Evaluation of Li$_3$N Accumulation in a Fused LiCl/Li Salt Matrix*

by

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INTRODUCTION

Pyrochemical conditioning of spent nuclear fuel for the purpose of final disposal is currently being demonstrated at Argonne National Laboratory (ANL), and ongoing research in this area includes the demonstration of this process on spent oxide fuel. In conjunction with this research a pilot scale of the preprocessing stage is being designed by ANL-W to demonstrate the in situ hot cell capability of the chemical reduction stage.

An impurity evaluation was completed for a Li/LiCl salt matrix in the presence of spent LWR uranium oxide fuel. A simple analysis was performed in which the sources of impurities in the salt matrix were only from the cell atmosphere. Only reactions with the lithium were considered. The levels of impurities were shown to be highly sensitive system conditions. A predominance diagram for the Li-O-N system was constructed for the device, and the general oxidation, nitridation and combined reactions were calculated as a function of oxygen and nitrogen partial pressure. These calculations and hotcell atmosphere data were used to determine the total number and type of impurities expected in the salt matrix, and the mass rate for the device was determined.

ANALYSIS

For this analysis, we only consider the reaction of the molten metal with either nitrogen or oxygen. The competing reactants consisted of different metal oxides, nitrates, nitrides and other compounds. A predominance diagram was constructed for the two vapor component as a function of partial pressure in the hot cell. First, the generic class of reaction equations were constructed:

\[
x_1 Li_{a}N_{b}O_{c} + O_{2} = y_1 Li_{u}N_{v}O_{w}
\]

\[
x_2 Li_{a}N_{b}O_{c} + N_{2} = y_2 Li_{u}N_{v}O_{w}
\]

\[
x_3 Li_{a}N_{b}O_{c} + O_{2} + mN_{2} = y_3 Li_{u}N_{v}O_{w}
\]  

(1)

where the first equation represents the class of oxidation reactions, the second equation represents the nitridation reactions and the the third equation allows for both reaction types.

In order to execute a solution, an apriori decision must be made concerning the reactants which will participate in a reaction. The device is assumed to be in equilibrium for the set of
reactions, so:

$$\Delta G_{yj} = -RT \ln K_{yj} \quad [j=1,2,3,...,r]$$

which is the temperature dependent free energy equation. For reactions which do not involve nitrogen, we can write:

$$K_1 = \frac{f_1}{P_{O_2}}$$

where $f_1$ is the predominance ratio for the non-nitridation components and is bound between zero and one. The equations defining predominance for a system with two compositional axes can be generalized as:

$$\ln P_j = \frac{\Delta G_j}{RT} \quad [j = 1,2]$$

and $P$ represents the partial pressure (in atm) of the atmospheric component in the reaction series. The equilibrium constant for reactions involving both nitridation and oxidation can be written:

$$K_3 = \frac{f_3}{P_{O_2} P_{N_2}^m}$$

By allowing the set of simultaneous reactions to occur at the two equilibrium limits for the predominance ratio the final thermodynamic expression can be constructed for the generalized reaction series:

$$\ln P_{O_2} = -m \ln P_{N_2} + \frac{\Delta G_3}{RT}$$

Equations 4 and 6 represent the predominance limits for the three classes of reactions in equation 1. Physically, these results allow the equilibrium domains to be partitioned according to reactant species and they can be displayed graphically as a function of the oxygen and nitrogen
partial pressures at a fixed reaction temperature. For a set of 21 feasible reactions, 6 were non-
nitrogen reactions, 4 were non-oxygen reaction and 11 were combined reactions. The method used
to arrive at these reactions is similar to the metal sulfide equilibrium evaluation of Morris. The
reaction phase boundary lines were calculated for the 11 competing reaction phases that exist. Triple
point coordinates were calculated and these results were used to construct the predominance diagram
shown in figure 1. Atmosphere limits for the device were superimposed on figure 1 so that reaction
types could be determined. The results indicate only Li₂O and Li₃N are likely.

RESULTS

The total interfacial reactivity was calculated by modifying the absolute rate formulation,
developed by Parry and Pulham, to account for a multicomponent, incompressible, perfect gas:

\[ k_j(T,P) = \frac{m}{\rho_j \chi_j A_c P}, \quad (7) \]

where \( k \) is the absolute rate constant, \( m \) is the mass of the reactant forming at the lithium-vapor
interface, \( \rho \) is the density, \( \chi \) is the mole fraction of the reactant, \( A_c \) is the reaction vessel cross
sectional area, \( P \) is the system pressure and the index refers to the reaction gas being considered.

The absolute rate constant \( k \) is a constitutive relation of the reaction gas being evaluated.
Chandrasekharaiah and Margrave have measured the temperature dependent nitrogen and oxygen
reaction rates with lithium in low pressure reaction vessels. Furthermore, they also reported that at
temperatures around 630 °C vessel corrosion interfered with the oxidation measurement, so no.
lithium oxidation rate measurements were reported. To date, no other lithium oxidation rate
measurement have been found in the literature making it impossible to evaluate an oxide loading rate
for the salt.

One of the most extensive nitrogen reaction rate evaluations in the literature was performed
by McFarlane and Tompkins. The kinetics of solid and molten lithium as a function of pressure
and temperature were measured. The reaction rate of solid lithium was found to be highly dependent
on pressure and nearly independent of temperature up to the breakaway temperature. However, at
fusion, the situation changes considerably, and the pressure dependance becomes negligible whereas
the temperature become activation energy dependent. Thus, the reaction rate is linear on an Arrhenius plot, and the pressure dependence is dropped:

\[ k_{N_2}(T) = A\exp(-b/RT) \]  \hspace{1cm} (8)

The rate constant in equation 8 is dependent on activation energy, which vary from 45.2 kJ/mole to 188.3 kJ/mole. The value obtained by Little \(^5\) at 49.8 kJ/mole was used in this work. From these results, the value of \(A\) is 2,980 cm/sec/atm, and \(b\) is 10,800 Kcal/K/mole.

The mass rate of nitride as an impurity taken up by the lithium can be calculated as a function of nitrogen mole fraction and temperature for the device. This is shown in figure 2. The mass rate is a fairly sensitive function of both temperature and reactant mole fraction and it decreases with decreasing values of both independent variables.

REFERENCES


Figure 1. Predominance diagram for the Li-N-O system at 650°C.
Figure 2. Temperature and pressure dependent nitridation rate in the PSOR device.