concentration.
- (ii) To detect possible intermediate products of the actinide.
- (iii) To avoid physical interference of the reduction possibly caused by excess Li.

Lithium chloride was also added to dilute the Li₂O, if the generation of Li₂O stopped. The general scheme of the addition of reagents is shown in Fig. 2.

Small samples of salt from the crucible, 100–200 mg, were taken every 2–3 h by quenching a small part of the salt in the crucible onto a stainless steel rod during day time, while overnight the system was just left with stirring. The total reduction times of each experiment were 59, 56, and 78 h in UO₂-1, PuO₂-1, and PuO₂-2, respectively.

2.3. Salt analysis

Lithium chloride samples taken during the reduction were analyzed mainly to determine the amount of Li₂O generated by the reduction. Samples were weighed and dissolved into H₂O in a gas burette. In this step, Li metal and Li₂O dissolving in LiCl react as follows:



The volume of H₂ gas generated by Li metal was accurately measured with the gas burette to calculate the amount of Li as follows:

$$\text{Li}(\text{mol}) = \frac{V_H (l)}{22.4} \frac{P (\text{hPa})}{P_0 (\text{hPa})} \frac{T_0 (\text{K})}{T (\text{K})} \quad (4)$$

$$(P_0 = 1013, T_0 = 273.16).$$

The solution was then titrated with 0.1 M HCl using phenol red as an indicator to estimate the amount of LiOH generated both from Li metal and from Li₂O.

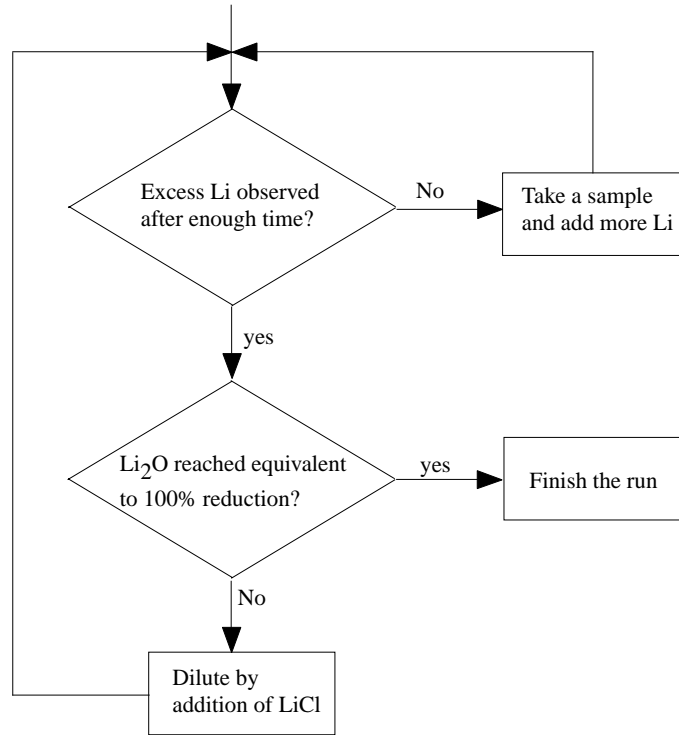
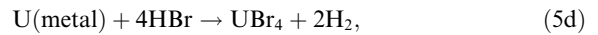
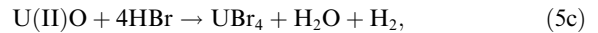
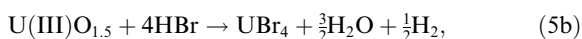
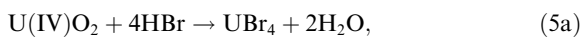


Fig. 2. Flow chart of the reduction experiments.

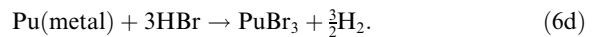
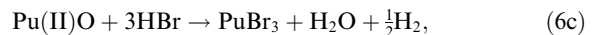
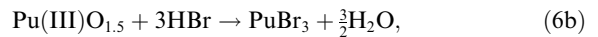
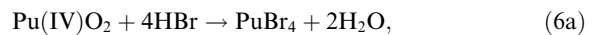
From the difference between the amount of LiOH and Li metal, the amount of Li₂O in the sample was calculated. The total amount of Li₂O in the crucible was calculated from the amount of Li₂O in each sample, the weight of the sample and total amount of LiCl in the crucible. The reduced fraction of AnO₂ was calculated from Eq. (1). In the experiments with PuO₂ the titrated solutions were then counted by gamma spectrometry to determine their Pu and Am contents.

2.4. Metal analysis

The actinide products were analyzed mainly to determine the fraction of actinide metal in the total actinide products. The samples on the bottom of the crucible were taken out by breaking the crucible and then washed with methanol to remove LiCl/Li₂O/Li metal. The products were then weighed, divided into several pieces, and dissolved into hydrobromic acid in a gas burette. The reactions of the actinides depend on their valence state. Follows are possible reactions of each valence state of actinide including reactions unlikely or very slow ((5a) and (6a)) and valence states unlikely ((5b), (5c) and (6c)).



⋮



Although actinides can form complex oxides such as LiAn(III)O₂ or oxychlorides such as An(III)OCl, the amount of hydrogen depends only on the valence state of the actinides and therefore the amount of metal can be calculated from the hydrogen volume as follows:

$$\text{U(mol)} = \frac{V_H \text{ (l)}}{22.4} \frac{1}{2} \frac{P \text{ (hPa)}}{P_0 \text{ (hPa)}} \frac{T_0 \text{ (K)}}{T \text{ (K)}}, \quad (7)$$

$$\text{Pu(mol)} = \frac{V_H \text{ (l)}}{22.4} \frac{2}{3} \frac{P \text{ (hPa)}}{P_0 \text{ (hPa)}} \frac{T_0 \text{ (K)}}{T \text{ (K)}}. \quad (8)$$

The HBr solution was counted by gamma spectrometry to determine the total amount of actinide. From the amount of actinide metal and total actinide, the reduced fraction was calculated as follows:

$$\text{Reduced fraction} = \frac{\text{An Metal from H}_2 \text{ (mol)}}{\text{Total An from gamma (mol)}} \quad (9)$$

3. Results and discussion

3.1. Solubility of Li_2O in LiCl

The solubility of Li_2O in LiCl is plotted in Fig. 3. The solubility of Li_2O was 8.8 wt% at 650 °C. The values of the solubility agreed well with published results [8]. Since the Li reduction process requires Li_2O to be dissolved into the LiCl solvent, the $\text{Li}_2\text{O}/\text{LiCl}$ ratio in the reduction process should be maintained at less than this solubility limit.

3.2. UO_2 -1 test

The Li_2O concentration in UO_2 -1 is plotted in Fig. 4 against the mass of Li added. The theoretical UO_2 reduction ratio was calculated from the amount of generated Li_2O as plotted in Fig. 4. The Li_2O concentration increased linearly with increasing weight of Li metal added and finally reached approximately 2.5 wt%. It can be seen from Fig. 4 that the final Li_2O concentration of

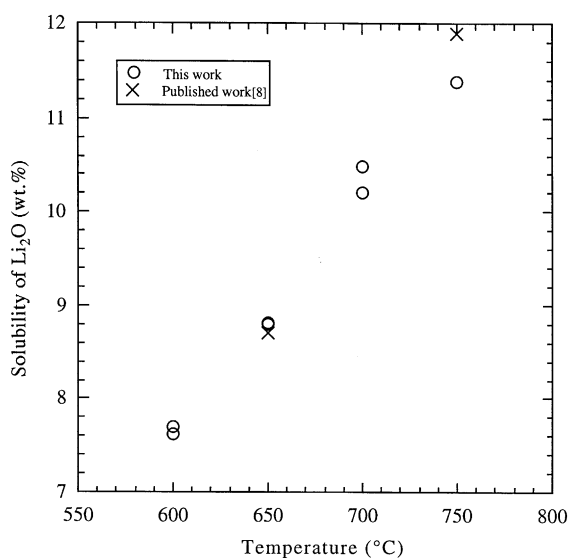


Fig. 3. Solubility of Li_2O in LiCl .

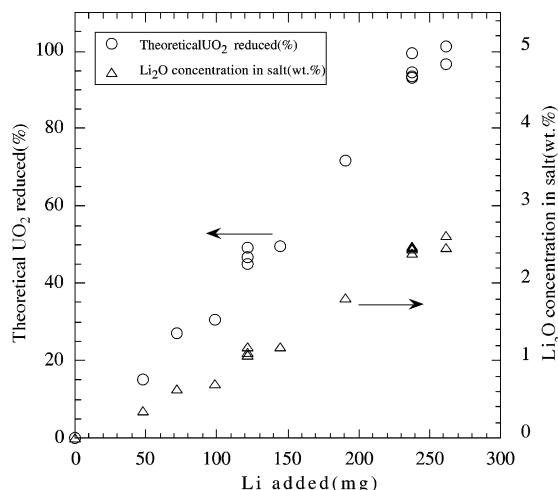


Fig. 4. Dependence of Li_2O concentration and reduction on the Li addition.

2.5 wt% corresponded to 100% theoretical UO_2 reduction. The total amount of Li added until the reaction stopped was 262 mg and agreed with the theoretical amount to reduce 2.32 g of UO_2 loaded.

After breaking the crucible at the end of the experiment, it was found that most of reaction product containing uranium was present in a layer of black particles at the bottom of the crucible, with a relatively small quantity of supernatant salt which was stained by a grey colour of uranium particles. In the next step, samples of U product taken from the layer on the bottom and the powdery product recovered from the stained salt were analyzed. A summary of the analytical results in Table 3 gives the weight of washed samples, their metal content derived from the volume of hydrogen measured by the gas burette, and the total amount of uranium calculated from the activity measured by γ -spectroscopy of the product solution. It can be seen that there is close agreement between sample weight and metal content.

Fig. 5 is an optical microscope photograph of the crucible fragment and reaction product from the experiment. The sample was mounted in resin, lightly ground using a 320 grit paper, followed by polishing with 6 and 1 μm diamond compounds. Lubrication was with a chlorinated solvent. As shown in the photograph, the particles in the layer appear to be spherical and brightened by the light provided by the microscope, indicating they are metallic. The particle is shown at higher magnification in Fig. 6. This photograph confirms the spherical shape of the product metal. The diameter of the particles is typically approximately 160 μm , which is close to the 200 μm diameter of the original UO_2 spheres, and product spheres appear to be macroporous, possibly because of the difference of molar volumes between original UO_2 and reduced U metal.

Table 3
Result of metal analysis of UO₂ reduction

Sample name	Mass (mg)	H ₂ (ml)	U metal (mg)	Gamma (Bq)	U from γ (mg)	Metal from mass (%)	Metal from γ (%)	Comment (see below)
Lump1-1	72	13.4	71.1	43.4	67.9	99	105	A
Lump1-2	86	16.3	86.3	51.1	79.9	100	108	A
Lump1-3	106	19.2	102.1	69.9	109.3	96	93	A
Lump2-1	80	15.4	82.0	50.0	78.2	102	105	B
Lump2-2	60	11.3	60.2	36.3	56.8	100	106	B
Lump3	118	23.2	123.5	72.4	113.2	105	109	C
Powder1	14	1.7	9.2	5.5	8.6	66	107	D
Powder2	43	7.3	38.9	23.9	37.4	90	104	D
Total	579	107.9	573.4	352.5	551.3	99 ^a	104 ^a	

^a Weighted average, A: part of Lump1 = 0.629 g, B: part of Lump2 = 0.986 g, C: Whole Lump3, D: Powder recovered from salt.

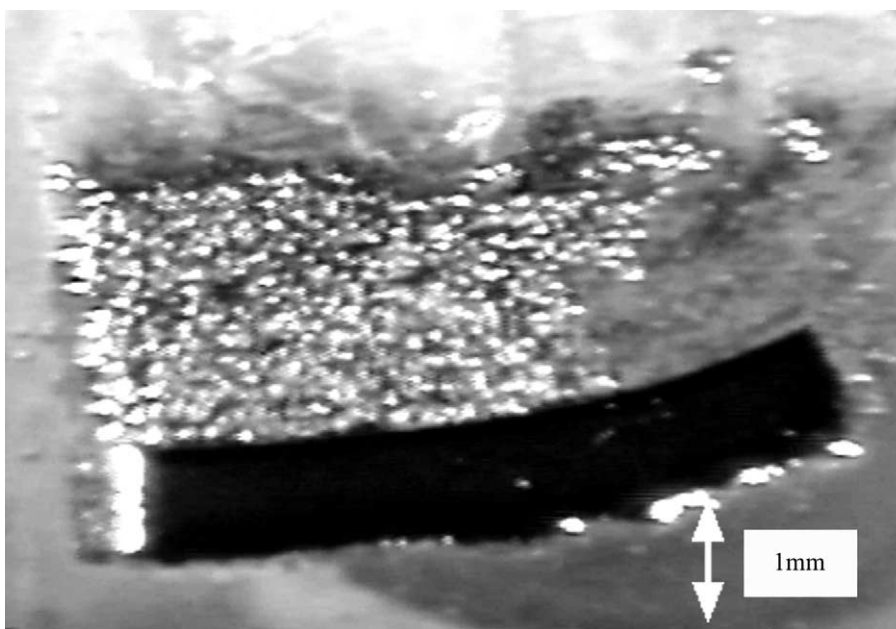


Fig. 5. Optical microscope photograph of the UO₂ reduction product on the crucible.

3.3. PuO₂-1 test

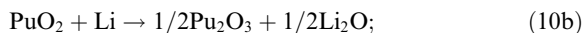
The Li₂O concentration in PuO₂-1 is plotted in Fig. 7 against the mass of Li added. The theoretical PuO₂ reduction ratio was calculated from the amount of generated Li₂O and was also plotted in Fig. 7. The Li₂O concentration increased linearly with increasing Li metal added and finally reached approximately 1.8 wt%. It can be seen from Fig. 7 that the final Li₂O concentration of 1.8 wt% corresponded to almost 100% reduction. The total amount of Li added until the reaction stopped was 248 mg and agreed well with the amount required to reduce the loaded PuO₂ completely to metal.

The linearity of Li₂O concentration in Fig. 7 suggests that PuO₂ did not make any intermediate product with Li or Cl because:

(i) If Pu(III) formed a complex oxide with Li by the following reaction, Li₂O should not increase



(ii) If Pu(III) did not form an intermediate product, the reduction of 1 mole PuO₂ to Pu(III) generates a 1/2 mole of Li₂O as follows:



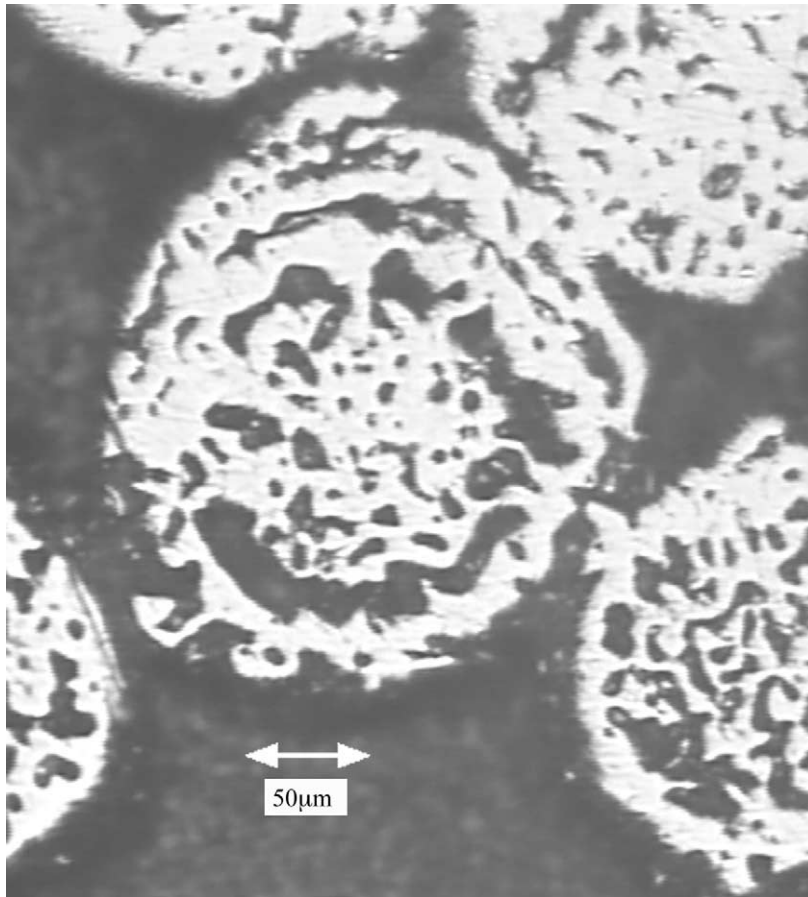


Fig. 6. High magnification optical microscope photograph of the UO₂ reduction product.

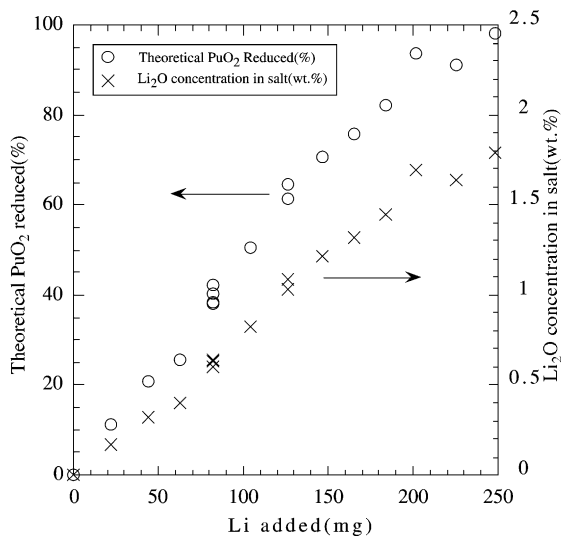


Fig. 7. Dependence of Li₂O concentration and Pu reduction on the Li addition in PuO₂-1 test.

(iii) If Pu(III) formed an oxychloride with Cl by the following reaction, Li₂O should increase twice as much as in forming Pu₂O₃

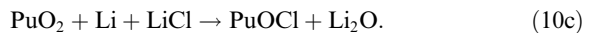


Fig. 8 shows the crucible fragments and reaction products from the experiment. It can be seen, in contrast to the UO₂ reduction experiment, that most of the plutonium product had coated the crucible with a shiny metallic surface rather than only being consolidated at the bottom. The plutonium had wetted all of the crucible in contact with salt, though the metal coating was thickest at the bottom, where it appeared to have small particle inclusions (on the left fragment in Fig. 8).

Results of the analysis of these materials associated with the crucible surface are shown in Table 4. This table gives the weight of plutonium metal derived from the hydrogen volume, those of total plutonium and americium calculated from the gamma activity, the reduced fraction, and Pu/Am ratio in these materials. An illustration of the inner wall of the crucible is shown in Fig. 9



Fig. 8. Photograph of the reduction product in PuO₂-1 test.

with sample numbers in Table 4. The data in Table 4 show the following features.

(i) The weight of plutonium metal measured by the gas burette agreed well with the weight calculated from the gamma activity. Thus, reduction of PuO₂ to metal was verified.

(ii) The average ratio of Pu/Am in the samples of the crucible fragment was 45, close to the value of ~40 for the PuO₂ feed material. The ratio did not scatter significantly among the parts of crucible where samples were taken. Since Pu metal melted in this experiment, if oxide of Am existed, it was not expected to be mixed

with Pu but dissolved in the salt or accumulated on the salt–metal interface. The Pu/Am ratio in the methanol used to wash the crucible fragment was also the same as the feed material. These facts suggest that Am was reduced to metal in the test conditions of PuO₂-1, the final Li₂O concentration of 1.8 wt%.

3.4. PuO₂-2 test

The Li₂O concentration in PuO₂-2 is plotted in Fig. 10 against the mass of Li added. The theoretical PuO₂ reduction ratio was calculated from the amount of

Table 4
Results of metal analysis of PuO₂-1 reduction test

Sample name	Metal in sample (mg)	Total Pu from gamma (mg)	Total Am from gamma (mg)	Reduced fraction (%)	Pu/Am
Pu#1-1	4.2	4.2	0.107	96.6	32.6
Pu#1-2	9.8	9.9	0.294	95.9	37.1
Pu#1-3	47.0	44.6	1.231	102.6	36.6
Pu#1-4	4.7	34.0	0.771	99.8	46.2
Pu#1-5	23.2	18.5	0.526	121.6	37.0
Pu#1-6	17.8	6.4	0.199	118.1	34.7
Pu#1-7	23.5	25.7	0.700	89.0	33.8
Pu#1-8	13.8	31.3	0.790	11.7	39.4
Pu#1-9	569.0	588.0	12.806	94.7	47.0
Pu#1-10	418.7	352.7	7.543	116.2	49.0
Total	1141.5	1115.2	24.966	100.1 ^a	44.7 ^a

^a Weighted average.

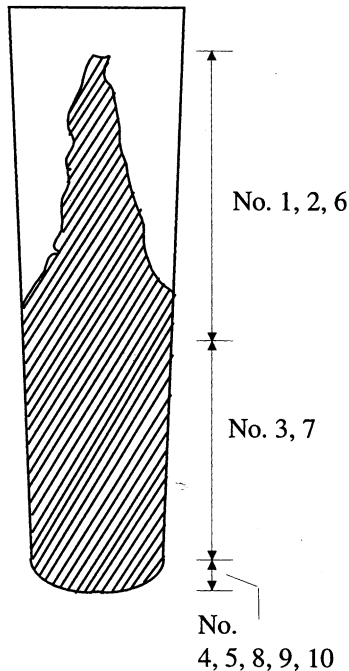


Fig. 9. Illustration of inner surface of the crucible (molten metal deposited on hatched area).

generated Li_2O as plotted in Fig. 10. As shown in this figure, the Li_2O concentration increased steadily until approximately 200 mg of Li had been added. The Li_2O concentration would have reached approximately 8.4 wt% at this point, so that any further Li_2O should not be dissolved in the solution. After dilution by addition of the extra 2.1 g of LiCl, the Li_2O concentration decreased to 8.0 wt%. This result indicated that the solid Li_2O was dissolved into LiCl, because the dilution without dissolution of the solid would decrease the Li_2O concentration to 7.3 wt%. From these results, it was shown that the reduction of Pu oxide had progressed even after the saturation of Li_2O . Fig. 10 also shows that the reduced fraction reached 100% after the dilution.

In the first two samples of salt taken for analysis, only 5.5 wt% of Li_2O was measured in the salt, although it should be 6.25 wt% based on the weights of Li_2O and LiCl initially loaded. This is equivalent to a ‘loss’ of 0.12 g Li_2O . The missing Li_2O was recovered after these two additions of Li, as seen in Fig. 10. At the first and second additions of Li, the temperature of the salt increased for a short time by about 1–2 °C. The other Li additions in $\text{PuO}_2\text{-2}$ and all Li additions in $\text{UO}_2\text{-1}$ and $\text{PuO}_2\text{-1}$ decreased the salt temperature by 1–2 °C, though the reduction is an exothermic reduction. These observations suggest possible formation of an intermediate product, although no details is given in the present study.

Fig. 11 is a photograph of the crucible fragment, salt, and reaction product in $\text{PuO}_2\text{-2}$. It can be seen that

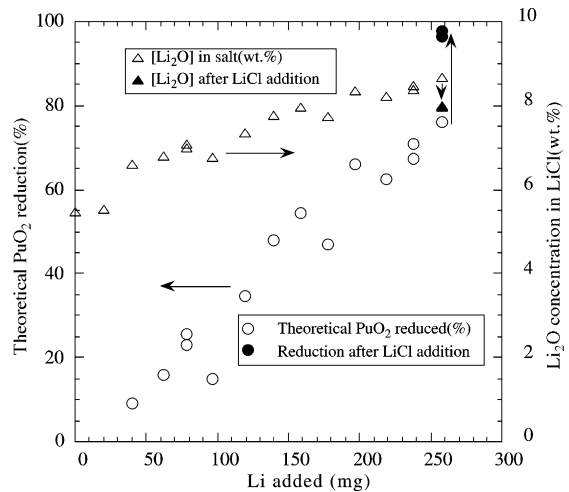


Fig. 10. Dependence of Li_2O concentration and reduction on the Li addition in $\text{PuO}_2\text{-2}$ test.

plutonium with shiny metallic appearance wetted not only the crucible but also the bulk salt. Results of the metal analysis are shown in Table 5. This table gives weight of plutonium metal derived from the hydrogen volume, those of total plutonium and americium calculated from the gamma activity, the reduced fraction, and Pu/Am ratio. Samples named W-x were recovered on the surface of the crucible fragments, while samples named S-x were recovered on the surface of the bulk salt. Generally, the weight of the metal calculated from the amount of hydrogen well agreed with the weight of plutonium measured by gamma spectroscopy. The agreement was especially good for large samples of which the analytical error is considered to be small, and therefore almost complete reduction of Pu in LiCl nearly saturated with Li_2O was verified. The reduced fraction was slightly lower for samples recovered on the surface of the bulk salt.

The Pu/Am ratio scattered much more than $\text{PuO}_2\text{-1}$. This heterogeneity would mean that Am took a chemical form immiscible with molten Pu metal. The average of the Pu/Am ratio was about 52 in the product, higher than original material, although the Pu/Am ratio in the salt was lower than the original material. From these points, Am was considered not to be completely reduced in $\text{PuO}_2\text{-2}$ conditions. In contrast to this result, americium was more miscible with Pu metal rather than salt and more homogeneous in the Pu metal in the $\text{PuO}_2\text{-1}$, where Li_2O concentration was lower and therefore the reduction was easier than $\text{PuO}_2\text{-2}$.

3.5. Behaviour of Pu and Am in the salt

The concentrations of Pu and Am in LiCl observed in $\text{PuO}_2\text{-1}$ are plotted in Fig. 12 against the reduced

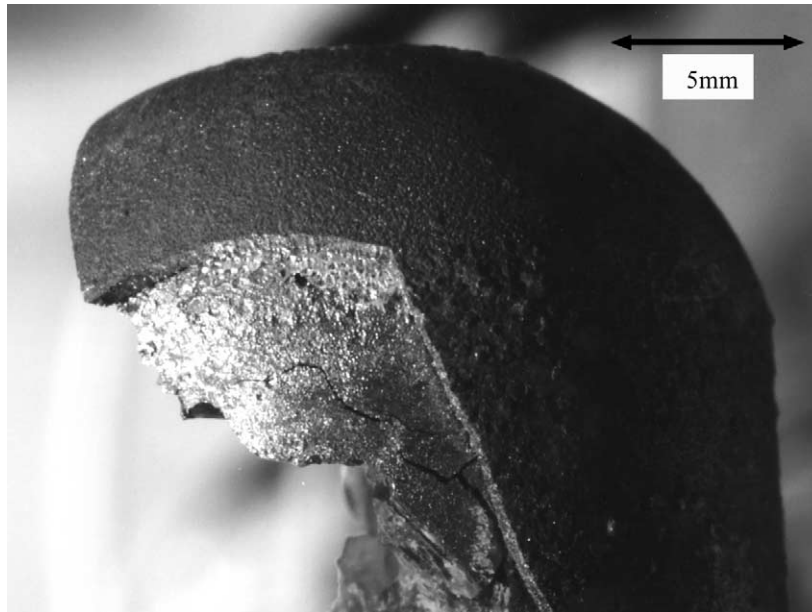


Fig. 11. Photograph of the reduction product in PuO₂-2 test.

Table 5
Results of metal analysis of PuO₂-2 reduction test

Sample name	Metal in sample (mg)	Total Pu from gamma (mg)	Total Am from gamma (mg)	Reduced fraction (%)	Pu/Am
W-1	372.4	338.0	6.168	108.2	54.8
W-2	54.5	38.4	0.768	139.2	50.0
W-3	40.0	29.1	0.470	135.4	61.9
W-4	61.0	51.1	0.973	117.0	52.5
W-5	344.0	336.2	6.822	100.3	49.3
W-6	7.5	18.1	0.603	40.2	30.1
S-1	54.1	61.4	1.148	86.6	53.5
S-2	75.6	76.7	1.600	96.5	47.9
S-3	13.3	18.4	0.500	70.4	36.9
S-4	93.0	93.0	1.678	98.2	55.5
S-5	120.4	124.7	1.999	95.0	62.4
S-6	107.7	109.6	2.066	96.5	53.0
Total	1343.5	1294.8	24.795	101.8 ^a	52.2 ^a

^a Weighted average.

fraction of PuO₂ shown in Fig. 7. It can be seen that the Pu concentration was almost constant, at approximately 60 ppm, until ~90% of PuO₂ had been reduced, and then suddenly decreased to <10 ppm. The concentration of Am in the salt increased to a maximum of about 30 ppm, after ~50% of PuO₂ had been reduced, and then decreased to ~3 ppm. The final masses of Pu and Am in the salt calculated from these concentrations are about 0.1 and 0.05 mg, respectively. This means that more than 99.9% Pu and Am were finally recovered into Pu metal phase.

Fig. 13 shows the concentration of Pu and Am in the salt observed in PuO₂-2. The concentration of Pu in the

salt was scattered with an average of about 1000–2000 ppm, and then decreased when more than 90% of the PuO₂ was reduced. The final amount of Pu in the salt was about 15 mg. This means that more than 99.9% of Pu was finally recovered into the Pu metal phase. The Am concentration stayed under 100 ppm until approximately 50% of Pu was reduced, and then increased. The final amount of Am in the salt was about 6 mg, namely, about 90% of Am initially loaded was recovered into the Pu metal phase.

The Pu/Am ratio in the salt in PuO₂-1 is shown in Fig. 14. In this test, the Pu/Am ratio decreased from approximately 20 to 1–2 as reduction progressed,

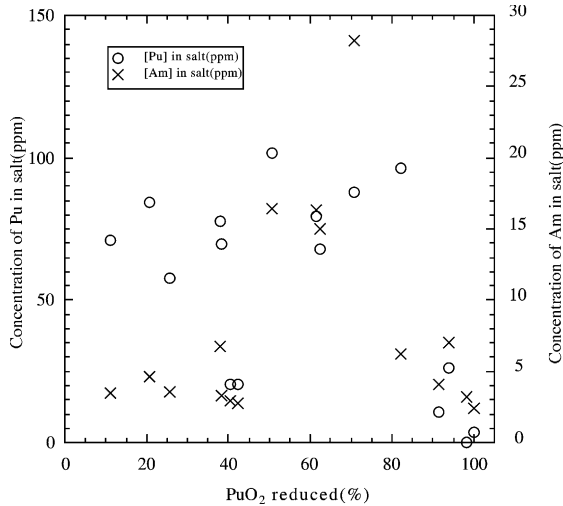


Fig. 12. Concentration of Pu and Am in the salt observed in PuO₂-1 test.

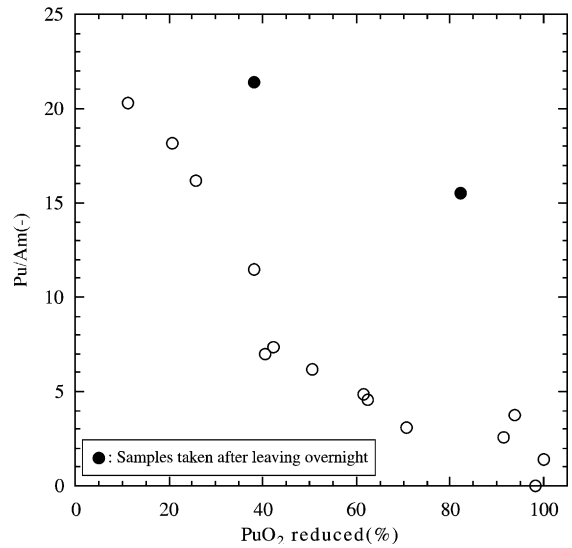


Fig. 14. Pu/Am ratio in PuO₂-1 test.

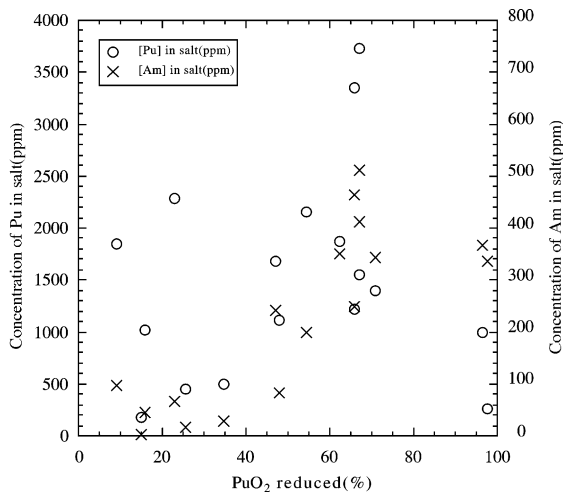


Fig. 13. Concentration of Pu and Am in the salt observed in PuO₂-2 test.

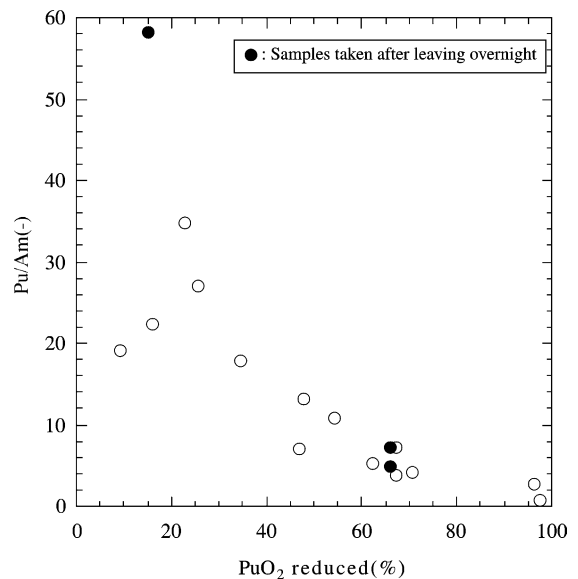


Fig. 15. Pu/Am ratio in PuO₂-2 test.

showing that the salt was always Am rich compared with the feedstock material (Pu/Am ~40) and the fraction of Am increased. However, 2 samples taken after leaving overnight for 13–14 h showed significantly higher Pu/Am ratio than other points around them as marked in the graph. Since stirring, temperature and atmosphere in the glove box were kept the same as day time, the difference of these 2 samples were supposed to be caused by stop of the Li addition or sampling or delayed/slow reaction. In test PuO₂-2, on the other hand, the Pu/Am ratio increased until about 25% reduction and then decreased gradually as shown in Fig. 15. The Pu/Am ratio of the salt taken after leaving overnight was higher than other points at 15% reduction but not different at 66%

reduction. In the latter case, the Li₂O concentration in the salt was about 8.3 wt% and the highest in these two tests. A further study may be needed to clarify the observed Am behaviour by considering the reaction mechanism and kinetics.

4. Conclusions

- (i) The solubility of Li₂O in LiCl was measured between 600 and 750 °C, and was 8.8 wt% at 650 °C.

(ii) Particles of UO_2 with diameter of 200 μm were completely reduced by Li metal at 650 $^\circ\text{C}$ in molten LiCl, and formed porous metal.

(iii) Plutonium dioxide was completely reduced by Li metal at 650 $^\circ\text{C}$ in molten LiCl with no intermediate product formation. The reduction of Pu can proceed even the Li_2O concentration in LiCl is just below the solubility limit.

(iv) The behaviour of AmO_2 contained in the PuO_2 depended on the concentration of Li_2O in LiCl. The AmO_2 was reduced in the condition that the final Li_2O concentration was 1.8 wt%, but not reduced at near saturation.

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