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STRATEGIC MINIMIZATION OF HIGH LEVEL WASTE FROM PYROPROCESSING OF SPENT NUCLEAR FUEL

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The pyroprocessing of spent nuclear fuel results in two high-level waste streams--ceramic and metal waste. Ceramic waste contains active metal fission product-loaded salt from the electrorefining, while the metal waste contains cladding hulls and undissolved noble metals. While pyroprocessing was successfully demonstrated for treatment of spent fuel from Experimental Breeder Reactor-II in 1999, it was done so without a specific objective to minimize high-level waste generation. The ceramic waste process uses "throw-away" technology that is not optimized with respect to volume of waste generated. In looking past treatment of EBR-II fuel, it is critical to minimize waste generation for technology developed under the Global Nuclear Energy Partnership (GNEP). While the metal waste cannot be readily reduced, there are viable routes towards minimizing the ceramic waste. Fission products that generate high amounts of heat, such as Cs and Sr, can be separated from other active metal fission products and placed into short-term, shallow disposal. The remaining active metal fission products can be concentrated into the ceramic waste form using an ion exchange process. It has been estimated that ion exchange can reduce ceramic high-level waste quantities by as much as a factor of 3 relative to throw-away technology.

I. INTRODUCTION

Pyroprocessing is currently being pursued by Idaho National Laboratory to treat spent fuel from the Experimental Breeder Reactor-II and is being included in designs for an advanced fuel cycle research facility under the Global Nuclear Energy Partnership (GNEP). In this non-aqueous technology, spent metal or oxide fuel is electrochemically separated into actinides and fission products. The fission products can be stabilized in principally two different kinds of waste forms—ceramic waste and metal waste. Active metal fission products such as alkalis, alkaline earths, and rare earths partition into the molten salt electrolytes used in pyroprocessing and can be immobilized in the ceramic waste.[1-2] Noble metal fission products such as Tc, Ru, Rh, and Mo remain undissolved in anode baskets along with cladding hulls and are melted to form the metal waste.[3]

There are a number of issues important for optimization of pyroprocessing. A major issue is minimization of the amount of waste generated relative to fuel treated. In the case of metal waste, most of the mass is due to cladding hulls. If cladding hulls can be effectively separated from the spent fuel with low fission product and actinide contamination, there is the potential to dramatically lower the amount of metal waste generated from the process. If the fuel is in the form of oxide fuel, this can be achieved via voloxidation.[4] Metal fuel, conversely, cannot be readily removed from cladding hulls prior to electrorefining due to the sodium bonding. However, it should be noted that the noble metal-loaded metal waste form has been developed using a stainless steel/zirconium matrix.[3] This stainless steel currently comes from cladding hulls. It is uncertain how much the metal waste volume could be reduced by separating out the cladding hulls and adding just enough stainless steel and zirconium to make a stable metal waste form alloy. Further experimental studies would be needed to establish to what degree the noble metal fission product concentration in the metal waste form could be increased.

The focus of this paper is, however, on the ceramic waste and options for minimizing its volume/mass. Two variants of advanced pyroprocessing, using oxide fast reactor and metal fast reactor fuel, are currently being considered under GNEP. The diagram shown in Figure 1 depicts a simplified and combined pyroprocessing flowsheet that accommodates both of these fuel options but focuses on salt recycle and waste. The objective of the analysis reported here was to minimize the rates of Cs-Sr ceramic waste (from oxide reduction) and high-level ceramic waste (from electrorefining) production. It is known from labscale oxide reduction experiments with spent fuel that Cs, Sr, and Ba convert to chlorides and accumulate in the LiCl-based electrolyte found in the oxide reduction unit.[5] The remaining active metal fission products similarly convert to chlorides and accumulate in the electrorefiner's LiCl-KCl electrolyte. This physical phenomenon is actually useful in the sense that it allows for the generation of a Cs-Sr waste form. Cesium and strontium are short-lived fission products but account for most of the fission product decay heat. This decay heat is a limiting factor for the capacity of a high-level waste repository. Thus, it is a GNEP objective to separate cesium and strontium into a non-high level waste form that can be placed in a shallow, short-term disposal site.

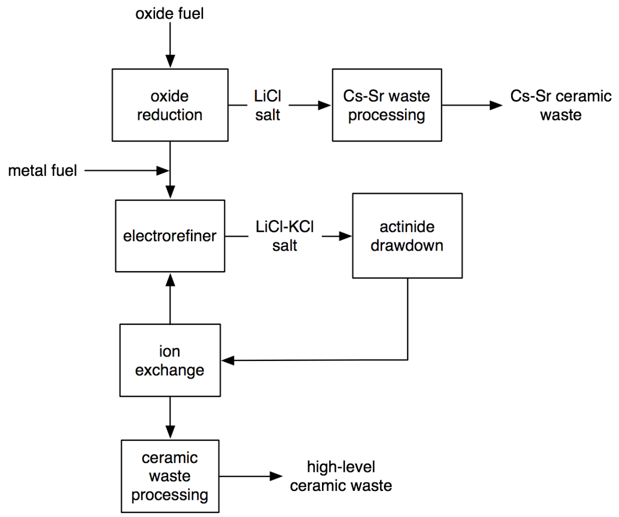

Figure. 1. Salt Recycle and Disposal Options for Pyroprocessing of Metal and Oxide Spent Fuel

The ceramic waste form for pyroprocessing is a glass-bonded sodalite that is formed from heating a mixture of salt-loaded zeolite-A and glass frit to temperatures ranging from 915 – 950°C. The salt-loaded zeolite can be formed via either a throw-away process or an ion exchange process. For the throw-away option, roughly a 9:1 mass ratio of zeolite and salt is blended in a high temperature v-blender to form salt-loaded zeolite. For the ion exchange option, zeolite is immersed in a molten pool of salt and allowed to reach equilibrium by exchanging cations with the salt. It has been found that fission products tend to have a higher affinity for the zeolite-A than does lithium and potassium. Thus, most of the LiCl-KCl can be recycled to the electrorefiner, while the fission products are concentrated in the zeolite. In theory, this will result in significantly lower amounts of ceramic waste than the throw-away option.

II. SALT WASTE MODEL

A batch model for pyroprocessing was developed based on the flowsheet shown in Figure 1 using the Matlab-Simulink platform. Calculations based on both metal and oxide fuels were performed. The composition of each fuel type is given in Table I, based on hypothetical fast reactor fuels.

TABLE I. Spent Fuel Composition.

Fast Reactor Oxide Fuel		Fast Reactor Metal Fuel	
	Mass Fraction		Mass Fraction
UO_2	0.294	U	0.271
Rb_2O	$1.57x10^{-3}$	Rb	$1.58x10^{-3}$
Y_2O_3	$2.12x10^{-3}$	Y	$1.84x10^{-3}$
La_2O_3	$1.03x10^{-2}$	La	$9.60x10^{-3}$
Ce_2O_3	$1.88x10^{-2}$	Ce	$1.76x10^{-2}$
$P_{r2}O_3$	$9.55x10^{-3}$	Pr	$8.96x10^{-3}$
Nd_2O_3	$3.00x10^{-2}$	Nd	$2.81x10^{-2}$
Pm_2O_3	$1.11x10^{-3}$	Pm	$1.08x10^{-3}$
Sm_2O_3	$9.07x10^{-3}$	Sm	$8.54x10^{-3}$
Eu_2O_3	$1.12x10^{-3}$	Eu	$1.06x10^{-3}$
Gd_2O_3	$1.04x10^{-3}$	Gd	$9.77x10^{-4}$
Tb_2O_3	$8.05x10^{-5}$	Tb	$7.58x10^{-05}$
Dy_2O_3	$6.54x10^{-5}$	Dy	$6.05x10^{-05}$
NpO_2	$2.20x10^{-2}$	Np	$2.37x10^{-2}$
PuO_2	$4.90x10^{-1}$	Pu	0.486
AmO_2	$4.88x10^{-2}$	Am	$4.89x10^{-2}$
CmO_2	$1.40x10^{-2}$	Cm	$1.28x10^{-2}$
SrO	$3.69x10^{-3}$	Sr	$3.44x10^{-3}$
Cs_2O	$3.02x10^{-2}$	Cs	$3.14x10^{-2}$
BaO	$1.23x10^{-2}$	Ba	$1.21x10^{-2}$
		Na	$3.06x10^{-2}$

The model was used to calculate changes in molten salt electrolyte compositions in the oxide reduction and electrorefiner units as additional batches of fuel were treated. When certain limits were reached such as total salt volume, concentration of fission products in the salt, and concentration of sodium in the salt, salt would be removed and sent to either Cs-Sr waste processing or actinide drawdown. As needed, additional LiCl and/or KCl would be added to each molten salt electrolyte batch to maintain the minimum volume and reduce the concentration of sodium and fission products.

Actinide drawdown was calculated based on a simple assumption that 99% of the actinides could be removed from the salt. The technology for achieving this drawdown is currently in the early testing phase but would likely involve either electrolysis or chemical reduction with an active metal such as lithium or calcium.

The fission product separation achieved from ion exchange was calculated using the equilibrium model published by Phongikaroon and Simpson.[6] Since that publication, the ion exchange parameters have been updated and are given in Table II. Note that since the experimental ion exchange studies are still in progress, several parameters had to be assumed to be the same as parameters for similar cations. All actinides were assumed to have the same parameters as U. Barium was assumed to be the same as strontium. And all rare earths were assumed to be the same as neodymium.

TABLE II. Ion Exchange Model Parameters

Cation	K^{IX}	K^{OCC}
U^{3+}	0.62	0.0046
Rb^{+}	0.056	2.0
Y^{3+}	0.71	0
La^{3+}	0.71	0
Ce^{3+}	0.71	0
Pr^{3+}	0.71	0
Nd^{3+}	0.71	0
Pm^{3+}	0.71	0
Sm^{3+}	0.71	0
Eu^{3+}	0.71	0
Gd^{3+}	0.71	0
Tb^{3+}	0.71	0
Dy^{3+}	0.71	0
Np^{3+}	0.62	0.0046
Pu^{3+}	0.62	0.0046
Am^{3+}	0.62	0.0046
Cm^{3+}	0.62	0.0046
Cs^{+}	0.18	2.2
Sr^{2+}	0	2.8
Ba^{2+}	0	2.8
Li^{+}	1	1
K^{+}	0.26	0.62
Na^{+}	1.17	0.055

III. RESULTS OF CERAMIC WASTE MODEL CALCULATIONS

For each fuel type, two treatment scenarios were considered—throw-away of salt from electrorefiner and ion exchange of salt from electrorefiner. The results of the calculations are given in Table II. For these calculations, it was assumed that fission products could not exceed 20 wt% in the electrorefiner and 20 mol% in the oxide reduction unit. Furthermore, sodium was limited to 30 mol% in the electrorefiner. Since there is a high concentration of sodium in the metal fuel and a low affinity for sodium cations in the zeolite-A, it is necessary to throw-away additional salt in the metal fuel case beyond what would be normally accommodated by zeolite ion exchange. Otherwise, the sodium concentration in the electrorefiner would reach a very high value before leveling off and would certainly raise the melting point of the salt. Another interesting observation from running the model was that lithium actually accumulates in the process if the zeolite-A used for ion exchange is 100% Li-exchanged. This would, in turn, increase the waste production rate, since it would be necessary to add KCl to keep the LiCl/KCl ratio close to the ideal eutectic. To get around this problem, the zeolite-A is assumed to be pre-exchanged with a combination of Li and K. Using 8.5 Li^{+} equivalents per unit cell and 3.5 K^{+} equivalents per unit cell yielded optimal waste generation numbers.

Hundreds of cycles were run by the model in which fuel was added followed by salt removal and treatment or disposal. In Table III, the steady-state mass of waste per mass of heavy metal is reported for four scenarios. From the standpoint of minimizing HLW with the given compositions, the best approach is to use oxide fuel and ion exchange to treat the ER salt. From the standpoint of minimizing all ceramic waste, a better approach is to use metal fuel with ion exchange to treat the ER salt. Ion exchange has clear and significant benefits over throw away—a factor of 1.8 for metal fuel and 3.0 for oxide fuel. The higher HLW number for metal fuel versus oxide fuel when using ion exchange is due to the need to throw away additional salt to keep the sodium concentration in the ER low. The ion exchange option for metal fuel is, thus, a hybrid of throw-away and ion exchange. The HLW throw-away numbers are very close for the two fuels, because sodium is only a limiting factor when the salt is recycled.

TABLE III. Results of Ceramic Waste Model Calculations

Fuel Type	OR Salt Treatment	ER Salt Treatment	Cs-Sr Waste (MT/ MTHM)	HLW ceramic (MT/ MTHM)
oxide	Throw-away	Throw-Away	2.9	8.5
oxide	Throw-away	Ion Exchange	2.9	2.8
metal	n/a	Throw-away	--	8.6
metal	n/a	Ion Exchange	--	4.9

IV. CONCLUSIONS

An analysis of salt recycle/disposal options for pyroprocessing of both oxide and metal fuel has yielded interesting observations. Currently, the only known way of achieving Cs-Sr separations from spent fuel pyrochemically is to start with oxide fuel and recover the Cs-Sr from the oxide reduction salt. This increases the total mass of ceramic waste compared to metal fuel treatment. But metal fuel treatment results in higher amounts of high-level waste, and the heat-load in that waste is high due to Cs and Sr. Whether using oxide or metal fuel, ion exchange shows clear benefits relative to salt throw-away. When there is no sodium in the fuel, ion exchange can reduce the mass of high-level waste by a factor of 3, while the improvement is a factor of 1.8 when using sodium bonded metal fuel. For sodium-bonded fuel, improved data to assess the impact of sodium on salt recycle and options for its selective removal from the salt should be evaluated. Additional experimental measurements of ion exchange parameters are planned, and this analysis will need to be updated accordingly.

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