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ABSTRACT

As part of the spent fuel treatment program at Argonne National Laboratory, a vacuum distillation process is being employed for the recovery of uranium following an electrorefining process. Distillation of a molten salt electrolyte, primarily consisting of a eutectic mixture of lithium and potassium chlorides with minor amounts of fission product chlorides, from uranium is achieved by a batch operation called cathode processing. Described in this paper are recent developments, both equipment and process-related, at the cathode processor during the treatment of blanket-type spent fuel. For the equipment developments, the installation of a new induction heating coil has produced significant improvements in equipment performance. The process developments include the elimination of a process step and the study of plutonium in the uranium product.

INTRODUCTION

The electrometallurgical treatment of Experimental Breeder Reactor-II (EBR-II) spent nuclear fuel at Argonne National Laboratory comprises a set of operations designed to separate uranium from radioactive fission products and place the fission products into acceptable waste forms [1]. A glass-bonded ceramic waste form and a stainless steel-based metallic waste form are the two types of high-level waste forms being qualified for disposal in a geological repository [2]. The low enriched uranium product is formed into ingots and stored pending a decision by DOE on final disposition. Treatment of the spent fuel is performed in the Fuel Conditioning Facility (FCF), a shielded hot-cell environment located at Argonne National Laboratory in Idaho. The treatment program for EBR-II spent fuel was initiated in June 1996 as a demonstration phase and continues currently on the balance of the spent fuels in a production phase.

Two types of EBR-II spent fuel are being treated at Argonne; driver and blanket. Driver fuel was utilized in the core region of the reactor and contains a highly enriched uranium-zirconium alloy. Blanket fuel consisting of depleted uranium surrounded the driver-core. Following the size reduction or chopping of the two types of fuel, two primary operations are utilized for the recovery of uranium from the spent fuel. The first, electrorefining, dissolves the spent fuel in a LiCl-KCl eutectic salt such that the transport of uranium to a cathode is possible [3-4]. In addition to the LiCl-KCl, other chloride species are present in the electrorefiner salt due to the oxidation of fission products, bond sodium, and actinides present in the spent fuel. Once transported, the uranium is collected from the cathode and further processed by a vacuum distillation operation for the removal of the adhering salts. Distillation of the salt is performed in a batch mode termed cathode processing to produce a consolidated uranium ingot [4-6].

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The cathode processor (Fig. 1) is an induction-heated furnace capable of temperatures to 1400°C and vacuums to less than 0.1 Torr. The furnace region contains a passively cooled induction coil and a graphite furnace liner that acts as the susceptor to heat the process materials. Removal of the chloride salts from the uranium in the cathode processor is accomplished by reducing the internal pressure to less than 1 Torr and heating to 1200°C. Standard batch sizes range from 20 kg to 50 kg depending on the fuel type, driver or blanket, respectively, with a typical salt fraction of 20 wt.%. Following the separation of the molten salts from uranium, the consolidated uranium ingot is further processed in a casting furnace where samples are taken for chemical analyses and isotopic dilution is performed for the driver stream. The dilution of the driver uranium is achieved by the addition of depleted uranium to lower the enrichment to less than 20 wt.%.

The context of this paper is to provide an update of activities associated with the FCF cathode processor based on recent developments. Since operations in FCF for the past few years have been primarily with blanket-type spent fuel, these developments are specifically related to blanket processing. The developments at the cathode processor include improvements for both the equipment and process aspects of the operations and are described in detail below.

EQUIPMENT DEVELOPMENTS

As part of the modifications to the cathode processor equipment for increased throughputs, a new induction heating coil has been designed and installed to increase the heating performance of the cathode processor [6]. Additional modifications to the ancillary cathode processor equipment will increase the capacities of both the process and receiver crucibles [7]. The implementation of these additional modifications is pending the completion of qualification testing. The redesign of the induction coil included three additional coil turns and a reduced insulation package allowing for a smaller coil diameter, see Table I. As expected, the power output for the new coil increased by approximately 25% to 15 kW resulting in the batch run times decreasing by at least 20%. Since production modeling efforts have indicated that the cathode processor operation is a potential bottleneck, the reduced batch time with the new coil will allow for improved productivity at the cathode processor.

Table I. Comparison of Old and New Induction Coil

Parameter	New	Old
Number of Turns	12	9
Coil ID (cm)	53	58
Power Output (kW)	15	12
Batch Run Time (hr)	7	9

Another benefit of the new coil has been a significant increase in distillation rates for salt due to the increased power output. Using the data plotted in Fig. 2, averaged distillation rates can be calculated for the two typical operating regimes (0.2 and 3.0 Torr) of vessel pressure. The measured distillation rates for the new and old coils are given in Table II for the two regimes. The quantity of salt distilled is calculated from the change in mass of the process crucible before and after the cathode processor operation. Distillation time is determined from inflections on the crucible and condenser temperature curves as shown in Fig. 3. Although the start and end points have been inferred from the curves without experimental correlation, comparison of data from batch to batch is nevertheless consistent. The distillation rates are higher at lower vessel pressures due to the enhanced diffusion rates of gas molecules under evacuated conditions.

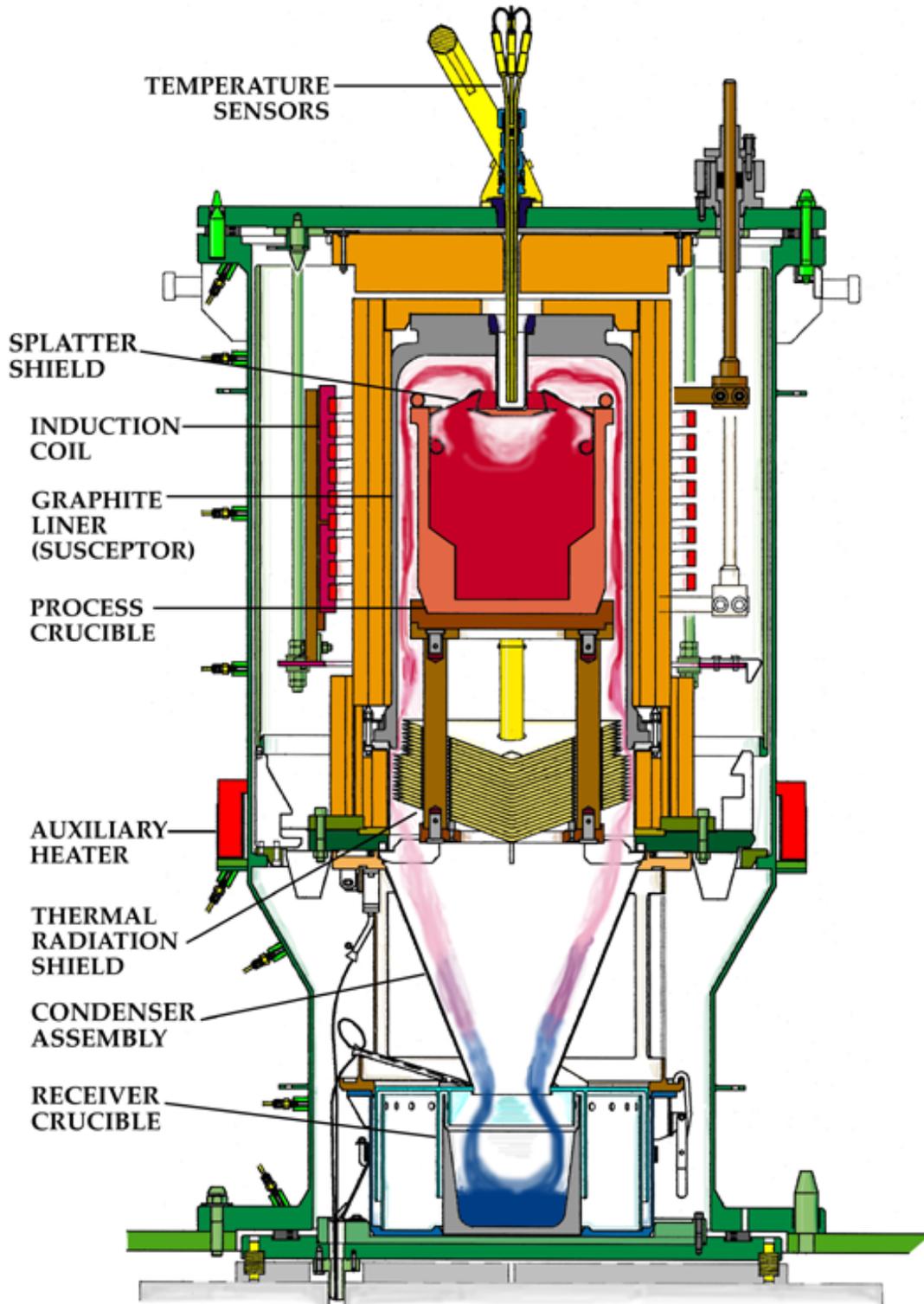


Figure 1. Schematic of Cathode Processor Equipment

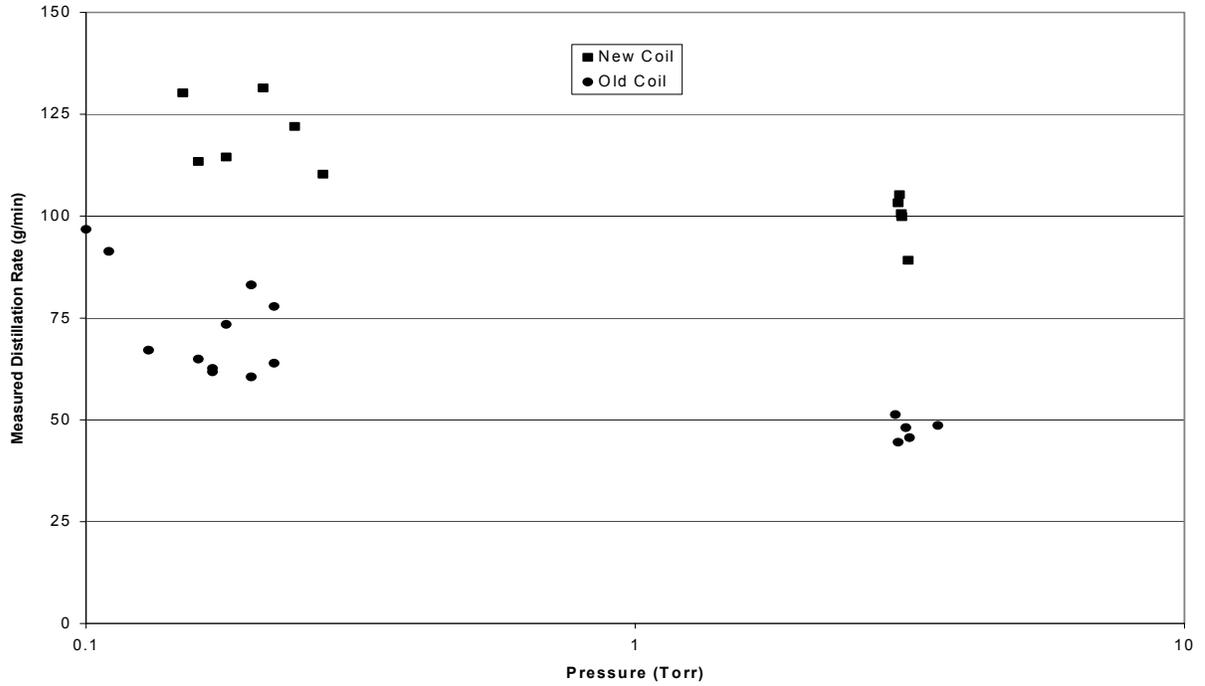


Figure 2. Comparison of Measured Distillation Rates for the New and Old Coils

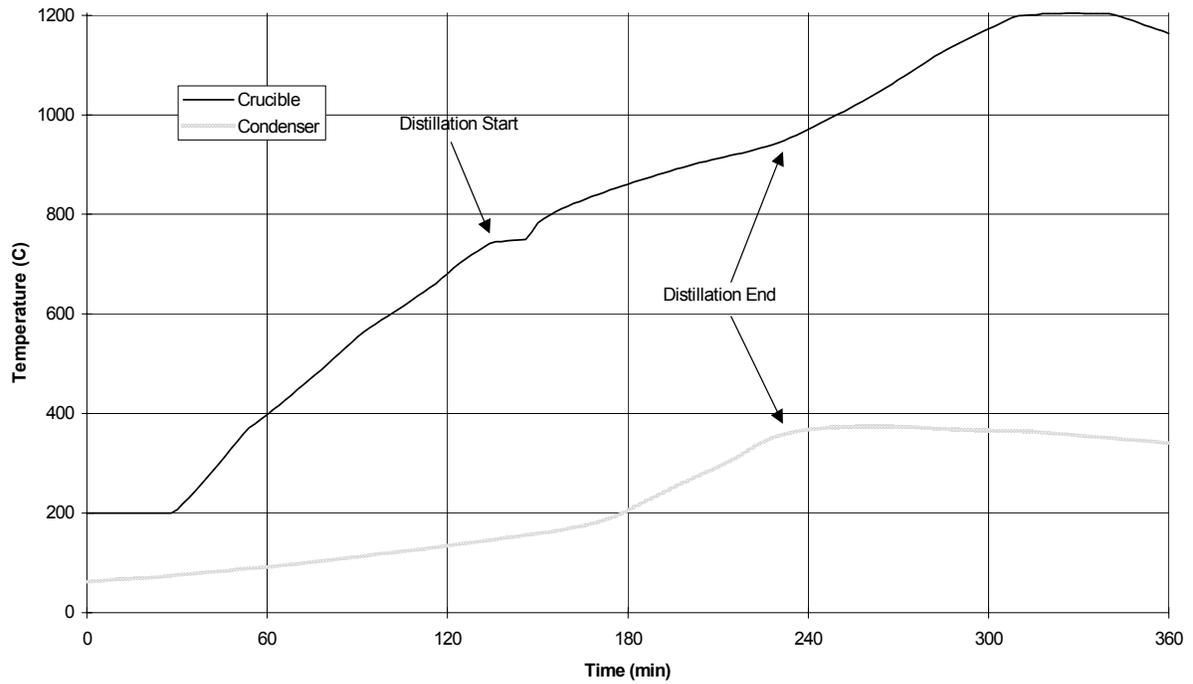


Figure 3. Typical Crucible and Condenser Temperature Curves

Table II. Distillation Rates as a Function of Coil and Vessel Pressure

Vessel Pressure (Torr)	New Coil			Old Coil		
	Measured Distill. Rate (g/min)	Measured Distill. Rate (g/min/cm ²)	Theoretical Distill. Rate (g/min/cm ²)	Measured Distill. Rate (g/min)	Measured Distill. Rate (g/min/cm ²)	Theoretical Distill. Rate (g/min/cm ²)
0.20	120.30	0.20	1.53	73.01	0.12	0.95
3.00	99.62	0.17	3.05	47.60	0.08	3.59

Taken a step further, the measured distillation rates can be applied to an area such that a comparison with theoretical rates is possible, see Table II. For simplicity, the assumed area or effective evaporating surface for distillation in the cathode processor is the inner diameter of the process crucible. The theoretical rates are based on the Hertz-Langmuir rate relation from the kinetic theory of gases [8-9]:

$$J = \frac{P}{\sqrt{2\pi MRT}} \quad (1)$$

where P is the gas pressure, M is the molecular weight, R is the gas constant, and T is the temperature. Use of the Hertz-Langmuir equation assumes that the distillation rate is solely controlled by vaporization at the surface and ignores such factors as the rate of vapor transport, heat transfer at the surface, and the presence of impurities. Thus, the measured rates are considerably less than the theoretical maximums. When compared to similar salt distillation data [10], the ratio of measured to theoretical is on the same order, that is, approximately 10%. It should be noted that although the theoretical rates appear to be increasing with pressure in Table II, higher temperatures are associated with the higher pressure data, thus enhancing the rates.

PROCESS DEVELOPMENTS

Currently, two process-related developments at the cathode processor are being pursued. The first, sampling of the cathode processor ingot, will increase the efficiency of the process while reducing cycle time on the casting furnace. The second, the investigation of plutonium in the final product, will assist in any future decisions related to the disposition of the uranium product from blanket operations.

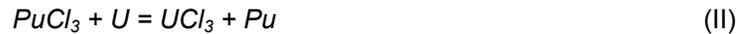
Until recently, samples for chemical analyses were taken at the casting furnace by injection casting molten uranium into quartz molds and then sampling the solidified pin. An alternative sampling method was considered in which samples were taken from the solidified cathode processor ingot by drilling of the ingot for shavings. A comparison of the two sampling methods is given in Table III for the total and isotopic (U-235) uranium contents of six batches. Based on the excellent agreement of the data, the casting operation has been discontinued during the processing of blanket-type fuel.

From the beginning of blanket processing, it was recognized that the plutonium content of the uranium product was significantly higher than that for driver processing. This was even more apparent when considering that the plutonium levels of the driver products can be further reduced by downblending the enrichments to that required for low-level waste (0.9% U-235) [11]. For blanket fuel, downblending is not an option since the products are already depleted. In an effort to provide more options for disposition, an understanding of the plutonium levels in the blanket products was desired so that the plutonium levels could either be reduced or controlled.

Table III. Cathode Processor Drill Sample and Casting Furnace Pin Sample Data

Batch	Total U		U-235	
	Drill	Pin	Drill	Pin
1	99.9214	99.9115	0.2287	0.2287
2	99.8696	99.9096	0.2150	0.2117
3	99.9196	99.9133	0.2120	0.2120
4	99.8662	99.8961	0.2190	0.2177
5	99.8609	99.8548	0.2157	0.2143
6	99.9008	99.8754	0.2050	0.2050

Two tests were performed in the cathode processor to determine the origin (electrorefining or cathode processing) of the plutonium in the blanket products. For both tests, salt containing plutonium was processed with uranium that was plutonium-free. The results of these two tests indicated the contamination of plutonium was occurring in the cathode processor according to the following reaction:



where plutonium results from the reaction of plutonium trichloride and uranium. Equation (II) is driven to the right by the evaporation of uranium trichloride with respect to plutonium trichloride.

A few additional tests were performed to rule out the possibility of undistilled plutonium trichloride. These tests were performed at higher than normal temperatures and longer processing times to assure distillation of the plutonium trichloride species. No significant changes in the plutonium levels were recognized for these tests.

Based on equation (II), another series of tests are currently being performed to reoxidize the plutonium metal and distill it as plutonium trichloride. These tests include the addition of various oxidants to form the plutonium trichloride. Preliminary results from these tests indicate that the plutonium levels of the blanket uranium products can be reduced by at least a factor of five.

A final series of tests have been proposed to determine the contribution of plutonium oxide to the contamination of the uranium products. A zirconia crucible coating is used during cathode processing and may react with the plutonium trichloride to form a plutonium oxide species. Tests are planned with different coating materials as well as a sacrificial liner to prevent contact of plutonium trichloride with zirconia.

CONCLUSIONS

- The following improvements have been implemented to increase throughputs during the spent fuel treatment program: a new induction heating coil has been installed in the cathode processor which reduces run times and the casting operation has been eliminated for blanket processing.
- The salt distillation rate at the cathode processor with the new coil has increased by at least 60%.
- The investigation of plutonium in the blanket uranium products is continuing with tests to reduce the plutonium content and understand the species of the plutonium.

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