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Global 2013

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October 2013

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Electrochemical processing of used nuclear fuel involves operation of one or more cells containing molten salt electrolyte. Processing of the fuel results in contamination of the salt via accumulation of fission products and transuranic (TRU) actinides. Upon reaching contamination limits, the salt must be removed and either disposed or treated to remove the contaminants and recycled back to the process. During development of the Experimental Breeder Reactor-II spent fuel treatment process, waste salt from the electrorefiner was to be stabilized in a ceramic waste form and disposed of in a high-level waste repository. With the cancellation of the Yucca Mountain high-level waste repository, other options are now being considered. One approach that involves direct disposal of the salt in a geologic salt formation has been evaluated. While waste forms such as the ceramic provide near-term resistance to corrosion, they may not be necessary to ensure adequate performance of the repository. To improve the feasibility of direct disposal, recycling a substantial fraction of the useful salt back to the process equipment could minimize the volume of the waste. Experiments have been run in which a cold finger is used for this purpose to crystallize LiCl from LiCl/CsCl. If it is found to be unsuitable for transportation, the salt waste could also be immobilized in zeolite without conversion to the ceramic waste form.
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I. INTRODUCTION

Electrochemical processing (aka "pyroprocessing") of used nuclear fuel is currently being developed and evaluated for potential commercial implementation by several nations. It is considered to have great promise for being applied to managing used nuclear fuel waste and potentially recycling actinides for use in either thermal or fast neutron spectrum reactors. A general form of the electrochemical processing flowsheet is given below in Figure 1.
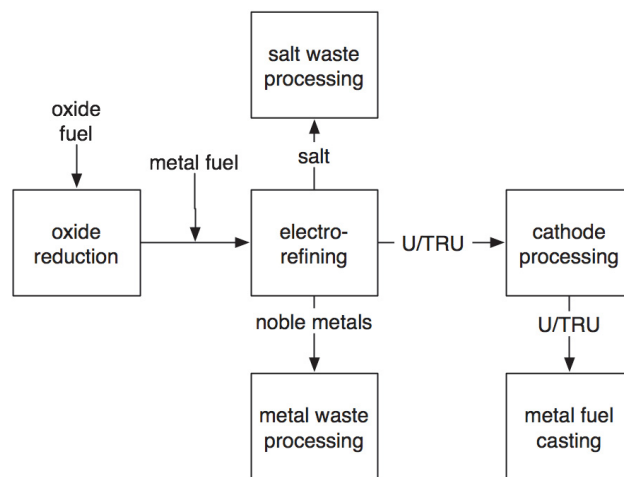

Fig. 1. General flowsheet for electrochemical processing of used nuclear fuel

This process is currently being used at Idaho National Laboratory (INL) to treat used fuel from Experimental Breeder Reactor-II (EBR-II) for final disposal (Ref. 1-2). This operation is being performed in the Fuel Conditioning Facility (FCF) at INL's Materials and Fuels Complex (MFC). Two electrorefiners are operating in FCF, each containing a large inventory of molten chloride salt (primarily LiCl-KCl) that is used as the electrolyte for electrorefining. As a result of processing approximately 4.7 metric tons (heavy metal) of EBR-II fuel out of the original inventory of 25.75 MT, this salt has become contaminated with fission products and mixed actinides. The current estimated salt composition in each electrorefiner is given in Table I.

TABLE I. Current Estimated Electrorefiner Salt
Composition (mass fractions)

Salt Compound	Mark-IV ER	Mark-V ER
LiCl	0.318	0.388
KCl	0.388	0.461
NaCl	0.0982	0.0579
RbCl	1.67E-03	5.90E-05
SrCl$_2$	4.98E-03	1.95E-04
YCl$_3$	3.50E-03	1.62E-04
CsCl	1.24E-02	6.91E-04
BaCl$_2$	7.20E-03	5.25E-04
LaCl$_3$	8.52E-03	3.57E-04
CeCl$_3$	1.62E-02	6.47E-04
PrCl$_3$	8.02E-03	2.94E-04
NdCl$_3$	2.73E-02	1.07E-03
PmCl$_3$	5.72E-04	2.19E-05
SmCl$_3$	5.20E-03	2.87E-04
EuCl$_3$	2.42E-04	1.49E-05
GdCl$_3$	1.62E-04	1.66E-05
NpCl$_3$	1.41E-03	7.28E-05
UCl$_3$	0.0685	0.0316
PuCl$_3$	0.0298	0.0575
AmCl$_3$	1.04E-05	1.30E-05

By the end of EBR-II fuel electrorefining operations, it is estimated that the mass of Mark-IV salt waste will be 1017 kg, and the mass of Mark-V salt waste will be 699 kg. The original plan for disposing of this waste involved first producing ceramic waste forms containing the salt and eventually shipping them to the permanent nuclear waste disposal repository in Yucca Mountain. With the cancellation of the Yucca Mountain Project and no definite plans for disposal of high-level nuclear waste, options for disposition of the salt waste are being reconsidered. One intriguing option is to directly dispose of it in a salt repository (similar to the Waste Isolation Pilot Plant (WIPP)) (Ref. 3). Such a repository would be formed inside of a geologic salt formation. If the direct disposal option is found to be unacceptable, the other options to consider include selective separation and recycle of useful salts (LiCl-KCl) back to the electrorefiner as well as immobilization of the salt in zeolite without subsequent conversion to a ceramic waste form. Those options and preliminary results of their assessment are given in this paper.

II. SALT WASTE DISPOSAL ASSESSMENT

The concept of direct disposal of ER salt waste in a salt repository was evaluated quantitatively by conducting a series of performance assessment (PA) calculations for its impact on the repository performance (Ref. 4). The generic salt PA model is an improved version of the model developed to evaluate a generic salt repository for disposal of heat generating commercial used nuclear fuel

(UNF) and defense high-level waste (DHLW) (Ref. 5 and 6).

Fig. 2 shows a schematic for the conceptual model of radionuclide (RN) release and transport pathways for a generic salt repository. The PA model assumes that the repository is situated in a thick-bedded salt formation below a carbonate aquifer, and is in saturated, anoxic reducing condition. These characteristics are consistent with the WIPP conditions. The RNs released from the waste package (WP) are transported to a nearby repository access shaft (assume 5 m diameter) and to the underlying interbed.

The RNs are released to overlying aquifer from the access shaft and transported advectively to a hypothetical biosphere located at the site boundary (5 km down-gradient from the repository footprint). The RNs released to underlying interbed remain in the interbed, as there is no hydrogeological feature for brine flow from the interbed to biosphere, and diffusive mass flux from the interbed upward to the overlying aquifer through intact salt rock and other overburden formations would be negligible.
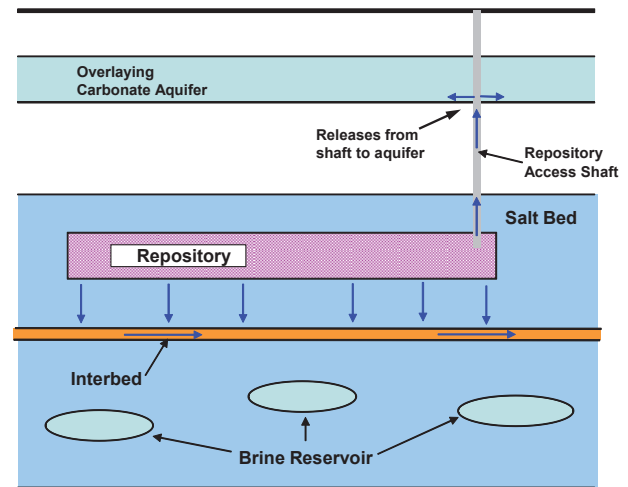

Fig. 2. A schematic illustrating the conceptual model for RN release and transport pathways of a generic salt repository.

The PA model used in the current analysis has incorporated the source term model and WP configuration that are specific to the two types of ER salt waste (i.e., Mark-IV and Mark-V ER salt waste). The source term model includes RN inventories, decay heat output profiles, WP failure, salt waste dissolution and RN releases upon WP failure, etc. The PA model also has incorporated the latest conceptual understanding and processes related to the long-term behavior of generic salt repository (Ref. 7). The PA calculations were conducted probabilistically with 100 realizations for each simulation.

The current WP configuration dictates salt waste is contained in thin-walled stainless steel canister and placed in thick-walled carbon steel overpack. Each WP contains 120 kg of ER salt waste. The PA analysis assumed the WP has 7.5-cm thick mild steel overpack as recommended in the recent analysis (Ref. 7), and the overpack thickness provides a very long WP containment lifetime (~100k years). The analysis demonstrated that a thinner-wall overpack may be sufficient for the ER salt WP.
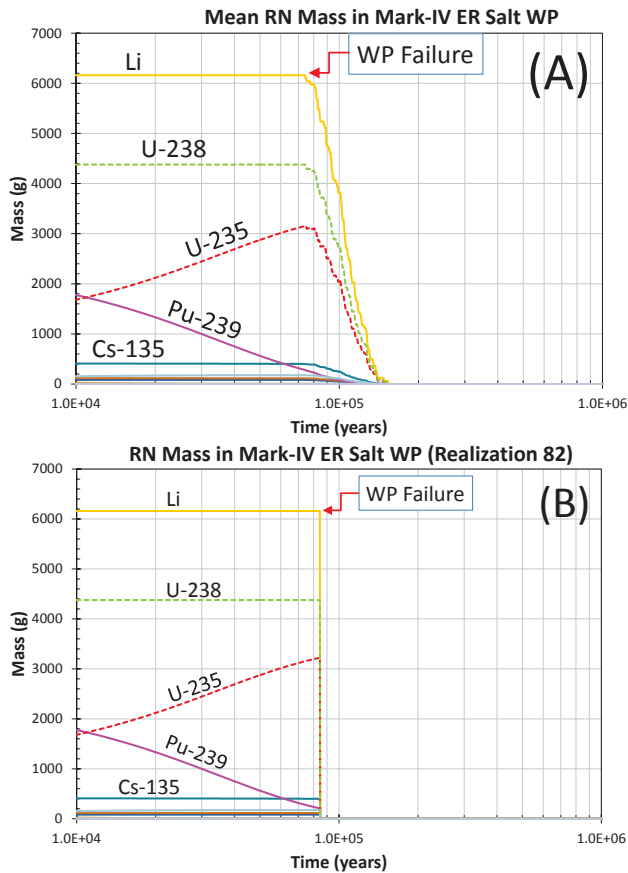

Fig. 3. Model result of RN releases from salt waste of Mark-IV ER salt WP: (A) Mean mass releases, and (B) Mass releases for Realization 82.

The salt waste dissolution and RN release rate is assumed conservatively to be congruent to the dissolution of LiCl, which is highly soluble in water; the PA model uses the LiCl solubility of 12.9 M, or the Li elemental solubility of 90 g/L. Fig. 3 shows the model results of the mean mass releases (Fig. 3-A) from salt waste upon WP failure and the releases for Realization 82 (Fig. 3-B). The mean releases are the mean of 100 values at each simulation time step. The modeled salt waste dissolution is better shown in individual realizations, and as shown in Fig. 3-B, the salt dissolution is fast, almost instantaneous relative to the simulation time steps. Decrease in Pu-239 mass and

increase in U-235 mass in the salt waste prior to the WP failure in the figures are due to the decay of Pu-239 (half-life of 2.41×10^4 years) to U-235. However, as shown in Fig. 4, most released RNs precipitate out subject to their solubility constraints in the chemically reducing condition that is assumed for the near-field environment of a generic salt repository (Ref. 8).
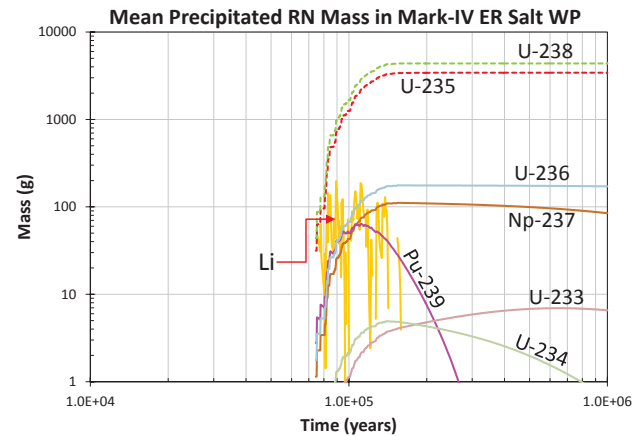

Fig. 4. Model result of mean precipitate mass of RNs released from salt waste of Mark-IV ER salt WP.

Fig. 5 shows the model result of the mean mass flux of RNs from the overlying aquifer to a hypothetical biosphere located at the repository site boundary. Only non-sorbing or weakly sorbing RNs (i.e., I-129 and Cl-36) with a significant inventory have calculated mass flux to the biosphere, and the mass release rates are insignificantly small. Although Li has the greatest flux, it is non-radioactive and not of interest. These RNs are those released from the access shaft to the overlying aquifer. As discussed above, the RNs released to the underlying interbed remain in the interbed, and do not contribute to the releases to the overlying aquifer or biosphere.
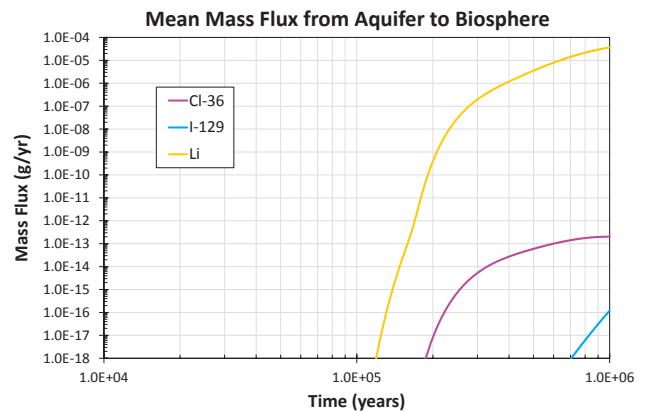

Fig. 5. Model result of mean mass flux of RNs from the overlying aquifer to the hypothetical biosphere located at the repository site boundary.

The model result of the mean annual dose at a hypothetical biosphere is shown in Fig. 6. The dose rates by the RNs (I-129 and Cl-36) are negligibly small and will not have any impact on the repository performance. The preliminary analysis demonstrates the ER salt waste can be disposed of safely without extensive treatments in a bedded salt repository (a type of salt formation for the generic repository of this study). The analysis also demonstrates how a PA tools can be utilized to develop guidance for HLW waste management strategy.
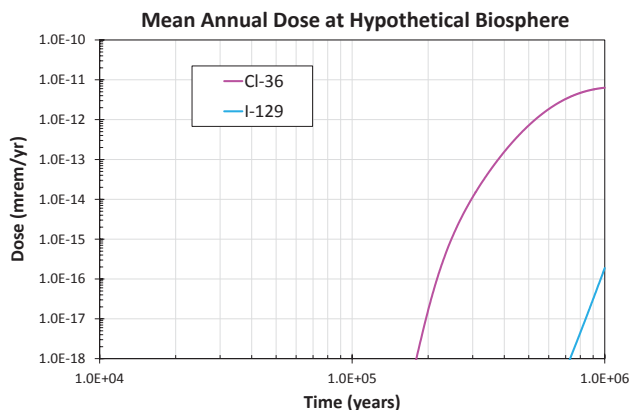

Fig. 6. Model result of mean annual dose at the hypothetical biosphere located at the repository site boundary.

III. SALT RECYCLING

As shown in Table I, a large fraction of the waste salt from the electrorefining performed at INL consists of LiCl and KCl. These are the two base salts for the electrolyte that need not be disposed if they can be separated from the fission product chlorides and returned to the electrorefiners. Various separation processes have been studied, and one of current interest is salt deposition on a cold finger. Based on the salt phase diagrams, it should be possible to create a purified salt deposit on a cold surface (such as a cold finger). This was tested using a mixture of LiCl-CsCl (5 wt%). This is an important salt mixture to consider, since the electrolytic reduction process uses LiCl as the electrolyte and CsCl is one of the contaminants introduced by used oxide fuel. The salt temperature was held at 650°C while a stainless steel tube cooled via argon gas flow was immersed in the salt for varying lengths of time. The argon gas flow rate ranged from 7.4 to 14.9 L/min. The time for immersion of the tube ranged from 5 to 30 min. Photographs of the resulting salt deposits are shown in Figure 7. These deposits were dissolved and analyzed for elemental composition using ICP-MS. The concentration of CsCl in those deposits is plotted in Figure 8 as a function of gas flow rate and deposition time.
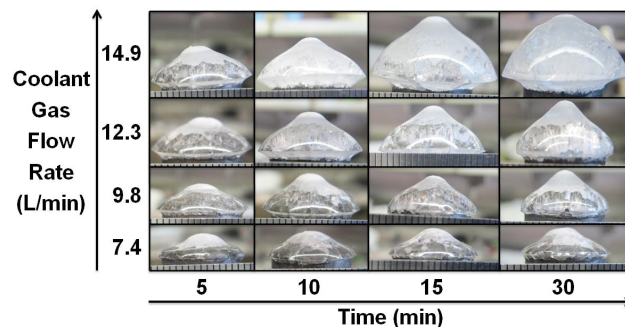

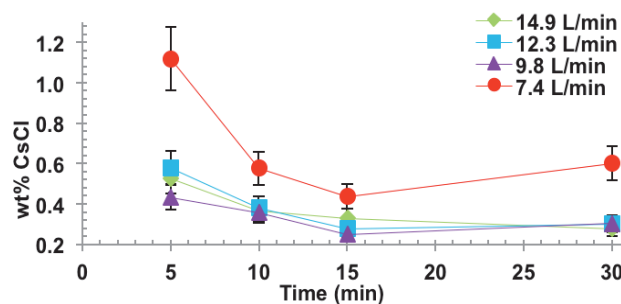Fig. 7. Salt deposits collected on a cold finger immersed in molten LiCl-CsCl (5 wt%).

Fig. 8. Cesium chloride concentration in salt deposits collected on a cold finger immersed in molten LiCl-CsCl (5 wt%).

As expected, the salt deposit sizes increased with both time and gas flow rate. The CsCl concentrations were highest in the smaller deposits. This is likely due to the ratio of mass of the actual deposit versus the mass of adhering salt from the bulk liquid. The solids that are formed within the molten salt liquid should be high purity LiCl. If such a deposit is relatively small, the amount of surface salt with the bulk composition would be more significant. Lowest impurity level measured in these deposits was 0.25 wt% CsCl.

The cold-finger process is expected to be readily scalable by increasing the surface area of the cold surface immersed in the salt. Increasing gas flow rate will increase the rate of heat removal from the surface, which should track the rate of salt deposition. Optimization of the process could include determining the ideal time to remove the deposits. Letting them grow for too long will likely result in insulation of the cold finger and a decrease in the rate of heat removal.

IV. SALT IMMOBILIZATION IN ZEOLITE

A ceramic waste process was developed at Argonne National Laboratory (ANL) that required occluding the electrorefiner salt into the pores of zeolite-4A followed by mixing with glass frit and thermally consolidating into a

glass-bonded sodalite (Ref. 9-10). The equipment for that process is shown in Figure 9. More details on the V-blender process and results of testing from laboratory through engineering scale are given elsewhere (Ref. 11).
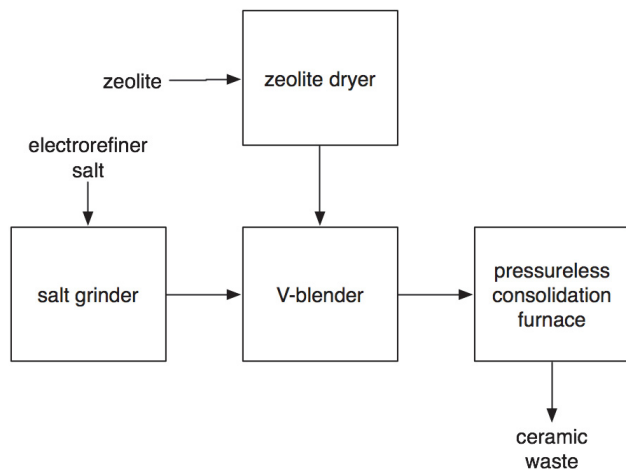

Fig. 9. Ceramic waste process for disposition of electrorefiner salt

Two major problems related to this process are waste loading and process throughput. Only about 7.5 wt% of the ceramic waste form is the actual salt. And the pressureless consolidation process can take over two weeks to process a single full-scale waste form (Ref. 10). A workaround to these problems is to stop the ceramic waste process after salt occlusion into the zeolite (V-blender operation). This would increase the waste loading to approximately 30 wt% salt in the zeolite. For the ceramic waste process, the salt content in the zeolite is limited by the conversion to sodalite. If sodalite need not be formed, then more salt can be loaded into the zeolite, and the glass frit can be left out of the waste form. Conventional thinking has been that the salt must be put into a waste form with durability comparable to that of high-level glass waste. But the previous analysis showed that even raw salt with no waste matrix is suitable for permanent disposal in a salt repository. Logically, it makes sense that a 30% salt/70% zeolite material would also be suitable for permanent disposal. If this process were to be coupled with a salt recycle step such as the cold finger process, effectively a further reduction in waste mass could be achieved.

Given that electrorefiner salt can be directly disposed of in a salt repository based on its long term performance, it would be reasonable to question why absorption of the salt into zeolite would even be considered. The issue of concern is transportation of the salt waste from its point of generation to the repository. This would likely occur on public roads, and various accident scenarios would need to be considered. If the salt were to be directly placed into waste canisters, a catastrophic transportation accident

could cause breaching of the canisters and exposure of the salt to water. Since the salt is highly soluble in water, this could result in a rapid and irreversible release of highly radioactive waste into the environment. In contrast, zeolite powder loaded with salt is relatively leach resistant. Standard testing of the salt-zeolite sorption process involves washing the salt-loaded zeolite in deionized water. It has been shown that the only salt that dissolves into the water is that which is on the surface of the zeolite (not absorbed in the pores) (Ref. 12). Thus, it is believed that salt-loaded zeolite would be a more acceptable waste material to transport to the final repository. The 3-fold increase in mass of the waste may ultimately be determined to be an acceptable price for dramatically improving transportation safety.

Note that the fact that performance assessment presented here was for salt repositories does not preclude consideration for other types of geologic repositories. The original plan for disposing of ceramic waste from the EBR-II spent fuel treatment process was to use the formerly proposed high-level waste repository at Yucca Mountain. Salt recycling could be combined with either direct salt disposal or with ceramic waste processing, in which case it could apply to disposal in a variety of different geologic repository types.

V. CONCLUSIONS

Through analysis of the impact of electrorefiner salt on a generic salt repository, it has been concluded that it can be directly disposed in such a repository. Direct salt disposal is highly attractive relative to the current baseline ceramic waste process because of the 13-fold decrease in mass coupled with elimination of ceramic waste process. This is expected to dramatically reduce the cost of completing the EBR-II spent fuel treatment project. And it improves the attractiveness of the electrochemical used fuel treatment process for potential commercial implementation with respect to waste disposal requirements. There is potential to couple direct salt disposal with a cold finger process to recycle a significant fraction of the LiCl-KCl back to the electrorefiner which should be further investigated. Despite the favorable performance of raw salt in the repository, it is anticipated that there may be problems with transporting electrorefiner salt on public roadways. Actually running part of the ceramic waste process—just up to and including the V-blender step—would likely mitigate the consequences of even a catastrophic transportation accident. The zeolite would effectively contain the salt in the environment for periods of time long enough to clean up such an accident. Further evaluation of transportation requirements is needed to draw conclusions regarding the

feasibility of these approaches to electrorefiner salt disposal.

ACKNOWLEDGMENTS

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