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Engineering-scale distillation of cadmium for actinide recovery

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Abstract

During the recovery of actinide products from spent nuclear fuel, cadmium is separated from the actinide products by a distillation process. Distillation occurs in an induction-heated furnace called a cathode processor capable of processing kilogram quantities of cadmium. Operating parameters have been established for sufficient recovery of the cadmium based on mass balance and product purity. A cadmium distillation rate similar to previous investigators has also been determined. The development of cadmium distillation for spent fuel treatment enhances the capabilities for actinide recovery processes.

Keywords: Actinide alloys; Vapor deposition

1. Introduction

Currently, the distillation of cadmium on an engineering-scale is being performed for two industrial applications; the purification of cadmium to high grade quality [1] and recovery from Ni–Cd battery wastes [2]. Both operations separate the cadmium at high temperature under vacuum conditions in kilogram quantities. Although the distillation of cadmium in the nuclear industry has been demonstrated for actinide recovery [3], until recently, the testing has not been conducted at an engineering-scale. Thus, a description of the equipment and experimentation for cadmium distillation at kilogram quantities is given.

Actinide products are being recovered from spent nuclear fuel by a pyrometallurgical treatment process at the Idaho National Laboratory (INL). The treatment process comprises a set of operations designed to separate actinides from radioactive fission products and place the fission products into acceptable waste forms [4–6]. Two distinct actinide products are recovered during spent fuel treatment; a low-enriched uranium product and a plutonium–uranium product. The low-enriched uranium products are currently being stored pending a disposition decision while the plutonium–uranium products are returned to the process to enable further testing.

Batch operations on the spent fuel include chopping, electrorefining, cathode processing, and casting. During electrorefining, fuel is anodically dissolved in a LiCl–KCl eutectic salt such that the transport of actinides as cathode material is feasible. 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, uranium cathode products are collected and further processed by a vacuum distillation operation for the removal of the adhering salts [7,8]. The plutonium–uranium products are produced by utilizing a liquid cadmium cathode for electrorefining and then removing the cadmium by distillation. Both distillation operations described are performed in the same piece of equipment, the cathode processor, to produce consolidated actinide ingots.

2. Experimental details

2.1. Equipment

Development of a distillation process for spent fuel treatment can be traced to efforts at the Argonne National Laboratory associated with the original Experimental Breeder Reactor II fuel cycle [9]. For this process, the uranium was separated from a zinc–magnesium solution by a vacuum retort furnace.

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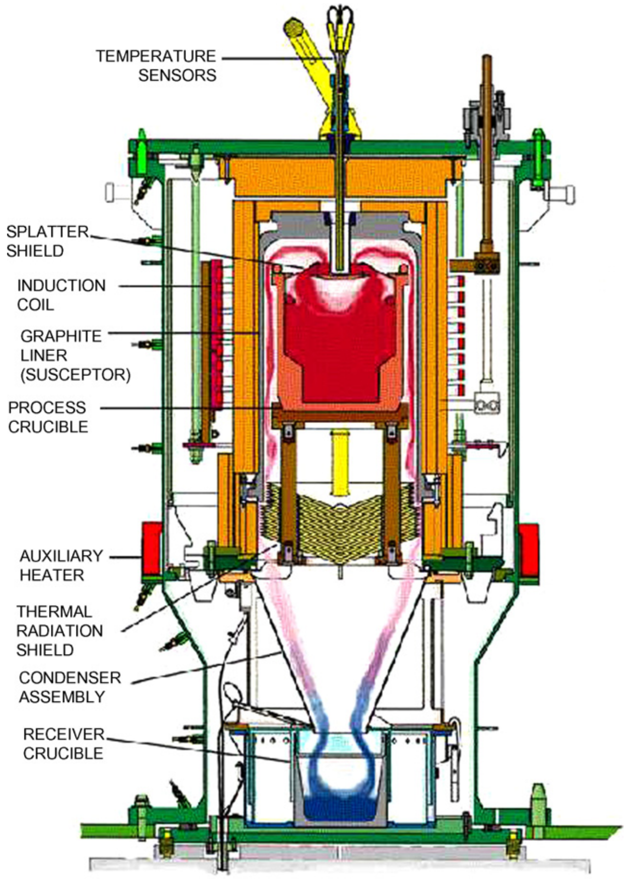

Fig. 1. Schematic of cathode processor.

The evolution of the current design of the cathode processor is based on this research.

Fig. 1 shows a layout of the cathode processor equipment. The crucible assembly (splatter shield, process crucible, radiation shield, condenser, and receiver crucible) is bottom loaded into the cathode processor vessel by translating the assembly to below the vessel and raising the assembly until seated. For ease of operation, the cathode processor vessel is elevated above the operating corridor. Horizontal motion of the crucible assembly is controlled by means of a trolley and rail assembly. With this configuration, the crucible assembly can be removed, dismantled, loaded or unloaded, and cleaned without disturbing the furnace components.

The furnace region of the cathode processor is heated by a passively cooled induction coil that suscepts to the graphite furnace liner which in turn heats the process crucible by radiation. The induction heating power supply is rated to 30 kW output at 2500 Hz, although only 10–15 kW is utilized for normal operations. Isolation of the induction coil from the crucible assembly is necessary to prevent the migration of vapor species to the coil during a run. The vacuum system consists of two oil-free mechanical pumps, either operated in parallel or independently, that are connected to the vessel through an assembly of piping, manifolds, and valves. Ultimately, the cathode processor is capable of temperatures as high as 1673 K and pressures less than 10 Pa. For typical distillations, it is only heated to 1473 K at less than 100 Pa to achieve sufficient separation of distillate from the actinide products.

The cathode processor is located in an argon atmosphere, shielded hot cell facility due to the radioactivity of the spent fuel. Both oxygen and moisture contents are maintained at less than 100 ppm in the argon cell of the facility. All operations in the hot cell, including those at the cathode processor, are performed remotely by overhead cranes, electromechanical manipulators, or manual manipulators.

2.2. Distillation experiments

Four experiments have been performed in the cathode processor for the separation of cadmium by distillation from actinide products. The first test utilized surrogate condensate materials (viz. cadmium and LiCl–KCl salt) with no actinides to confirm the operating parameters developed during equipment qualification testing. A small amount (<500 g) of salt is expected to be collected in the liquid cadmium cathode operation due to submersion of the cathode in the salt pool during electrorefining. The next three experiments in the cathode processor were with plutonium–uranium products following a liquid cadmium cathode operation in the electrorefiner.

For all four experiments, the process conditions for cadmium distillation consist of evacuating the cathode processor vessel to 100 Pa, isolation of the vacuum system from the vessel to prevent the migration of cadmium vapor, heating to 973 K at 8 kW, and then heating to a maximum crucible temperature of 1473 K at 15 kW (Fig. 2). Although the pressure is approximately 100 Pa initially, it increases slightly with temperature due to isolation. The reduced power level controls the rate of cadmium distillation initially while the 973 K temperature is considered high enough to achieve thermal decomposition of any plutonium–cadmium compounds. A crucible temperature of 1473 K was necessary to overcome the melting point of uranium (1405 K) which was added as diluent for facility safeguard purposes. Also given in Fig. 2 is the condenser temperature from which the start and end of cadmium distillation can be inferred from inflection points. The overall run time (from induction power start to finish) for the four cadmium distillation experiments averaged less than nine hours per run.

Gravimetric measurements were taken both before and after the cathode processor experiments so that a mass balance of the condensates (salt and

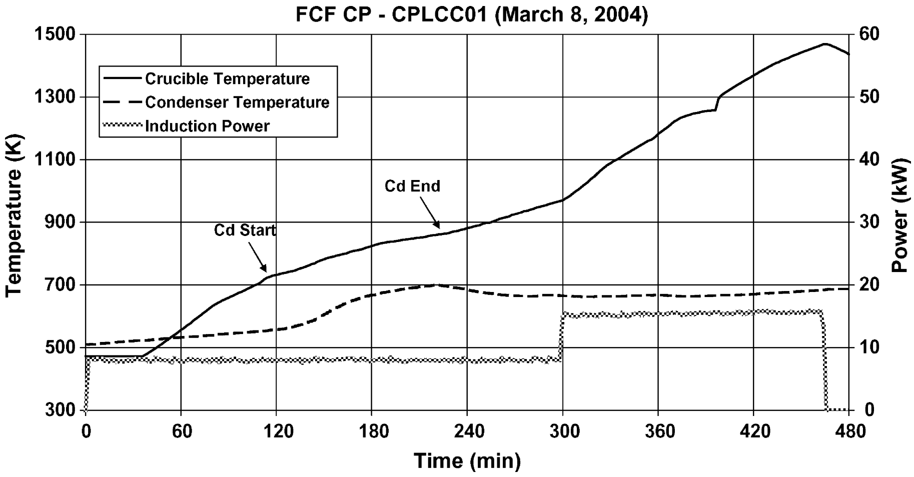

Fig. 2. Temperature and power data for cadmium distillation in cathode processor.

Fig. 3. Photograph of plutonium–uranium ingot following cadmium distillation experiment.

cadmium) could be performed. The three consolidated plutonium–uranium ingots were then processed in the casting furnace for sampling purposes. Molten samples were taken during the casting operations from the homogenized melt for chemical analyses. No cathode processor ingot was produced for the surrogate test since the charge materials did not include actinides. The actinide product ingots following casting were returned to the electrorefiner in order to continue tests with the liquid cadmium cathode. Samples were also taken from both the cadmium and salt portions of the condensate material. Although the four condensate ingots were not specifically reused in subsequent recovery operations, the intention is for reuse.

3. Results and discussion

Following cadmium distillation in the cathode processor, the three plutonium–uranium ingots were removed from the process crucible by inverting the crucible using a dumping operation. No difficulties were encountered on ingot dumping and the appearance of the ingot is shown in Fig. 3. The condensate ingot was also dumped from its crucible with no adherence problems (Fig. 4). The conical upper section of the condensate ingot is a result of material partially solidifying in the condenser region and dripping into the crucible forming the metallic stalagmites. The dark material seen from the mid-section up is salt which distills after the cadmium and is deposited on top.

Fig. 4. Photograph of condensate ingot following cadmium distillation experiment.

The mass balance data for the four cadmium experiments performed in the cathode processor are given in Table 1. Condensate charged was calculated from the difference of before and after cathode processing weight measurements on the process crucible. As seen by the recovered values, the amount of condensate collected differs from that charged for every experiment. This is due to condensate either being held-up in the components of the cathode processor or being released from previous runs. Following each cadmium distillation experiment, an additional cleanout operation was performed by reheating the lower region of the cathode processor to drive condensate to the receiver crucible. Values given in Table 1 for recovered condensate include the condensate recovered in the cleanout run.

Also shown in Table 1 is the cadmium levels detected in the plutonium–uranium ingots following the casting operation. For

Table 1
Summary of engineering-scale cadmium distillation experiments

Cathode processor batch	Date	Condensate[a] charged (kg)	Condensate[a] recovered (kg)	Condensate[a] recovered (%)	Cadmium in Pu–U ingot (ppm)
CD001	6/17/2003	28.513	28.224	99	–
LCC01	3/8/2004	26.505	26.545	100	<20
LCC02	7/21/2004	26.531	26.662	100	<25
LCC03	8/9/2005	25.901	25.988	100	<85

[a] Includes both cadmium and salt.

Table 2
Distillation rates for cadmium and zinc from various sources

Metal distillate	Quantity	Operating pressure (kPa)	Distillation rate (g/min)	Distillation rate per area (g/min/cm^2)	Source
Cadmium	Kilogram	0.7	242.776	0.406	This study
Cadmium	Gram	1.3	6.955	0.343	Tomczuk et al. [10]
Cadmium	Gram	1.0	Unavailable	0.357	Holtz et al. [11]
Cadmium	Gram	101.3	0.043	0.004	Wu et al. [12]
Zinc	Kilogram	0.1	16.000	0.320	St. Clair and Spendlove [13]
Zinc	Kilogram	0.1	153.397	0.434	Caldwell et al. [14]

all three plutonium–uranium ingots, the amount of cadmium detected was less than the detection limits of the analytical technique (ICP-OES). The results for samples taken of the condensate material were difficult to evaluate in terms of plutonium content due to cross-contamination of cadmium and salt. Regardless, the condensate is intended to be reused thus rendering the results inconsequential.

Using the start and end times for cadmium distillation from the condenser temperature data, an averaged distillation rate for the cathode processor can be calculated and compared against previous work as shown in Table 2. Since no kilogram-scale distillation data are available for cadmium, the rates for this study are compared against those from either gram-scale cadmium distillations or kilogram-scale zinc distillations. Zinc and cadmium are similar chemically such that their vapor pressures are comparable. Prior to the comparison of distillation rates, it should be recognized that distillation rate is dependent on three important factors; the atmosphere or operating pressure, the power level of the equipment, and the applied surface area. The applied surface area for the data in Table 2 is the cylindrical cross-sectional area characterized by crucible geometry. Despite the apparent differences in metal distillation rates, comparable values are determined by normalizing the rates with the applied evaporating surfaces for the different investigators. The low distillation rate for Wu et al. [12] can be attributed to the higher operating pressure. It is assumed that the power input for these distillations are all on the order of 5–10 kW although data is not specifically available for Wu et al. [12] and Caldwell et al. [14].

4. Conclusions

For the four cadmium experiments performed in the cathode processor, a batch greater than 25 kg of cadmium was distilled and greater than 99 wt.% was recovered for reuse. The plutonium–uranium products for three experiments contained levels of cadmium below the detection limits of analytical chemistry. A cadmium distillation rate of 0.41 g/min/cm^2 was determined which compares favorably with previous investigators. In conclusion, a successful separation of cadmium from actinide products was achieved at the engineering-scale to support further research efforts in actinide recovery.

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