

DEVELOPMENT OF ELECTROREFINER WASTE SALT DISPOSAL PROCESS FOR THE EBR- II SPENT FUEL TREATMENT PROJECT

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The results of process development for the blending of waste salt from the electrorefining of spent fuel with zeolite-A are presented. This blending is a key step in the ceramic waste process being used for treatment of EBR-II spent fuel and is accomplished using a high-temperature v-blender. A lab-scale system was used with non-radioactive surrogate salts to determine optimal particle size distributions and time at temperature. An engineering-scale system was then installed in the Hot Fuel Examination Facility hot cell and used to demonstrate blending of actual electrorefiner salt with zeolite. In those tests, it was shown that the results are still favorable with actinide-loaded salt and that batch size of this v-blender could be increased to a level consistent with efficient production operations for EBR-II spent fuel treatment. One technical challenge that remains for this technology is to mitigate the problem of material retention in the v-blender due to formation of caked patches of salt/zeolite on the inner v-blender walls.

KEYWORDS : Pyroprocessing, Ceramic Waste, Zeolite, Molten Salt, V-Blender

1. INTRODUCTION

The Experimental Breeder Reactor-II (EBR-II) was a sodium-cooled, fast reactor that employed sodium-bonded binary (U-Zr) metal fuel during its operation at Argonne National Laboratory-West from 1961 to 1994 [1]. Two types of fuel assemblies were employed—drivers with high U-235 enrichment (55-76%) alloyed with Zr and blankets that were essentially depleted U (U-238) [1]. The driver assemblies were used to support the fission reactions, while the blanket assemblies were used for breeding Pu-239 from neutron capture. In 1995, the reactor was shutdown based on a shift in programmatic priorities for the U.S. Department of Energy (DOE), and reactor decommissioning was initiated. Due to the presence of highly reactive sodium metal bonding between the fuel slugs and cladding, it was determined that some treatment of this fuel was necessary before it could be shipped to a long-term storage facility or geologic repository. Cutting of the fuel followed by distillation of the sodium was one option considered. This is not a clean approach, however, in the case of the driver assemblies, which encountered high burn-up. The fuel slugs developed porosity, allowing the sodium to migrate into the fuel's pores and allowing some fission products such as Cs to migrate into the bulk of the sodium bonding. It

was, thus, determined to be impractical to attempt to distill all sodium from the fuel pins. And even if this distillation could be achieved, it would be problematic to deal with the Cs contamination in the sodium. The preferred processing alternative was to use electrochemical processing technology to separate the sodium from the spent fuel and produce chemically-stable products. In electrochemical processing of spent fuel, fuel segments are placed into anode baskets and lowered into an electrorefiner containing a molten salt (LiCl-KCl-UCl_3) electrolyte. The sodium and active metal fission products react with UCl_3 to form chlorides such as NaCl , CsCl , SrCl_2 , etc. that accumulate in the molten salt. An electrical potential is then applied which leads to oxidation of the U at the anode with simultaneous reduction and deposition at the cathode. A dendritic U deposit forms at the cathode. After collecting these dendrites and distilling the salt, a high purity U product can be collected. Depending on the enrichment and economics of fuel fabrication, this U can either be refabricated into new fuel or disposed of as a waste. The sodium and fission products continue to accumulate in the salt, which can accommodate significant quantities of both without interfering with the electrorefining process. Once the fission product and sodium concentration in the salt is so high that either fission product decay heat is excessive or its melting point is too high, salt must be

removed from the electrefiner and either discarded into a waste form or treated and returned to the electrefiner. Noble metal fission products and trace quantities of actinides remain in the cladding hulls in anode baskets and are sent to the metal waste furnace. In the metal waste furnace, salt is removed from the cladding hulls via distillation, and a metal alloy is formed that contains the noble metals, 15% Zr, and stainless steel (balance). A flow diagram that illustrates this process is shown in Fig. 1.

Of particular interest for this paper is the fate of the active metals, which accumulate in the electrefiner salt. In this case, active metals are defined as those that form more stable chlorides than uranium trichloride on a basis of kJ per mole of Cl. This includes Group I and II metals in addition to lanthanides and transuranic actinides (TRU). As more and more fuel is processed, the contamination level of the fission products and sodium in the salt increases. Since the salt's melting point is initially low (approx. 350°C) due to the presence of a eutectic LiCl-KCl ratio in the electrolyte, there is concern that this contamination will eventually be high enough to increase the melting point above an acceptable level relative to the operating temperature of the electrefiner (500°C). Other concerns regarding the salt composition are in regard to plutonium concentration and heat load from decay of short-lived fission products (Cs and Sr).

There are principally two options for dealing with the contaminated electrefiner salt. It can either be discarded directly into a waste form or can be treated to selectively remove some of the fission products and sodium and then be returned to the electrefiner. A previously published paper discusses the merits of each of these options and shows potential waste volume reduction from choosing the selective process [2]. While there are obvious benefits to treating the salt and recycling it to the electrefiner, the baseline process for EBR-II spent fuel treatment includes a simple throw-away of the salt [3-6]. In this process, the waste salt is absorbed by dry zeolite-4A via high temperature powder blending [7-8]. The salt-loaded zeolite, which is in granular form, is then blended with granular glass frit and heated to over 915°C to form a glass-bonded sodalite waste form [9-11]. A process flow diagram for the ceramic waste process is given in Fig. 2.

In this paper, important findings for the development of the salt/zeolite blending operation are presented. This process has been studied and optimized using a two-pronged approach of performing small-scale experiments with non-radioactive surrogate salts and large-scale experiments with both surrogate and actual radioactive salts extracted from the electrefiners. The small-scale experiments provide rapid, inexpensive test results for narrowing down the operating parameter range. While the large-scale

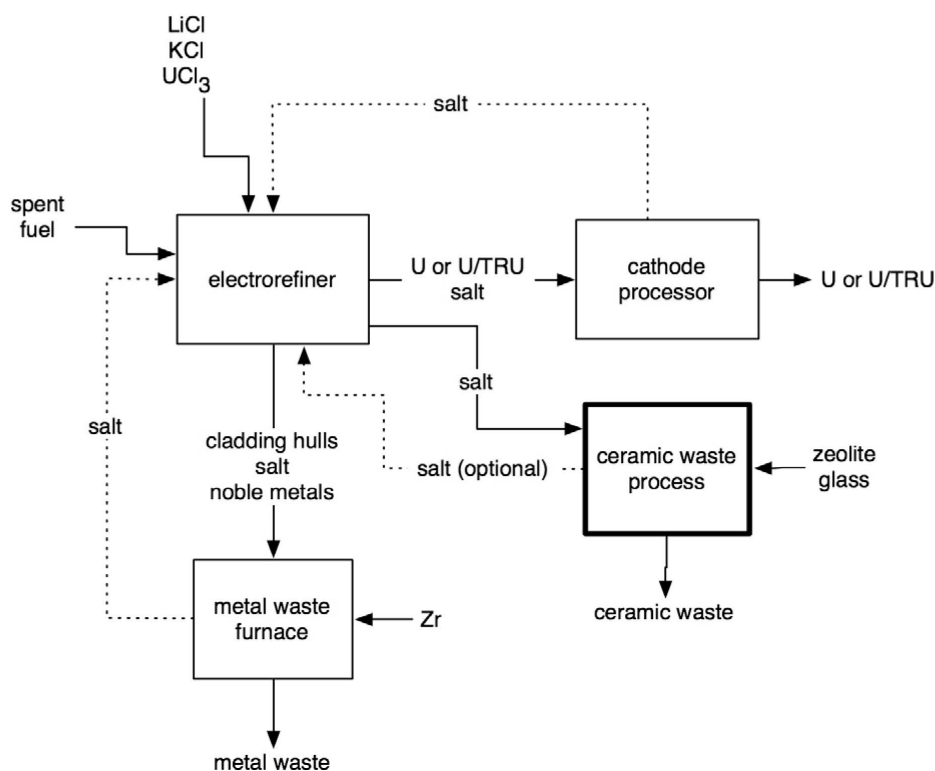


Fig. 1. Process Flow Diagram for EBR-II Spent Fuel Treatment

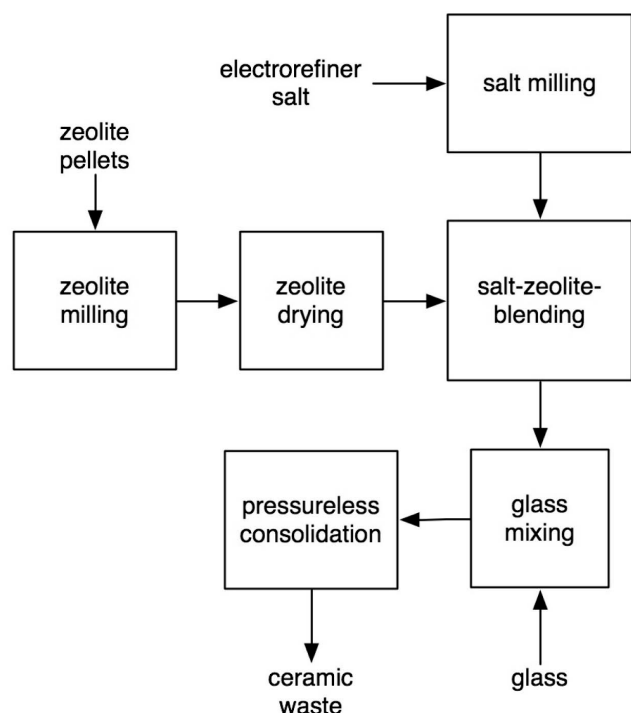


Fig. 2. Process Flow Diagram for the Ceramic Waste Process

experiments examine potential scale-up issues and provide data for testing with actinide-loaded salt. This approach has been found to be effective in that the v-blender operation for the ceramic waste process is considered mature with few technical issues yet to be resolved.

2. EXPERIMENTAL

Zeolite-4A was obtained from UOP in the form of 2-mm diameter pellets, which contain a proprietary inorganic binder that nominally comprises 10% of their mass. They were milled and sieved to the specified particle size distributions using a variety of methods. Then the zeolite was dehydrated by heating to 550°C under vacuum. The residual moisture concentrations were measured by a variety of methods including TGA, near infrared absorbance, and Karl-Fischer titration. The moisture concentration in the zeolite after drying ranged from 0.1 to 0.5 wt%.

Three different types of salt powders were used for salt/zeolite blending tests reported here. Small-scale tests involved either LiCl-KCl eutectic (44.3 wt% LiCl and 55.7 wt% KCl, Aldrich APL) or that same eutectic salt combined with various fission product surrogates. Large-scale tests used actual fission product-contaminated salt from the Mark-IV electrorefiner that was used for treating

EBR-II driver fuel. The compositions of the surrogate and Mark-IV ER salts are shown in Table 1. The values given for the Mark-IV salt were determined from samples analyzed using ICP-MS. The values given for the surrogate salt were calculated based on masses of added salts. With the exception of KI and KBr, all salts used were chlorides. After melting to form a solution, the surrogate salt was solidified, crushed, milled, and sieved to a 45 to 425 μm particle diameter range. The LiCl-KCl eutectic was crushed, milled, and sieved to remove particles with diameters greater than 425 μm . Test sieves were then used to characterize its particle size distribution over specified ranges. The results of these measurements are given in Fig. 3. The Mark-IV electrorefiner salt was milled using a high speed impact mill/classifier (Prater) in the Hot Fuel Examination Facility (HFEF) hot cell. Sieving was only performed to measure its particle size distribution, not to remove any particles outside of a specified range. For that salt, only one size distribution was used with 50.8 wt% of the particles being between 45 and 300 μm diameter.

Table 1. Compositions of Mark-IV Electrorefiner and Surrogate Salts

Element	Mark-IV salt (wt%)	surrogate salt (wt%)
K	21.3	25.7
Li	5.87	6.34
U	5.49	0
Na	1.9	2.45
Rb	not measured	0.1
Nd	0.7	0.9
Cs	0.62	0.82
Ce	0.42	0.53
Pu	0.29	0
Ba	0.25	0.31
Pr	0.21	0.27
La	0.21	0.29
Sm	0.16	0.15
Sr	0.15	0.25
Y	0.12	0.13
Fe	0.066	0
Np-237	0.0265	0
Eu	0.01	0.011
Cl	balance	61.7
Br	not measured	0.0061
I	not measured	0.063

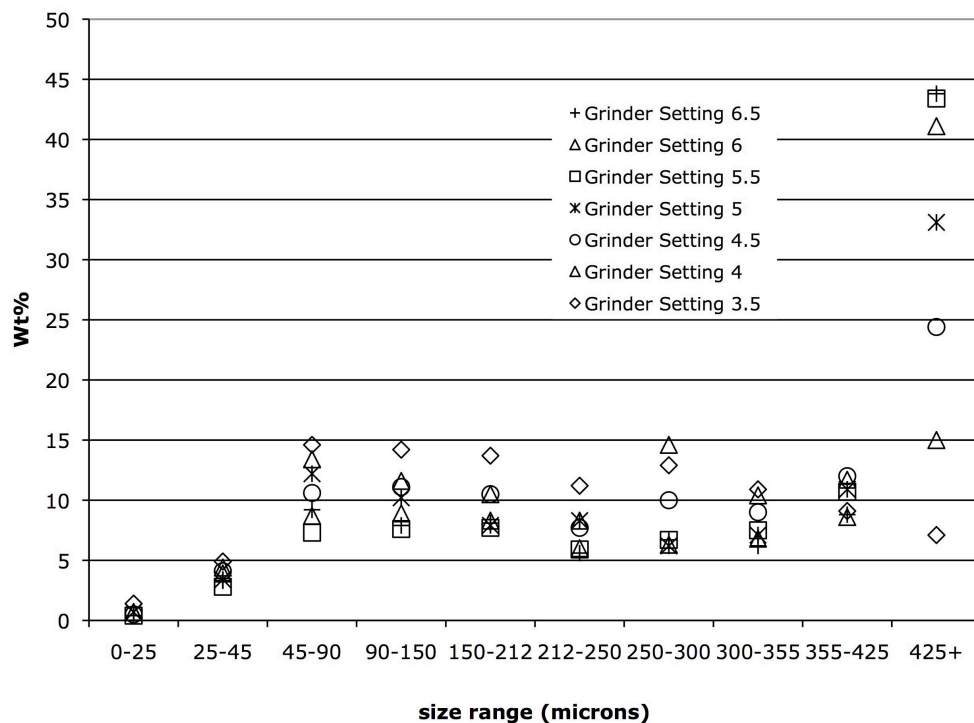


Fig. 3. Particle Size Distributions for LiCl-KCl Salt Batches

Labscale salt/zeolite blending experiments were performed using a 4-liter, stainless steel v-blender (Ability Engineering). It was heated externally by a ceramic furnace that was mounted on rails to allow it to easily slide into and out of place. A thermocouple ran through the shaft and into the vessel. The temperature control was based upon feedback from the internal thermocouple, but thermocouples were also placed near heating elements to prevent the furnace from over-heating. The vessel itself was air-tight and was initially filled with dry argon gas prior to loading it with salt and zeolite. The end caps on the v-blender were sealed using Grafoil® gaskets that were discarded after each run. It was not possible to take samples of salt-loaded zeolite in situ. Samples could only be taken after the v-blender and its contents had cooled to near room temperature. A drawing of the labscale v-blender system is shown in Fig. 4.

Rotation of the v-blender was set at 17 rpm for all testing. For each run, the salt and zeolite were pre-mixed in a plastic bottle and poured into the v-blender in such a way as to minimize entrainment of air into the vessel. After sealing the v-blender, the material was cold mixed for 30 minutes prior to initiating a 5°C/min heat-up to 500°C. After holding the v-blender at a temperature of 500°C for the specified period of time, the heaters were turned off while the v-blender continued to rotate. Once the temperature had reached a temperature low enough to

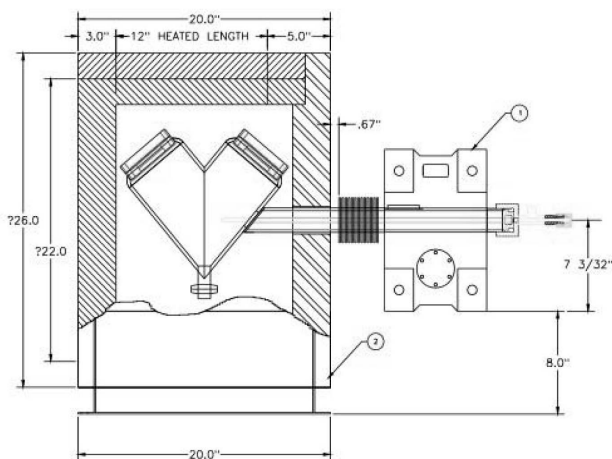


Fig. 4. Labscale High Temperature V-Blender Used for Testing with Non-Radioactive Salt

allow safe handling, the v-blender was pulled out of the furnace, opened, and unloaded into a plastic bottle.

For engineering-scale tests with actual radioactive salt, a larger v-blender (Ability Engineering) was installed in the Hot Fuel Examination (HFEF) hot cell. A drawing of this system is given in Fig. 5. Its vessel has an

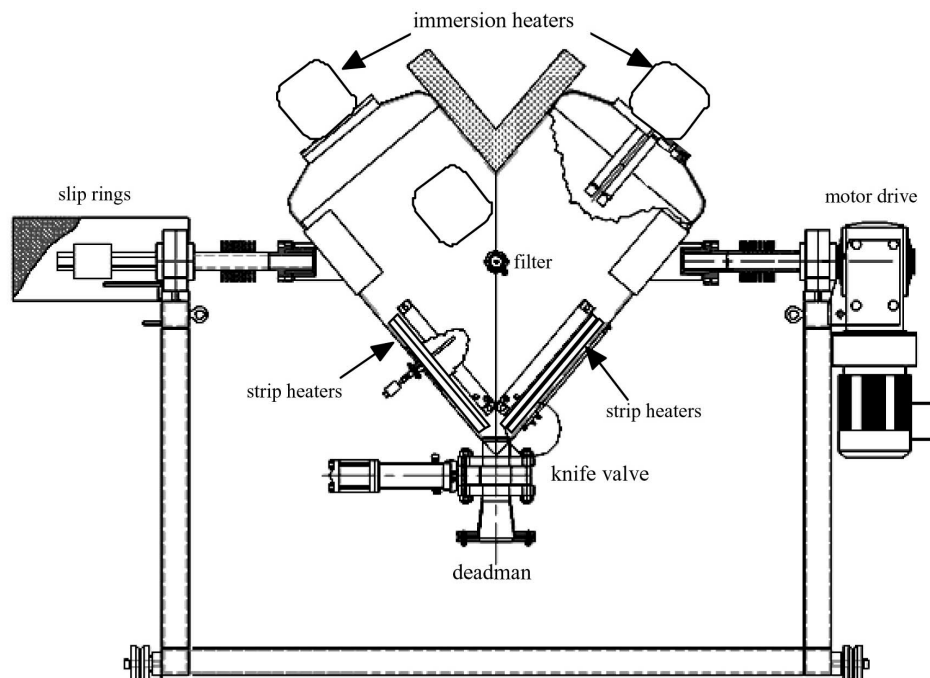


Fig. 5. High Temperature V-Blender Installed in the Hot Fuel Examination Facility Hot Cell

internal volume of 230 liters, was constructed of 316H stainless steel, and was designed for a nominal 50 kg batch size. Two types of heaters were used to heat the contents of the vessel--immersion heaters and strip heaters. The immersion heaters consist of coils that extend into the vessel and come in direct contact with the salt/zeolite. The strip heaters were fastened to the outside of the v-blender vessel walls and covered with insulation (10 cm of Unifrax® Durablanket-S). In actual operation, both heaters were used to achieve the target temperature for the salt/zeolite of 500°C as quickly as possible. As in the case of the lab-scale v-blender, this system was rotated at a rate of 17 rpm.

For testing with both the lab-scale and engineering scale v-blenders, the extent of salt adsorption into zeolite was quantified using a free chloride measurement. It is assumed that all salt that is not adsorbed by the zeolite will dissolve in a water wash in one minute or less. One gram of salt-loaded zeolite is, thus, washed with 60-ml of nanopure water for a minute. Wash solution is then extracted through a 0.45 µm filter and analyzed using a free chloride ion specific electrode (Accumet). The free chloride concentration is calculated using the following formula.

$$\text{Free Chloride Concentration} = 100\% \bullet \frac{C_{Cl} \left(\frac{\mu\text{g } Cl^-}{\text{ml } H_2O} \right) \frac{\text{g } Cl^-}{10^6 \mu\text{g } Cl^-}}{m_{\text{sample}} (\text{g})} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Lab-scale V-Blender Experiments

Lab-scale experiments with surrogate and eutectic salt were performed in order to determine the effect of time at maximum temperature, zeolite particle size, and salt particle size on the free chloride concentration. Based on the known thermal stability of the zeolite, the maximum temperature of the blending process was never raised above 500°C. The results of tests in which the time at temperature was varied for two different zeolite particle size distributions is shown in Fig. 6. For these tests, the surrogate salt shown in Table 1 was used. As can be seen, there is benefit to using the smaller particle sizes, but the effect is not dramatic. Whether 45 to 125 µm or 75 to 250 µm zeolite is used, the free chloride concentration reaches a minimum well below 0.5 wt% after approximately 10 hrs at 500°C. There is minimal improvement in going from 16 to 20 hrs at the maximum temperature.

To study the effect of salt size distribution on free chloride concentration, additional lab-scale blending tests were run using LiCl-KCl eutectic that had been milled with different grinder settings. The different particle size distributions for the salt are shown in Fig. 3. From that figure, it is apparent that the major differentiating characteristic between the different salt samples is the mass fraction with particle diameters greater than 425 µm.

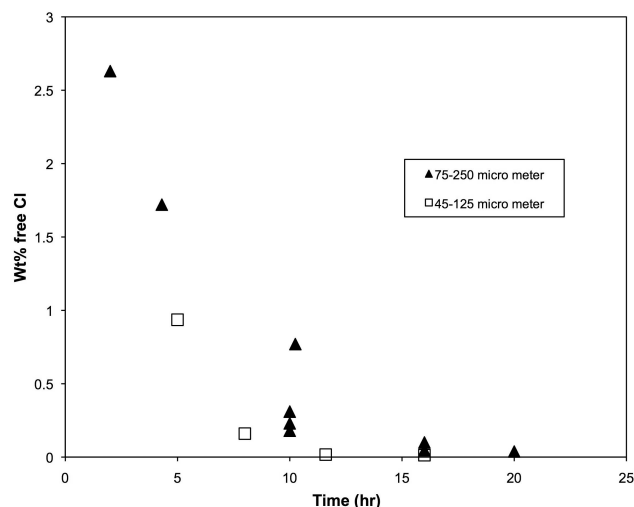


Fig. 6. Effect of Time at Maximum Temperature (500°C) on Free Chloride Concentration of Salt-Loaded Zeolite From Labscale Blending Experiments with Surrogate Salt

In Fig. 7, the relative size of this coarse fraction is plotted versus the free chloride concentration. There is a readily discernible correlation where higher coarse content in the salt leads to higher free chloride concentration.

When considering all of the lab-scale testing results, it is apparent that smaller particle sizes for both the salt and zeolite are beneficial for the kinetics of the salt sorption. This can be explained in a number of ways, including using surface area and diffusion arguments. For developing an optimized salt/zeolite blending process, it might seem logical to make both the salt and zeolite particles as small as possible. However, reducing particle size of a powder generally worsens its handling characteristics, and the powders used in this study already suffer from handling difficulties. Container to container transfers are essential to minimize dusting problems and rehydration of hygroscopic materials in the hot cells. And it is often necessary to use mechanical agitation from pneumatic vibrators to complete these transfers. It was, thus, decided to focus on minimizing the fraction of salt particles greater than 425 μm while using a wide zeolite particle size distribution (45 to 250 μm). The zeolite size

was actually driven more by the next step of the ceramic waste process--pressureless consolidation. This size was found to result in good and consistent waste form solidification.

3.2 Engineering-Scale V-Blender Experiments with Electrefiner Salt

For treating the waste salt from the electrefiners used for EBR-II spent fuel treatment, a practical batch size for a v-blender would be in the 100-200 kg range to facilitate treatment of all of the salt in a reasonable length of time. For the initial demonstration of the technology, an engineering-scale v-blender was obtained (as discussed in the experimental section) and installed in the Hot Fuel Examination Facility (HFEF) hot cell to demonstrate the process at the 50 kg scale. Three tests were run in this v-blender with salt extracted from the Mark-IV electrefiner after 100 driver assemblies had been processed. The composition of this salt is given in Table 1. As shown in Table 2, these tests were done with different batch sizes, zeolite particle sizes, and average heating rates. The free chloride concentrations in all cases were considered to be acceptable.

Since each test involved heating the salt/zeolite mixture at 500°C for 15 hrs, it is apparent that the free chloride results are slightly higher than encountered in the lab-scale tests. This could be due to the differences between actual and surrogate electrefiner salt composition. It could also be due to the differences in salt particle size. There was a relatively high fraction of the salt larger than 300 μm in the engineering-scale tests. Examining Fig. 7, it can be seen that such a high fraction of large particles can explain the high free chloride concentrations. Or the batch sizes investigated, there was not a significant effect of batch size on the free chloride concentration. This leads to the conclusion that the v-blender used for the 50-kg demonstration can also be used for 100-kg scale production operations.

In addition to achieving a low free chloride concentration, another important consideration for performance of the blending process is material hold-up. In early developmental testing before the v-blender was moved into the hot cell, it was observed that small patches of salt/zeolite form in certain locations on the inside wall of the v-blender. The precise mechanism for this "caking" is unknown but is suspected to be tied to the presence of fine salt particles

Table 2. Summary of Salt/Zeolite Blending Tests in HFEF-Installed V-Blender. (Zeolite:salt ratio = 8.7, $t=15$ hrs at 500°C)

Test	zeolite particle size (μm)	Batch Size (kg)	Avg heating rate ($^{\circ}\text{C}/\text{min}$)	wt% Free Cl
HV-1	75-250	38.7	3.2	0.15
HV-2	75-250	84	2.9	0.19
HV-3	45-250	54.2	1.4	0.078

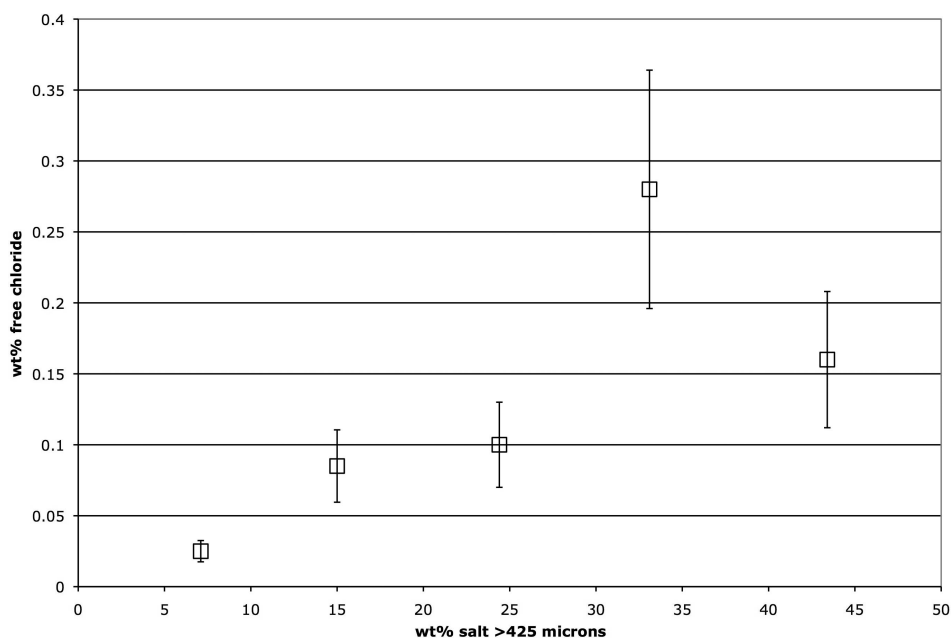


Fig. 7. Effect of Coarse LiCl-KCl Eutectic Salt Particles on Free Chloride Results for Small-Scale V-Blender Tests. Zeolite-4A Particle Size Range was 45 to 250 μ m for All Tests

that have a tendency to adhere to the vessel walls. When the temperature of the vessel exceeds the salt melting point, this salt probably melts without being able to be fully absorbed by the zeolite. When the v-blender cools, this salt re-freezes and forms hard, crusty patches. Due to the difficulty in remotely cleaning the inside of the v-blender, this phenomenon was carefully monitored in these tests. The first and easiest way to determine if this was occurring in the HV-series runs was to estimate material hold-up after each run. After HV-1, the hold-up was estimated at 290 grams. After HV-2, the cumulative holdup had increased to 750 g. An inspection of the interior of the vessel with a remotely-operated video camera verified the existence of some caking of powder on the walls. A small patch of this material was seen adjacent to each of the two immersion heaters. And the immersion heaters were coated with a layer of powder.

In order to meet material control and accountability requirements for a nuclear facility, sampling of most feed

and product streams is carried out and mass balances of accountable material (U and Pu) are calculated. If the sample analysis results are in poor agreement with what is expected, it may be impossible to close the material balance for the accountable material. This would be a very serious problem that would certainly slowdown or even stop operations. Thus, a sample was taken after the salt-loaded zeolite from HV-1 had been mixed with glass frit. It was analyzed for U and Pu isotopes, with the results compared to what was expected based on the measured masses and the measured composition of the 100-driver electrefiner salt. The results of the analysis are given in Table 3.

From this table, it is evident that there was close agreement between the concentrations in the salt-loaded zeolite/glass samples and those expected based on the concentrations in the salt. If the results from each of the two samples are averaged, it can be shown that the actual versus expected concentrations deviated by no more than

Table 3. Uranium and Plutonium Concentrations in a Salt-Loaded Zeolite/Glass Sample from V-Blender Batch HV-1

	Sample 1	Sample 2	Predicted based on salt composition
Elemental Concentration (wt%)			
Total U	0.528	0.544	0.557
Total Pu	0.0218	0.0224	0.0225

4%. The material balance, thus, appears to be excellent. However, there was a slight deficiency in U and Pu concentrations in both samples relative to what was expected based on the salt analysis. This may be attributed to U and/or Pu hold-up in the v-blender. Practically, there is only one route by which U and/or Pu can be envisioned to be retained in the v-blender in a higher concentration than at some other elements in the salt-loaded zeolite/glass mixture. This again refers to the problem of salt caking on the walls. Analysis of this caked material indicated that it had a high salt concentration of approximately 50 wt%. So, whenever caking occurs in the v-blender, the concentration of U and Pu in the samples of salt-loaded zeolite/glass should be lower than anticipated if there was no such caking. Indeed, the deficiency shown in Table 3 is consistent with a 70-150 g quantity of salt-rich cake retained in the v-blender.

4. SUMMARY

The results presented in this paper show how the salt/zeolite blending step in the ceramic waste process has been developed at Idaho National Laboratory using both lab-scale experiments with non-radioactive, surrogate salts and engineering-scale experiments with actual electrorefiner salt contaminated with active metal fission products and actinides. The reference zeolite-A particle size distribution is 45 to 250 μm , which leads to acceptable salt sorption kinetics while still maintaining decent powder handling characteristics and good performance in the pressureless consolidation step. The important characteristic of the salt particle size distribution is that it should have a minimal fraction of particles coarser than 425 μm . Running at a maximum temperature of 500°C leads to acceptable free chloride concentrations after approximately 15-16 hours of heating at this temperature. The only significant issue that needs to be further studied in this area is mitigation of the material caking that has been observed on the inner v-blender walls. This leads to a hold-up problem and potentially impacts the homogeneity of the ceramic waste form. It is speculated that the caking can be addressed via further fine-tuning of the salt particle size distribution and possibly via optimizing the temperature cycle for the v-blender.

For the continued treatment of spent fuel from EBR-II, the engineering-scale v-blender that is currently installed

in HFEF is considered to be the production unit. Additional engineering-scale tests out-of-cell with surrogate salts are planned in the near future to provide final process qualification data.

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