Literature Review of Metal Corrosion Sensitivity in High Temperature, High Impurity Hot Cell Atmospheres

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INTRODUCTION
The pyrochemical conditioning of spent nuclear fuel for the purpose of final disposal is being demonstrated at Argonne National Laboratory (ANL). One aspect of this program is to develop a lithium preprocessing stage for the Fuel Conditioning Facility (FCF)\[^1-3\]. One of the design considerations under investigation in this program is the system’s corrosion response in the presence of irradiated commercial fuel as well as atmospheric impurities. Static corrosion coupon tests have been completed which demonstrate the potential corrosivity of the salt matrix in a worse case environment as well as provide a boundary for allowable impurities in the system during operation \[^4\].

The literature concerning corrosion of either fused salts or molten metals consistently emphasizes three similar features which are common to both systems: (1) the overall corrosion rate is strongly dependent on temperature, impurity concentration and flow velocity; (2) many different mechanisms can be involved in a specific corrosion process; and (3) corrosion rates will significantly increase as all three of these independent variables are increased \[^5\]. The qualitative and quantitative understanding of these corrosion results is important for this spent fuel program since all of these variables will increase as the process scale increases. The purpose of this work was to determine if any data existed which could provide a quantitative expectation for corrosion rates of refractory metals in a lithium chloride salt bath.

LITERATURE REVIEW
There are at least ten general fused salt corrosion mechanisms which can cause the corrosion of container alloys used in fused salt processes. They include but are not completely limited to selective attack, pitting, electrochemical reactions, thermal gradient induced mass transport, salt constituent reactions with the alloy, alloy constituent depletion into the salt, salt impurity reactions with the alloy, fluxing of the alloy’s oxide layer, flow velocity enhanced corrosion and stress corrosion cracking \[^6\].

These corrosion mechanisms are generalized results taken from studies which have emphasized alloy corrosion with nitrate, nitrite and fluoride salts as well as hydroxide, sulfate and carbonate salts \[^7\]. For the most part fused LiCl does not appear to have any wide base industrial applications except as a brazing flux, so corrosion problems for this salt-vessel system are unique \[^8\]. Corrosion data for the eutectic salt LiCl-KCl has been studied in high purity systems, but since the system temperatures and impurity levels for these data are so much lower than for the oxide reduction system, the information is not generally applicable \[^9\].
Overall, the mechanisms of corrosion for fused salts are more numerous than for aqueous solutions.

RESULTS
It is currently difficult to provide a quantified upper bound for the impurities that will exist in the salt matrix of the oxide reduction system. Furthermore, the elemental concentration of impurities will change over time. This transient nature of the impurities will occur for at least three reasons. First, fission products and other waste products can accumulate in the salt and potentially can create impurity build-up in the vessel. Second, the concentration of moisture and nitrogen will increase with time; however impurities will fluctuate as the salt is regenerated and replaced. Third, several fission product oxides can exist that are not reduced by liquid lithium. These oxides might be partially reduced in the electrowinning process, but as the regenerated solution is recharged in the reduction vessel, this will create a continually increasing mass of oxide impurities.

The sensitivity of refractories to temperature and impurity can be demonstrated by examining some of the historic fused salt data. The data from Gill has been reevaluated in figure 1. For titanium in lithium chloride (LiCl-KCl used below 614°C) it can be seen that in all of the tests that temperature sensitivity increases as:

\[ R \propto T^4 \]  

The upper bound data are air atmosphere tests and the lower bound data are vacuum tests. Here a synergistic influence of temperature and impurity can be clearly seen. At 625°C the change in the corrosion rate is about 33% and increases to almost 300% at 850°C. Furthermore, the order of the corrosion rate in equation 1 is usually second order for molten metal systems, so this experience many not be useful in evaluating the oxide reduction process.

CONCLUSIONS
The corrosivity of molten salts increases over time as they become more oxidized and more contaminated. As a general rule, molten alkali salts become more corrosive as temperature, oxide concentration, impurities and flow rates are increased in alkali salts. Also, the alkali metal oxides tend to be good fluxes and can easily react with protective oxide films of heat resistant alloys. These reactants form compounds that become a solute in the salt, so that passivation is not usually possible.

REFERENCES


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Corrosion Rate of Titanium in LiCl, 3hr Tests