



## Light element thermodynamics related to actinide separations

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### Abstract

The accumulation of waste from the last five decades of nuclear reactor development has resulted in large quantities of materials of very diverse chemical composition. An electrometallurgical (EM) method is being developed to separate the components of the waste into several unique streams suitable for permanent disposal and an actinide stream suitable for retrievable storage. The principal types of nuclear wastes are spent oxide or metallic fuel. Since the EM module requires a metallic feed, and oxygen interferes with its operation, the oxide fuel has to be reduced prior to EM treatment. Further, the wastes contain, in addition to oxygen, other light elements (first- and second-row elements) that may also interfere with the operation of the EM module. The extent that these light elements interfere with the operation of the EM module has been determined by chemical thermodynamic calculations. © 1997 Elsevier Science B.V.

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### 1. Introduction

Many different types of wastes have accumulated from the operation of nuclear power reactors. These wastes contain actinide elements, fission product elements, and structural materials. In addition, the wastes may contain various light elements such as oxygen from oxide fuels, aluminum from production reactors, and sodium coolant. Since the actinide elements have potential value for energy production, it is desirable to separate them from the other materials so that the latter can be placed in permanent storage and the actinides in retrievable storage. This paper will focus on selected facets of the electrorefining process to illustrate the capability of the method and also to characterize the impact that light elements may have in creating chemical complexity into the electrorefiner system.

The focus of the fuel-cycle effort is on fuel treatments and advanced pyrochemical techniques. An electrorefining process is being developed for the treatment of spent fuel from DoE owned reactors and commercial light water reactors (LWRs). A beneficial feature of this process is the removal of transuranics from the spent fuel, significantly reducing the quantity of long-lived radionuclides that would

otherwise be disposed in a geologic repository. Waste treatment processes are also being developed to concentrate the metal and salt wastes from the electrorefiner and to convert the treated waste materials into forms suitable for disposal in a licensed high-level waste repository.

To develop a cost effective treatment for these diverse nuclear wastes, Argonne national laboratory (ANL) has developed an electrometallurgical (EM) method [1–3], that can be used to separate the actinide elements from the other elements. The processing approach is to treat the various fuel types with a customized head-end step to produce either a metal or an oxide product. The oxide fuels are first reduced to metals by using lithium metal reductant. The metallic feed to the EM module is electrolytically separated into three output streams: a stream containing actinide elements; a stream containing Cs, Sr, Ba, and the rare earths, elements that are chemically more reactive than the actinide elements; and a stream containing elements (noble metals) that are chemically less reactive than the actinide elements. The active elements and the actinide elements are oxidized (i.e., electrons are removed) into the molten salt electrolyte, and by adjustment of the voltage, the actinides are deposited either as the pure metal in the case of uranium, or as intermetallic compounds in a liquid cadmium anode in the case of the other actinides. While the uranium is free of other elements, the other actinides contain significant amounts of the rare-earth fission products. Periodically, the molten salt electrolyte is treated with

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zeolite to remove the active fission products, and the salt is recycled to the EM module. The fission-product loaded zeolite is mixed with glass and formed into a waste suitable for permanent storage. The elements less reactive than the actinides are left as a noble metal waste, which is alloyed with other metals and formed into a waste suitable for permanent storage.

The basic separation methodology involves oxidation–reduction processes in which the actinides are separated from other elements by differences in the equilibrium partition between two phases. Usually, these processes consist of two steps. The first step involves partitioning between two phases where the elements less active than the actinides are left in one phase, and the actinides remain in the other phase. In the second step, the redox potential of the system is adjusted so that the actinides remain in one phase, while the more active elements remain in the other phase. Since these are equilibrium partitions and the physical separations are never 100% complete the end result is usually that the actinides are contaminated with more active or less active elements. This has turned out to be a desirable result since it makes the recovered actinides very radioactive and, therefore, not easily diverted to undesired uses. Most of the separation processes that have been or are being considered involve the partition between a metallic phase and a molten salt phase, the latter either a chloride or fluoride salt.

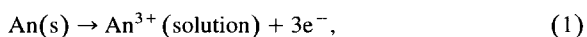
The key to the successful operation of this treatment method is the ability to electrolytically oxidize the actinide elements at the anode. These then disperse into the molten salt electrolyte as a soluble ionic species that can be electrolytically reduced to the metallic form at the cathode. If the feed to the EM module contains elements that reduce the actinide activity, then it may not be possible to achieve the oxidation into the molten salt. For example, the actinide oxides are not readily ‘oxidized’ into the salt as ionic species and, therefore, are reduced chemically prior to being introduced into the EM module.

## 2. Electrometallurgical method

In this section, the chemistry of the EM module will be considered with respect to the impact that light elements (e.g., oxygen, sodium) might have on its operation. There are three areas of the system where this impact might be observed: (1) anodic oxidation of actinides and the more active elements into the salt, (2) ionic species that are formed in the molten salt, and (3) cathodic reduction of the actinides.

### 2.1. Anodic oxidation

The desired oxidation reaction may be written:



where An represents an actinide element (U, Np, Pu, Am,

etc.) in the metallic state. The half-cell voltage for this reaction depends on the activities of the actinide in the metallic state (which might be an alloy) and in the molten salt solution. The lower the activity in the metallic state, the greater the voltage needed for this oxidation, while the lower the activity in the molten salt solution, the smaller the voltage required for the oxidation. In the case where the spent fuel is an oxide, the oxygen is removed prior to introduction into the EM module by chemically reducing the oxide to metal. When the waste fuel is a nitride, silicide, or aluminide, a method for the separation of the light element must be devised so that a metallic actinide stream is available as feed for the EM module. In some cases the proportion of the light element to the waste is large, as in the reactor fuel consisting of uranium aluminide in a matrix of aluminum. It is desirable to produce a light element stream that can be disposed of as a low level waste. In the case of the oxide and the nitride an ideal waste would be the pure gases. In the case of the silicide and aluminide fuels, both light elements are possible constituents of glass waste forms. However, some of these waste fuels contain such a large amount of aluminum in that there is an advantage in separating the aluminum if it could be obtained free of significant amounts of radioactive contaminants so it could be disposed of as a low level waste. The volume of the waste can be reduced by a factor of about 1.7 if the aluminum is obtained as the metal rather than the oxide.

### 2.2. Ionic species in molten salt

In the reference EM module, the actinides are present as trivalent halides (chlorides). While these actinide chlorides have negative deviations from ideal solution behavior due to the formation of chloride complexes, they participate in simple oxidation–reduction reactions at the anode and cathode. The other cation species have, in general, oxidation potentials greater than the actinides. Hence, when the EM module is operated, the actinides are preferentially deposited at the cathode. The equilibrium between uranium and the other actinides is such that pure uranium is obtained at a solid uranium cathode. The transuranic actinides are separated from the molten salt by changing to a liquid cadmium cathode. Because the activity coefficients of the transuranic actinides are much smaller than that of uranium in liquid cadmium, these elements can be preferentially stripped from the molten salt (rare-earth fission products will accompany the transuranic actinides).

### 2.3. Cathodic reduction

A large amount of research [4] has been done to define the conditions that yield the best separation of uranium from the other actinides and the actinides from the more active fission product elements. Critical to the EM module operation is obtaining high separations of the other ac-

tinides from the active fission products. This is dependent on the satisfactory operation of the liquid cadmium cathode. It has been discovered, and predicted by theory [5], that the Pu to U ratio in the molten salt must not exceed a critical value for satisfactory operation of the liquid cadmium cathode. If the ionic species in the molten salt is significantly different from the simple chloride complex, then cathodic deposition will be effected. Not only might the maximum extent of the deposition be changed but the morphology of the deposit. Currently a mass of large crystals of uranium is obtained. These crystals are readily consolidated into a single ingot by melting. In the case of the transuranium actinides, by the regulation of the Pu to U ratio in the molten salt, the growth of dendrites of the actinide metal–cadmium intermetallic at the surface of the liquid cathode can be avoided.

### 3. Spent fuels

Electrometallurgical technology that was developed for treatment of commercial LWR spent fuel forms the basis for treatment of DoE-owned spent fuels. The objective is to convert unstable or at-risk spent fuels to waste forms that are suitable for interim storage and repository disposal. The DoE spent fuels include non-metal fuels that are inadequately contained, such as the Three Mile Island – 2 rubble; fuels that are reactive in the environment, such as hydride fuels from the training reactor isotopes general atomic (TRIGA); and highly enriched oxide fuels that pose the possibility of post-emplacment criticality. The objective of the current studies at ANL is to develop a process that can convert this wide variety of fuel types into a single waste-form type acceptable for repository disposal.

The processing approach is to treat the various fuel types with customized head-end steps to produce either a metal or an oxide product. The metal fuel is fed directly to an electrorefiner, where pure uranium is separated from the other fuel components. The oxide fuels are first reduced to metals by using lithium metal reductant, then the metal product is fed to the electrorefiner. The pure uranium can be either blended for use as fuel in light water reactors or disposed of as low-level waste. The remaining transuranic elements and fission products are incorporated in a stable waste form that is the same, regardless of the type of fuel type being treated.

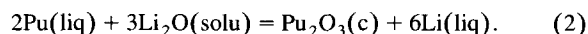
The electrorefiner is capable of separating the spent fuel into three waste streams: (1) pure metallic uranium stream or uranium mixed with other actinides, (2) a noble metal (e.g., Nb, Ru) alloy stream, and (3) a glass containing the more active fission product elements (Cs, Rb, Sr, Ba, and the rare-earth elements). The transuranic element stream will also contain a significant amount of the rare-earth elements and will, therefore, be highly radioactive. The radioactivity of the noble metal and active element streams is significantly reduced by the separation of the

transuranic elements such that the time that these waste streams will be radioactive is reduced by several orders of magnitude.

### 4. Effect of oxygen

The presence of oxygen in the molten salt affects the EM method in several ways. For example, metallic reactor fuel has sodium as a heat transfer medium between the fuel and cladding. When the fuel pins are separated from the fuel assembly hardware and chopped into segments, the sodium is exposed to the cell atmosphere. Even though the water and oxygen content of the cell atmosphere is maintained at ppm levels, the oxygen or water will react with the sodium to form either  $\text{Na}_2\text{O}$  or  $\text{NaOH}$ . When the fuel pin segments are fed to the electrorefiner, these sodium oxygen compounds will dissolve in the molten electrolyte and react with the  $\text{UCl}_3$  to form  $\text{UOCl}$ , which has a low solubility in the  $\text{LiCl}$ – $\text{KCl}$  eutectic. Should there be an accidental loss in the control of the cell atmosphere, it is likely that larger amounts of oxygen or water would be introduced and lead to additional oxide formation in the molten salt electrolyte. The uranium oxides that accumulate must eventually be recovered. In the present process scheme, it is planned to filter the electrolyte and reduce the actinide oxides to metal by using metallic lithium as the reductant.

In addition to the accidental introduction of oxygen, either with contaminated sodium or from the cell atmosphere, lithium oxide will be introduced with the salt coating the metallic feed to the electrorefiner from the lithium reduction step. In the EM method, oxide fuels are reduced to metals using elemental lithium as the reductant. Lithium was selected for the reduction step because reaction vessels made from mild steel can be used for the process, the lithium oxide product of the reduction can be readily reduced electrochemically and the resulting oxygen disposed of as a gaseous waste, and the lithium can be recycled. The development of the lithium reduction step led to several interesting applications of the use of thermodynamics to select reaction conditions. An early observation was that at temperatures of  $650^\circ\text{C}$ , not all of the plutonium oxide was reduced. This was found to be due to the back reaction of the Pu metal with  $\text{Li}_2\text{O}$  to form the sesquioxide:

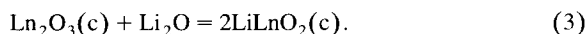


Lithium oxide has a significant solubility in the molten salt, and its thermodynamic activity can vary as the reduction reaction proceeds. Since these fuels contain more uranium than plutonium, the reactant quantities were computed on the basis of reaction with the  $\text{UO}_2$  so that all of the  $\text{Li}_2\text{O}$  produced would remain in solution. It was found that the free energy of Eq. (2) went from a small positive value to a small negative value at about  $530^\circ\text{C}$ . To reduce

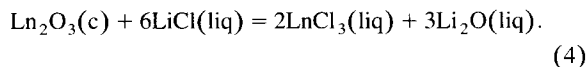
the tendency for this reaction at 650°C, the temperature of the reduction step, it was necessary to limit the activity of the  $\text{Li}_2\text{O}$  in the molten  $\text{LiCl}$  solution. It was found that if the concentration of  $\text{Li}_2\text{O}$  in the molten salt was not allowed to go above about 5 mol% (the saturated value is 12 mol%) that all of the plutonium was reduced to metal. The final concentration of  $\text{Li}_2\text{O}$  in a reduction experiment, where incomplete reduction of the plutonium oxide was observed, was about 6 mol%. Once the importance of this reaction was realized and the final concentration of  $\text{Li}_2\text{O}$  adjusted complete reduction of the plutonium oxide was achieved.

### 5. Mixed oxides

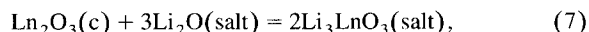
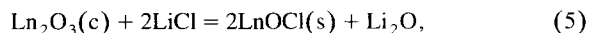
Upon the reduction of a simulated mixture of actinide and lanthanide oxides, a brightly colored solid was found with the metallic reaction product. This solid was found to be a mixed oxide compound that formed between the lanthanide sesquioxides and  $\text{Li}_2\text{O}$ :



These mixed oxide compounds have been reported and their X-ray diffraction patterns are known. Except for europium and samarium, it was not expected that the lanthanide sesquioxides would be reduced with metallic lithium. In addition, a significant concentration of the light lanthanides was found in the molten salt after the reduction [6]. It was not expected that the sesquioxides would be soluble in the molten salt since the following reaction has a large positive free energy:



In view of the formation of the mixed oxide compounds, it was assumed that complex oxide species may form in the molten salt, which increased the solubility by decreasing the  $\text{LnCl}_3$  activity. These can be represented by the following:



where 'salt' indicates a molten salt solution, and the  $\text{LnO}^+$  cation is assumed to react with chloride ion to form the slightly soluble lanthanide oxychloride. On the basis of these reactions, it was found that for small additions of  $\text{Li}_2\text{O}$ , as during the early stages of the reduction, the sesquioxide is the expected equilibrium solid phase. However, when the  $\text{Li}_2\text{O}$  concentration is increased, the mixed oxide compound would begin to form and precipitate from solution, i.e., when its solubility limit was reached. If  $\text{Li}_3\text{LnO}_3(\text{salt})$  does not form, then the lanthanide concentration in the molten salt should remain constant after the

equilibrium phase changes to  $\text{LiLnO}_2(\text{c})$ . However, the lanthanide concentration in the molten salt continued to increase as the  $\text{Li}_2\text{O}$  concentration of the molten salt was increased. Experimental measurements were made of the lanthanide concentration of the molten salt as a function of the  $\text{Li}_2\text{O}$  concentration. The solid phase in equilibrium with the molten salt was also separated and identified by X-ray diffraction measurements. These data [6] yielded information on both the dependence of the 'solubility' on the  $\text{Li}_2\text{O}$  concentration and the nature of the solid equilibrium phase.

The dependence of the 'solubility' on the  $\text{Li}_2\text{O}$  mole fraction when the sesquioxide is the equilibrium phase is given by the relation

$$x_{\text{Ln}(\text{salt})} = \left( K_1^{1/2} + K_2^{1/2} x_{\text{Li}_2\text{O}} \right) x_{\text{Li}_2\text{O}}^{1.2}, \quad (8)$$

where  $K_1$  is the equilibrium constant for Eq. (6) and  $K_2$  the equilibrium constant for Eq. (7), the two terms correspond to the formation of the  $\text{LiLnO}_2$  and  $\text{Li}_3\text{LnO}_3$  species in the solution. The  $x$ s are mole fractions. A plot of the ratio of the mole fraction of the lanthanide to the square root of the mole fraction of  $\text{Li}_2\text{O}$  versus the mole fraction of  $\text{Li}_2\text{O}$  should yield a straight line. From the y-axis intercept and the slope of this line, the values of the two equilibrium constants can be computed. When the mixed oxide compound is the equilibrium solid phase, the 'solubility' is given by the relation

$$x_{\text{Ln}(\text{salt})} = K_3 \left[ 1 + (K_2/K_1)^{1/2} x_{\text{Li}_2\text{O}} \right], \quad (9)$$

where  $K_3$  is the  $\text{LiLnO}_2$  species concentration in the molten  $\text{LiCl}$  when  $\text{LiLnO}_2(\text{c})$  is the solid phase. A plot of the mole fraction of the lanthanide vs. the mole fraction of  $\text{Li}_2\text{O}$  will give a straight line from whose slope and intercept the value of  $K_3$  may be computed. Eqs. (8) and (9) indicate that the solubility dependence on the  $\text{Li}_2\text{O}$  concentration should yield a curved line in the region where the sesquioxide is the equilibrium phase, and a straight line where the mixed oxide compound is the equilibrium phase. The comparison of these predictions with the experimental data are shown for the neodymium system in Fig. 1. The calculated curve is based on the analysis of the experimental data as just described. The curved line segment represents the 'solubility' of neodymium sesquioxide, while the straight line segment represents the 'solubility' of  $\text{LiNdO}_2$ . If the second soluble species,  $\text{Li}_3\text{NdO}_3$ , were not formed, the concentration of Nd in the molten salt should be constant in the region where  $\text{LiNdO}_2$  is the equilibrium solid phase. Calculated concentrations of  $\text{LiNdO}_2$  species in the molten  $\text{LiCl}$  is also shown, which remains constant in the region where  $\text{LiNdO}_2(\text{c})$  is the equilibrium phase. This line is given by the first term in Eq. (8) when  $\text{Nd}_2\text{O}_3$  is the equilibrium solid phase and is equal to  $K_3$  when  $\text{LiNdO}_2$  is the equilibrium solid phase. Note that the  $\text{Li}_3\text{NdO}_3$  species is a large fraction of the soluble Nd species. Similar results were obtained for the cerium system.

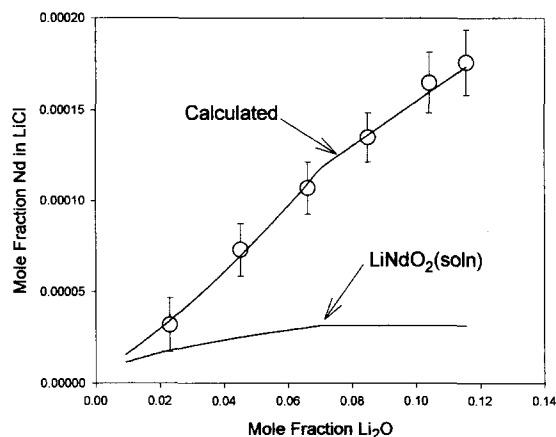


Fig. 1. Comparison of calculated and experimental Nd concentrations in molten LiCl at 650°C as a function of Li<sub>2</sub>O concentration.

From the values of the equilibrium constants obtained from the solubility data, the free energies of formation of the two soluble species and LiNdO<sub>2</sub>(c) can be obtained using the following relations:

$$\Delta G_f(\text{LiNdO}_2, \text{salt}) = \frac{1}{2}(-RT \ln K_1 + \Delta G_f(\text{Nd}_2\text{O}_3(\text{c})) + \Delta G_f(\text{Li}_2\text{O}, \text{salt})), \quad (10)$$

$$\Delta G_f(\text{Li}_3\text{NdO}_3, \text{salt}) = \frac{1}{2}(-RT \ln K_2 + \Delta G_f(\text{Nd}_2\text{O}_3(\text{c})) + 3\Delta G_f(\text{Li}_2\text{O}, \text{salt})), \quad (11)$$

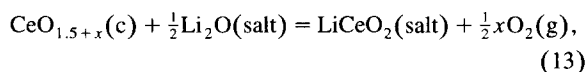
$$\Delta G_f(\text{LiNdO}_2(\text{c})) = -RT \ln K_3 + \Delta G_f(\text{LiNdO}_2, \text{salt}), \quad (12)$$

where 'salt' refers to the species dissolved in the molten LiCl and the  $K$ s have the same definitions as used in Eqs. (8) and (9). The values for the standard free energy of formation of LiNdO<sub>2</sub>(c) and LiCeO<sub>2</sub>(c) were found to be -1014 and -1006 kJ/mol, respectively at 650°C. These values may be used to compute the free energies of formation from the oxides, which were found to be -2900 and -900 J/mol for LiNdO<sub>2</sub>(c) and LiCeO<sub>2</sub>(c), respectively. These values for the free energy of formation from the oxides are consistent with the small values usually found for mixed oxide compounds and lends support to the method of analysis used. From a study of the influence of dissolved nitrogen and carbon on the reaction of lithium with cerium oxides, Barker and Alexander [7] have deduced that the free energy of formation of LiCeO<sub>2</sub>(c) at 600°C is between -996 and -1022 kJ/mol.

## 6. Behavior of multiple-valence lanthanides

The experimental studies were done with excess lithium metal, which does not enter into the reactions in Eqs. (3)–(7). As a check on our results, experiments were done

without the use of lithium metal. The results for the neodymium system were the same as found when lithium metal was present. However, the cerium system without lithium yielded lower Ce 'solubilities', which were not reproducible. This is believed to be due to the fact that, without lithium metal, the oxygen potential of the experimental system was not fixed but varied in a random manner depending on how much oxygen (or water) was present. There are a number of non-stoichiometric cerium oxides in the phase diagram between Ce<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>. The activity of Ce<sub>2</sub>O<sub>3</sub> under these conditions will be less than one, its value depending on the composition of the particular cerium oxide phase that is stable at the oxygen potential of the system. The formation of the LiCeO<sub>2</sub> species in solution will involve the following reaction:



where 'salt' refers to lithium oxide dissolved in the molten LiCl. The value of  $x$  will depend on the oxygen partial pressure (oxygen potential), increasing as the partial pressure increases. The greater the value of  $x$ , the smaller the activity of 'Ce<sub>2</sub>O<sub>3</sub>'. Also, as the oxygen partial pressure increases, this reaction will be shifted to the left, leading to a lower concentration of Ce in the molten salt. Since the actual oxygen partial pressure of the system was not known, it was not possible to compare computed solubilities with experimental values. The values of the free energies of formation of the non-stoichiometric cerium oxides, while reported [8,9], are still uncertain. If our original experiments had not been done with an excess of metallic lithium present to control the oxygen potential, we might not have discovered the existence of these soluble, mixed oxide species.

## 7. Effect of mixed oxides on EM process

The formation of these mixed oxide compounds and their significant solubilities in the salt probably will only have negligible effect on the reduction step, but will affect the electrotransport of the actinides to the cathode. Their solubility in the reduction salt, as well as the decrease in their solubility as the Li<sub>2</sub>O concentration is reduced, will lead to their precipitation as the Li<sub>2</sub>O concentration is decreased in the lithium electrowinning step of the reduction process. Whether this precipitate of the sesquioxide will adhere to the oxygen electrode used in the electrowinning (these compounds exist as LnO<sub>2</sub><sup>-1</sup> anions in the molten salt) and interfere with its operation is not known. The carryover into the electrorefiner of the lanthanides mixed oxide compounds with the metallic product of the lithium reduction step will also carry over slightly more oxygen (O/Ln = 2) than would be the case if the lan-

thanides remained as the sesquioxides ( $O/Ln = 1.5$ ). The mixed oxide compounds are not stable enough to reduce the tendency of reacting with the  $UCl_3$ . It is expected that the reaction will yield the insoluble uranium oxychloride and possibly the lanthanide chloride, although the free energy change for the reaction of  $LnOCl$  with  $UCl_3$  to yield  $LnCl_3$  is only slightly negative ( $-29$  kJ) and, considering the probable accuracy of the data, uncertain. Regardless of whether the lanthanide is converted to the chloride or not, significant formation of uranium oxychloride is expected. The amount is probably larger because the lanthanides enter the electrorefiner as the mixed oxide compounds. A method is needed for dealing with the formation of uranium oxides or oxychlorides in the electrorefiner.

### Acknowledgements

The thermodynamic models presented in this report were developed as an aid to the understanding of the experimental results and the solution of process development problems. The experiments were done by one or more of our colleagues: W.E. Miller, Z. Tomczuk, R.D.

Pierce, G.K. Johnson, J.L. Willit, and K.V. Gourishankar. Special acknowledgments are made to K.V. Gourishankar who worked with the author (I.J.) in the development of the explanation for the large solubilities of the lanthanide sesquioxides in the presence of lithium oxide.

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