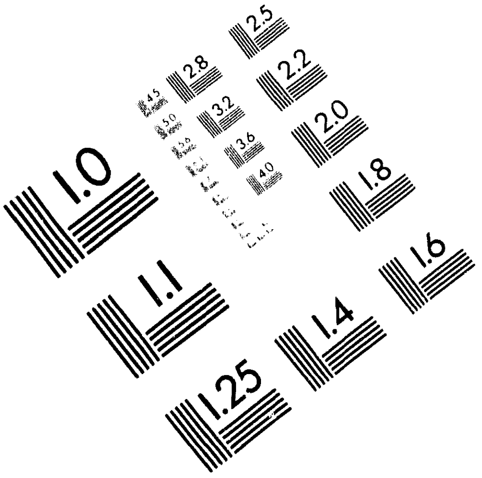
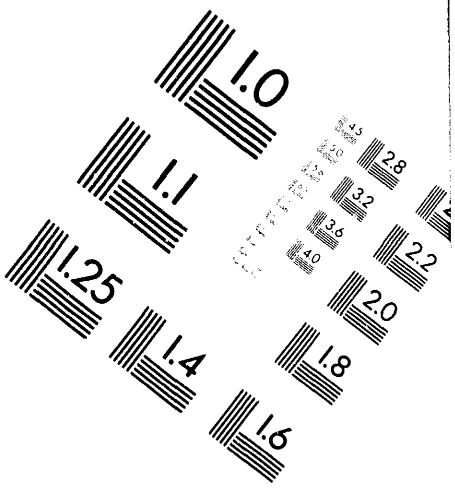


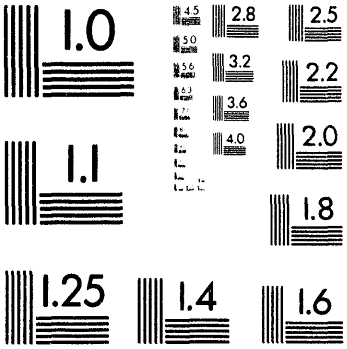
AIIM

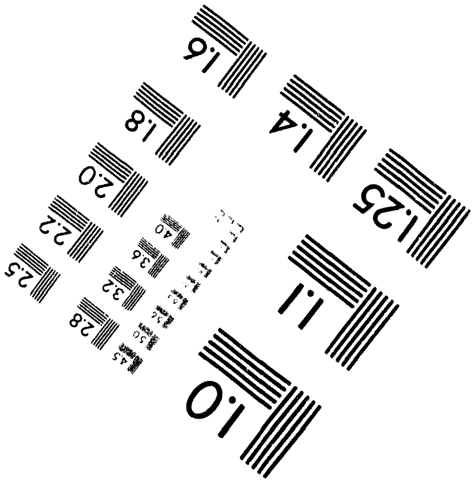
Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910

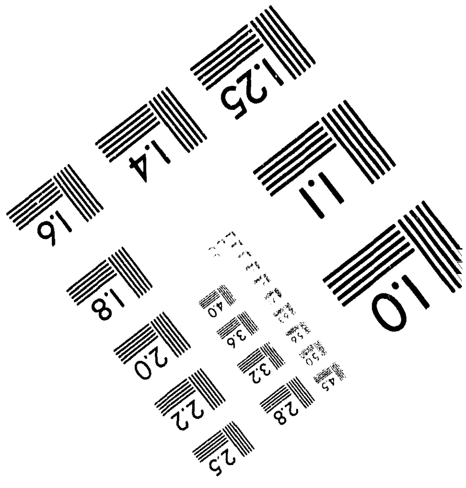
301/587-8202







MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.



1 of 1

ANL/CMT/CP--80022
Conf-940204--6

DEFINING A METAL-BASED WASTE FORM FOR IFR PYROPROCESSING WASTES*

S. M. McDeavitt, J. Y. Park, and J. P. Ackerman

Argonne National Laboratory
Chemical Technology Division
9700 South Cass Avenue
Argonne, Illinois 60439-4837

To be presented at

The International Symposium on Actinides:
Processing & Materials
1994 TMS Annual Meeting
San Francisco, CA

February 27-March 3, 1994

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

---

*Work supported by the U.S. Department of Energy, Nuclear Energy Research & Development Program, under Contract W-31-109-Eng-38.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DEFINING A METAL-BASED WASTE FORM FOR IFR PYROPROCESSING WASTES

S. M. McDeavitt, J. Y. Park, and J. P. Ackerman

Argonne National Laboratory
Chemical Technology Division
9700 S. Cass Ave.
Argonne, IL 60439-4837

Abstract

Pyrochemical electrorefining to recover actinides from metal nuclear fuel is a key element of the Integral Fast Reactor (IFR) fuel cycle. The process separates the radioactive fission products from the long-lived actinides in a molten LiCl-KCl salt, and it generates a lower waste volume with significantly less long-term toxicity as compared to spent nuclear fuel. The process waste forms include a mineral-based waste form that will contain fission products removed from an electrolyte salt and a metal-based waste form that will contain metallic fission products and the fuel cladding and process materials. Two concepts for the metal-based waste form are being investigated: (1) encapsulating the metal constituents in a Cu-Al alloy and (2) alloying the metal constituents into a uniform stainless steel-based waste form. Results are given from our recent studies of these two concepts.

Introduction

The Integral Fast Reactor (IFR) system being demonstrated by Argonne National Laboratory includes a metal-fueled advanced liquid metal reactor (ALMR) with the associated fuel cycle and waste management capabilities located at one "integral" facility [1] or at a centralized location serving several ALMRs. The ALMR design for the IFR system is based on over 30 years of operating experience with metal nuclear fuels at the Experimental Breeder Reactor II (EBR-II). Metal fuel helps confer important safety advantages on the IFR [1]. It is also highly compatible with pyrochemical processing, which involves electrorefining of the spent fuel in a molten salt electrolyte. Pyroprocessing results in a compact, economical fuel cycle that is highly proliferation resistant; it returns nearly all transuranic (TRU) elements (Pu, Np, Am, and Cm) to the reactor to be used as fuel; and it results in small waste volumes. Because pyroprocessing equipment is compact enough to be combined with a reactor facility, spent fuel need not be transported to an independent reprocessing facility. Recycling and burning the fissionable TRU elements will not only remove the long-lived actinides from the waste stream, but it will also improve the utilization of available resources.

From the onset of IFR pyroprocess development, emphasis has been placed on addressing waste disposal issues to minimize waste volumes; to provide economical, effective waste forms; and to establish a data base to support future waste form acceptance petitions after the IFR system is deployed commercially. Our intent is that the commercial waste generators will only have to demonstrate that their facility or facilities are capable of producing waste forms that meet previously established waste form acceptance specifications. "Waste form" is the designation for radioactive materials and any encapsulating or stabilizing matrix that will then be placed in a "waste package" [2].

Two different waste forms are being developed to contain all the IFR process wastes. They are (1) a mineral-based waste form, described elsewhere [3], that will contain fission products removed from the electrolyte salt by ion exchange onto zeolite beds and (2) a metal-based waste form that will contain metallic fission products and the fuel cladding and process materials (which are primarily stainless steel).

For the metal-based waste form, two concepts are being evaluated to immobilize the waste materials. The first concept involves the encapsulation of the steel materials with the metallic fission products dispersed in the matrix as intermetallic phases or in solution in a Cu-Al alloy. The second concept involves melting and casting the stainless steel cladding and process materials as an alloy matrix which incorporates the metallic fission products into a homogeneous waste form alloy. These metal-based concepts are being evaluated to select one as the primary approach. The present paper defines the IFR metal waste streams, describes the metal-based waste forms, and discusses some preliminary tests with the candidate waste form materials.

Background

IFR Fuel

The fuel alloys to be used in IFR systems are U-10 wt % Zr and U-20 wt % Pu-10 wt % Zr[4]. Uranium-based alloys have been used in the reactor core of EBR-II for over 30 years. Metal fuel pins are fabricated by vacuum casting fuel slugs and placing the slugs in stainless steel cladding. The current reference cladding is HT-9 (ASME S42100), a martensitic stainless steel based upon Fe-12 wt % Cr-1 wt % Mo [5]. A gap between unirradiated fuel and the cladding accommodates fuel swelling. This gap is filled with sodium to provide a thermal bond between the fuel and the cladding. The plenum volume above the fuel accommodates noble gas fission products.

During reactor operation, the actinides undergo fission, introducing a wide variety of fission product elements into the fuel. As the actinides are consumed and fission products build up, the fuel becomes less reactive and must eventually be removed from the reactor. Table I presents estimates for the elemental content in a typical, high-burnup U-Pu-Zr fuel pin (only the most abundant solid fission products are shown) [6]. Concentrations are included for the bond sodium and the HT-9 cladding components that will be processed along with the fuel. Gaseous fission products, such as xenon, are not included because they are released when the pins are chopped for processing and collected in the controlled atmosphere of the processing cell. A typical batch of fuel for pyroprocessing contains about 20 kg of actinides.

The elements in Table I are categorized into groups according to their behavior during electrorefining. The actinide elements are recovered by electrorefining. The rare earth elements (lanthanides), noble metal elements, and other fission products remain in the electrorefiner and eventually enter the waste streams, as discussed below. The rare earth, noble metal, and other significant fission products in Table I only constitute 1.8 wt % (1.5 at %), 1.5 wt % (2.2 at %), and 1.2 wt % (1.0 at %) of the fuel rod, respectively. These values do not include the zirconium from the fuel rod, the bond sodium, or the HT-9 components (Fe, Cr, Mo, Ni, Ti, and Mn).

Table I. Estimated Composition of High Burnup IFR Fuel Pin
(Weight %) [6]

Actinides		Rare Earths		Noble Metals				Other	
U	43.1	La*	0.23	Ti**	0.066	Tc*	0.016	Na	0.69
Np	0.066	Ce*	0.42	Cr**	3.65	Ru*	0.59	Mg	0.003
Pu	12.2	Pr*	0.22	Mn**	0.064	Rh*	0.020	Rb*	0.040
Am	0.087	Nd*	0.66	Fe**	26.2	Pd*	0.41	Cs*	0.75
Cm	0.007	Pm*	0.18	Co**	0.003	Ag*	0.043	Sr*	0.90
		Sm*	0.018	Ni**	0.15	Cd*	0.029	Ba*	0.27
		Eu*	0.024	Mo**	0.91	Sn*	0.002	I*	0.066
		Gd*	0.018	Zr	7.38	Sb*	0.008	Se*	0.006
		Y*	0.051			Te*	0.12		

*Fission product elements.
**HT-9 constituents.

Some actinide nuclides have radiological half-lives up to 10^9 years [7]. This makes the long-term disposal of these elements a challenge. Most of the radioactive fission products, on the other hand, have significantly shorter half-lives than the actinides [7]. Since the actinides are absent from the IFR waste, the long-term toxicity in the IFR waste forms will be significantly less than that of non-reprocessed spent nuclear fuel.

IFR Waste Streams

The current process for electrorefining IFR fuel [6] begins by chopping the spent fuel and its cladding into small pieces that are placed in a basket and submerged in molten LiCl-KCl salt at 500°C (Fig. 1). The bond sodium and the rare earth and active metal fission products are oxidized into the salt as chlorides. The actinides are transferred from the spent fuel by electrotransport. Metallic uranium is collected at a solid cathode, whereas the TRU elements and some uranium are deposited in a liquid cadmium cathode. Some rare earths are also present in the TRU + U product, which will be returned to the reactor as recycled fuel. The noble metal elements do not form chlorides under the process conditions; they remain in the basket or fall into the process vessel as metallic particulates.

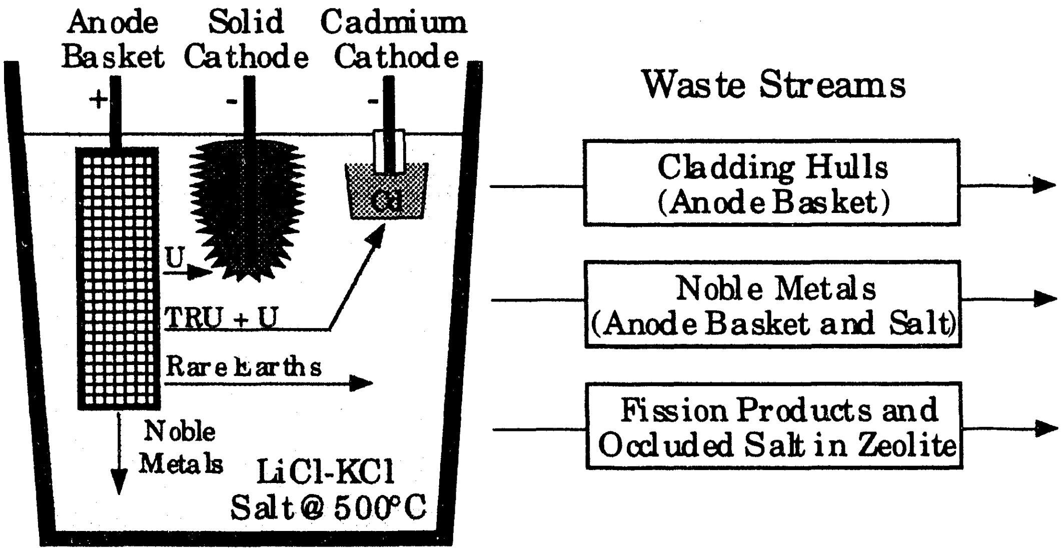


Figure 1. Schematic Diagram of IFR Electrorefiner and Waste Streams

After many batches of spent fuel have been processed, the accumulated fission product wastes in the process vessel will be removed. There are three waste streams that will originate in the pyroprocess, as indicated in Fig. 1. These waste streams are the cladding hulls from the anode basket; the insoluble noble metal fission products, which will be removed by filtering the salt; and the fission product ions, which will be collected on a zeolite bed by ion exchange. The cladding hulls and noble metal fission products will be incorporated in the metal-based waste form. The fission product chlorides together with some occluded salt will be immobilized in the mineral-based waste form [3]. Only the small fraction of the process salt that is entrained in the zeolite will be disposed as waste. Two methods are being evaluated for dealing with the rare earth chlorides in the process salt. In the first, the rare earth chlorides could be removed from the salt through reduction to their respective metals before the salt is filtered through zeolite. This reduction has been demonstrated by adding lithium metal to the salt, and the product metals have been collected in a liquid cadmium solution [6]. Following this step, active fission products such as Cs and Sr would be incorporated in the mineral-based waste form, while the rare earth fission products would be incorporated in the metal-based waste form along with the noble metals and cladding hulls. The second approach avoids reduction of the rare earths; they are removed with the other active metal fission products in the zeolite bed. The first approach would distribute the fission products and their associated decay heat between the two waste forms. However, it would involve an additional step, making the waste treatment process more complex and expensive. The potential benefits of separating the rare earths from the active metals must be balanced against the cost of additional processing, but the primary concern for choosing between the approaches will be the quality of the resulting waste form.

Concepts for Metal-Based Waste Form

Copper-Alloy Waste Form

In this approach, the cladding hulls are encapsulated in a Cu-Al alloy, with the metallic fission products dispersed in the alloy matrix as intermetallic phases or in solution. The encapsulated hulls will not be melted, so that the resulting waste form will be heterogeneous. The noble metal fission products that fall out of the anode basket will be removed from the electrorefiner by extraction using liquid cadmium as a solvent. The rare earth fission products would be reduced from the spent salt and extracted into a cadmium solution, as described above. The noble metal dissolution and the optional rare earth reduction could be carried out simultaneously, placing all the metal fission products into a single solution containing fission products and cadmium.

The cadmium could be distilled from the fission product solution, but the resulting metal ingot would be extremely hot from the concentration of fission product decay heat. Also, distillation of the last fractions of cadmium, as required to avoid forming mixed hazardous waste, requires excessively long times and/or high temperatures. Therefore, instead of distilling the cadmium, the fission products would be extracted from the cadmium by contacting the solution with a molten aluminum or Cu-Al alloy. The solubility of cadmium in aluminum is very low, and the fission products have a much lower activity in aluminum than in cadmium [3]. Therefore, by this process, the fission products would be transferred from cadmium into aluminum or Cu-Al and the cadmium would be distilled and reused. The content of the vessel bottom would be cycled back into the extraction process, thereby avoiding the slow distillation of the last fraction of cadmium. This extraction process is discussed in more detail elsewhere [3].

The Al-Cu-fission product alloy would then be enriched with copper to generate the desired waste form composition, which is being selected. The resulting alloy would be cast as the waste form matrix around the cladding hulls. All processing would be carried out at relatively low temperatures, 600°C to 800°C, in an inert environment.

Steel-Based Waste Form

In this approach, the stainless steel cladding hulls would be melted and consolidated into a dense waste form with the metal fission products dispersed in the alloy. The noble metal particulates in the spent salt would be removed from the salt by using stainless steel filters, and the hulls and filters would be melted together in a high temperature furnace to form a homogeneous alloy waste form. This alloying melt would be carried out under an oxidizing salt flux to oxidize residual uranium or TRU elements that might remain on the hulls. These elements would be removed from the waste stream as chlorides. The salt flux with the uranium and TRU chlorides would then be cycled back into the electrorefiner.

However, if the rare earths were disposed in the metal-based waste form instead of the mineral-based waste form, the noble metal dissolution and rare earth reduction, discussed above for the copper-alloy waste form, would be necessary. The cadmium could then be distilled, leaving a fission product ingot. To avoid handling this ingot, which would be very radioactive and thermally hot, the cadmium could be distilled in the waste-form melting apparatus, and then the steel cladding material could be added to generate the waste form alloy. The cladding hulls would be melted separately under a salt flux to remove actinides from the waste stream, as in the previous scenario. To avoid oxidizing the rare earths, this should be carried out before alloying the steel with the fission products. Because of these complexities, we anticipate that the rare earths will be placed in the mineral-based waste form if the stainless steel waste form is selected.

Two methods for melting cladding hulls to reduce waste volumes have been demonstrated previously for Zircaloy and stainless steel materials [8-12]. The first method, inductoslag melting [8-10], involves induction melting of cladding hulls fed into a water-cooled copper container from above. The melt is under a molten salt flux, and the cast product is continuously drawn from below the furnace. This process was developed at Pacific Northwest Laboratory [8,9], and an industrial-scale process (up to 3 kg) for radioactive materials was built by the Commissariat à l'Energie Atomique (CEA) in France [10]. However, a continuous casting process such as this would have to be modified for IFR use because the fission product concentrations will need to be well controlled. With at least three different feed streams having wide variations in properties, the potential for fission product segregation would be high.

In a second method, induction melting [11,12], the metal was melted in a refractory crucible in an induction furnace and then cast into a mold by passing the melt through a hole in the bottom of the crucible or by tilting the crucible. A facility for the volume reduction of large quantities of low level waste, called the Waste Experimental Reduction Facility (WERF) [12] has been built at the Idaho National Engineering Laboratory (INEL) by EG&G. This facility has successfully consolidated the reactor piping (not fuel cladding) for the decommissioned SPERT III reactor through induction melting and mold casting.

Laboratory-Scale Experiments

Copper-Alloy Waste Form

Copper-aluminum alloys have been prepared with five different compositions (20, 33, 40, 55, and 60 wt % Cu) to provide samples for corrosion tests and information for selecting an optimum alloy composition. The alloys were generated by mixing pure aluminum and copper with commercial master alloys of 33.2 wt % Cu (Heat No. 7U681), 52.6 wt % Cu (Heat No. 7U635), and 50.4 wt % Cu (Heat No. 7U32).[1] The mixtures were melted at 700°C in a controlled argon environment, followed by a remelting step in a vacuum furnace at 900°C. The castings were made in cylindrical alumina crucibles of 2.5 cm diameter.

Upon handling the 55 and 60 wt % Cu alloys, we observed that they were very brittle and easily fractured, making them unacceptable as waste-form matrix materials. The Al-Cu binary phase diagram (Fig. 2) shows that the brittle alloys should be dominated by the intermetallic q-phase (Al_2Cu) and h-phase (AlCu). Because of their brittle nature, these alloys will no longer be considered as waste form candidates. The other prepared alloys showed more fracture resistance and span the two-phase field, q + Al(Cu), which has a eutectic at 33 wt % Cu. Also, alloys having very high (>70 wt %) copper content, aluminum bronzes, are expected to show superior corrosion resistance, so investigations of these alloys have recently begun.

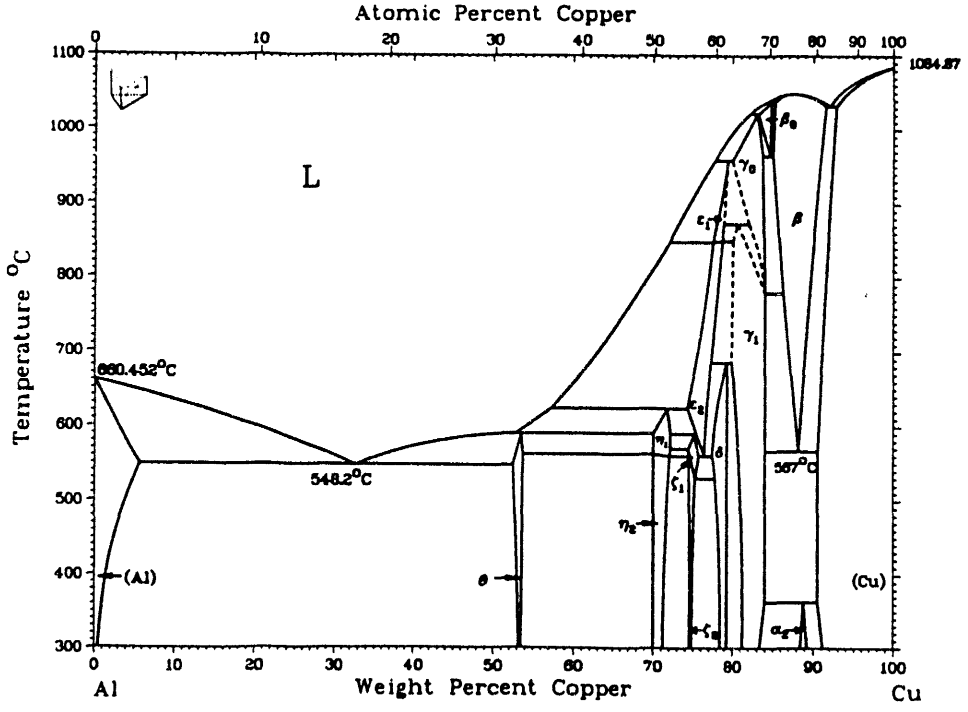


Figure 2. Aluminum-Copper Phase Diagram [13]

---

[1] Courtesy of KB Alloys, Inc.

Alloy castings with 1.9 wt % Ce were prepared for the three remaining alloy compositions (20, 33, 40 wt % Cu). The added cerium simulated the presence of rare earth fission products in the matrix. Figures 3 and 4 show scanning electron micrographs of horizontal cross sections from the 1.9 wt % Ce-32.6 wt % Cu-Al alloy at 45 mm and 3 mm from the bottom of the ingot, respectively. The laminar eutectic structure is evident in the matrix for both micrographs, where the area in light contrast corresponds to copper-rich phase, and the dark area corresponds to aluminum-rich phase.

The large features in Fig. 4 are intermetallic Ce-Cu-Al precipitates which have settled to the bottom of the ingot. The cerium concentration near the top of the ingot (Fig. 3) was estimated to be less than 1 wt %, whereas the average cerium concentration near the bottom (Fig. 4) was estimated to be 5 wt %. These estimated were based on results from energy dispersive X-ray analysis. These microstructures indicate that the rare earth fission products will most likely form discrete intermetallic phases in this alloy system. The gravitational phase segregation of the intermetallic particles evident from Figs. 3 and 4 would not be tolerable in the final waste form.

Steel-Based Waste Form

Using the information from Table I, the reference composition for the laboratory-scale steel-based waste form was defined to be 12.5 wt % Zr; 7.5 wt % rare earths (3 % Nd, 2 % Ce, 1 % La, 1 % Pr, and 0.5 % Y); 5.0 wt % noble metals (2 % Ru, 1.5 % Pd, 1 % Te, and 0.5 % Ag); with the balance being HT-9. In the event that the rare earth fission products are not to be included in the metal-based waste form, the reference composition would be 12.5 wt % Zr and 5.0 wt % noble metals in HT-9. The most abundant and readily available metals were selected, with the exception of the noble metal, rhodium, which was excluded because of its high cost. Only pure, unirradiated metals were used to represent the chemical behavior of the waste materials and simulate the waste form. Half of the zirconium expected from the fuel pin is currently included in the reference composition, but work is underway to develop methods to recycle most of the zirconium with the actinides.)

Several small samples (Table II), typically ~20 g, were prepared and melted under helium at ~0.2 atm in a high temperature furnace, and the small ingots were rapidly cooled, but not quenched. Sample HT9-1 consisted of HT-9 tubing alone, which was melted at 1800°C in a zirconia (ZrO_2) crucible. After the cast ingot was sectioned, a portion of HT9-1 was annealed at 600°C for six hours. The corrosion resistance of the as-cast and annealed samples was tested along with several other alloys, as discussed later. Samples HT9-2 to HT9-4 were alloys with zirconium to survey the effect of including 100 % (HT9-2) or ~50 % (HT9-3 and HT9-4) of the zirconium from an IFR fuel pin in the metal waste stream. Because of an interaction between molten zirconium and ZrO_2 and because of the relative stability of the rare earth oxides, yttria (Y_2O_3) crucibles were used whenever zirconium and rare earths were melted. Sample HT9-5 included rare earths and sample HT9-6 included rare earths and noble metals. Melt temperatures for all samples are given in Table II.

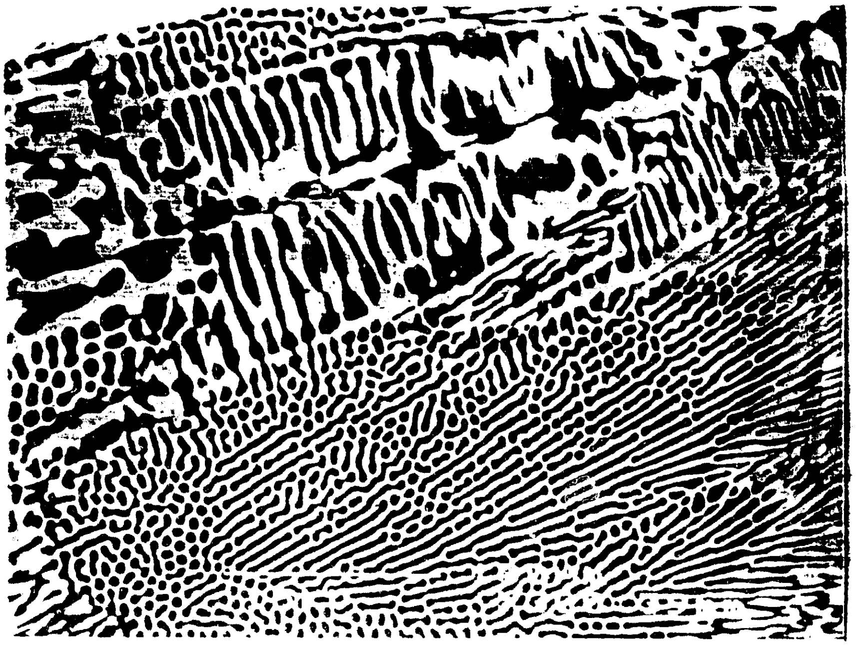


Figure 3. Scanning Electron Micrograph of the 1.9 wt % Ce-32.6 wt % Cu-Al Sample 45 mm from the Bottom of the Ingot

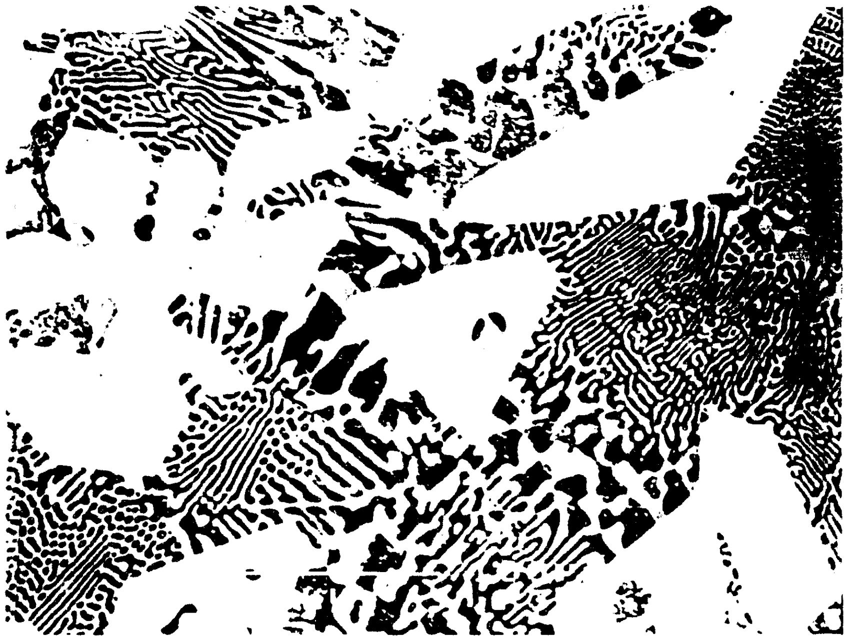


Figure 4. Scanning Electron Micrograph of the 1.9 wt % Ce-32.6 wt % Cu-Al Sample 3 mm from the Bottom of the Ingot

Table II. Composition of Steel-Based Waste Form Experiments
(wt %)

Sample Number	Melt Temp. (°C)	HT-9	Zirconium	Rare Earths*	Noble Metals**
HT9-1	1850	100.0	•	•	•
HT9-2	1900	76.0	24.0	•	•
HT9-3	1900	86.5	13.5	•	•
HT9-4	1800	87.5	12.5	•	•
HT9-5	1800	80.5	12.5	7.0	•
HT9-6	1800	75.0	12.5	7.5	5.0

*3% Nd, 2% Ce, 1% La, 1% Pr, and 0.5% Y.
**2% Ru, 1.5% Pd, 1% Te, and 0.5% Ag.

The samples HT9-2 through HT9-4 exhibited differences that can be explained by considering the Fe-Zr phase diagram (Fig. 5). This system forms a eutectic between Fe and Fe_3Zr at ~14 wt % Zr. Specimen HT9-2 was Zr-rich (~10 wt % above the eutectic composition), so precipitation of Fe_3Zr would be expected, whereas specimen HT9-4 was relatively near to the eutectic composition, so precipitation would be limited upon rapid cooling. As expected, an array of dendritic, Zr-rich features was evident throughout HT9-2, as indicated by the light-colored phases in Fig. 6. Energy dispersive X-ray (EDX) analysis revealed that the dendritic phase was approximately 61 wt % (70 at. %) Fe-34 wt % (24 at. %) Zr-5 wt % (6 at. %) Cr, which correlates well with the expectation of Fe_3Zr.

In contrast to the Zr-rich sample, HT9-4 lacked gross Zr-rich structural features, with the exception of small zirconium precipitates. The precipitates contained no iron, chromium, or other elements and were probably formed because the zirconium gettered impurities from the alloy matrix. The laminar steel microstructure, which is also evident in the matrix of HT9-2 in Fig. 6, was dominant, and most of the zirconium was in the alloy matrix (not in the precipitates). The zirconium from the fuel will, therefore, affect the waste form microstructure through the formation of the Fe_3Zr intermetallic compound, especially if none of the zirconium is recycled and the waste form is zirconium-rich.

The last two survey specimens, HT9-5 and HT9-6, included additions of the simulated fission products. Because the metals used to produce the reference alloy are highly reactive, they were handled in a glovebox. The reactive metals were combined as powders or small pieces of metal and sealed in HT-9 capsules to be transferred from the glovebox to the furnace. The capsules were placed into Y_2O_3 crucibles with the inert alloying additions, Zr and Ag, and melted.

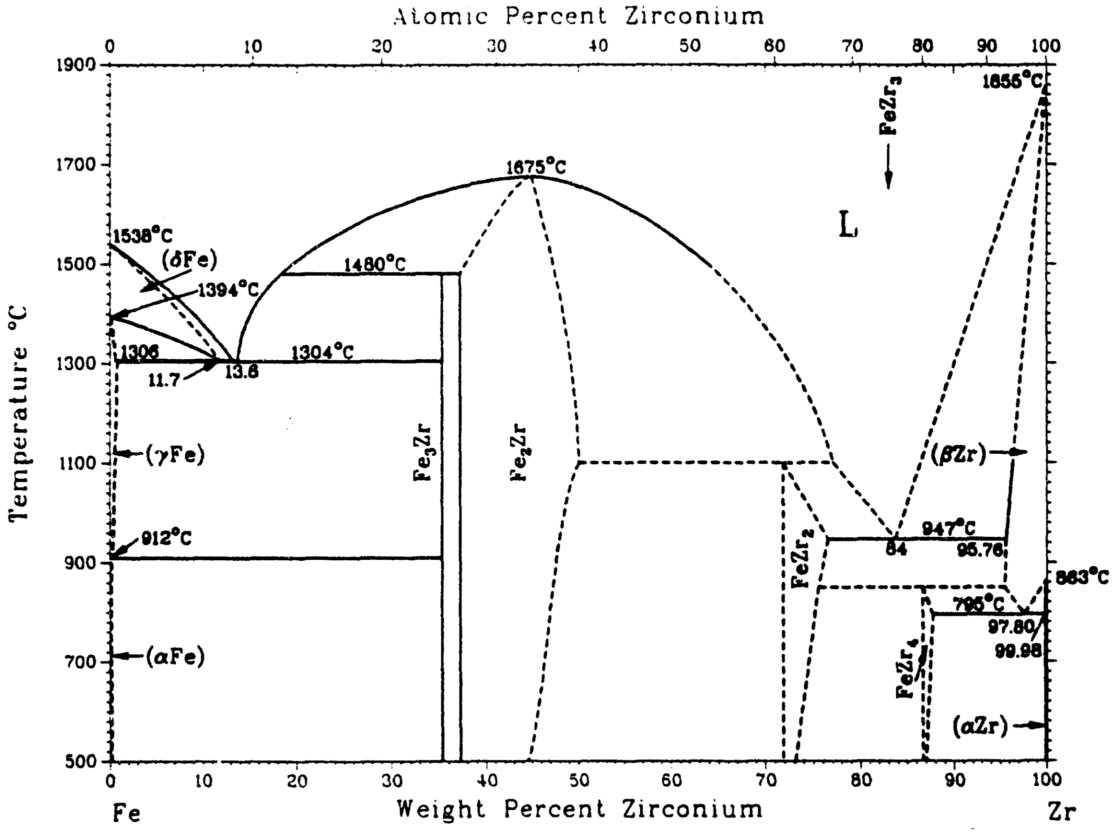


Figure 5. Iron-Zirconium Phase Diagram [14].

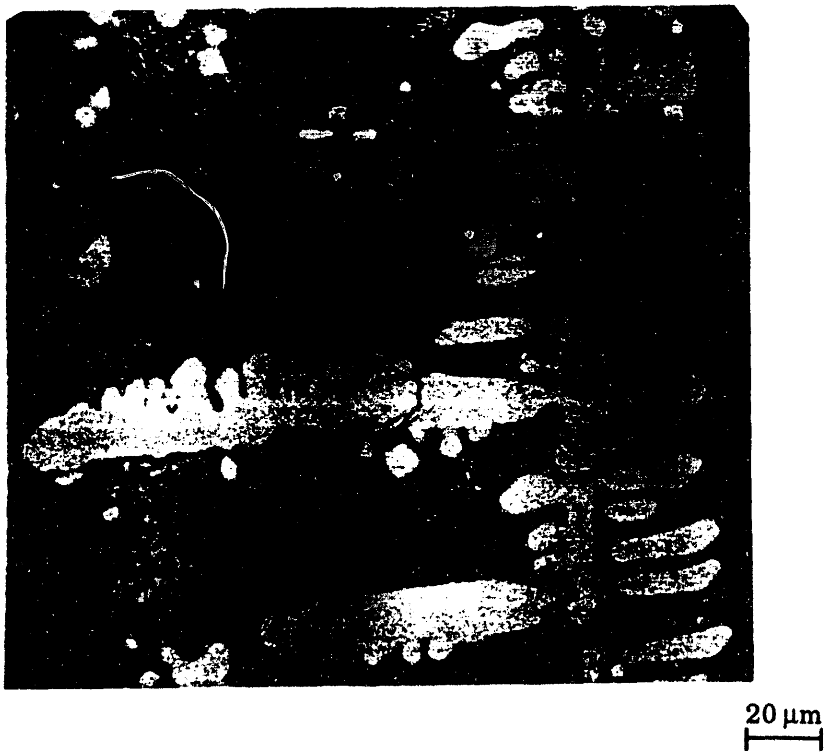


Figure 6. Scanning Electron Micrograph Showing Dendritic Fe3Zr Phase in the HT-9 Matrix (backscattered electron image)

The microstructure of both samples was characterized by a laminar, two-phase steel structure with uniformly dispersed globular phases on the order of 5 to 30 µm in diameter, as shown for sample HT9-6 in Fig. 7. The lamellae in these samples were slightly larger than those in the zirconium alloys, as may be seen by comparing Figs. 6 and 7. For HT9-5, the globular phases were irregularly shaped, whereas for HT9-6, the globular phases were typically round, as seen in Fig. 7.

The globules were analyzed by EDX methods and found to contain the rare earth elements, some zirconium and iron, and, in HT9-6, some of the noble metal elements (notably Ag and Pd). The steel matrix was devoid of the rare earth and noble metals alloying components, with the exception of trace amounts of ruthenium detected in the matrix of HT9-6. These results indicate that many of the metal fission products will form dispersed precipitates in the steel-based waste form.

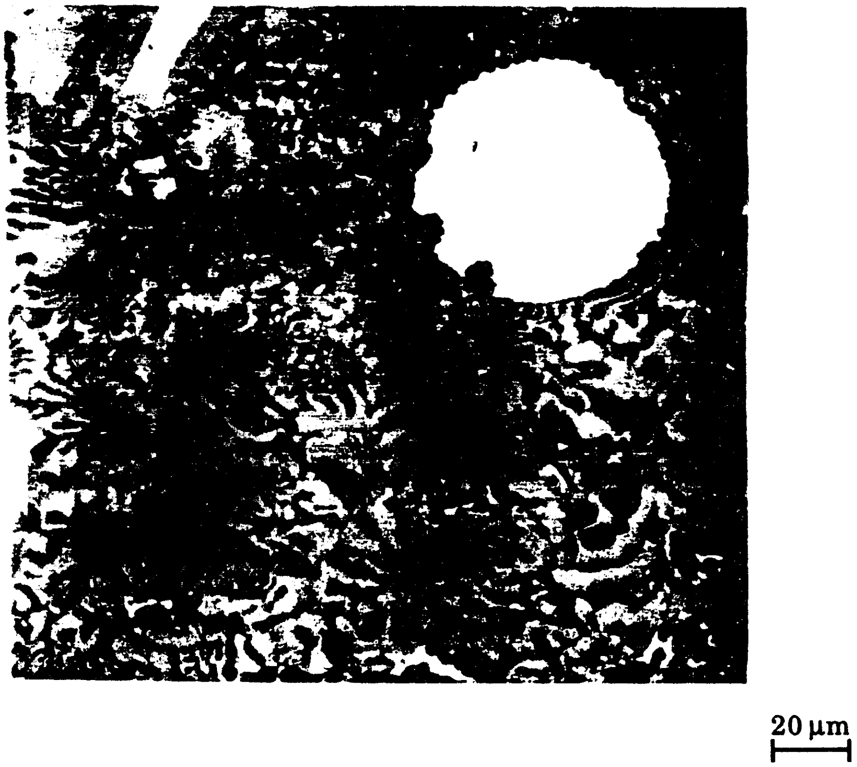


Figure 7. Scanning Electron Micrograph Showing HT9-6 (backscattered electron image)

Corrosion Tests

General corrosion tests were completed to survey the behavior of the copper and stainless steel alloys. Round disk specimens, 15.9 mm in diameter and 3 mm thick, were fabricated from the experimental materials. The initial materials tested include three 32.6 wt % Cu-1.9 wt % Ce-Al samples, one 33 wt % Cu-Al sample, and the as-cast and annealed HT-9 stainless steel samples described above. The specimens were polished, cleaned, and immersed in simulated J-13 well water at 363 K (90°C) at 1 atm for 28 days. The J-13 well water is representative of the groundwater at the Yucca

Mountain site in Nevada, which is a proposed location for a high-level nuclear waste repository [15]. A typical ion composition (units of mg/L) of J-13 well water is 11.5 Ca, 1.76 Mg, 45.0 Na, 5.3 K, 0.06 Li, 0.04 Fe, 0.001 Mn, 0.03 Al, 30.0 Si, 2.1 F^-, 6.4 Cl^-, 18.1 SO_4^{2-}, 10.1 NO_3^-, 143.0 HCO_3^-, and 5.7 dissolved oxygen [15].

The MCC-1 Static Leach Test Method [16] was used as a guide for the corrosion tests. The specimens were ultrasonically cleaned with ethanol and immersed in the test solution in a 60-mL Teflon vessel, which was sealed and placed in an oven maintained at 90°C. The ratio of specimen surface area to test solution volume was constant at 0.1 cm^{-1}. After 28 days, the vessels were cooled to room temperature, and the specimens were removed, rinsed with distilled water and ethanol, dried, and examined with a scanning electron microscope.

Qualitatively different corrosion behaviors were observable for different specimens. The 33 wt % Cu-Al specimen had a relatively smooth and uniform corrosion surface layer, whereas the 33 wt % Cu-Al-Ce specimens had a rough surface, primarily due to differential corrosion between the Ce-Cu-Al precipitates and the eutectic Cu-Al matrix of the material. Neither the as-cast nor annealed HT-9 stainless steel specimens had evidence of appreciable corrosion, with the exception of some localized corrosion surrounding a pre-existing cavity on one face of the annealed specimen. This cavity was part of a pipe cavity formed during casting. The results are qualitative and preliminary, but they validate the expectation that the Cu-Al alloy is less resistant to corrosion in an aqueous environment than HT-9 stainless steel. A more detailed discussion of the corrosion test results is forthcoming, after further testing is completed.

Summary

Two metal-based waste form concepts are being evaluated for the immobilization and disposal of metal IFR process wastes. These are a copper-alloy waste form and a steel-based waste form. Corrosion tests and other laboratory experiments are being conducted to provide a basis for the selection of one concept as the primary waste form candidate. The present observations provide guidance and baseline information for the further evaluation of the waste form concepts.

For the copper-alloy waste form, several Cu-Al alloys were fabricated, and we observed that the intermetallic q-phase (Al_2Cu) was too brittle to be used as a waste form matrix. When cerium was added to simulate the behavior of the rare earth fission products in the Cu-Al system, intermetallic phases on the order of 100 μm in size were formed, and they became segregated in the alloy matrix by settling. For the steel-based waste form, six samples were fabricated to survey the microstructural consequences of incorporating various metal waste constituents in this waste form. The addition of rare earths to HT-9 stainless steel also produced secondary phase precipitates, which were 5 to 30 μm in size. Precipitates such as these would concentrate fission products into discrete heat sources and would not disperse heat throughout the alloy in solid solution. This finding provides further motivation to consider incorporating the rare earth elements in the mineral-based waste form instead of the metal-based waste form.

The results of the static corrosion test verified that the HT-9 steel alloy is more resistant to corrosion than the Cu-Al alloy in a simulated groundwater at 90°C. It has yet to be established whether the corrosion rate of the Cu-Al alloy would be acceptable for the metal-based waste form. For the next level of corrosion testing, the corrosion rates and the corresponding fission product release rates must be evaluated for the candidate waste form alloys.

Acknowledgments

The authors would like to acknowledge T. R. Johnson and A. Newman for their insights in fission product extraction. This work was supported by the U.S. Department of Energy, Nuclear Energy Research & Development Program, under contract W-31-109-Eng-38.

References

1. C. E. Till, "Looking to the Future with the IFR," Nuclear Engineering International, 30 (1985), 20.

2. "Standard Practice for Prediction of the Long-Term Behavior of Waste Package Materials Including Waste Forms Used in the Geologic Disposal of High-Level Nuclear Waste" (Philadelphia: American Society for Testing and Materials Standard, C 1174-91, 1991).

3. J. P. Ackerman, T. R. Johnson, and J. J. Laidler, "Waste Removal in Pyrochemical Fuel Processing for the Integral Fast Reactor" (this proceedings).

4. G. L. Hofman et al., "Swelling Behavior of U-Pu-Zr Fuel," Metallurgical Transactions A, 21A (1990), 517.

5. L. Leibowitz and R. A. Blomquist, "Thermal Conductivity and Thermal Expansion of Stainless Steels D9 and HT9," International Journal of Thermophysics, 9 (5) (1988), 873.

6. J. P. Ackerman, "Chemical Basis for Pyrochemical Reprocessing of Nuclear Fuel," Ind. Eng. Chem. Res., 30 (1) (1991), 29.

7. Chart of the Nuclides, 13th ed., (Knolls Atomic Power Laboratory, 1983).

8. R. G. Nelson, M. P. Schlienger, and E. V. Tiesenhausen, "Selection of a Melting Furnace for Consolidation of Nuclear Fuel Hulls" (Pacific Northwest Laboratory Report BNWL-1968, 1976).

9. R. G. Nelson and D. R. Montgomery, "The Cladding Hull Decontamination and Densification Process" (Pacific Northwest Laboratory Report PNL-3166, 1980).

10. N. Jacquet-Francillon et al., "Hull Melting" (Third International Conference on Nuclear Fuel Reprocessing and Waste Management: RECOD '91 Proceedings, vol. 2, Sendai, Japan, 1991), 909.

11. D. R. Montgomery, "Consolidation of Simulated Nuclear Metallic Waste by Vacuum Coreless Induction Melting" (Pacific Northwest Laboratory Report PNL-5254, 1984).

12. M. M. Larsen, J. N. Davis, and J. A. Logan, "Sizing and Melting Development Activities Using Contaminated Metal at the Waste Experimental Reduction Facility" (Idaho National Engineering Laboratory Report EGG-2411, 1985).

13. T. B. Massalski, ed., Binary Alloy Phase Diagrams, vol. 1 (Metals Park, OH: American Society for Metals, 1986), 106.

14. T. B. Massalski, ed., Binary Alloy Phase Diagrams, vol. 2 (Metals Park, OH: American Society for Metals, 1986), 1129.

15. J. Y. Park, W. J. Shack, and D. R. Diercks, "Crack Growth Behavior of Candidate Waste Container Materials in Simulated Underground Water," Application of Accelerated Corrosion Tests to Service Life Prediction of Materials, Eds. G. Cragnolino and N. Sridar, (Philadelphia: American Society for Testing and Materials, ASTM STP 1194, 1993).

16. "MCC–1P Static Leach Test Method" (Materials Characterization Center, Pacific Northwest Laboratory, 1985).

DATE FILMED

6/22/94

END