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ABSTRACT

We are investigating the precipitation of actinides, lanthanides, and fission products from molten chloride melts by the formation of an insoluble nitride. If successful, this method could be used as a final cleanup step in treating salt wastes that contain radioactive components generated by the electrometallurgical treatment of spent nuclear fuel. In the development of an acceptable waste form for this salt waste, these radioactive components, such as the fission products, which are the major heat producers (i.e., Sr, Cs), need to be removed to substantially reduce the volume of high-level waste that requires disposal. To extract the fission products from the salt, a nitride precipitation process is being developed. Nitrides cannot be added directly to the salt phase because they would be destroyed by chemical reactions with the molten salt. Accordingly, the salt waste is contacted with a molten metal. After the salt phase is in equilibrium with the metal phase, a nitride is added to the metal phase. The fission product then forms an insoluble nitride and can be removed from the metal phase. The insoluble nitrides can be recovered and converted to a borosilicate glass after air oxidation. For a bench-scale experimental setup, a crucible was designed to contact the salt and metal phases. Solubility tests were performed with candidate nitrides and metal nitrides for which there are no solubility data. Experiments were performed to assess the feasibility of the precipitation of metal nitrides from chloride melts.

Introduction

We are investigating the precipitation of actinides, lanthanides, and fission products from molten chloride melts by the formation of an insoluble nitride (an invention report for this process has been filed at ANL [TOMCZUK]). If successful, this method could be used as a final cleanup step in treating salt wastes that contain radioactive components generated by the electrometallurgical treatment of spent nuclear fuel. It also has the potential application for cleanup of fluoride salts from the Molten Salt Reactor Experiment (MSRE). These fluoride salts were generated at Oak Ridge National Laboratory during reactor development activities, and details of this process are given elsewhere [PERETZ].

Other extraction processes for treating salt waste include chemical reduction, oxygen sparging, and zeolite ion exchange. However, the chemical reduction process generates additional waste streams, phase separation in the oxygen sparging process is difficult, and zeolite ion exchange cannot be used with fluoride salts. Unlike the other processes, nitride precipitation is a simple process, which reduces the volume of waste that requires disposal and is not limited by the type of salt waste. Nitrides cannot be added to the salt phase because they would be destroyed by chemical reactions with the molten salt. Accordingly, a salt waste is contacted with a molten metal. Then, to enhance the extraction of the radioactive component into the metal phase, a nitride is added directly to the metal phase, where the actinide, lanthanide, or fission product forms an insoluble nitride. The insoluble nitrides can be recovered and converted to a borosilicate glass after air oxidation.

A series of experiments was performed to (1) assess the compatibility of select metals and nitrides and (2) determine if lanthanum can be extracted from a salt and precipitated as a nitride. These experiments and results are discussed.

Experimental

Experiments were conducted using a graphite crucible with a volume of 116 cm³ (3.8-cm diameter, 10.2-cm height) at ~500 °C (773 K). Salts used for the experiments were reagent grade and obtained from APL Engineering Materials, Inc. Metals and nitrides used for these experiments were reagent grade and obtained from Johnson Matthey Alfa Aesar and Cerac, Inc. Experiments performed were designed to test (1) metal-nitride compatibility, (2) metal-nitride extraction, (3) metal-salt extraction, and (4) metal-salt-nitride extraction. A discussion of these experiments follows.

Metal-Nitride Compatibility Experiment

The purpose of the metal-nitride compatibility experiment was to find a molten metal/nitride combination in which the nitride is insoluble in the molten metal, and the nitride does not react with the metal. Based on thermodynamic data (free energies of formation given in [PANKRATZ]), the following combinations were tested: Zn-Ca₃N₂, Zn-Li₃N, Zn-BN, Sn-Li₃N, and Bi-BN.

Each metal (~400 g) was added to the graphite crucible, heated to 500 °C (773 K), and sampled using a tantalum tube under reduced pressure. After sampling of the metal, 1 wt% nitride was added directly to the metal. The metal was sampled 1, 24, and 48 h after the nitride addition. The metal content was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES,) and the nitrogen content was determined using Kjeldahl distillation, followed by ion chromatography.

Metal-Nitride Extraction Experiment

This experiment was performed to demonstrate that lanthanum can be extracted as lanthanum nitride by addition of calcium nitride to a zinc-lanthanum solution. Lanthanum was chosen as a stand-in for the radioactive component in the salt. Calcium nitride (2.5 g) was added to a zinc-0.1 wt% lanthanum alloy (250 g) and was sampled 1, 24, and 48 h after the nitride addition. The samples were then analyzed by ICP-AES.

Metal-Salt Extraction Experiment

This experiment was performed to determine if lanthanum can be extracted into a metal phase from a LiCl/KCl/LaCl₃ (1 wt% La) salt when contacted with molten zinc. The salt used for this experiment is a lithium chloride-potassium chloride eutectic (58.2 mol% LiCl, 41.8 mol% KCl) with a eutectic point of 352 °C [JANZ]. Zinc metal (250 g) was added to the graphite crucible, heated to 535 °C, and sampled. Then, LiCl/KCl/LaCl₃ salt (72 g) was added to the molten zinc and sampled 4, 24, 48 and 75 h after addition. All samples were analyzed by ICP-AES.

Metal-Salt-Nitride Extraction Experiment

Currently, a crucible is being fabricated for the metal-salt-nitride experiment (see Fig. 1). The design challenges for the crucible include contacting the salt and metal phase, sampling each phase, and adding a nitride directly into the metal phase, which is the denser phase. Also, the crucible material is molybdenum, which is fabricated in sheets and cannot be rolled without annealing at high temperatures. The chimney design (two concentric squares) shown in Fig. 1 was chosen so that the metal phase would be contained in the inner and outer regions (or squares) of the crucible, and the salt phase would be contained in the outer region of the crucible only. The openings in the bottom of the inner crucible allow the metal phase to be distributed between the inner and outer regions of the crucible. The nitride will be added to the metal phase by use of a 28-mesh basket, which is connected to a stirrer.

A metal-salt-nitride extraction experiment was performed to determine if lanthanum is extracted as a nitride into a metal phase from a LiCl/KCl/LaCl₃ salt when contacted with molten zinc. While the crucible is being fabricated, a temporary setup was used where zinc (250 g) was added to the graphite crucible, and an addition tube (a molybdenum rod with 1.9-cm OD and a 100-mesh screen covering the end) was placed in the molten metal so that the nitride (1.5 g) could be added directly to the metal phase. The salt phase (72 g) was added to the molten zinc, and after the temperature was raised to 525 °C (798 K), the nitride was added to the crucible through the molybdenum tube. The salt was sampled 24, 48, and 72 h after nitride addition. All samples were analyzed by ICP-AES.

Results and Discussion

The results of the metal-nitride compatibility experiment (Table 1), show that all of the metal-nitride combinations tested are compatible since less than 4% of the nitride reacted with any metal.

Table 1. Results of Metal-Nitride Compatibility Experiment

Metal-Nitride Combination	Nitride Conc. (ppm)	% Nitride Reacted
Zn-Ca ₃ N ₂	45	2.41
Zn-Li ₃ N	150	3.78
Zn-BN	< 20	0.36
Sn-Li ₃ N	90	2.27
Bi-BN	< 20	0.36

Since all of the metal-nitride combinations tested were compatible, we decided to evaluate the Zn-Ca₃N₂ combination first. In earlier experiments, Moriyama et al. tested metal phases of bismuth, zinc, tin, and cadmium and successfully extracted lanthanides and actinides from molten salt (66.7 mol % LiF-BeF₂) into molten metal using a lithium reductant [MORIYAMA]. For this study, Moriyama et al. concluded that to extract lanthanum from the salt phase into the metal phase at 600 °C (873 K), the order of extractability is Sn < Zn < Cd < Bi.

Another experiment was performed to determine if lanthanum would react with calcium nitride and form lanthanum nitride in molten zinc media as given in



Table 2. Results of Metal-Nitride Extraction Experiment

Time after Nitride Addition (h)	La Conc. (ppm)	Ca Conc. (ppm)	% La Reacted to Form LaN
0	127	0	0
1	51	5	60
24	< 5	128	>96
48	25	118	80

The results from the metal-nitride extraction experiment (Table 2) indicate that the lanthanum concentration decreases as the calcium concentration increases. Greater than 96% of lanthanum reacted to form lanthanum nitride 24 h after the addition of calcium nitride.

The metal-salt extraction experiment was done without the nitride to serve as a baseline for future tests in which a nitride will be added to the metal phase. The results in Table 3 show that ~10% of La was extracted into the metal phase (initially 1 wt% La was added to the salt as LaCl_3).

Table 3. Results of Metal-Salt Extraction Experiment

Time after Nitride Addition (h)	La (wt% in salt phase)	% La extracted
4	0.92	8
24	0.85	15
48	0.87	13
75	0.90	10

The metal-salt-nitride experiment was performed to determine the feasibility of the nitride precipitation process using the $\text{Zn-Ca}_3\text{N}_2$ combination. The results in Table 4 show that 29% of the lanthanum was extracted from the salt phase. To improve the extractability of lanthanum from the salt phase, we will test different metal-nitride combinations and will also explore the feasibility of adding a reductant to the salt phase.

Table 4. Results of Metal-Salt-Nitride Extraction Experiment

Time after Salt Addition (h)	La (wt% in salt phase)	% La extracted
24	0.72	28
48	0.71	29
72	0.71	29

Summary

The zinc-calcium nitride system was able to extract 29% of the lanthanum from the chloride salt phase into the metal phase. To improve the extractability of lanthanum from the salt phase, we will test different metal-nitride combinations and will also explore the feasibility of adding a reductant to the salt phase. Future experiments will be done in the crucible shown in Fig. 1, which will increase the metal-salt contact area by increasing the surface area and also stirring the system.

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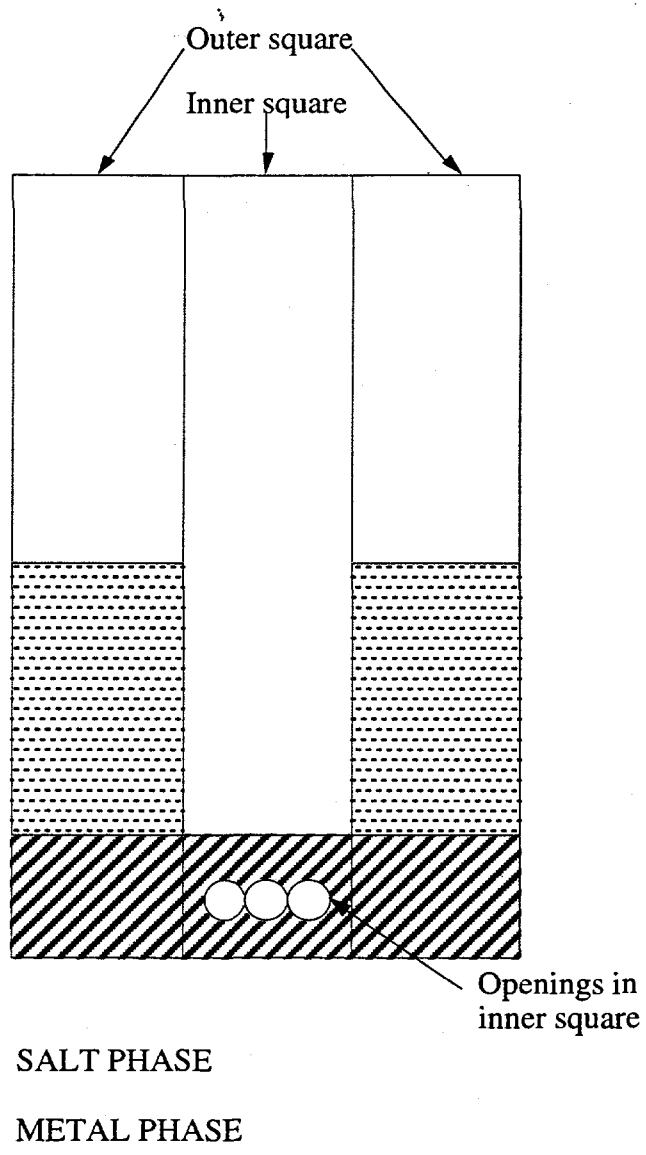


Figure 1. Crucible for Experimental Tests with Dimensions (side view) of 15.2-cm Height, 7-cm Outer Square Base, and 3.8-cm Inner Square Base