CONTAMINATION OF ZIRCONIUM METAL BY CADMIUM DISSOLVED IN MOLTEN LiCl-KCl SALT

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Cadmium contamination of the metal waste stream in the pyroprocessing of used nuclear fuel from the Experimental Breeder Reactor-II (EBR-II) has become a significant concern as it creates a mixed hazardous/radioactive high-level waste product. It has been hypothesized that this contamination is a result of a reaction between the zirconium (Zr) in the undissolved fuel segments and metallic cadmium (Cd) dissolved in the molten LiCl-KCl salt inside the Mark-IV electro-refiner. To test this theory, Zr metal pellets were immersed in a molten LiCl-KCl salt bath sitting above a layer of molten Cd and sampled over time. Salt samples were taken at time intervals, and analyzed via inductively coupled plasma mass spectrometer (ICP-MS) to measure the Cd concentration in the salt. The ICP-MS results revealed that the addition of Li metal significantly lowers Cd concentration in the salt. Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) of the cross-sections of the Zr pellets was used to measure the relative concentrations of Zr, Cd, and Cl along line-scans from the surface to the interior of the pellets. These results indicate that Cd appears to concentrate at the salt/Zr interface and its concentration in the Zr was consistent across samples.

I. INTRODUCTION

The Experimental Breeder Reactor II (EBR-II) was a sodium-cooled fast breeder reactor that operated from 1965 to 1994. One of its features was the use of metallic U-Zr fuel, which has the advantages of being easier to form into desired shapes through casting and superior thermal conductivity compared to oxide fuel. The EBR-II core consisted of a central region of HEU-Zr driver pins encased in a blanket region of LEU-Zr pins for the purpose of breeding Pu-239. To enable secure, on-site separation of the Pu and refabrication of U-Pu-Zr metal fuel, pyroprocessing was selected as the reprocessing technology. In this process, electro-refiners (ERs) are used to electrochemically separate the components of used metallic fuel by dissolving and transporting them through a molten salt electrolyte.

While EBR-II and the mission to develop an Integral Fast Reactor (IFR) system were shut down in 1994, R&D of pyroprocessing technology has continued for the purpose of stabilizing its fuel for permanent disposal. In the Fuel Conditioning Facility (FCF) at the Idaho National Laboratory (INL), the Mark-IV ER is used to process used driver fuel.

The Mark-IV ER is a cylindrical, airtight stainless steel vessel with access ports located in its top cover to allow the insertion of electrodes and instruments (Fig. 1). The ER is filled with eutectic LiCl-KCl (44.2 wt% LiCl, 55.8 wt% KCl) molten salt electrolyte that floats above a liquid Cd cathode (LCC) pool. The headspace of the vessel is filled with dry argon (Ar) gas. Chopped sections of used EBR-II driver fuel containing U, Pu, fission products and minor actinides are loaded into baskets, which are then immersed in the salt. An electrical potential is then applied between the anode baskets and solid cathode mandrels also immersed in the salt. The uranium, actinides, and fission products electrolyze into

Fig. 1. Diagram of the Mark-IV electrorefiner.
the salt and leave zirconium and other noble metals behind. The uranium is electrodeposited onto the solid cathodes as very pure metallic dendrites. The growth of these dendrites must be constrained by mechanical scrapers to prevent shorts with the vessel walls. The LCC pool serves to dissolve these fallen scrapings and prevent HEU from piling up under the solid cathodes and creating a criticality concern. The LCC is also used to collect Pu and minor actinides, which can then be recovered later. Active metal fission products accumulate in the salt and must eventually be removed and discarded as waste. The cladding hulls left in the anode baskets contain undissolved actinides, noble metals, and zirconium. Adhering salt is distilled off and the hulls are then processed in a metal waste furnace to consolidate the metal into an ingot waste form.

I.A. Operational challenges

The LCC pool in the Mark IV ER is useful for collecting dissolved Pu with minor actinides and U that has been scraped off of the solid cathode. However Cd is a RCRA-listed toxic metal and has a relatively high vapor pressure in the ER operating temperature (500°C). Any Cd contamination of either of the waste streams (salt or cladding hulls) may complicate eventual acceptance of the waste at a disposal site. Analysis of samples of the cladding hulls from the anode baskets by INL researchers has indicated a relatively large Cd contamination, which could complicate operation of the metal waste furnace and disposal of the metal waste forms.

To address this problem, the mechanism for the Cd contamination needs to be understood. The anode baskets never come in direct contact with the Cd pool, but in previous studies by Goff it has been shown that Cd is slightly soluble in the LiCl-KCl molten salt. In addition, small but measurable quantities of dissolved cadmium metal vaporize at the salt surface into the Ar headspace, and then condense onto exposed interior surfaces of the ER. Thus, two mechanisms seem to be plausible: the reaction of dissolved Cd from the salt phase with the cladding hulls and the condensation of Cd vapor on the basket as it is being pulled out of the salt.

Given that this contamination has uniquely been a problem with the cladding hulls, it is hypothesized that Cd may be reacting with Zr in the hulls to form one or more of several intermetallic compounds that can form at these temperatures. As such reactions occur rapidly, it is thought that the entire process is rate-limited by the diffusion of Cd through the salt.

Cd may diffuse through the salt physically as neutral Cd and chemically as CdCl₂ (the formation of which is not favored by accepted salt chemistry). Goff et al. measured total Cd concentrations in excess of their expected combined contributions and hypothesized that O and C impurities (measured by Goff as ranging from 1.2 to 2.0 wt%) in the salt could react with Li to form LiCO₃ and enhance the oxidation of Cd by Cl, augmenting the otherwise minimal CdCl₂ transport pathway. Possible sources of C include CO₂ from the glove-box atmosphere and C from the low-carbon steel crucibles used in Goff’s study. Goff attempted to correct for this by adding U or Li (as a surrogate for U) to the salt with the aim of reducing the hypothesized excess CdCl₂. This produced a marked decrease in total Cd concentrations.

An alternative explanation is that the dissolution of U or Li in the salt could be physically displacing neutral Cd from the salt. This concern is particularly relevant due to the large quantity of Li that Goff alloyed with the Cd pool (28.6 wt%). Separately measuring the concentrations of neutral Cd and CdCl₂ in the LiCl-KCl salt would be the most explicit means of resolving this question.

It should be noted that the effects of electrochemical reactions were not considered in this study and no potential was applied.

II. EXPERIMENTAL PROCEDURE

II.A. Materials and Equipment

A KerrLab Auto Electro Melt Maxi furnace was used to heat CoorsTek 100 ml alumina ceramic crucibles in these experiments. For some portions of the experiment, a stand was utilized to support a stainless steel basket that could be lowered into the crucible. All procedures using this equipment were carried out in an MBraun LABmaster glovebox filled with an industrial-grade argon gas (<10 ppm water and <10 ppm oxygen).

A high purity (99.999%) anhydrous eutectic LiCl-KCl mixture (44.2 wt% LiCl, 55.8 wt% KCl) from the stock used by the Mark-IV ER was used for the salt bath. Cd of 99.999% purity was supplied by Alfa Aesar as were 3-6mm Zr pellets (99.8% purity excluding Hf, 4% max Hf). In all experiments, the crucible was loaded with 60g of eutectic LiCl-KCl mixture and 20g of Cd metal (Fig. 2).
II.B. Investigative Procedure

The first objective was to determine the solubility and rate of dissolution of Cd in the salt bath under lab conditions. The loaded crucible was heated at a rate of 10 °C per minute to 500 °C. A sample was taken from the surface of the salt once it had liquefied (also recording the current temperature) followed by four additional samples taken every hour thereafter. The temperature of the salt was directly measured with an alumina-sheathed thermometer at each sampling.

The next stage of the experiment investigated the hypothesized presence of CdCl$_2$ in the salt. Here, 0.08g of Lithium (Li) metal was added to the salt solution to reduce any CdCl$_2$ that may have been present. This amount was chosen to be sufficient to reduce the excess CdCl$_2$ hypothesized by Goff$^3$. Lithium should react to completion with any CdCl$_2$ in the salt to form Cd and LiCl (a role performed by U in the Mark-IV). Reacted Cd will either dissolve in the salt or settle into the Cd pool. Samples of salt were taken from its surface every 30 minutes for 2.5 hours with measuring the temperature of the salt at each sampling. The Li metal formed a bead on the surface of the salt, the bead was swirled around gently after the second sampling and between the third and the forth. The swirling did not appear to facilitate the bead’s dissolution. The furnace was then set to cool to 300°C and turned off after reaching this temperature. The crucible was then removed from the glove box, and a Zr pellet was selected from each for Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis. The selected pellets were mounted in epoxy and then polished with an electric grindstone to expose a cross section to prepare them for the SEM. Three line-scans were made from each pellet at different sites perpendicular to the perimeter of the cross section.

II.C. Results

Cadmium concentrations measured using ICP-MS indicated that the addition of Li metal lowered the solubility of Cd in the molten salt (Fig. 3). While it appears that the Cd concentration in the unadulterated salt was approaching a value of ~0.0055 wt%, the measurement duration was insufficient to ensure that equilibrium concentration had been reached; therefore, the true value may have been higher. The addition of Li metal to the salt clearly resulted in a decrease in Cd concentration, as can be seen in Fig. 3.
Fig. 3. Cd concentration as a function of time and addition of Li metal.

The SEM was used to measure the relative concentrations of Cd, Zr, and Cl via EDS line scans for samples of the Zr pellets as shown in Fig. 4. Note that the pellets were not washed to remove salt, thus they were all coated with LiCl-KCl.

This raw EDS data was analyzed in three ways. The counts for Cd, Cl, and Zr vs. position were first normalized to their maximum values for each line scan so that they could be plotted and compared on the same scale. From each sample, the line scan with the least random variability in normalized Cd counts was selected as the “best”. The Cd counts vs. depth of these best line scans were then plotted together. Lastly, the mean plateau Cd/Zr ratios from the all line scans were plotted vs. time.

The normalized Zr counts vs. position were consistent across line scans from all samples in that they rose sharply and then plateaued at the surface of the pellet, as seen in the SEM micrograph included in Fig. 5. The position of the Zr count plateau “edge” was helpful in defining the surface of the pellet. The normalized Cl counts vs. position were also consistent in peaking at the nugget surface from adherence and then decreasing sharply to near zero in the interior.

The normalized Cd counts vs. position were, in contrast, highly variable between line scans but still revealed several trends. Normalized Cd counts either peaked at the surface and decreased to a non-zero plateau value in the interior (Fig. 5) or simply plateaued at the surface with no clear surface peak (Fig. 6). For all line scans, the normalized Cd counts varied greatly for small changes in position along the line scan. Line scans with a surface Cd peak generally had less variability in counts for small changes in position.

The Cd counts vs. position data from each selected “best” line scan were then shifted on the position axis to center the peaks at zero (Fig. 7). This data set was intended to provide a basis for estimating the diffusion coefficient of Cd in the Zr (thought to be on the order of 10^-5 cm^2/s.) Unfortunately there was no observable difference in the aligned data sets across samples, precluding such analysis. It is also unknown what effect the formation of intermetallic compounds would have on Cd diffusion.
The mean Cd/Zr ratios in the interior-plateau regions of all line scans (Fig. 8) were remarkably consistent. Across all samples and line scans, the Cd-Zr ratio was approximately 0.0152 ± 0.0006. This data shows that the Cd-Zr ratio in the interior of the Zr pellets (to the depths measured by the line scans) was constant over the time period studied.

III. CONCLUSIONS

This study attempted to replicate the transport of Cd through molten LiCl-KCl eutectic salt to interact with Zr metal found in electro-refined spent fuel segments. The study solely used non-radioactive materials to facilitate working in a glove box instead of a shielded hot-cell.

The Cd content of the LiCl-KCl salt samples was measured with ICP-MS and yielded maximum concentrations of about 0.0055 wt% Cd. This was of the same order of magnitude as the 0.004 wt% Cd in Li/U reduced salt measured by Goff et. al.\(^3\) The addition of relatively small quantities of Li caused a large drop in the measured Cd concentration. It is worth noting that this experiment used alumina crucibles rather than steel ones as used by Goff, which might have been a source of contaminants that would facilitate excess CdCl\(_2\) formation he proposed.

The investigation of the interaction of dissolved Cd with Zr yielded mixed results. The SEM-EDS detected Cd on both the surface and interior of the Zr pellets. It is theorized that the Cd peaks at the surfaces of some line scans are due to local pellet geometries exposing surface adhering Cd in background of the line scan focal plane. There appeared to be no increase in Cd concentrations over the time frame studied (4 hrs). This precluded the estimation of the diffusion coefficient of Cd in Zr.

There are a number of potential avenues for future research. With regard to the transport of Cd in the salt, experiments are planned to separately measure the concentrations of Cd metal and CdCl\(_2\) in the salt both with and without the addition of U and Li. There are also plans to see if the crucible material has any effect on the salt-Cd chemistry. This should be sufficient to achieve a complete understanding of Cd transport in LiCl-KCl eutectic salt.

The uptake of Cd by Zr metal immersed in the salt bath also has opportunities for future study. The effect of intermetallic formation on Cd diffusion into Zr needs to be characterized. It has been established that Cd-Zr intermetallic compounds can be distinguished from each other and the Zr matrix via x-ray diffraction\(^5\). The relative populations of these compounds might be used to estimate the local Cd concentration and with their known energies of formation, draw conclusions about reaction rates.

The mean interior Cd concentrations (~1.5 mol% Cd) were nearly identical across samples. The significance of this is unknown as Cd does not saturate in Zr and instead forms increasing Cd rich intermetallic compounds.

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