Molten Salt Systems for FHRS and MSRS: Chemistry and Mass Transport

Galvanic Reduction for Actinide Recycling in a Molten Chloride Fast Reactor

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INTRODUCTION

Molten chloride salts have recently gained interest from the advanced reactor development community for their proposed use as fuel matrixes in a fast neutron spectrum reactor. To achieve the full potential of high level waste minimization using an MCFR, it is advantageous to dispose of actinide-free salt containing fission products. This paper presents one viable scheme for separating the actinides from MCFR that is passive and has been experimentally demonstrated using molten chloride salts used for pyroprocessing spent nuclear fuel.

Process Design and Theory

The process is fundamentally based on the relative reduction potentials of metal chlorides—including actinides, fission products, and base salt components such as Na and K. The order of potentials in MCFR molten chloride salts can be shown by calculation to be as follows:

$$U^{4+} > U^{3+} > Pu^{3+} > Gd^{3+} > La^{3+} > Na^{+} > K^{+} > Cs^{+}$$
 (1)

Thus, if a solid metal object made of a rare earth metal such as Gd or La was to be inserted into the salt and electrically connected to the vessel wall or another inert metal object such as a stainless steel basket, the galvanic coupling would drive U and Pu metal to deposit onto the inert metal surface. The resulting salt would be essentially cleansed of actinides and would only contain fission products and base salts (NaCl, KCl, etc.). This actinide-free salt could be drained and converted to a stable waste form via occlusion/ion exchange in zeolites or vitrification using a compatible glass matrix. Then the actinide metal could be re-oxidized via a variety of different chemical or electrochemical oxidation processes to re-dissolve in the salt as chlorides. One notable challenge with such a process would be to keep the salt molten, since its liquidus temperature is lowered by UCl₃ and/or UCl₄. With each mole equivalent of uranium chloride extracted from the salt, it is replaced by a mole equivalent of a rare earth chloride. Fortuitously, rare earth metal chlorides have the same effect as uranium chlorides on the liquidus temperature of NaCl in mixtures. Phase diagrams for NaCl-TbCl3 and NaCl-DyCl3 have been measured and reveal eutectic melting temperatures well below the melting point of NaCl can be achieved, typically under 600°C [1]. Thus, in the proposed process, a one for one mole equivalent exchange of uranium with rare earth metals in the salt should maintain

the liquidus temperature sufficiently low for the salt to remain liquid.

RESULTS

To assess the viability of galvanic reduction to meet this goal, tests were run in which eutectic LiCl-KCl loaded with either 0.17 mol% UCl₃ was contacted with a galvanic couple of stainless steel and Gd metal at 500°C [2,3]. The Gd rod was physically separated but electrically contacted with the SS basket, which was rotating at 100 rpm. Salt samples were taken every 15 min and analyzed by ICP-MS. The results are shown in Figure 1. Within 0.5 hr, 98.5% of the UCl₃ had been removed from the salt. Within 2 hr, the UCl₃ concentration was below the limit of detection for ICP-MS.



Fig. 1. Result of Gd-galvanic reduction of LiCl-KCl-UCl₃

Since this process has only been demonstrated for conditions representative of electrorefiners used for pyroprocessing spent nuclear fuel, further testing is needed with MSR candidate salts, including NaCl-UCl₃, NaCl-KCl-UCl₃, etc. Maintaining a liquid salt is predicted but needs to be verified.

REFERENCES

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