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**PYROCHEMICAL SCRAP RECOVERY IN THE FABRICATION
OF LEU MONOLITHIC U-MO FUEL FOR HIGH-PERFORMANCE
RESEARCH REACTORS**

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ABSTRACT

The NNSA Global Threat Reduction--Conversion program is currently engaged in the development of a nuclear fuel that would enable conversion of US high-performance research reactors from high-enriched uranium to low-enriched uranium alloy fuel, monolithic uranium-10wt% molybdenum (U-10Mo). Approximately 2400 kg of scrap from the initial U-10Mo fuel meat used to create fuel foils for the five U.S. high-performance research reactors will be recycled annually. A design concept has been developed for a pyrochemical processing system to recover low enriched uranium from the U-10Mo fuel scrap. A summary of the system and a design concept for the proposed scrap recovery line will be presented. Building upon our successful laboratory-scale electrorefining experiments, results from the engineering-scale electrorefining experiments with zirconium bonded U-10Mo scrap are discussed. The applicability of the pyrochemical process for treating used HPRR fuel will be briefly described.

Introduction

The NNSA Global Threat Reduction--Conversion program is currently engaged in the development of a nuclear fuel that would enable conversion of US high-performance research reactors (HPRR) from high-enriched uranium to low-enriched uranium alloy fuel, monolithic uranium-10wt% molybdenum (U-10Mo). The conceptual process proposed for conversion will generate ~2400 kg of scrap from the initial U-10Mo fuel meat used to create fuel foils for the five U.S. high-performance research reactors [1]. A design concept has been developed for a pyrochemical processing system to recover low enriched uranium (LEU) from the U-10Mo fuel scrap available for recycling annually. A summary of the system, mass flowsheet, and the design concept for the proposed scrap recovery line is presented. The experimental setup and the results from the laboratory and engineering-scale electrorefining experiments with zirconium bonded U-

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10Mo scrap are discussed. The applicability of the pyrochemical process for treating used HPFR fuel will be briefly described.

Pyroprocessing Flowsheet of Zr-bonded U-10Mo Scrap

Uranium recovery from the proposed HPFR aluminum-clad zirconium-bonded U-10Mo fuel is essentially a five step process. Figure 1 is a conceptual flowsheet of the pyroprocess proposed to treat scrap U-Mo fuel. The first step is the chemical decladding of the outer aluminum layer by immersing the fuel within an aqueous 10% by mass sodium hydroxide solution. The NaOH solution will selectively remove the aluminum from the fuel and leave the zirconium-bonded U-Mo fuel intact. Once the fuel is declad, the material must be chopped or shredded to reduce the size of the fuel into pieces that can be loaded into the electrorefiner anode baskets. The size reduction also serves to increase the exposure of the internal U-Mo fuel meat that as received as scrap is almost entirely coated with the zirconium bonding layer. The third step is the primary pyroprocessing operation. The loaded anode-baskets, containing the U-10Mo scrap, are treated in an electrorefiner and uranium is selectively recovered from the other fuel components. The uranium product that is collected undergoes a final salt-removal and consolidation step to meet the product purity specifications of the HPFR fuel fabrication process. The molybdenum and zirconium fuel components that remain within the anode baskets are forwarded to the salt distillation process to remove the adhering salt and prepared for disposal. The waste generated from the process is composed of Al-containing aqueous waste, Mo/Zr waste, and baskets/crucibles that are unable to be recycled.

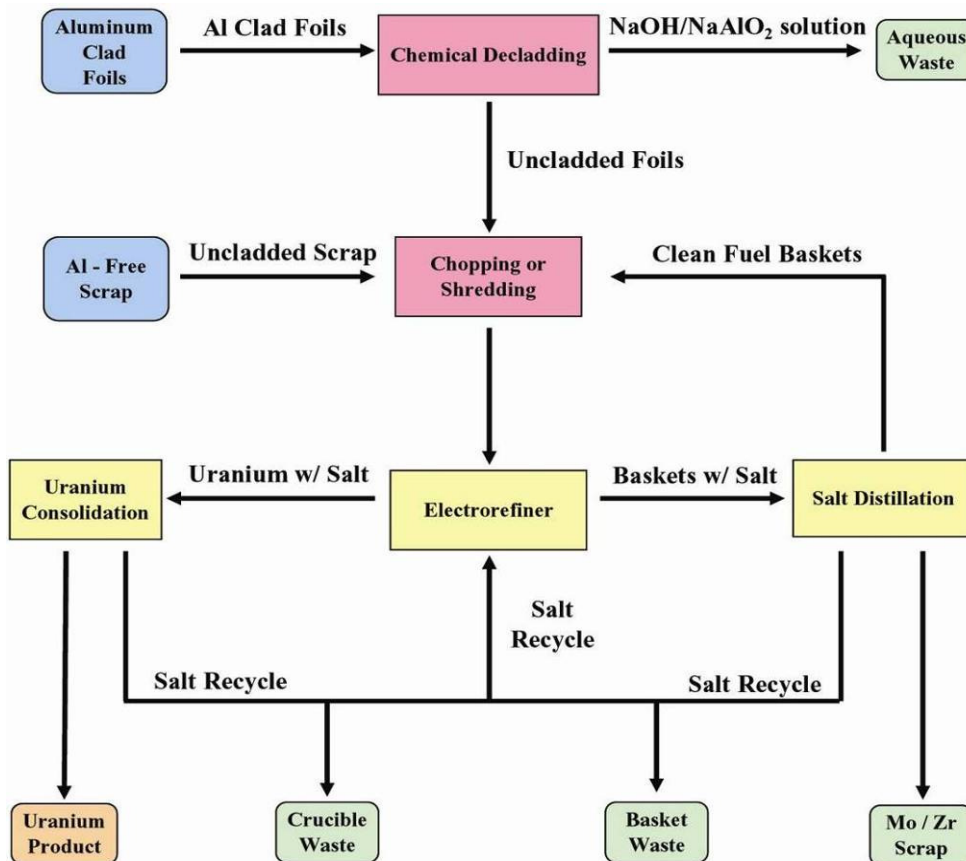


Figure 1. Conceptual Flowsheet for Pyrochemical Recycle of Zr-bonded U-10Mo Scrap

Pyroprocessing Salt Recycle

A critical component of the pyrochemical flowsheet presented in Figure 1 is salt recycle. The LiCl-KCl-UCl₃ salt electrolyte originates in the electrorefiner as the media by which uranium ions are transferred from the anode basket to the cathode. At the anode basket, the uranium found as U-Mo alloy is electrolytically transferred into the bulk salt as a positively charged trivalent uranium ion. At the cathode, the positively charged trivalent uranium ion is reduced and deposited at the electrode as pure uranium metal. An important note is that the rate that uranium ions are transferred into the salt at the anode equals the rate that the uranium metal is deposited at the cathode. This equilibrium ensures that the concentration of UCl₃ in the bulk remains constant. What does change, however, is the total amount of salt in the electrorefiner because the uranium product and the residual noble metals (Mo and Zr) that remain in the anode will retain up to 20wt% salt that must be recovered in the next processing steps.

At the uranium consolidation and salt distillation operations, the retained salt is removed from the products by distillation and captured in a condenser assembly. The salt is then recovered from the condenser and returned to the electrorefiner to maintain a constant salt height in the processing vessel. The entire salt path is ideally a closed system with complete recycling. The greatest likelihood for a loss of salt is during the transfer of materials between operations where the salt could fall onto the surface of the glovebox. If those losses can be minimized, then there is no limit on the number of times the salt can be recycled. The salt does not degrade over the course of pyroprocessing and can be reused indefinitely. The bulk electrolyte used in the engineering-scale experiment described below has been in use for ~25 years and shows no signs of degradation.

Pyroprocessing Development

The principle operation in the recovery of uranium from zirconium-bonded U-Mo scrap is the electrorefiner. Experimental validation was performed to demonstrate the feasibility of recycling the material using an electrorefining process at a laboratory and engineering scale. The experimental setup and the results of that work are presented.

Experimental Setup

The laboratory-scale experiments were performed on both a U-Mo foil and on a zirconium bonded U-Mo foil. Figure 2 is a schematic of the laboratory-scale test cell and figure 3 is a photo of the actual setup used during experimentation. The tests were conducted within an inert atmosphere glovebox that maintains moisture levels and oxygen levels below 10 ppm. The primary salt vessel was fabricated from steel and was electrically isolated from the glovebox using a ceramic oxide insulator. The anode basket was made of stainless-steel mesh and contained the scrap fuel, which was cut into thin strips. A smooth stainless-steel rod was used as the cathode to collect the uranium product. Ceramic-oxide tubes were used to isolate the electrodes from the heat shield package and the glovebox. A Ag/AgCl reference electrode, inserted into the bulk electrolyte maintained at 500°C, completed the experimental setup.

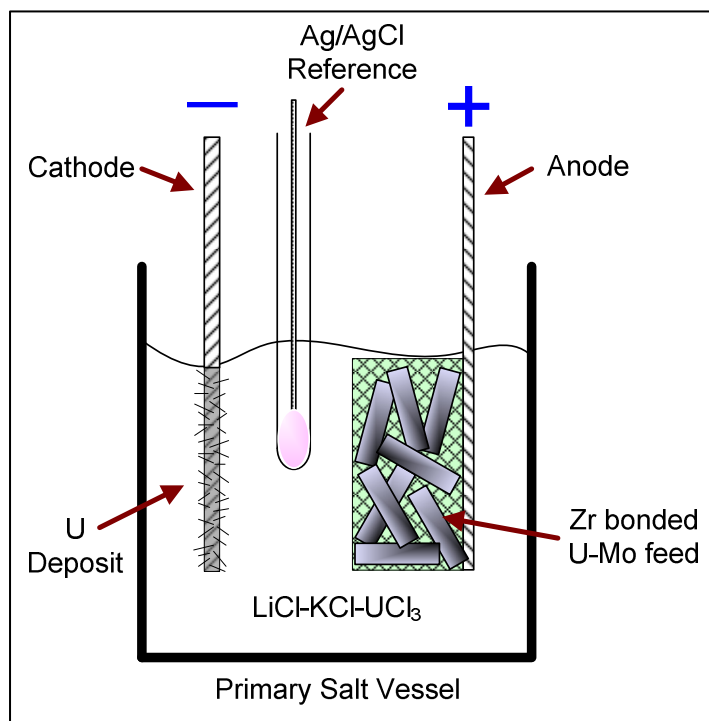


Figure 2. Schematic of Feasibility Test Cell

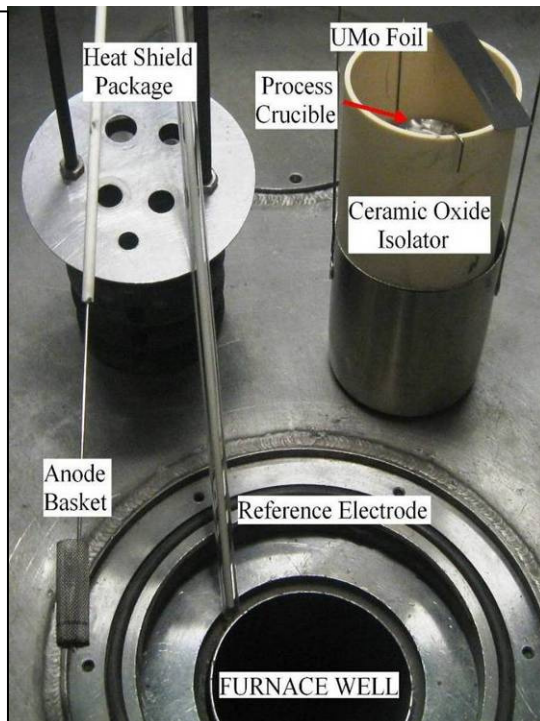


Figure 3. Test Cell for Feasibility Study

The engineering-scale experiments are being performed using Argonne National Laboratory's planar electrode electrorefiner (PEER). PEER is a prototype module of a possible commercial planar electrorefiner that could be used to treat U-Mo scrap. Figure 4 is a sketch of the planar electrorefiner. Two different types of fuel scrap were used during the initial qualification tests. Approximately 3 kgs of uncoated U-8wt%Mo fuel scrap were treated followed by 2 kgs of zirconium-bonded U-10Mo fuel scrap. The bonded fuel was coated with a zirconium layer, which had been cold-rolled onto the alloy. In both cases, fuel was placed in the anode of the electrorefiner and uranium was recovered at a series of cathodes. The electrorefiner was operated using galvanostatic conditions throughout the experiment. Voltage limits were set to ensure that uranium was the only transport species deposited at the cathode. After a specified number of coulombs had been passed, the cathodes were scraped to prevent the buildup of material between cathode and anode. Occasionally, PEER was examined before scraping the cathodes to determine the character of the deposit on the cathodes. Throughout the experiments, voltage data were collected between the cathode and the anode. The engineering-scale tests did not contain a reference electrode as used in the laboratory-scale tests. Several operating parameters were varied throughout the qualification tests such as electrode spacing and the size of the initial fuel strips to determine the relative affect on the current efficiency and to establish a set of test parameters.

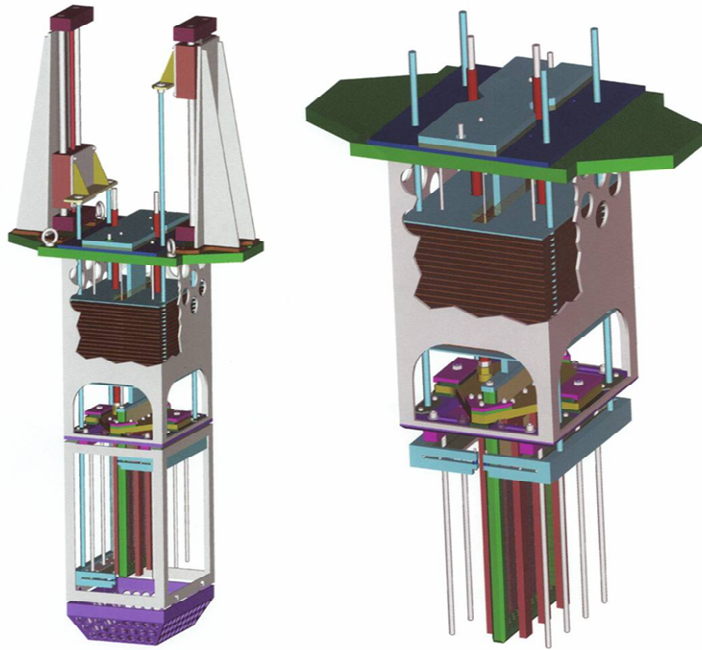


Figure 4. Sketch of the Planar Electrorefiner Used for the Engineering-Scale Test

Results and Discussion

The laboratory-scale feasibility studies successfully demonstrated that uranium could be recovered from zirconium-bonded U-10Mo fuel scrap. Figure 5 is a photo of the uranium product that was deposited from the test. Analytical samples were collected and the uranium was determined by mass spectrometry to be free from molybdenum and zirconium contamination. The anode residue consisted of Mo and Zr as well as unreacted fuel scrap. The salt samples contained no Mo and Zr impurities in the molten salt electrolyte.



Figure 5. Uranium Product from the Laboratory-Scale Feasibility Test

The engineering-scale qualification tests were completed exploring a wide range of variables. The results from the tests identified the preferred range for many of the operating parameters for the electrorefiner. For example, during one of the tests it was found that electrical shorting was occurring between the cathode and anode due to uranium growth across the gap. This short did not stop the uranium transport process but introduced inefficiency. Thus, the gap was subsequently increased to reduce the electrical inefficiencies that occur when a short exists between the electrodes. In all the tests, uranium was successfully recovered and a photograph of one of the deposits is shown in Figure 6. The purple tint to the uranium product shown in Figure

6 is due to UCl_3 in the salt that adheres to the metal product. The salt is removed from the product in a subsequent operation. Test results using mass spectrometry analysis show that the uranium collected as dendritic solid on the cathode has excellent quality and was free from Mo and Zr contamination. Molybdenum was also shown to be contained within the anode. Additional scrap material is being manufactured to complete the engineering-scale tests to determine the process recovery efficiency, further establish the product quality, and optimize operating parameters for the electrorefining process.



Figure 6. Uranium Product from the Engineering-Scale Test

Conceptual Facility Layout

The pyroprocessing facility contains two major pieces of equipment. The glovebox contains window stations for chopping foils, electrorefining, and basket/crucible preparation. A diagram of the equipment can be seen in Figure 7. The glovebox is estimated to be 16' x 8' or 12 m². Figure 8 is an example of the size of glovebox that would be necessary to house the equipment for the pyrochemical recycle of Zr-bonded U-10Mo Scrap. The uranium consolidation and salt distillation equipment consists of a high-temperature induction furnace located next to glovebox, which allows for direct material transfer, and is estimated to be 16' x 8' or 12 m².

Chop / Shred Foil	Storage		Basket Harvesting / Cleaning	Crucible Preparation
	U-Mo	Salt		
Basket Loading	Electro- refiner		Uranium Dendrite Harvesting	Salt Harvesting

Figure 7. Engineering-Scale Glovebox Design



Figure 8. Engineering-Scale Glovebox Prototype

Pyroprocessing Flowsheet of Used HPRR fuel

Pyrochemical processing is also applicable for the treatment of spent HPRR fuel and is the preferred treatment option. Pyroprocessing uses molten-salt electrochemical methods to separate and recycle uranium from the fission products contained in the used fuel. The technology was developed for treating fuel discharged from advanced liquid-metal-cooled reactors and its feasibility demonstrated by conditioning fuel discharged from the Experimental Breeder Reactor II (EBR II), which is located in Idaho [2]. The process used in Idaho was designed to treat U-10 wt% zirconium (U-10Zr) fuel but it shares many of the same key separation operations that would be required to recover uranium metal from used HPRR fuel consisting of zirconium-bonded uranium-10wt% molybdenum (U-10Mo) fuel with aluminum cladding. In fact, a higher degree of uranium recovery is expected from the U-10Mo fuel because of the difference in electrochemical properties between molybdenum and zirconium.

The flowsheet describing the pyrochemical process to treat used HPRR fuel is shown in Figure 9. The process is composed of seven principle operations that begin with a chemical decladding step to remove the aluminum cladding. Once the fuel is declad, the material is mechanically

chopped and placed into fuel baskets. The fuel baskets are transferred to an electrorefiner that electrolytically recovers uranium. Active-metal fission products partition to the molten salt and the noble metal fission products remain in the fuel baskets. Uranium product with residual salt is transferred from the electrorefiner to the cathode processor to consolidate the metal and remove any adhering salt, and then it is recycled to fuel fabrication. Salt distillation is also performed on the noble-metal fission products and fuel components, such as molybdenum and zirconium that remain within the fuel baskets, to create a stable metal waste form and allows the residual salt to be recovered. The molten salt collected from the uranium consolidation and noble-metal product processing operations is recycled to the electrorefiner after it undergoes treatment to remove the salt soluble fission products and a replenishment process to generate uranium trichloride oxidant, which is required by the electrorefining process due to the presence of active metal fission products in the fuel. The waste generated from the process is composed of aqueous waste, a noble-metal and an active-metal fission product waste.

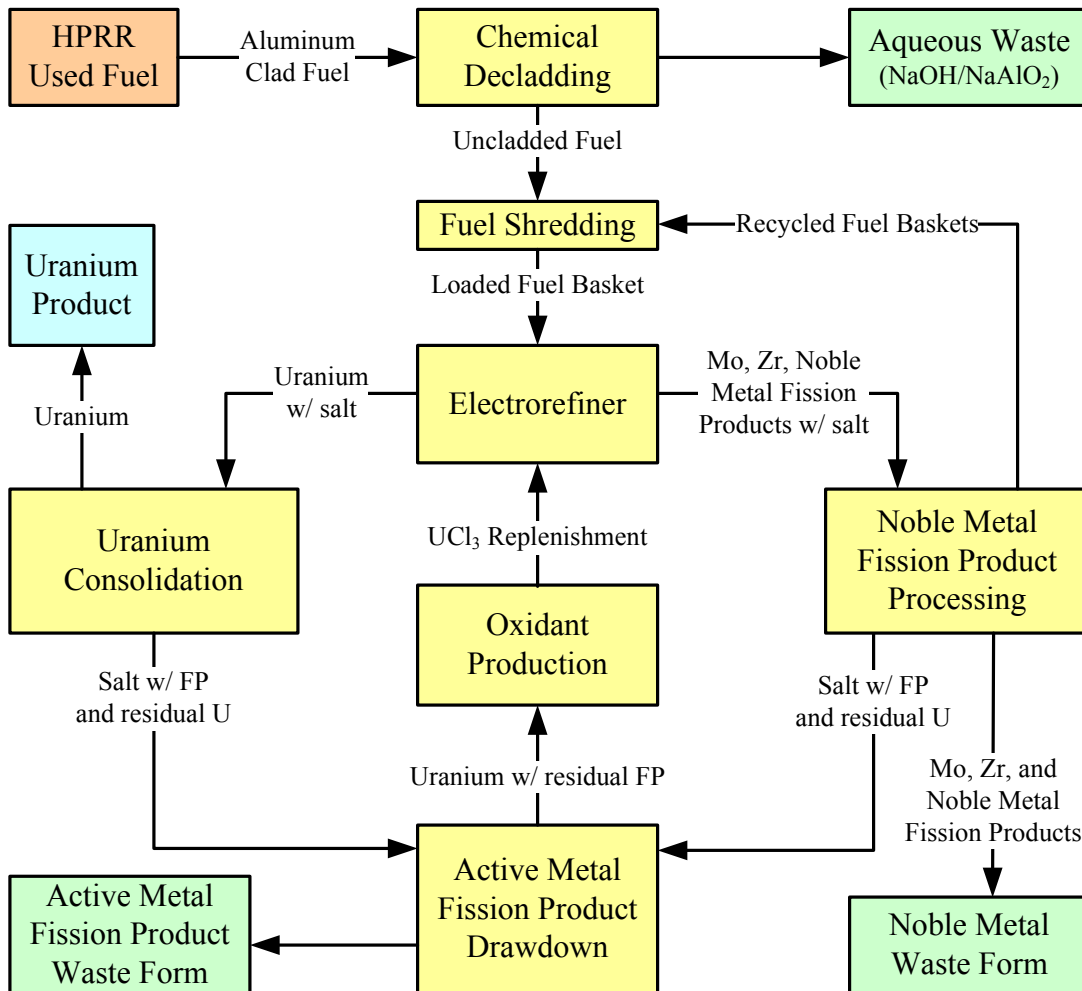


Figure 9. Conceptual Pyrochemical Process to Treat Used HPRR Fuel

Conclusions

The ultimate goal for pyroprocessing is to develop a commercially-viable technology to recover uranium from U-Mo fuels for recycle into HPRR fuel production. The system must produce high quality products, limit waste production, be easily scalable and, most importantly, be economical. The research performed at the laboratory-scale was the first step to validate the process by confirming that uranium recovery from Zr-bonded U-Mo fuel scrap was feasible. The second step using the engineering-scale electrorefiner has verified the laboratory-scale work but additional scrap material is being manufactured to complete the engineering-scale tests in order to determine process recovery efficiency, establish the product quality, and optimize operating parameters for the electrorefining process. A mass balance has been developed and the results of the engineering-scale experiments will be used to test the flowsheet assumptions for the U-Mo scrap process. Future work for U-Mo scrap process also involves (1) testing the uranium consolidation operation to demonstrate that the electrorefining product meets fuel specifications and (2) conducting a detailed heat and energy balance for the system. For the spent U-Mo treatment process, the plans focus on performing laboratory-scale electrorefining tests with U-Mo foil irradiated by the Argonne linear accelerator to validate uranium recovery from irradiated fuel and fission product behavior in the process.

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