ANL/TD/CP-93948
CONF-971004--9

HOT STARTUP EXPERIENCE WITH ELECTROMETALLURGICAL TREATMENT OF SPENT NUCLEAR FUEL

by

R. W. Benedict, M. J. Lineberry, H. F. McFarlane, and R. H. Rigg

Technology Development Division
Engineering Division
Argonne National Laboratory-West
P. O. Box 2528
Idaho Falls, ID 83403-2528

To be Presented
at
Global '97
International Conference on Future Nuclear Systems
October 5-10, 1997
Yokohama, Japan

*Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology, and the Office of Environmental Management, under contract W-1-109-Eng-38.

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R. W. Benedict, M. J. Lineberry, H. F. McFarlane, R. H. Rigg
Argonne National Laboratory - West
P.O. Box 2528
Idaho Falls, ID 83403-2528 USA
Tel: 208-533-7166 Fax: 208-533-7655 E-mail: robert.benedict@anl.gov

ABSTRACT

The treatment of spent metal fuel from the EBR-II fast reactor commenced in June of 1996 at the Fuel Conditioning Facility on the Argonne-West site in Idaho, USA. During the first year of hot operations, 20 fuel assemblies entered processing and 6 low enrichment uranium product ingots were produced. Results are presented for the various process steps with decontamination factors achieved and equipment operational history reported.

I. BACKGROUND

For approximately 10 years, Argonne National Laboratory worked on developing a fast reactor fuel cycle based on dry processing.[1] When the U.S. fast reactor program was canceled in 1994, the fuel processing technology, called the electrometallurgical technique, was adapted for treating unstable spent nuclear fuel for disposal. While this technique, which involves electrorefining fuel in a molten salt bath, is being developed for several different fuel categories, its initial application is for sodium-bonded metallic spent fuel. In June 1996, the Department of Energy (DOE) approved a hot demonstration program in which 100 spent driver assemblies and 25 spent blanket assemblies from the Experimental Breeder Reactor-II will be treated over a three year period. This demonstration will provide data that address issues in the National Research Council's evaluation[2] of the technology. The planned operations will neutralize the reactive components (elemental sodium) in the fuel and produce a low enriched uranium product, a ceramic waste and a metal waste. The fission products and transuranium elements, which accumulate in the electrorefining salt, will be stabilized in the glass-bonded ceramic waste form. The stainless steel cladding hulls, noble metal fission products, and insoluble residues from the process will be stabilized in a stainless steel/zirconium alloy. Upon completion of a successful demonstration and additional environmental evaluation, the current plans are to process the remainder of the DOE sodium bonded fuel.

The fuel treatment demonstration will utilize the Fuel Conditioning Facility (FCF). The process steps are shown in Figure 1 and include fuel assembly dismantling, element chopping, electrorefining, cathode processing, casting and waste processes. Fuel assembly dismantling removes the individual stainless steel clad elements from the assembly hardware. These elements are sheared at the element chopper into fuel segments which contain the metal fuel. The driver elements (~4.1 kg uranium per assembly) are sheared with a small existing chopper while a larger blanket element chopper will be installed for the larger diameter blanket elements (~47 kg uranium per assembly).

The driver segments will be placed in anode baskets that are placed in the MK-IV Electrorefiner. This electrorefiner[3,4] has a 1 m diameter vessel with a 10 cm layer of molten cadmium and a 30 cm layer of molten salt held at 450-500°C. The electrorefiner has four ports for two anodes and two cathodes which can process two 10 kg loads of uranium, simultaneously. For blanket fuel treatment, which will demonstrate higher throughput, a second (MK-V) electrorefiner will be installed in FCF in late 1997. It has an identical vessel with four ports; however, each port has a concentric anode cathode module that holds 37 kg loads of uranium. The four anode-cathode modules (total of 150 kg uranium) can be processed simultaneously. The process principles of electrorefining are the same in both electrorefiners and have been described previously.[5]

After electrorefining, the cathode products are transferred to the cathode processor, an induction-heated vacuum distillation furnace. The residual salt and cadmium are removed from the uranium and recycled to the electrorefiner. The consolidated uranium product is transferred to the casting furnace. This furnace is also an induction-heated device using a yttria coated graphite crucible. The uranium product is mixed with depleted uranium to produce a homogeneous low enriched uranium product (< 20% ^{235}U). Samples for chemical analysis are taken by injection casting while the product is molten at 1500°C.

A metal waste form is produced from the stainless steel cladding hulls which are removed from the electrorefiner and processed through the cathode processor and casting furnace. The process steps are very similar to the uranium cathode process steps except a pure yttria crucible is used in the casting furnace. The cladding hulls are mixed with 15% zirconium to make the waste form.[6,7] For production operations, a new casting furnace would be required to handle the higher throughputs.

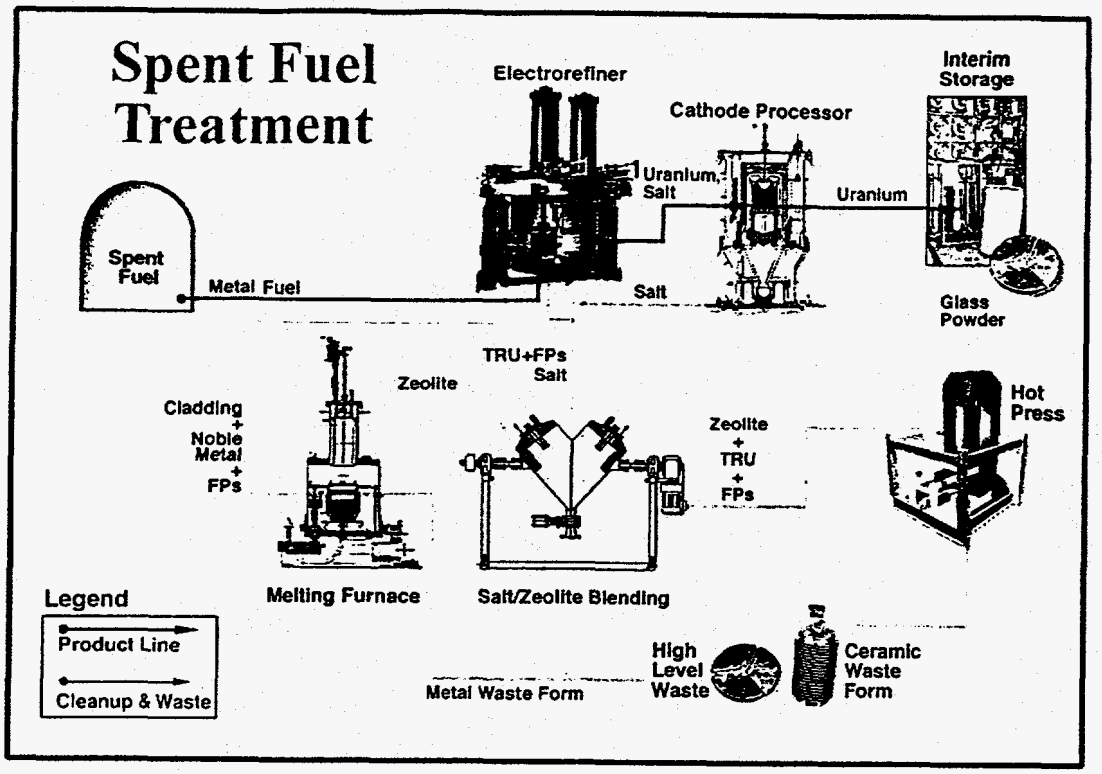

Figure 1. EBR-II Spent Fuel Treatment Process Steps

The majority of the fission products and transuranic elements will accumulate in electrorefiner salt. A major demonstration objective is to show that these fission products can be incorporated into a stable waste form that is suitable for a geologic waste repository. A portion of the fission product and transuranic elements will be incorporated into the ceramic waste which has been developed by Argonne.[8] In the demonstration, the electrorefiner salt will be mixed with zeolite powder in a hot mixer. This mixer is a V-blender that can operate up to 600°C. After the salt is absorbed into the zeolite, glass materials will be mixed with the zeolite. This powder mixture will be loaded into waste cans that are evacuated and seal welded. The cans are transferred to a hot isostatic press which is capable of operation up to $2x10^8$ N/m^2 and 900°C. These processes convert the material to a ceramic monolith which will be characterized for waste performance.

II. PROCESS RESULTS

The main process steps (element chopping, electrorefining, cathode processing and casting) have been operating in FCF since June 1995. Initially, depleted uranium and cast depleted uranium-zirconium alloy were used to test the process equipment. In addition, a metal waste casting has been completed in the hot cells and initial testing has been completed on the demonstration ceramic waste form. This section summarizes the process experiences to date.

A. Electrorefining Experience

The Electrorefiner has processed 59 kg depleted uranium, 28 kg uranium-zirconium alloy and 82 kg irradiated driver fuel. The unirradiated runs produced thirty-one cathodes and showed similar performance to engineering-scale glovebox operations in Illinois. With irradiated operations, the electrorefiner experiments have been studying the effects of fission product carryover at different operating voltages and deposition modes. The two primary deposition modes are direct transport and deposition. In direct transport, the uranium is directly electrotransported from the fuel dissolution baskets to the cathode. For deposition mode, the uranium is electrotransported to the cadmium pool and then transferred to the cathode. A third operating mode combines these two modes in one experiment. Table 1 shows some of the primary process conditions that have been investigated and the resulting cathode weights.

A difficulty in interpreting the results is that the composition of the product has to be calculated from the composition of the casting product. Table 2 shows the decontamination factors for the cathodes that have been processed, sampled and analyzed. Decontamination factor is defined as the concentration of the element in the irradiated uranium divided by the concentration of the same element in the uranium metal in the cathode product. Although these results are very preliminary, several observations can be made. The active metals (Cs)

Table I. Electrorefiner Process Parameters for Irradiated Cathode Summary

Cathode #	Date	Transport Mode	Ave. Volts	Weight kg	Collection Eff.%
32	June 96	Direct	1.09	7.9	61
39	Nov. 96	Direct	1.19	7.3	65
43	Feb. 97	Direct	0.66	8.0	70
45	Mar. 97	Direct	0.28	7.5	60
36	Sep. 96	Deposition	0.67	11.5	42
38	Oct. 96	Deposition	0.62	3.8	78
42	Jan. 97	Deposition	0.39	4.6	45
46	Apr. 97	Deposition	0.38	6.2	77
37	Oct. 96	Direct/Dep.	1.16/0.49	6.5	43
40	Dec. 96	Direct/Dep	1.21/0.53	7.8	45
41	Jan. 97	Dep./Direct	0.55/0.93	8.1	56

Table II. Cathode Ingot Decontamination Factors[9]

CP Ingot	1	2	3	4	5	6
Cathode(s)	33 & 34	36	35, 37, & 38	39	40	41
Transport	DT/DP & DP	DP	DP/DT/DP &DP	DT	DT/DP	DP/DT
Mn54	3000	500	800	300	400	500
Co60	NA	NA	18,300	7,000	7,500	3,700
Nb95	100	10	2	1	1	1
Zr95	100	20	20	10	10	50
Ru106	1,400	126,200	100	20	20	30
Sb125	1,800	127,300	100	30	20	40
Cs134	31,300	NA	NA	NA	NA	NA
Cs137	44,600	3,274,100	319,200	480,200	352,500	71,500
Cd144	31,000	481,600	181,000	862,300	NA	25,200
Eu155	54,300	332,200	NA	NA	NA	10,600
Pu239	4,000	2,600	NA	600	300	500

DT = Direct Transport from anode to cathode
DP = Transport from anode to Cd pool followed by transport to cathode

and rare earths (Eu & Ce) have very high decontamination factors. The noble metals appear to have an entrainment mechanism which cannot be explained by simple thermodynamics. The zirconium transport does appear to be influenced by electrorefiner voltages. However, the results are not yet available for the runs that investigated this phenomenon in a more controlled manner.

B. Cathode Processing/Casting

Seven batches of cathodes from depleted uranium, four batches of cathodes from depleted uranium-zirconium and nine batches from irradiated fuel have been processed through the cathode processor and casting furnace. The eleven nonirradiated runs showed that complete salt distillation could be achieved by operating the cathode processor at 1200°C and 1 torr pressure. Argonne National Laboratory - East runs demonstrated that yttria coatings on the graphite crucibles could not be used in the presence of salts. After the initial runs, zirconia has been used to coat the process crucible. The irradiated runs have concentrated on the complete removal of the salt at lower temperatures (1150°C) and studying if the fission product salts are being completely removed. The initial results indicate complete removal but additional data are needed as the fission product concentrations increase.

The uranium product purity and the associated radioactive decontamination have been tracked to determine possible materials disposition options. Table 3 shows the low enriched ingot composition including the added depleted uranium. In addition, the ingot radiation dose rates have been measured through the 1.2 cm thick storage container and have varied from less than 10 mSv to more than 600 mSv. Based on gamma spectroscopy, this dose is dominated by the fission product ^{106}Ru and its decay products. This is a decay process dominated by the one year half-life of ^{106}Ru and calculations show that even the hottest ingots will be below 10 mSv within 15 years, so process factors affecting Ru transport and decontamination factors are only relevant for this time period after fuel treatment. The most important process parameter for Ru transport appears to be the electrorefiner cutoff voltage (and thus maximum current and uranium transport rate) in the electrorefiner. Lower allowable voltages or transport from the cadmium pool favor retention of Ru in the electrorefiner or in the cladding hulls and thus lower radiation levels.

C. Waste Processing Experience

Two batches of unirradiated cladding materials and two batches of irradiated cladding materials have been processed through the cathode processor. An operating condition of 1000°C and 1 torr was successful for salt removal from the unirradiated hulls but complete removal was not achieved for the irradiated hulls. Operation at 1100°C has provided complete salt removal. One ingot of unirradiated and one irradiated cladding hull ingot have been cast. The irradiated ingot is currently waiting remote sampling and chemical analysis.

The demonstration scale hot isostatic press has been used to produce 65 samples of non-radioactive simulated waste. The heated V-mixer has been procured and will be tested starting in the Fall of 1997. The ceramic waste process equipment will be tested in a glovebox facility with non-radioactive simulated waste before installation in the hot cells.

III. EQUIPMENT OPERATION HISTORY

The remotely operated equipment required for the four main treatment processes was either already in place from previous missions in fast reactor research, or had completed its development and qualification well before the start of hot operations in June of 1996.

Table III. Low Enriched Uranium Product Composition[9]

Ingot#	U wt.%	Zr wt.%	O ppm	C ppm	Si ppm	Fe ppm	Cr ppm	Ni ppm	Mo ppm	Ru ppm	Ba ppm	Pu ppm
1	99.7	0.21	50	63	210	156	13	ND	ND	ND	ND	1
2	98.3	1.54	30	209	286	123	40	8	ND	ND	17	1
3	99.4	0.53	6	24	187	158	40	55	118	60	ND	ND
4	99.1	0.73	19	25	245	180	40	81	248	134	ND	4
5	99.1	0.75	25	11	260	150	ND	ND	233	ND	ND	7
6	99.6	0.11	12	2437	142	150	ND	ND	133	ND	ND	4

ND = Not Detected

The element chopper is the piece of equipment with the highest duty cycle, making up to 60 individual chops for each of the 122 fuel elements in a batch. The greatest concern from a design viewpoint was the lifetime of the chopping blades, but this has not turned out to be a problem. The current blade material (RDS, a tool steel) is lasting about 40,000 cycles, or nearly half a year at our current processing rate. The mechanical problems have primarily been with replaceable parts such as motors and drive train components in the element feed system, where some items were discontinued by the manufacturer in the eight years since the machine was designed.

The electrorefiner has been at operating temperature since November of 1994, and has not yet experienced any failures in its heaters or heater control circuits. Cadmium does diffuse through the salt layer and accumulate as a vapor deposit on metal surfaces in the gas space. Electrical shorting has caused minor problems when deposits bridge the insulators in the bearing systems for the rotating electrodes. Periodic remote cleaning of the insulators and design changes to minimize condensation of cadmium vapor at these locations have been implemented and minimize these shorts.

The cathode processor is the piece of equipment with the most difficult combination of high operating temperature and moderately high vacuum requirements. The basic induction power circuitry and vacuum sealing features have been trouble free but there have been a few mechanical failures in some of the various pumps in the vacuum system, in particular the turbo- molecular pump. These components were designed from the start to be remotely replaceable, and have been successfully repaired.

The casting furnace has the highest operating temperature and has seen the greatest magnitude of changes in its mission since its installation in cell, but the actual physical changes to components thus far have been minor and implemented without problems. In both this and the cathode processor, the transition from "hands-on" to remote cleaning and recoating of the graphite crucibles between runs has resulted in poorer coating performance and decreased reusability of the crucibles. Work is continuing on incremental improvements and alternative materials are being investigated.

IV. CONCLUSIONS AND FUTURE PLANS

The successful startup and hot operation of the EBR-II Spent Fuel Treatment project has been underway for more than one year. In that time we have started treatment of 20 fuel assemblies and completed processing and analysis of 6 uranium ingots for interim storage. Processing rates are scheduled to double in August 1997. Blanket treatment operations with the new MK-V electrorefiner and blanket element chopper will start in March 1998.

Ceramic waste form production equipment has been procured and is undergoing qualification compatible with a schedule milestone of February 1999 for the start of hot operations. Equipment operation and reliability has been satisfactory thus far, and the demonstration is scheduled for completion in June 1999.

V. ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance provided in the preparation of this paper by B. R. Westphal, R. D. Mariani, D. E. Vaden, K. M. Goff, G. L. Lentz, S. S. Cunningham, P. J. Colborn, and L. J. Christensen. This work was funded by DOE Contract No. W-1-109-ENG-38.

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