ANL/CSE-13/14

Pyrochemical Recovery of Uranium from Monolithic U-10Mo Fuel Scrap

Chemical Science and Engineering Division

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PYROCHEMICAL RECOVERY OF URANIUM FROM MONOLITHIC U-10Mo FUEL SCRAP

1 INTRODUCTION

This report provides a description of a pyrochemical processing system designed to recover low enriched uranium from uranium 10 wt% molybdenum alloy (U-10Mo) scrap that is bonded to aluminum cladding. Approximately 44 wt% (2327 kg) of the initial U-10Mo fuel meat used to create fuel foils for the five U.S. high-performance research reactors will be recycled annually (Wachs et al. 2008). The U-10Mo recycle stream is a mixture of materials including casting scrap from the uranium down-blending process, shearing losses from foil sizing, rejected fuel elements, and material from hold-up in crucibles and other contaminated equipment. A description of the process chemistry, processing equipment including size, and approximate footprint of the proposed scrap recovery line is presented. In addition, a mass balance flowsheet that identifies and quantifies product streams, waste streams, and process reagent requirements is provided for the proposed recycle process.

2 FEED MATERIALS

The monolithic fuel fabrication process produces four distinct feed streams to the recycling process. Three of these streams are a result of the fuel failing quality assurance inspections. The fourth stream results from material hold-up on, for example, crucibles and equipment. The distinctive characteristics, specific quality assurance failures, and any pre-conditioning steps required prior to pyrochemical processing are described for each stream. Overall, 85 wt% of the material available for recycle is assumed to be treated by pyroprocessing. Uranium could be recovered from the remaining material but the material would need to be treated by other methods prior to pyroprocessing. The four fuel streams are as follows.

1. *Down-Blending and Casting Scrap*—The material from the down-blending and casting steps is primarily composed of hold-up that is strongly bonded to process crucibles or has failed feed specifications. The bulk of this feed stream must be treated by physical methods to release the alloy from the crucibles. Investigation into the strength of the bond between the alloy and the crucibles, along with exploration into mechanical techniques required to harvest the hold-up, is needed to determine the amount of casting scrap that could be recovered for subsequent pyrochemical treatment. This stream accounts for 19 wt% of the overall material sent to recycle; for the purposes of this report, an extremely conservative estimation is that only 20 wt% of this stream will be recovered from the crucibles and treated by the proposed pyrochemical process. Further research and development of mechanical harvesting techniques could lead to significantly higher uranium recovery percentages from this stream.

2. *Rolling and Shearing Scrap*—The scrap from the rolling and shearing steps has visible surface deformities or consists of leftover shearing pieces that do not meet foil specifications. This stream accounts for 31 wt% of the overall material available for recycle and may require additional mechanical manipulations such as chopping or shredding so that the material meets the size requirements of the electrorefiner fuel baskets. The maximum fuel meat thickness from the five U.S. research reactors is only 0.03 in. and would be easily converted into acceptable feed by a commercial chopper (Wachs et al. 2008). The chopping equipment would be operated within an inert atmosphere to eliminate any possibility of oxide formation on the chopped scrap.

3. *Boundary Layer Coating Scrap*—The scrap foil from the boundary layer coating steps has irregular zirconium or aluminum-silicon alloy diffusion layers that failed quality assurance inspections. This stream accounts for 24 wt% of the overall material available for recycle and requires aqueous chemical stripping with an alkaline solution to remove the Al-Si diffusion layer prior to pyrochemical treatment (Moore et al. 2008). The Al-Si layer must be removed from the feed stream to avoid competing electrochemical

reactions within the uranium electrorefiner. After pre-treatment, the foil will undergo mechanical manipulation such as chopping or shredding to meet the size requirements of the electrorefiner fuel baskets and to expose the inner U-10Mo fuel meat within the Zr boundary layer.

4. *Plate and Element Scrap*—The plate and element scrap material has failed a variety of quality assurance inspections due to the presence of surface defects, dimensional irregularities, or abnormalities in the aluminum bond. This stream accounts for 26 wt% of the overall material available for recycle and will first require disassembly of the plate/element hardware. Following disassembly, the aluminum cladding and the Al-Si boundary layer will be removed by aqueous alkaline dissolution before proceeding to the chopping operation.

3 MASS BALANCE

The Global Threat Reduction Initiative (GTRI) sponsored by the National Nuclear Security Agency has estimated that the proposed manufacturing process for fuel conversion will require 5288 kg of U-10Mo annually (Wachs et al. 2008). Using the net material–to–qualified fuel element efficiency factor of 56%, approximately 2327 kg of U-10Mo scrap will be generated. Assuming that 85 wt% of the overall feed stream will be treated by pyrochemical separations, a flowsheet was designed to treat 2000 kg of U-10Mo annually. The flowsheet assumes the facility would be operated for 200 days per year with an average daily processing rate of 10 kg of U-10Mo scrap. Detailed criticality safety analysis was not part of this study. The other assumptions used in developing the mass balance flowsheet are given below.

General Assumptions

1. Facility designed for 2000 kg U-10Mo/yr.
2. Facility operated 200 days/yr.

Casting Feed Stream

1. 20 wt% of down-blending and casting scrap recovered from crucibles.

Disassembly and Mechanical Separations of Plates and Elements

1. No U-10Mo losses with hardware waste.

Aluminum Aqueous Stripping

1. No U-10Mo losses to waste stream.
2. Complete removal of aluminum cladding by aqueous methods.
3. Complete removal of Al-Si layer by aqueous methods.
4. Density of Zr boundary layer estimated at 6.52 g/mL.
5. Density of Al-12 wt% Si boundary layer estimated at 2.66 g/mL.
6. Thickness of Zr and Al-Si boundary layers estimated at 0.001 in.

Chopping and Shredding

1. No material losses in the chopping and shredding of alloy.
2. Bulk packing density of chopped fuel in electrorefiner baskets estimated at 2.5 kg/L.

Electrorefiner

1. Feed alloy contains no oxides.
2. Uranium retention in baskets estimated at 0.5 wt%.
3. Mo and Zr completely retained within baskets.

4. Complete recovery of uranium metal from cathode.
5. Residual salt on products estimated at 20 wt%.
6. Fuel baskets require annual replacement.

Uranium Consolidation

1. Complete separation of uranium metal from salt.
2. Uranium retention in crucibles estimated at 0.1 wt%.
3. Crucibles require annual replacement.

Salt Distillation

1. Complete separation of U, Mo, and Zr metal from electrorefiner salt.
2. Crucibles require annual replacement.

A simplified schematic of the conversion process and mass balance is shown in Figure 1. The mass balance flowsheet has a theoretical uranium recovery efficiency of 99.4 wt% from the U-10Mo scrap. The waste from the process is composed of hardware from the plate disassembly process, aluminum scrap, and Mo/Zr metal scrap. Broken fuel baskets and unsuitable crucibles that cannot be recycled will also contribute to the waste generated. The LiCl-KCl molten salt is continually recycled from the uranium consolidation and salt distillation operations to the electrorefiner. Impurity buildup in the LiCl-KCl salt would be slow, so salt purification would not be required until after several years of normal operation. All uranium-bearing waste streams generated could be accumulated with the remaining down-blending and casting scrap and potentially be recycled by other separation technologies.

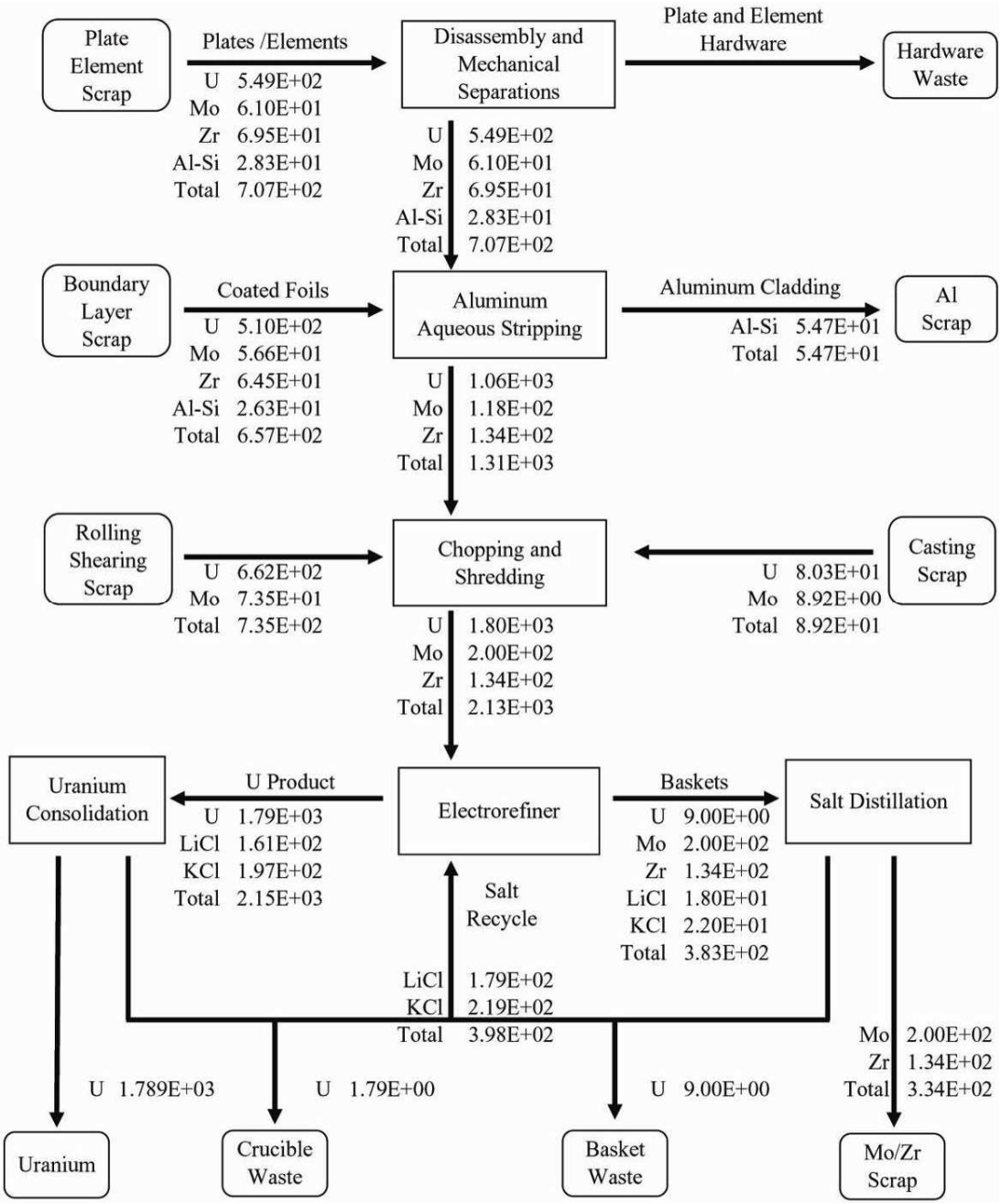

FIGURE 1 Mass Balance Flowsheet in kg/yr

4 UNIT OPERATIONS

4.1 ELECTROREFINING

Uranium electrorefining and the associated process chemistry needed to yield a purified uranium product are an established technology that has been demonstrated for a variety of programs, including the Integral Fast Reactor Program, and for treatment of spent fuel from the Experimental Breeder Reactor II (Battles et al. 1991; Gay et al. 1996). Electrorefiners, such as the planar electrorefiner being developed at Argonne National Laboratory, have demonstrated the capability to meet the annual throughput requirements of the U-10Mo scrap recovery process.

4.1.1 Chemistry

Electrorefining is an electrochemical process used to produce a purified metal from an impure feed material. In the case of uranium, it is performed in a molten salt such as LiCl-KCl eutectic at 500°C. The operating conditions of the electrochemical cell are controlled to only allow the transport of uranium from the anode baskets to the cathode. As electrical current is applied to the cell, uranium in the anode fuel baskets is oxidized to trivalent uranium ions that dissolve into the molten salt. Simultaneously, trivalent uranium ions in the molten salt are reduced at the cathode, yielding a metallic uranium deposit. The uranium metal that is deposited on the cathode is harvested and sent to a salt distillation and consolidation process. The zirconium and molybdenum present in the fuel are electrochemically less reactive than the uranium and remain in the fuel baskets. They are mechanically recovered from the fuel baskets after the electrorefining process and sent to waste after residual salt is removed by distillation. Previous experimental work with U-10 wt% Zr fuel, coupled with the knowledge that Mo is nobler than Zr, suggests that higher operating potentials can be used for the U-10Mo scrap, which will lead to better separations. All product transfers from the electrorefiner can contain up to 20 wt% residual chloride salts; hence the need for distillation. The recovered salt is recycled to the electrorefiner.

4.1.2 Equipment

The electrorefining process is performed in a furnace well contained within an inert atmosphere (argon) glovebox. The system is sized to accommodate approximately 55 kg of scrap alloy per loading. An operations schedule that would meet the desired throughput requirement of 10 kg of U-10 Mo scrap treatment per day is as follows: 1 day for fuel basket loading, 3 days for U electrotransport, and 1 day for product recovery plus cell clean-up. However, the electrorefiner design can be easily modified to accommodate different batch sizes and operational schedules.

The fuel baskets would be constructed of stainless steel sized to contain approximately 23 L of material (assuming a conservative bulk density of 2.5 kg per liter). The original monolithic U-10Mo fuel matrix can have uranium densities up to 16.5 kg U per liter, but the packing density within the fuel baskets will be considerably lower (Lemoine and Wachs 2007).

A set of six baskets 24 in. wide × 1 in. thick × 10 in. tall would contain this material. The basket dimensions are limited to 10 in. tall to simplify the product loading and the harvesting process. The six-basket set has an estimated empty mass of 55 kg and a fully loaded mass of 110 kg with the U-10Mo alloy scrap. It is estimated that the fuel baskets will require annual replacement. The overall basket assembly footprint would be approximately 2 ft × 2 ft and fit within the electrorefiner vessel opening, which is sized to be 3 ft × 3 ft.

4.2 URANIUM CONSOLIDATION

Uranium product consolidation, also known as cathode processing, is required to remove residual salt that adheres to the uranium dendrites and consolidate the uranium into an ingot (Westphal et al. 2001; Brunsvold et al. 2000). In current practice, the uranium metal coated with residual salt is recovered from the cathode of the electrorefiner cell and placed into a crucible that is installed in an induction furnace. The furnace is first evacuated to a slight vacuum (e.g., 50 torr) and the crucible is heated to 850°C to allow the salt to distill from the uranium-metal dendrites. This salt is collected in a condenser and eventually recycled to the electrorefiner system. The crucible is then heated to 1200°C to melt the uranium product into an ingot. Melting the uranium into an ingot is required to ensure that any residual salt within the dendrites is released, so that purity specifications are met for fuel fabrication. After cool-down, the uranium ingot is removed from the crucible and recycled to fuel fabrication.

4.2.1 Equipment

The principle components of the cathode processor include a stainless steel vessel, the loading/unloading trolley, an induction furnace, vacuum pumps, and the condenser assembly. Many of these components are commercially available and require few modifications before installation. The equipment is sized to process up to 50 kg of U per batch. The primary crucible is constructed of hafnium-nitride-coated niobium (empty mass of approximately 90 kg). Although it is estimated the crucible will be replaced annually, process experience may show that it can be used for longer periods. The overall footprint of the cathode processor is approximately 8 ft × 16 ft. Due to this large footprint and the desire to maintain low glovebox capital costs, only the loading and unloading of the cathode processor would be performed in the inert glovebox. A trolley rail system would be designed to deliver the crucible to the consolidation vessel while maintaining an inert atmosphere. The consolidation vessel would be located next to the glovebox to minimize the distance that the crucible must travel.

4.3 SALT DISTILLATION

Removal of residual salt from the molybdenum and zirconium is accomplished by the same method as for uranium. The salt-coated molybdenum and zirconium scrap is harvested from the fuel baskets and transferred into a crucible, which is designed for use in an induction furnace. The furnace is evacuated to a slight vacuum (e.g., 50 torr) and the crucible is heated to 850°C to allow the salt to distill. The salt is collected in a condenser assembly and eventually

recycled to the electrorefiner system. After the salt is distilled, the remaining Mo and Zr scrap are cooled to room temperature, collected from the crucible, and packaged for disposal.

4.3.1 Equipment

The principle components used to distill the chloride salt are identical to the equipment required for the uranium product consolidation. The difference between these two operations is shorter processing time, as the Mo and Zr scrap does not require consolidation into an ingot. Operational scheduling would be designed to perform both the salt distillation and the uranium consolidation operations within the same piece of equipment. Sharing the equipment greatly reduces the facility footprint and capital cost. Alternative technologies, such as a commercially available rotary kiln, could be used to distill the chloride salts from the Zr/Mo scrap. Rotary kilns are continuous operations that can treat smaller amounts of material while still achieving the desired throughput and potentially have an advantage over batch processors. However, use of a rotary kiln for the Zr/Mo would increase the facility footprint.

5 FACILITY DESCRIPTION

The recycle facility would be composed of a scrap preparation area, a pyrochemical glovebox, uranium consolidation area, and a storage area. The size of the overall facility would depend on storage requirements and on the design of scrap-preparation area. Figure 2 shows a conceptual facility design that is 36 ft × 44 ft, an area of 1584 ft^2, that accommodates all functions. An overhead bridge crane would be shared across the facility and equipped to handle equipment installations and product transfers.

5.1 SCRAP PREPARATION AREA

The scrap preparation section of the facility is 28 ft × 17 ft. The preparation area has three stations: casting crucible recovery (8 ft × 10 ft), aluminum stripping by aqueous methods (10 ft × 10 ft), and plate/element disassembly (10 ft × 10 ft) operations. This area also includes two hoods that are available for analytical or chemistry support work. Future research and development on scrap preparation, specifically U-10Mo recovery from crucibles, would help to provide a more detailed design of this area.

5.2 PYROCHEMICAL GLOVEBOX AND CONSOLIDATION AREA

The pyrochemical glovebox and consolidation area is compactly contained within a 24 ft × 20 ft area (Figure 3). This area contains an inert glovebox, a consolidation processor, a glovebox atmosphere purification system, and a system control panel. Additional equipment located in this area includes power supplies, material transfer systems, and vacuum components. The glovebox is fitted with a specialized trolley system designed to deliver the U dendrites or Zr/Mo crucible to the consolidation vessel while maintaining an inert atmosphere. Due to the large footprint of the consolidation system and the desire to reduce the glovebox manufacturing costs, this design would only house the loading and unloading of crucibles within the glovebox. The trolley would utilize glovebox transfer locks to transfer the loaded crucible to the induction furnace and return the uranium ingot or cleaned Zr/Mo scrap along with the salt condenser after the cycle is completed.

5.3 PYROCHEMICAL GLOVEBOX

The argon-atmosphere glovebox shown in Figure 4 is 16 ft long × 8 ft wide and contains four distinct areas: (1) chop/shred, (2) electrorefining, (3) crucible preparation for product consolidation, and (4) storage. The chop and shred area is one station, 4 ft × 4 ft, that is used to cut the feed alloy into a size suitable to fill the electrorefining fuel baskets. The chopping operation is performed in an inert atmosphere to eliminate any possibilities of oxide formation on the chopped scrap. The electrorefining area requires four separate window stations, each 4 ft × 4 ft wide. These stations comprise the heated salt well, fuel basket loading, basket harvesting/cleaning, and uranium dendrite harvesting. The product consolidation area is made up

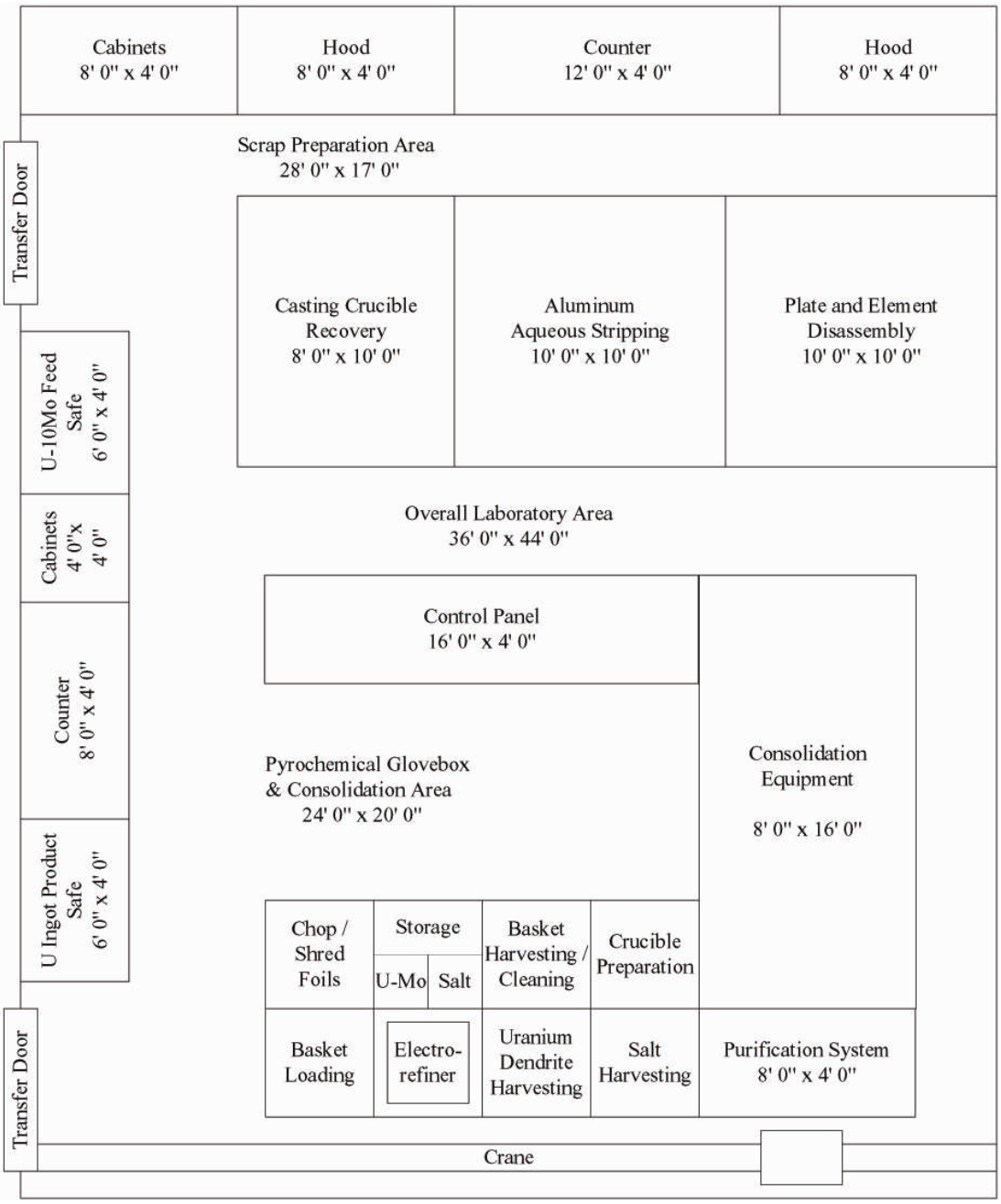

FIGURE 2 Conceptual Facility Layout

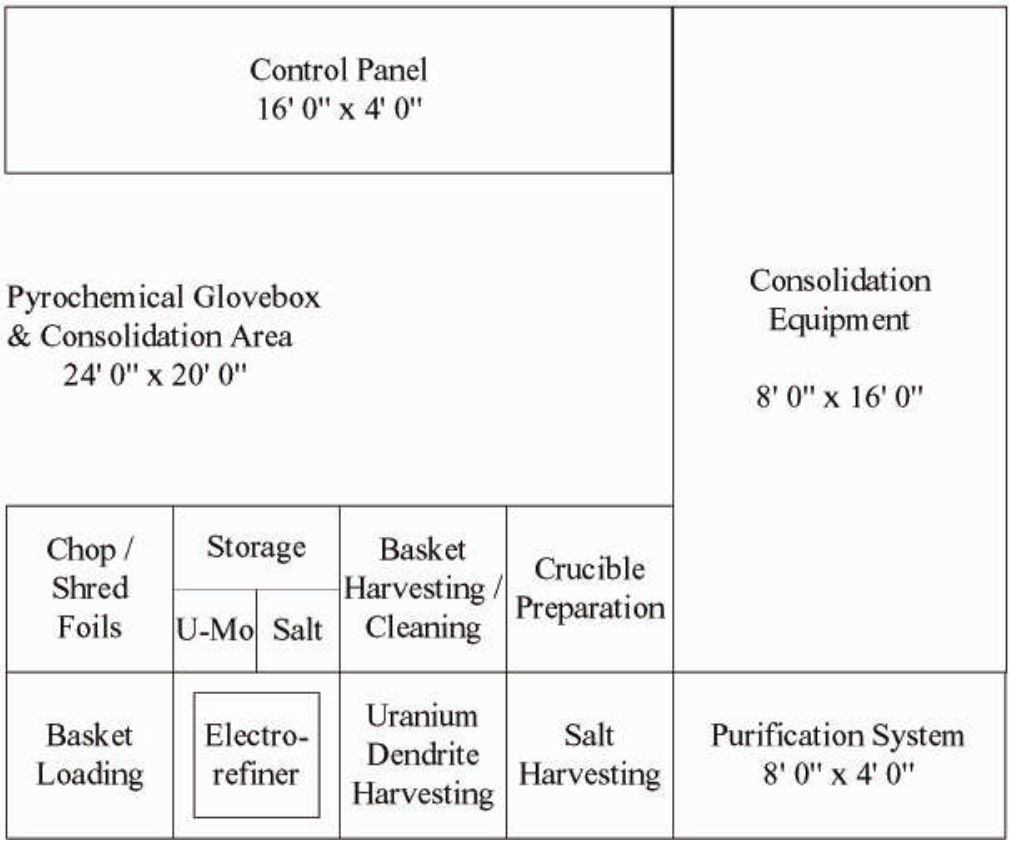

FIGURE 3 Pyrochemical Glovebox and Consolidation Area

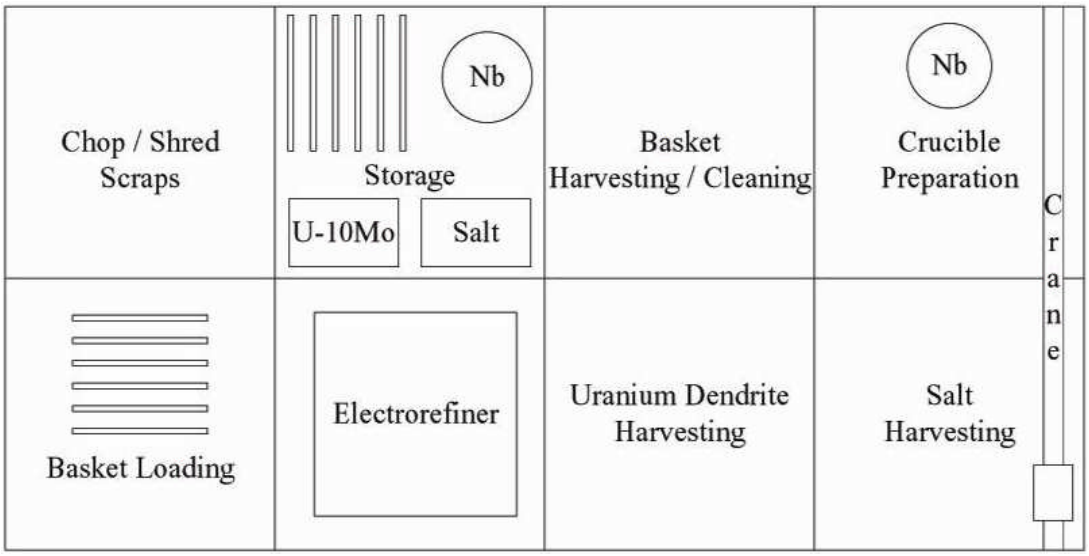

FIGURE 4 Glovebox Layout

of two stations used for crucible preparation and salt harvesting. The crucible-preparation station is used to load uranium dendrites into the consolidation trolley and to harvest uranium ingots. This station is also used for Zr/Mo crucible loading and unloading. The salt harvesting station is used to recover the electrorefiner salt, distilled from uranium or Mo/Zr, from the induction furnace condenser. The final station in the glovebox is dedicated for shared storage of fuel baskets, crucibles, electrorefiner salt, uranium ingots, and tools. Ingots formed in the cathode processor are stored in wells within this station prior to release to fuel fabrication. An overhead bridge crane is shared across the glovebox stations and equipped to handle both equipment installations and product transfers. The pressure in the glovebox would be maintained negative to the facility to protect workers from possible uranium dust releases. The glovebox argon atmosphere would be maintained at low (parts per million; ppm) oxygen, moisture, and nitrogen levels using a dedicated purification system.

6 SUMMARY

The facility envisioned for manufacturing the U-10 wt% Mo fuel used in high-performance research reactors would produce over 2000 kg of U-bearing scrap material annually. A pyrochemical process is proposed to treat the four major streams that account for approximately 85 wt% of the scrap created. Electrorefining is the main pyroprocess needed to recover the uranium from the scrap fuel for recycle to fuel fabrication. Experience in recovering uranium from U-10Zr fuel indicates process viability for U-10Mo fuel treatment. In fact, we expect a higher degree of U recovery from the U-10Mo fuel because of the difference in electrochemical properties between Zr and Mo. The uranium product from the refining process is consolidated into an ingot, after residual salt is removed, and recycled. Zirconium and molybdenum scrap recovered from the fuel baskets is prepared for disposal after residual salt is removed from the surface by distillation. The electrorefining and salt-distillation/uranium-consolidation processes have been developed to an engineering scale for a similar application, but they require additional development at the scale proposed by this study.

A theoretical mass balance flowsheet was developed for the pyrochemical treatment process. Uranium recovery was calculated to be at >99% efficiency for the proposed process. The waste streams created in this process consist of approximately 55 kg of Al-Si boundary layer waste and 334 kg Mo/Zr scrap per year. In addition, fuel baskets (55 kg) and Nb crucibles (180 kg) that are estimated to require annual replacement will contribute to the waste mass generated. The amount of uranium retained on the discarded baskets and crucibles is conservatively estimated to be 11 kg annually. All uranium-bearing waste streams generated could be accumulated with the remaining down-blending and casting scrap and be recycled by other separation technologies. However, the capital and operating cost of the recovery process would have to be less than the economic discard limit for the uranium-bearing wastes.

A conceptual facility layout was developed for the scrap recycling process. The overall laboratory area was approximately 1600 ft^2. Refinement of equipment design and placement would optimize the laboratory space needs and could lead to a reduced facility footprint. The pyrochemical glovebox and consolidation area is compactly enclosed within a 500 ft^2 area. Sharing the processing equipment for both uranium consolidation and salt distillation operations was key to maintaining a small footprint. The use of alternative technologies, such as a commercially available rotary kiln that could distill the chloride salts from the electrorefiner products, may allow treatment of the material and still achieve throughput requirements, but this would come at added facility footprint.

Follow-on research and development studies at the laboratory and engineering scale would provide valuable data that could be used to develop detailed equipment design information and optimize the facility layout. Laboratory-scale electrorefining experiments using U-10Mo fuel would confirm process viability and provide current density information that can be used to refine throughput calculations and equipment size. Coupled testing of the electrorefining and distillation/consolidation processes would define the amount of uranium retained in the system and provide additional insight into the amount of waste generated by the process. Validated electrorefining and uranium consolidation experiments would also provide

impurity and chloride content data for the uranium ingots, which is important for fuel fabrication. Lastly, investigation of the mechanical harvesting techniques used to remove the casting scrap from the crucibles could lead to significantly higher percentages of feed materials that could be sent to pyrochemical treatment.

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