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INCORPORATION OF RADIONUCLIDES FROM THE ELECTROMETALLURGICAL TREATMENT OF SPENT FUEL INTO A CERAMIC WASTE FORM

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ABSTRACT

An electrometallurgical process is being developed at Argonne National Laboratory to treat spent metallic nuclear fuel. In this process, the spent nuclear fuel is electrorefined in a molten salt to separate uranium from the other constituents of the fuel. The treatment process generates a contaminated chloride salt that is incorporated into a ceramic waste form. The ceramic waste form, a composite of sodalite and glass, contains the fission products (rare earths, alkalis, alkaline earth metals, and halides) and transuranic radionuclides that accumulated in the electrorefiner salt. These radionuclides are incorporated into zeolite A, which can fully accommodate the salt in its crystal structure. The radionuclides are incorporated into the zeolite by high-temperature blending or by ion exchange. In the blending process the salt and zeolite are simply tumbled together at >450°C (723 K), but in the ion exchange process, which yields a product more highly concentrated in fission products, the molten salt is passed through a bed of the zeolite. In either case, the salt-loaded zeolite A is mixed with glass frit and hot isostatically pressed to produce a monolithic leach resistant waste form. Zeolite is converted to sodalite during hot pressing. This paper presents experimental results on the fission product uptake of the zeolite as a function of time and salt composition.

INTRODUCTION

In the electrometallurgical treatment of spent nuclear fuel, metallic nuclear fuel is electrorefined in a molten salt to separate uranium from the other constituents of the fuel.[1,2] The salt retains the rare earth, alkali, and alkaline earth fission products, as well as the transuranic radionuclides originally present in the spent fuel. Two options are currently under study for treating this salt. In one option, it is directly incorporated into zeolite and, eventually, a ceramic waste form. Fresh salt is then introduced into the electrorefiner to treat additional fuel.[3] In the second process, the radionuclides are removed from the salt by an ion-exchange process using zeolite columns. The radionuclides are concentrated in the zeolite, which also retains a portion of the salt. The effluent salt from the column is used to treat additional spent fuel, reducing the quantity of salt that must be disposed of.[4, 5, 6] In both processes, the salt and radionuclides are first incorporated into zeolite A, then combined with glass frit and consolidated by hot isostatic pressing. During consolidation, the salt-loaded zeolite is converted to sodalite, resulting in a monolithic composite of sodalite and glass.[7]

In this paper we will discuss the incorporation of fission products into zeolite by ion exchange and some of the factors that play a role in incorporating the zeolite into a waste form. We are determining the effectiveness of the ion exchange process by examining the fission product uptake of the zeolite as a function of time and salt composition. From these tests we obtain kinetic and equilibrium data with which to model the ion exchange process in a column system and compare with results of

laboratory-scale column tests.[4] The waste form development and testing are being done in parallel with the column and batch ion exchange tests. [7, 8, 9]

EXPERIMENT

The batch ion exchange experiments were conducted by immersing zeolite beads in a large excess of a salt containing non-radioactive fission product species that will remain in the salt after treatment of spent fuel from Experimental Breeder Reactor II (EBRII). The zeolite was supplied by UOP Inc. in the sodium form as 8x12 mesh beads containing 7 to 12% clay binder and also as a fine (<20 μm) powder containing no binder. The zeolite was dried in flowing nitrogen at 525°C and stored under argon prior to use. The moisture content was estimated by differential scanning calorimetry. Lithium chloride and potassium chloride (LiCl/KCl) were obtained as a mixture at the eutectic composition (~58 mol.% LiCl) from Lithcoa Inc. The other salt components were obtained as pure anhydrous or ultra-dry halides from Aldrich Chemical Co. and Alfa Aesar Inc. The test salts were prepared by combining the LiCl/KCl with the pure components at room temperature; the mixture was then lowered into a furnace and heated to 500°C under an argon atmosphere. Once molten, the salts were stirred overnight. The compositions tested are listed in Table 1. Composition 1 is the reference composition used for waste form fabrication.

The ion exchange tests were carried out with two ion exchange steps. First, 390 g of dehydrated zeolite beads was placed in a stainless steel tube. Approximately 1500 g of LiCl-KCl eutectic salt was passed through the column at a flow rate of 1.5 cm^3 per minute to replace the sodium in the beads with lithium and potassium. The zeolite contained 1.3% sodium, 6.4% lithium, 14.4% potassium, and 35% chloride. In the second step, approximately 1.5 g of these salt-loaded beads was placed in a pouch made from a stainless steel mesh. The pouch was attached to a stirring rod. The pouches were then immersed in 500 g of the simulated waste salt at 550°C and stirred. Samples of zeolite were immersed in the waste salt mixtures for times ranging from 0.5 to 72 hours.

RESULTS AND DISCUSSION

The ion exchange process relies on the ability of the zeolite to selective sorb fission products and actinides from the LiCl-KCl electrolyte in which they accumulate. The ion exchange of molten salts has been examined in several previous studies [4, 5, 9-11]. The salt compositions that are used are given in Table 1. The compositions include two different waste salt compositions and three single component salts. Composition 1 is the composition expected after treatment of EBRII spent fuel. For composition 2, the salt of composition 1 was diluted with LiCl/KCl by a factor of ten. The salt compositions with a single fission product contain 5 equivalent per cent of the fission product chloride with the balance LiCl/KCl salt. In our study, zeolite shows good selectivity for all of the fission products present in the molten waste salt compared to lithium or potassium. Results of batch ion exchange tests with composition 1 are shown in Figure 1. Results for composition 2 are shown in Figure 2. Results of single component tests are shown in Figure 3. '

The data in Figure 1 show the relative rates of ion exchange for several fission products into zeolite A from a molten salt. Uptakes were determined by chemical analysis of the zeolite after ion exchange. The data in Figure 1 indicate a competitive exchange between the divalent alkaline earths and the trivalent lanthanides. As the duration of the tests increases, the concentration of the alkaline earths goes through a maximum and then falls to a lower value. Cesium and yttrium show similar behavior, though less pronounced. Initially the lanthanide concentration increases steadily with time for all salt compositions. However, in Figure 1 at 24 hours, the behavior of the rare earths begin to vary. Lanthanum and cerium continue to increase while the other rare earths begin to decrease.

Table 1: Salt compositions used in ion exchange experiments

SALT	COMP. 1	COMP. 2	CS SALT[A]	SR SALT[A]	LA SALT[A]
LiCl	31.9	44.1	39.6	43.4	43.5
KCl	37.3	51.7	46.6	51.0	51.1
NaCl	15	2.07	*	*	*
RbCl	0.3	0.05	*	*	*
CsCl	2.42	0.35	13.8	*	*
KI	0.15	0.02	*	*	*
KBr	0.02	0.003	*	*	*
$SrCl_2$	0.92	0.14	*	5.6	*
$BaCl_2$	1.11	0.17	*	*	*
YCl_3	0.6	0.10	*	*	*
$LaCl_3$	1.13	0.17	*	*	5.4
$CeCl_3$	2.25	0.32	*	*	*
$PrCl_3$	2.46	0.16	*	*	*
$NdCl_3$	3.82	0.54	*	*	*
$SmCl_3$	0.59	0.10	*	*	*
$EuCl_3$	0.05	0.001	*	*	*

*Not added to salt. [a] 5 equiv.% Cs, Sr, or La in LiCl-KCl.

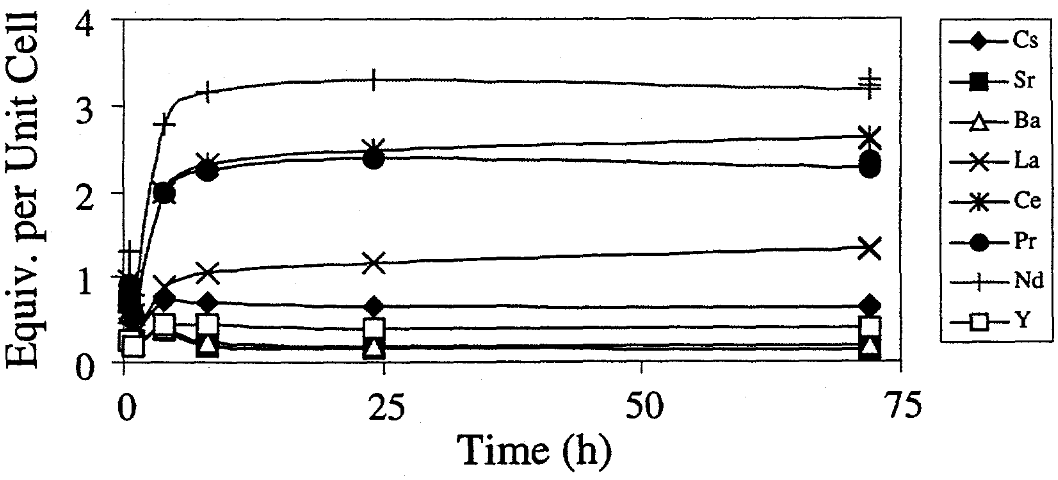

Figure 1: Uptakes for ion exchange tests with salt composition 1.

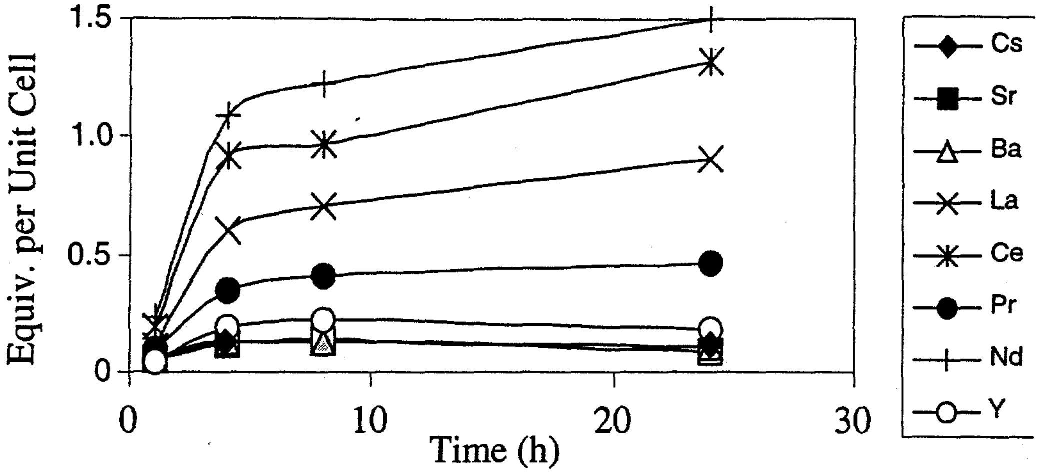

Figure 2: Uptakes for ion exchange tests with salt composition 2.

The data for salt composition 2 are not as extensive as for composition 1. Some differences are apparent, however. The competitive exchange evident in Figure 1 is not as apparent. This is expected since at low fission product concentrations, there are relatively more exchange sites available for the various types of cations. The alkaline earths do not go through a maximum. The curves for praseodymium and lanthanum switch order between Figure 1 and 2, because the praseodymium in salt composition 1 is more concentrated relative to the other rare earths.

The data in Figure 3 show the differences in the rate of exchange. Relative to the higher charge species, cesium uptake reaches a maximum value within one hour after initial immersion. The cesium uptake is steady through 24 hours, but somewhat lower at 72 hours. Strontium reaches a maximum uptake after 4 hours. There is a slight dip in the strontium uptake with time as well, but this is within the uncertainty of the chemical analysis. Lanthanum uptake is slowest of the three. The rate of uptake shifts between 8 and 24 hours, and a maximum is not yet achieved after 24 hours. The results of these tests are consistent with the results obtained for the mixed salt compositions.

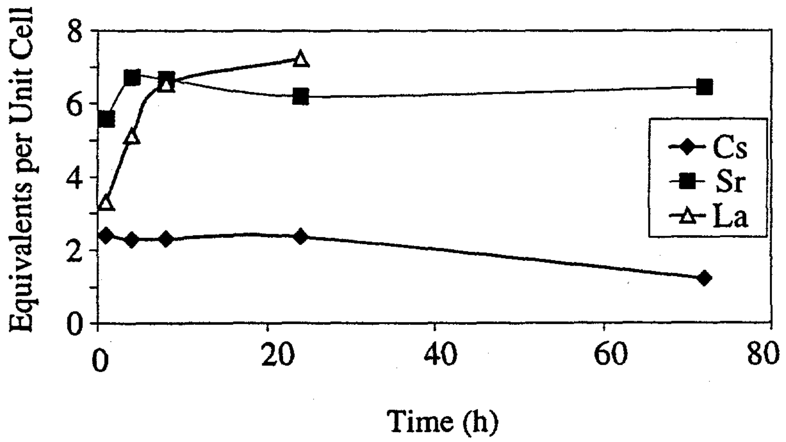

Figure 3: Uptakes for single-component ion exchange tests.

In order to test the possibility that the rare earths were reacting to form oxides or oxychlorides we looked at the reversibility of the ion exchange. Zeolite beads that had been immersed in salt of composition 1 for 72 hours were subsequently immersed in LiCl-KCl for an additional 24 hours at 500°C. The composition of the zeolite after immersion in each of the salts is given in Table 2. Essentially all of the cesium, barium, and strontium were exchanged out of the zeolite by the LiCl-KCl. However, only approximately two thirds of the rare earths in the zeolite were exchanged out. These results suggest that the rare earths may react with the zeolite or water to form oxides or oxychlorides, which are insoluble in the salt. If the rare earth elements were present as ions the ion exchange should be fully reversible.

Table 2: Composition of Zeolite Before and After Reverse Ion Exchange

Equivs Per UC	Cs	Sr	Ba	La	Ce	Pr	Nd	Y	Re
72	0.6273	0.1398	0.1726	1.3114	2.5915	2.288	3.225	0.4035	9.8194
96	0.0176	0.0137	0.0466	0.7615	1.0285	0.7011	0.7839	0.0942	3.3691

In molten salt, the zeolite has a particular affinity for the highly charged ions, such as the rare earths, although uptake is slower for these ions than for cesium or the alkaline earths. Exchange factors (EF's) can be calculated as a measure of the selectivity of the zeolite for fission products. Exchange factors for the reaction

$$^1/_n\,XCl_n + {}^1/_m\,YZ = {}^1/_m\,YCl_m + {}^1/_n\,XZ$$

are calculated from the following equation:

$$EF = (x_z/x_s)^{1/n}(y_s/y_z)^{1/m}$$

where x_i and y_i are the mole fractions of each species in the zeolite (z) or salt (s). Table 3 gives the EF's for each of the ions present in waste salt for the different compositions examined. Since exchange factors are based on an equilibrium composition, the values given in Table 3 are based on 72-hour tests. The EF's indicate that a column should effectively remove fission products from the salt and concentrate them in the zeolite with one exception. The EF calculated for strontium at composition 1 (0.83) indicates that exchange is not favored. This is a curious result in that it differs dramatically from the result with composition 2, the Sr salt, and results reported previously.(1) However, with this curious exception, the zeolite can effectively "clean" the salt for reuse. We do see an increase in the value of the exchange factor at the more dilute composition, indicating that the exchange factors are a function of concentration. All of the tests were run under identical conditions.

CONCLUSIONS

The incorporation of radionuclides into the ceramic waste form can be accomplished by simply using the zeolite to soak up all of the salt. However, the ion exchange data presented here indicate that zeolite does selectively sorb fission products from waste salt. This makes ion exchange an attractive method for reducing waste form volumes by concentrating radionuclides in the waste form. Incorporation of an ion exchange step into the electrometallurgical treatment process by use of ion exchange columns is currently under study.

Table 3: Exchange Factors of Representative Fission Products into Zeolite A Referenced to Sodium after 24-Hour Immersion in Salts

SALT	COMP. 1	COMP. 2	CS SALT	SR SALT	LA SALT
Li	1.33	2.17	2.28	2.96	1.47
K	1.00	1.00	1.00	1.00	1.00
Na	1.01	1.70	*	*	*
Cs	5.94	9.50	3.2	*	*
Sr	0.83	3.67	*	4.0	*
Ba	1.04	11.1	*	*	*
Y	1.98	2.05	*	*	*
La	5.34	6.50	*	*	2.8
Ce	4.54	5.99	*	*	*
Pr	3.75	5.67	*	*	*
Nd	3.67	5.60	*	*	*

Note that I, Br, Rb, Eu, and Sm were not measured.

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