



Lithium reduction of americium dioxide to generate americium metal

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Abstract

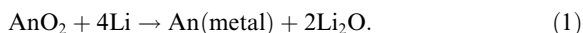
The lithium reduction process has been developed for application to a pyrochemical recycle process for oxide fuels. This process uses lithium metal as a reductant to convert oxides of actinide elements to metal. Lithium oxide generated as a product of the reduction would be dissolved in a molten lithium chloride bath to enhance reduction. In this work, the reduction of americium dioxide to its metal was experimentally confirmed. At the end of the reduction, more than 99.9% of the Am was recovered from the salt phase to a solid Am phase. It was also shown that the lithium oxide concentration in lithium chloride is required to be kept under 5.1 wt%. When the concentration of lithium oxide was between 5.1 and 6.3 wt%, americium formed monoxide. © 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 for application to nuclear fuel reprocessing [1–5]. As a part of the process, a pyrochemical reduction of spent oxide fuel to metal is being developed before introduction into an electrorefiner. The technology named the ‘Lithium reduction process’ employs lithium (Li) metal as a reductant and lithium chloride (LiCl) as a solvent [6–10]. Since the melting point of LiCl is about 610 °C, the Li reduction process is operated at 650 °C.

In the reduction step, 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 lithium reduction process has significant advantages over other technologies which employ other reductants, such as calcium and magnesium, because: (i) it does not require a ceramic container; (ii) it would require a lower temperature process; (iii) recycle of the reductant would be easier than other processes. However, it was observed in plutonium reduction tests that behaviour of americium included in PuO₂ depended on Li₂O concentration and that Am was not reduced to metal when the final Li₂O concentration was about 8.0 wt% [10]. The difference of the behaviour was caused because the standard Gibbs energy of formation (ΔG_f°) of Li₂O and americium sesquioxide (Am₂O₃) are so close [11] and thermodynamic data suggest that Am₂O₃ is more stable than Li₂O. The relation of the stability of Am₂O₃ and Li₂O means that the progress of the reduction may depend on the concentration of Li₂O in LiCl, i.e. the chemical activity of Li₂O. Since the final distribution of Am depends on the valence state of Am, it is important to determine the upper limit of the Li₂O concentration below which Am can be reduced to metal.

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The experiment reported in this article was carried out to measure the upper limit of Li_2O concentration in LiCl , below which AmO_2 can be reduced to metal by Li and to show that Am metal can be obtained by the Li reduction process.

2. Experiments

The reduction experiment and product analyses were carried out in argon atmosphere glove boxes to treat chemically reactive materials. A high purity argon atmosphere glove box equipped with a furnace well used for reduction tests had 5–10 ppm oxygen and approximately 20 ppm of water vapor while a lower purity glove box was used for chemical analysis. The nitrogen concentration was estimated to be four times larger than that of oxygen as in air. The crucible and stirring rod used in the reduction test were made of tungsten to avoid possible reaction with Am metal. The temperature difference in the crucible with 20 mm diameter and 150 mm height was less than 5 °C.

2.1. Reduction of oxide

In the reduction experiment, 1.08 g of AmO_2 , 16.17 g of LiCl and 1.05 g of Li_2O were loaded into the crucible. The 1.08 g of AmO_2 generates 236 mg of Li_2O when completely reduced, which is equivalent to about 1.5 wt% in 16 g of LiCl . Since Am was reduced to metal when the final concentration of Li_2O was 1.8 wt% in a plutonium reduction test, extra Li_2O was added to make the Li_2O concentration high enough to stop the reduction of Am . The Li_2O had been calcined at 1000 °C in the air to remove possible impurities before use. Lithium chloride used in the experiments was purchased from Anderson Physics Laboratory. The AmO_2 was a fine powder of pure Am-241 .

The amount of Am in each sample was determined from the 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 Li_2O 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 Li_2O , in case the generation of Li_2O stopped. The gen-

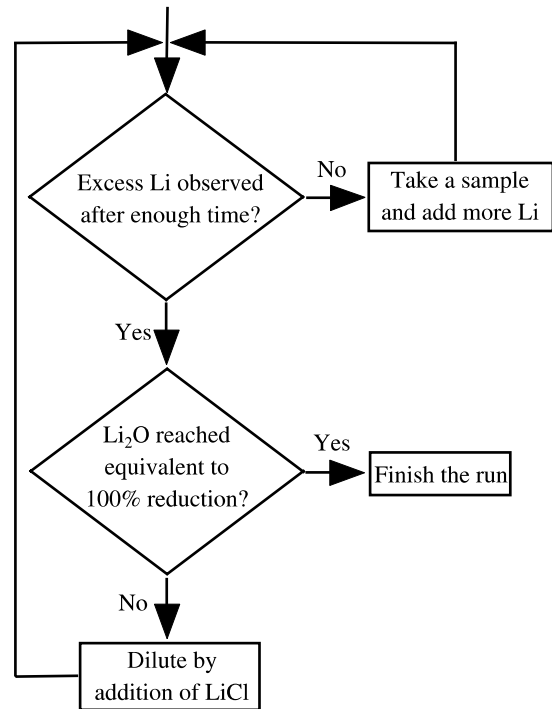


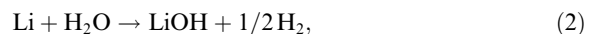
Fig. 1. Flow chart of the reduction experiments.

eral scheme of the addition of reagents is shown in Fig. 1.

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 daytime, while overnight the system was just left with stirring.

2.2. Salt analysis

Lithium chloride samples taken during the reduction were analyzed mainly to determine the amount of Li_2O generated by the reduction. Samples were weighed and dissolved into H_2O in a gas burette. In this step, Li metal and Li_2O dissolving in LiCl react as follows:



The volume of H_2 gas (V_{H}) generated by Li metal was accurately measured with the gas burette to calculate the amount of Li at the pressure (P) as follows:

$$\text{Li (mol)} = \frac{V_{\text{H}} \text{ (l)}}{22.4} \times 2 \times \frac{P \text{ (hPa)}}{P_0 \text{ (hPa)}} \times \frac{T_0 \text{ (K)}}{T \text{ (K)}} \quad (4)$$

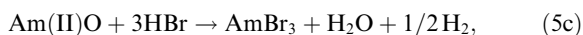
$$(P_0 = 1013, T_0 = 273.16).$$

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. 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 AmO₂ was calculated from Eq. (1). Titrated solutions were then counted by gamma spectrometry to determine their Am contents.

2.3. Metal analysis

The reduction product of Am was analyzed mainly to determine the fraction of Am metal in the total Am amount. The Am products on the bottom of the crucible were taken out with small amount of salt by breaking the crucible and then measured reduction yield with the following two methods.

Method 1: Three representative samples of Am products were washed with methanol to remove the salt containing Li and Li₂O assuming that Am metal does not react with methanol. Washed products were dried, weighed and then dissolved into hydrobromic acid (HBr) in a gas burette. The reactions of the Am depend on their valence state. The following are possible reactions of each valence state of actinide including reactions unlikely or very slow (5a):



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

$$\text{Am (mol)} = \frac{V_{\text{H}_2} (l)}{22.4} \frac{(1)}{3} \frac{P (\text{hPa})}{P_0 (\text{hPa})} \frac{T_0 (\text{K})}{T (\text{K})}. \quad (6)$$

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

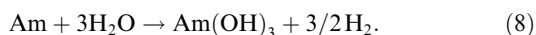
$$\text{Reduction yield} = \frac{\text{Am metal from H}_2 \text{ (mol)}}{\text{Total Am from gamma (mol)}}. \quad (7)$$

Because a very slow reaction of the Am product with methanol was observed in the analysis with *Method 1*,

two more analyses were carried out by a more complicated method to obtain more accurate value.

Method 2:

- (i) Americium products along with adherent Li/Li₂O/LiCl were weighed and then washed using H₂O, a small amount of Am metal reacted as follows:



In this case, all the Li also reacted as Eq. (2). Therefore the total amount of Li and the amount of Am metal reacted with H₂O were determined by means of this dissolution.

- (ii) When the reaction became negligible, the Am products were taken out and dried. The aqueous solution was titrated with 0.1 M HCl. The dissociation constant of Am(OH)₃ was sufficiently small to separate it with filtration, and therefore titrated alkali was only equivalent to LiOH generated from Li and Li₂O. In this step the total amount of Li and Li₂O was determined by means of this titration.
- (iii) The dried Am products were dissolved into 4.3 M HBr in a gas burette to measure the volume of hydrogen generated by the reaction (5d). From the hydrogen volume, the amount of Am metal which has not reacted in (i) was determined.
- (iv) Aqueous solutions from (i) and (iii) were analyzed by gamma spectroscopy to determine the total amount of Am. From the total amount weighed in (i) and the amount of Am, the weight of Li–Li₂O–LiCl is calculated. Since the concentration of Li₂O in LiCl was given from the analytical result of final salt sample and the weight of Li was negligible compared with LiCl, the amount of LiCl and Li₂O each could be obtained. The difference between the amount of LiOH analyzed in (ii) and that of Li₂O gave the amount of Li metal. From the difference between the hydrogen volume obtained in (i) and that of Li metal, the amount of Am metal reacted in (i) could be obtained. Here the total Am metal estimated from this calculation and from (iii) can be compared with the amount of total Am evaluated from the gamma analysis to calculate the reduction yield.

3. Results and discussion

3.1. Results of salt analysis

Plotted in Fig. 2 are the concentration and total amount of Li₂O in LiCl, the amount of Li added, and the total amount of LiCl in the crucible. The *x*-axis of the graph shows the run number which increases with the progress of the experiment. This graph exhibits the following features.

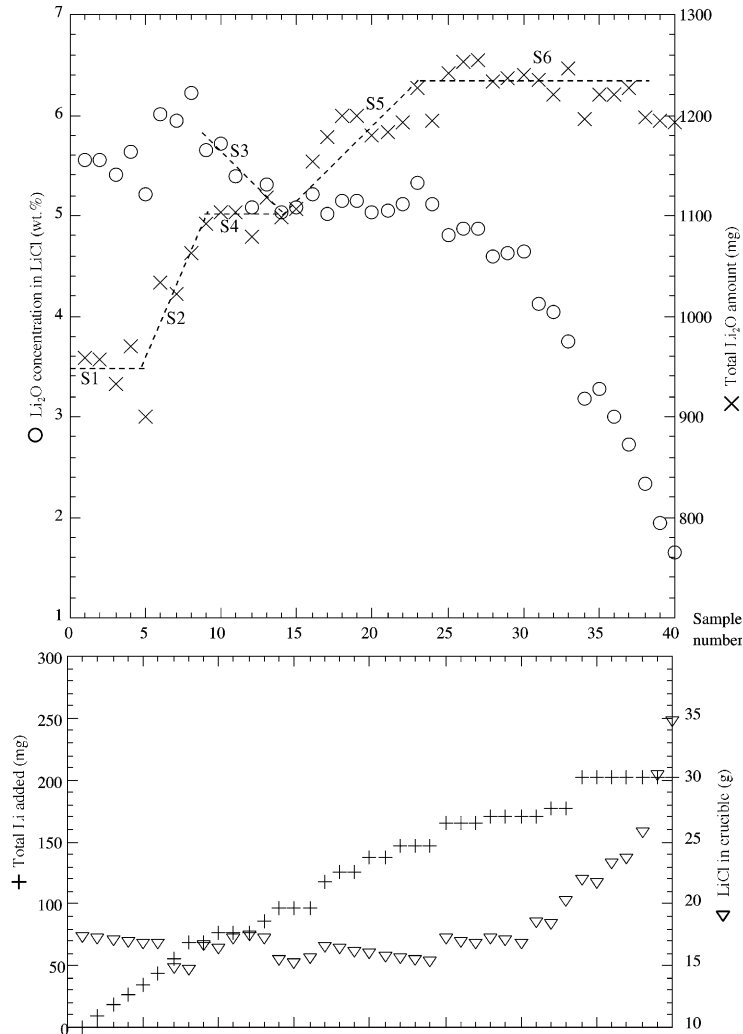


Fig. 2. Concentration and total amount of Li_2O in LiCl , the amount of Li added, and the total amount of LiCl .

- (i) In the early stage of the experiment, the amount of Li_2O did not increase (broken line S1 in the figure) although added Li was consumed. It means that AmO_2 and Li reacted without generating Li_2O . The amount and the concentration of Li_2O suddenly began to increase after sample no. 5. The total amount of Li added until the sample no. 5 was taken was 40 mg, i.e. 3.6×10^{-3} mol, and was nearly equal to the amount of loaded AmO_2 , 3.8×10^{-3} mol. This good agreement of the amounts suggests that the reaction in the early stage was



- (ii) The amount of Li_2O which started to increase after sample no. 5 continued to increase linearly with Li addition (broken line S2) until sample no. 9 was taken. After that both the consumption of Li , i.e.

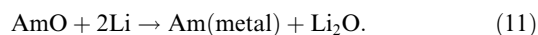
the progress of the reduction, and the increase of Li_2O stopped. The amount of Li added between sample nos. 5 and 9 was 43 mg, 6.2×10^{-3} mol, and agreed well with the amount of Li_2O (150 mg, 5.0×10^{-3} mol), generated in the same period. From the good agreement, the reaction in this stage was supposed to be as follows:



Since the reaction stopped at this point when the Li_2O concentration was 6.3 wt%, it can be assumed that AmO is not reduced by Li in the LiCl including 6.3 wt% of Li_2O .

- (iii) To restart the reduction, LiCl was added repeatedly (arrows in the lower part of the graph) until sample no. 16 was taken. Between sample nos. 9 and 14, the Li_2O concentration decreased along broken line S3

while the total amount of Li_2O stayed constant as broken line S4. This means that Li_2O was just diluted without restart of the reduction. However, the amount of Li_2O started to increase again around sample no. 15 when the Li_2O concentration reached approximately 5.1 wt%. The total amount of Li_2O increased with Li addition (broken line S5) and finally became constant, approximately 1240 mg (broken line S6). The amount of Li_2O generated between sample nos. 14 and 23 was about 120 mg. This amount, approximately 4.0×10^{-3} mol, is nearly equal to the amount of Am in mol, and therefore it can be said that AmO was reduced to metal as follows when Li_2O concentration was lower than 5.1 wt%:



- (iv) The addition of LiCl was continued after sample no. 23 to ensure that no more reaction occurred. The total amount of Li_2O stayed constant while the concentration decreased by dilution. From these results, completion of the reaction at sample no. 23 was confirmed.

Fig. 3 shows the concentration of Am in the salt with the same sample numbers as Fig. 2. Even measured concentration scattered a lot, following two features were clearly observed:

- Some samples from the initial stage of the experiment showed higher Am concentration than others.
- Americium concentrations were constantly decreased after the reduction was completed around sample no. 23.

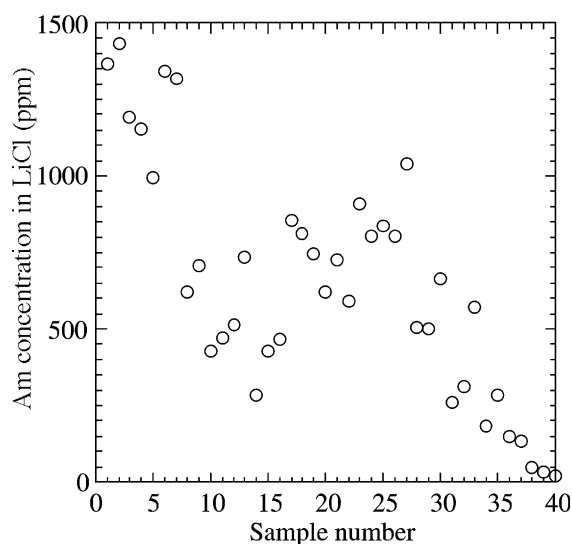


Fig. 3. Concentration of Am in the salt.

These observations may mean:

- Am(IV) has higher solubility than other valence states in LiCl with high concentration of Li_2O .
- Dilute AmO in LiCl was slowly reduced and precipitated.
- Metal Am is soluble in LiCl depending on Li_2O concentration.

However, further experiments under controlled condition are necessary to ensure the reason. The final amount of Am in LiCl was about 1.3 mg in total and more than 99.5% were recovered into solid Am phase.

3.2. Results of metal analysis

For metal analysis, five Am samples associated with crucible fragments were chosen from the bottom part at random. Table 1 shows the analytical results, i.e. amount of Am metal and total Am, and reduction yields. Reduction yields were nearly 100% (105.4% in weighted average) and suggested that AmO_2 was almost completely reduced to metal. The amount of Am metal was slightly larger than total amount of Am due to experimental errors. Errors inherent in the measurement of H_2 from HBr and the measurement of gamma activity were estimated to be about 2% and 3%, respectively from control experiments. The other part of the error was thought to be mainly inherent in the measurement of H_2 from the methanol and H_2O . Since measured H_2 volume from methanol and H_2O generally scattered more widely than that from HBr, the total error of experiments was supposed to be about 10%. It can also be seen from the table that reduction yields measured by two methods agreed well, therefore reaction between Am metal and methanol was negligible.

3.3. Discussion on the free energy of formation of AmO

The Gibbs free energy of formation of AmO was evaluated based on the regular solution model. Reaction of Eq. (11) is rewritten as follows:

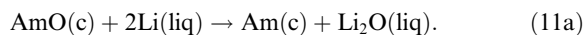


Table 1
Results of metal analysis

Sample	Analytical method	Am metal (mg)	Total Am (mg)	Reduction yield (%)
AM1	Method 1	122.7	119.8	102.4
AM2	Method 1	17.1	16.0	106.7
AM3	Method 1	92.6	87.3	106.0
AM4	Method 2	109.3	104.3	104.8
AM5	Method 2	60.8	54.6	111.3

The Gibbs energy change of this reaction is

$$\Delta G_{\text{reaction}} = \Delta G_{\text{Li}_2\text{O}}^0 + RT \ln a_{\text{Li}_2\text{O}} - \Delta G_{\text{AmO(c)}}. \quad (12)$$

Since the reaction is in equilibrium at an Li_2O concentration of 5.1 wt%,

$$\Delta G_{\text{reaction}} = 0$$

at 5.1 wt% of Li_2O concentration.

Therefore,

$$\begin{aligned} \Delta G_{\text{AmO(c)}} &= \Delta G_{\text{Li}_2\text{O}}^0 + RT \ln a_{\text{Li}_2\text{O}(5.1 \text{ wt}\%)} \\ &= \Delta G_{\text{Li}_2\text{O}}^0 + RT \ln(\gamma_{\text{Li}_2\text{O}} \cdot X_{\text{Li}_2\text{O}}^{5.1 \text{ wt}\%}). \end{aligned} \quad (13)$$

Here, $\gamma_{\text{Li}_2\text{O}}$ is activity coefficient of Li_2O , and $X_{\text{Li}_2\text{O}}^{5.1 \text{ wt}\%}$ is molar ratio equivalent to 5.1 wt%, 0.0708.

Assume that $\gamma_{\text{Li}_2\text{O}}$ is independent of the molten salt composition,

$$\gamma_{\text{Li}_2\text{O}} = a_{\text{Li}_2\text{O}(\text{saturated})} / X_{\text{Li}_2\text{O}}^{\text{saturated}}. \quad (14)$$

Since the solubility of Li_2O in LiCl is 8.8 wt% [10], $X_{\text{Li}_2\text{O}}^{\text{saturated}}$, the solubility in molar ratio, is 0.120.

Thus $\Delta G_{\text{Li}_2\text{O}}^0$ and $a_{\text{Li}_2\text{O}(\text{saturated})}$ are necessary to be calculated.

At first, $\Delta G_{\text{Li}_2\text{O}}^0$ is evaluated. Since the melting point of Li_2O is higher than the boiling point of Li , pure super-cooled Li_2O is necessary to be considered.

Thus $\Delta G_{\text{Li}_2\text{O}}^0$ is calculated as total Gibbs energy of the following two reactions:

- $2\text{Li}(\text{liq}) \rightarrow 2\text{Li}(\text{gas})$.
- $2\text{Li}(\text{gas}) + 1/2\text{O}_2(\text{gas}) \rightarrow \text{Li}_2\text{O}(\text{liq})$.

From ΔG^0 of each reaction shown in Ref. [11], it is calculated that

$$\begin{aligned} \Delta G_{\text{Li}_2\text{O}}^0 &= 2(-0.0930T + 150.766) + (0.2672T - 811.140) \\ &= 0.0812T - 509.608 \text{ (kJ/mol)}. \end{aligned} \quad (15)$$

The value of the ΔG^0 at 923 K is -434.660 kJ/mol.

In the next, $a_{\text{Li}_2\text{O}(\text{saturated})}$ is evaluated. Since

$$\Delta G_{\text{Li}_2\text{O}}^{\text{sol}} = \Delta G_{\text{Li}_2\text{O}}^{\text{liq}} + RT \ln a_{\text{Li}_2\text{O}(\text{saturated})} \quad (16)$$

in saturated solution,

$$a_{\text{Li}_2\text{O}(\text{saturated})} = \exp\{(\Delta G_{\text{Li}_2\text{O}}^{\text{sol}} - \Delta G_{\text{Li}_2\text{O}}^{\text{liq}})/RT\}. \quad (17)$$

Here, $\Delta G_{\text{Li}_2\text{O}}^{\text{sol}}$ can be calculated from the ΔG in Ref. [11] as

$$\Delta G_{\text{Li}_2\text{O}}^{\text{sol}} = 0.1377T - 604.127 \text{ (kJ/mol)} \quad (18)$$

and $\Delta G_{\text{Li}_2\text{O}}^{\text{liq}}$ is same as (15). Therefore

$$\begin{aligned} a_{\text{Li}_2\text{O}(\text{saturated})} &= \exp\{[(0.1377T - 604.127) \\ &\quad - (0.0812T - 509.608)]/RT\} \\ &= \exp\{(0.0565T - 94.519)/RT\}. \end{aligned} \quad (19)$$

The value of ΔG^0 at 923 K is 4.00×10^{-3} , and therefore $\gamma_{\text{Li}_2\text{O}} = 4.00 \times 10^{-3}/0.120 = 3.33 \times 10^{-2}$.

By using these value and Eq. (3),

$$\begin{aligned} \Delta G_{\text{AmO(c)}}^0 &= -434.660 + RT \ln(3.33 \times 10^{-2} \times 0.0708)/1000 \\ &= -481.1 \text{ kJ/mol} \end{aligned}$$

at 923 K.

4. Conclusions

- (1) Americium dioxide can be reduced to Am metal by Li when Li_2O concentration in LiCl is lower than 5.1 wt%. In this case, more than 99.9% of Am is recovered from molten salt phase into solid Am phase.
- (2) Americium dioxide is reduced to AmO by Li when Li_2O concentration in LiCl is between 5.1 and 6.3 wt%.
- (3) Standard Gibbs energy of formation of AmO was estimated to be -481.1 kJ/mol at 923 K.

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