ANL/CSE-13/25

Uranium Dioxide Conversion

Chemical Science and Engineering Division

About Argonne National Laboratory
Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via DOE's SciTech Connect (http://www.osti.gov/scitech/)

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):
U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandra, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703) 605-6000
Fax: (703) 605-6900
Email: **orders@ntis.gov**

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: **reports@osti.gov**

Disclaimer
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

ANL/CSE-13/25

Uranium Dioxide Conversion

by
J. Figueroa and M.A. Williamson
Chemical Science and Engineering Division, Argonne National Laboratory

prepared for
U.S. Department of Energy, National Nuclear Security Administration,
Office of Defense Nuclear Nonproliferation

August 30, 2008

CONTENTS

1 Introduction 1

2 Baseline Conversion Process 2
2.1 Mass Balance 2
2.1.1 General Assumptions 3
2.1.2 Hydrofluorination 3
2.1.3 Calciothermic Reduction 3
2.1.4 Waste Treatment 3
2.2 Hydrofluorination 4
2.2.1 Fluidized Beds 5
2.2.2 Moving Bed Furnace 6
2.3 Calciothermic Reduction 6
2.4 Billet-Salt Separations 7
2.5 Off-gas Treatment 8
2.6 Facility Description 8
2.6.1 Laboratory Area 8
2.6.2 Basement Area 10
2.7 Cost Estimate 11

3 Alternative Process 12
3.1 Mass Balance 12
3.1.1 General Assumptions 12
3.1.2 Electrolytic Reduction 13
3.1.3 Cathode Processing 13
3.1.4 Waste Treatment 13
3.2 Electrolytic Reduction 14
3.3 Uranium Cathode Processing 15
3.4 Facility Description 15
3.4.1 Electrolytic Reduction Glovebox 15
3.4.2 Cathode Processor 16
3.4.3 Laboratory Area 17
3.5 Cost Estimate 18

4 Summary 19

5 References 20

FIGURES

1 Mass Balance Flowsheet for Baseline Conversion Process 4

2 Schematic of Hydrofluorination Fluidized-Bed Configuration 5

3 Moving Bed Furnace Diagram 6

4 Reduction Glovebox Diagram 7

5 Off-gas Treatment 9

6 Baseline Facility Layout 10

7. Alternative Facility Mass Balance Flowsheet 13

8 Reduction Glovebox Diagram with Crucible Loading/Unloading Station 16

9 Reduction Glovebox Diagram and Uranium Consolidation 16

10 Alternative Facility Layout 17

TABLES

1 Baseline Equipment Costs 11

2 Alternative Equipment Costs 18

URANIUM DIOXIDE CONVERSION

1 INTRODUCTION

The Global Threat Reduction Initiative (GTRI) sponsored by the National Nuclear Security Agency is responsible for converting the five U.S. research reactors from high enriched uranium (HEU) to low enriched uranium (LEU) fuel. A description of the facility envisioned for manufacturing the LEU fuel from HEU feedstock is given by Wachs et al. (2008). In that document, they estimate that the proposed fuel manufacturing process would have an overall fuel manufacturing efficiency of 56% (net material to qualified fuel elements). The remaining 44% of the material accounts for more than 2000 kg of LEU to be recycled annually. The uranium recycle stream would be composed of a mixture of materials ranging from casting scrap from the downblending process, shearing losses from foil sizing, rejected fuel elements, and material from hold-up in crucibles and other contaminated equipment. In order to treat such a complex uranium recycle stream, an aqueous purification process was selected to remove the impurities via solvent extraction. Uranyl nitrate, the product from the solvent extraction process, is calcined to yield uranium dioxide, which is ultimately converted through nonaqueous processes to metallic uranium that is recycled to fuel fabrication. This report provides a flowsheet, process description, and material balance including waste streams for a baseline and alternative method to convert uranium dioxide from the aqueous purification process to uranium metal. In addition, a brief description of the process equipment, a facility layout, and cost estimate is provided for each conversion method.

2 BASELINE CONVERSION PROCESS

The baseline process consists of two well-established unit operations for converting uranium dioxide to uranium metal: hydrofluorination and calciothermic reduction. They are routinely used in the uranium enrichment and metal production processes. Over the years, the chemistry and engineering of these processes has been optimized to yield high quality product while minimizing waste production.

The hydrofluorination process converts uranium dioxide to uranium tetrafluoride by reaction with hydrogen fluoride gas. The chemical equation describing the process is

$$UO_2(s) + 4\ HF(g) = UF_4(s) + 2\ H_2O(g). \tag{1}$$

This solid-gas reaction is typically completed in a fluidized-bed reactor at temperatures in the range 300°C to 500°C. Complete conversion of the UO_2 to UF_4 is routinely achieved on an industrial scale.

The calciothermic reduction process chemically reduces the UF_4 with calcium metal to produce uranium metal. The chemical equation describing the process is

$$UF_4(s) + 2\ Ca = U(s) + 2\ CaF_2(s). \tag{2}$$

The reduction process is carried out in a batch reactor with a reaction initiation temperature of approximately 500°C. The enrichment level of the feed material and equipment design dictate batch size. As with the hydrofluorination process, complete conversion of the UF_4 to U is routinely achieved on an industrial scale. The product metal is separated from the CaF_2 and residual Ca in a billet-salt separation process. This mechanical operation removes the residual salt from the reduced metal to produce a clean ingot.

In addition to the major U conversion operations, there are auxiliary operations required to deliver the reagents and condition the waste streams. These supporting operations include the HF vaporizer for the hydrofluorination system, the off-gas treatment system, reduction vessel cleaning, and product and waste storage.

A simplified schematic of the conversion process and mass balance is presented in the next section of this report. A description of the proposed conversion equipment and facility follows the mass balance information.

2.1 MASS BALANCE

The GTRI has estimated that the proposed manufacturing process for fuel conversion will require 4759 kg of LEU annually (Wachs 2008). Using the overall efficiency factor of 56%, approximately 2094 kg of uranium scrap will be generated annually. The scrap uranium conversion facility is designed to treat 2500 kg annually, giving approximately 15% excess

capacity. The current facility would be required to operate for 250 days per year with an average daily processing amount of 10 kg of U. A detailed criticality safety analysis was not part of this study. Other assumptions used in developing the mass balance flowsheet are given below.

2.1.1 General Assumptions

1. Annual amount of uranium scrap is 2094 kg
2. Facility designed for 2500 kg/yr
3. Aqueous separations provide feed material in the form of UO_2

2.1.2 Hydrofluorination

1. Hydrofluorination process efficiency is 100%
2. 15 mol% excess HF gas is required to achieve conversion efficiency
3. Particle entrainment in gas phase is 0.01 wt% of total material
4. Entrained particle recycle efficiency is 90% by weight
5. UF_4 product particle size is adequate for reduction process

2.1.3 Calciothermic Reduction

1. Reduction efficiency of UF_4 to U is 100%
2. Batch size is limited to 10 kg U product
3. 15 mol% excess calcium required to achieve reduction efficiency
4. 5 mol% Li used to enhance reactivity and facilitate metal-salt separation
5. No salt is retained inside uranium billet
6. Ceramic crucibles have one-time use
7. Salt retention on uranium billet is 2 wt% or less
8. Product retention in crucible is 1 wt% or less
9. Unrecoverable product losses are 1 wt% or less

2.1.4 Waste Treatment

1. Excess HF can be recycled to aqueous separations
2. CaF_2, LiF, and excess Ca metal can be recycled to aqueous separations

A simplified schematic of the conversion process and mass balance is shown in Figure 1. The mass balance flowsheet reveals 98.8% efficiency for the production of U from UO_2. The residual uranium-bearing materials are sent to the aqueous separations process for recovery, purification, and recycle. Calcium fluoride (1590 kg/yr) and calcium (145 kg/yr) are sent to aqueous processing to recover the residual uranium and stabilize the waste. In addition, 145 kg of HF is delivered to aqueous separations as dilute hydrofluoric acid for treatment of process waste from fuel fabrication and uranium conversion (e.g., dissolution of refractory materials or

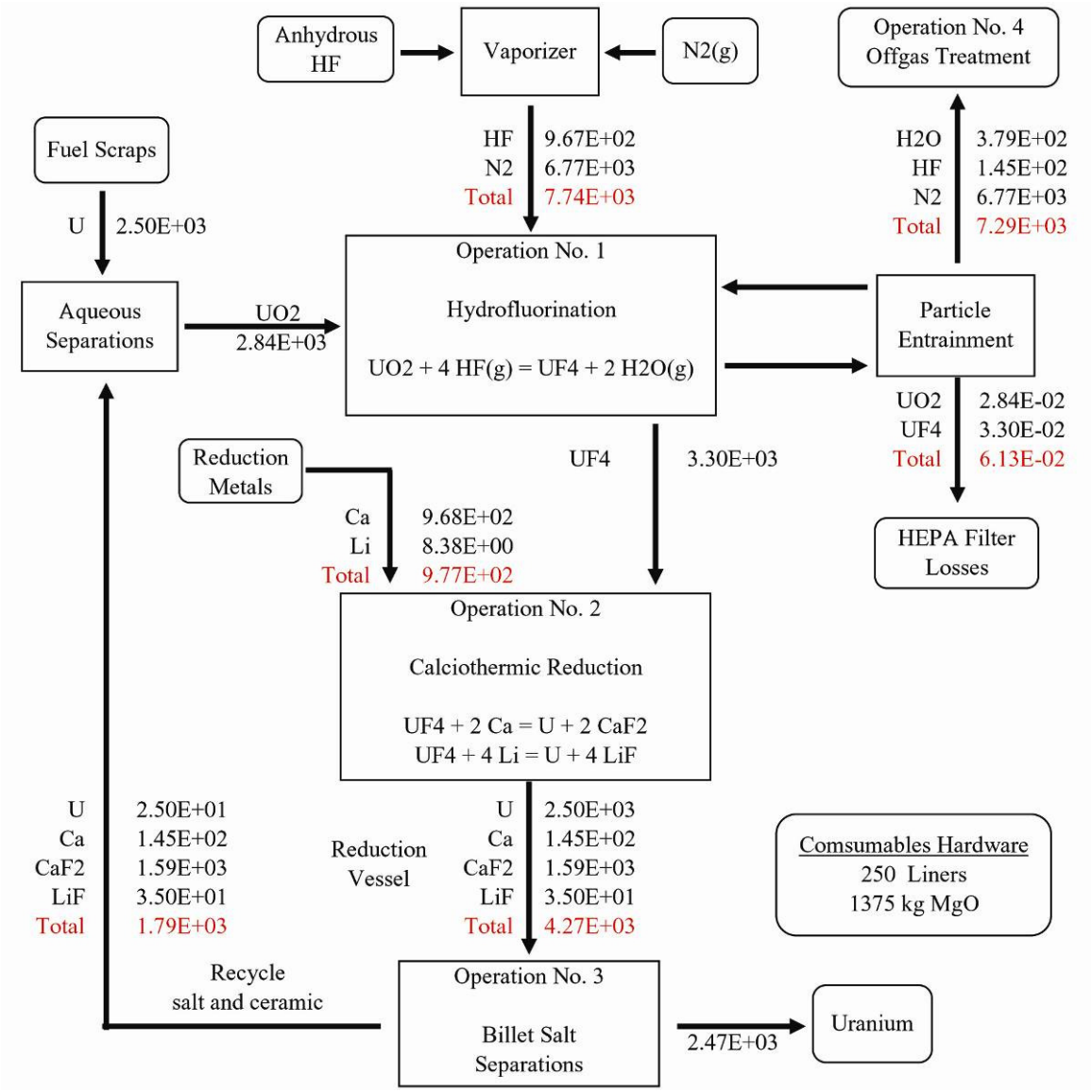

FIGURE 1 Mass Balance Flowsheet for Baseline Conversion Process (kg/yr)

off-specification fuel). The largest waste stream from the baseline process is the one-time-use magnesia liner or crucible (1375 kg/yr). This material is sent to aqueous separations so that any residual uranium can be recovered prior to disposal.

2.2 HYDROFLUORINATION

Both dry and wet hydrofluorination processes are used in commercial applications to convert uranium dioxide to uranium tetrafluoride. Dry hydrofluorination uses anhydrous hydrogen fluoride gas at elevated temperatures within fluidized or moving bed reactors (IAEA 1999; Edwards and Oliver 2000). For the conversion process, 10 to 25 mol% excess

HF gas is required to ensure the complete conversion to UF_4 (Perkins 1982; Patisson and Ablitzer 2002; Roddy et al. 1977). The excess HF gas is collected using a scrubber system and recovered in the form of dilute hydrofluoric acid, which can be recycled to the aqueous process (IAEA 1999). In contrast, wet hydrofluorination uses aqueous hydrofluoric acid and precipitates the UF_4 from solution (Edwards and Oliver 2000). This approach minimizes the cost of the HF scrubber systems but requires drying the UF_4 product (Edwards and Oliver 2000). It is more commonly used in uranium enrichment where the next step is conversion to UF_6 rather than the metal production process.

2.2.1 Fluidized Beds

Two vertical fluidized-bed reactors in series with countercurrent flow of solid and gas would be used for the hydrofluorination process (Perkins 1982; Roddy et al. 1977; Goorevich 1998). A schematic of the hydrofluorination step with fluidized beds is shown in Figure 2. The first bed is operated at 300°C, where the UO_2 feed, which is charged by a steel hopper, is partially converted to UF_4. An approximately 70% conversion rate can be expected for this first bed. The effluent stream from this process consists of steam and approximately 15% HF gas.

The second bed has anhydrous HF added directly to the partially converted UO_2 at 500°C to finish the conversion process. A screw feeder powered by an electric motor will charge the second reactor with the partially converted UO_2 from the first reactor. Conversion efficiencies of approximately 100% are quite common with the hydrofluorination process.

The UF_4 product is discharged from the second bed into a storage hopper for transfer to the reduction operation. Nitrogen gas is used to prevent caking in the fluidized bed (approximate flow rate of 100 scfm). Stirring can also be employed to prevent caking but may not be required. The typical footprint for a 50-kg batch fluidized-bed system is approximately 32 ft^2 with bed dimensions of 3 ft high by 0.5 ft in diameter. A pair of horizontal counter-current fluidized beds with ribbon stirrers could also be used for the hydrofluorination operation, but this approach may

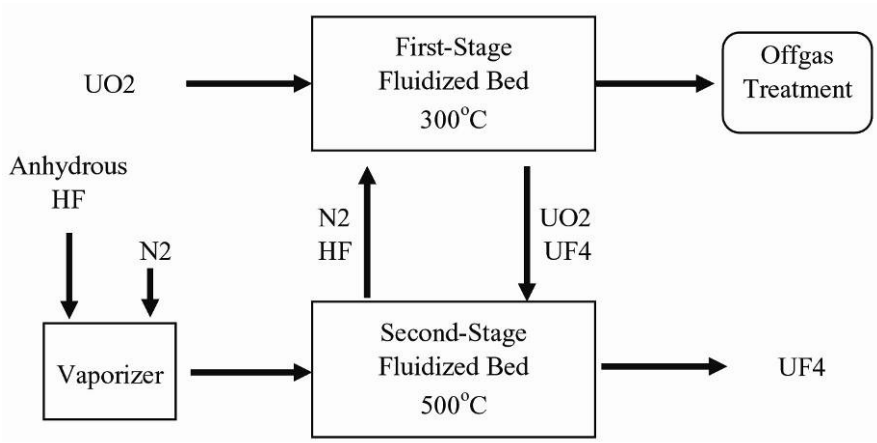

FIGURE 2 Schematic of Hydrofluorination Fluidized-Bed Configuration (Source: Perkins 1982)

lead to a larger facility footprint. The materials of construction for the equipment and subsequent piping in contact with HF (wet or dry) is Hastelloy, Inconel, or Monel (Goorevich 1998; Bonini et al. 1998).

2.2.2 Moving Bed Furnace

An alternative to the fluidized-bed reactor is a moving-bed furnace (Dussoubsa et al. 2002, 2003a,b). A diagram of the furnace is shown in Figure 3. The system consists of two distinct zones that behave similarly to the two independent fluidized beds. The UO_2 is gravity fed through the top of the moving-bed furnace and is preheated to 200°C prior to entering the furnace. The average particle size of the UO_2 entering the vertical zone is 6 mm or less to ensure high efficiency conversion to UF_4. The vertical zone temperature is carefully controlled with heat exchangers capable of cooling the vessel, if the exothermic reaction drives the temperature above the desired range of 300°C to 700°C. The partially reacted UO_2 automatically enters the horizontal zone of the moving-bed furnace.

An Archimedes screw is used to transport the material through the horizontal zone. The screw also prevents the material from caking. Counter-flow anhydrous HF is introduced at 340°C into the horizontal zone of the furnace and proceeds up through the vertical zone. The gas velocity through the vertical zone is approximately 2 ft/s while the solid flow is about 2×10^{-2} ft/s in the opposite direction. The process time from entrance into the vertical zone to exit of the furnace is approximately six hours.

The approximate footprint of the furnace system is 32 ft^2 and 16 ft in height. The moving-bed furnace is several meters high with a diameter up to 1.6 ft.

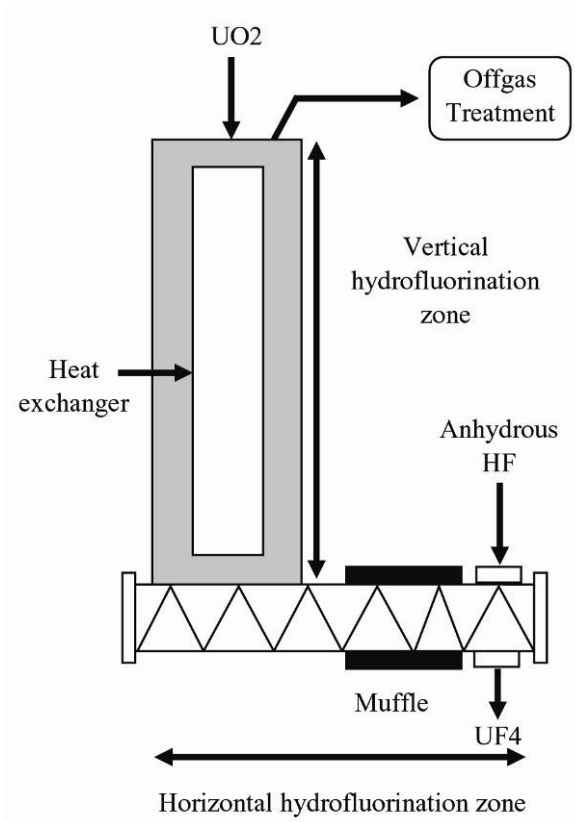

FIGURE 3 Moving Bed Furnace Diagram (Source: Dussoubsa et al. 2003a)

2.3 CALCIOTHERMIC REDUCTION

Uranium metal is produced by reacting the uranium tetrafluoride from the hydrofluorination operation with calcium metal. The major by-product of the process is calcium fluoride. Excess calcium metal, 10 to 25 mol%, is required to completely convert the UF_4 into U. Magnesium, which is more economical than calcium, may also be substituted as the reducing agent; however, calcium produces a higher quality uranium billet (Goorevich 1998).

Calcium reduction often uses iodine and/or lithium metal as a booster to lower the salt slag melting point from approximately 1360°C to the uranium melting point of approximately 1150°C (Sheller 1961). Without the addition of iodine or lithium, the salt will solidify before the uranium and become entrapped within the uranium billet. The addition of iodine and lithium also reduces the initial starting temperature of the reaction from 515°C to approximately 410°C (Sheller 1961; Baker et al. 1945).

Process equipment used for the calciothermic reduction is an inert glovebox, an induction furnace, a ceramic crucible or liner, and a steel containment or bomb assembly (Baker et al. 1945). A dolomitic lime (fused CaO-MgO) or MgO liner is one of the key components of the reduction process because of its inertness with liquid uranium (Goorevich 1998; Bonini et al. 1998). The liner, with a mass of about 5.5 kg, would be used once and discarded.

The inert argon atmosphere glovebox is 12 ft long × 4 ft wide × 8 ft high and contains three separate stations: (1) reduction vessel loading, (2) reduction and subsequent vessel cleaning, and (3) billet-salt separation and storage. Figure 4 is a diagram of the glovebox proposed for reduction and billet-salt separation. The glovebox should be maintained at negative pressure to the facility to protect workers from possible uranium dust releases in the event of a glove failure. The argon atmosphere in the glovebox would be maintained at low (ppm) O_2, H_2O, and N_2 levels using a dedicated purification system.

2.4 BILLET-SALT SEPARATIONS

The uranium billet produced in the calciothermic reduction operation is readily separated from the ceramic liner and salt slag. The molten uranium forms a puck at the bottom of the liner while the lower density CaF_2 salt solidifies above. The separation process involves cracking the ceramic liner and segregating the CaF_2 from the billet. Mechanical cleaning and polishing of the billet requires a small (~10 ft^2) section of the glovebox to separate the uranium product from the

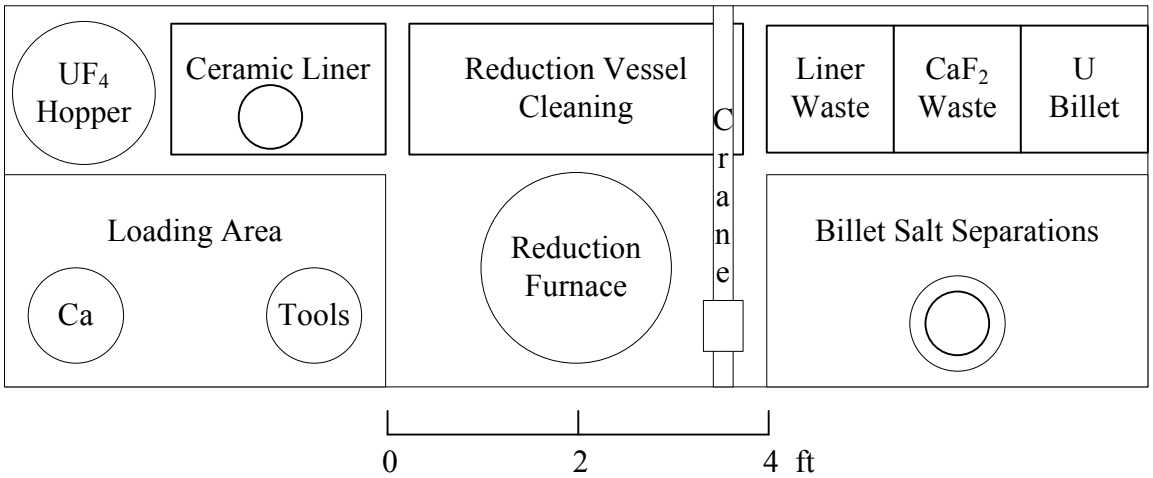

FIGURE 4 Reduction Glovebox Diagram

salt. The uranium billet that is collected would be stored in a well prior to transfer out of the glovebox for use in fuel fabrication or long-term storage. The salt slag and the broken ceramic liner are also stored within their respective locations in the glovebox prior to discharge to the aqueous recovery process. The reduction vessels will undergo mechanical cleaning to remove residual salt and calcium metal prior to being reused.

If mechanical polishing does not effectively remove the salt from the billet, a chemical wash can be performed in an adjacent area outside the reduction glovebox. Two chemical wash schemes are reported to work effectively. In one scheme, the billet is placed in a dilute acetic acid solution, followed by a water rinse, and, lastly, acetone for through drying (Baker et al. 1945). The other scheme involves a four step process: (1) immersion of the billet in an alkali metal salt bath, (2) a water quenching step, (3) a warm nitric acid bath, and (4) a water rinse (Banker et al. 1981).

2.5 OFF-GAS TREATMENT

The gaseous HF and N_2 that flow through the hydrofluorination equipment will capture fine UO_2 and UF_4 particles. The entrained particles are captured using carbon-metal filters that in combination trap 99.999% of the dust particles (Perkins 1982; Roddy et al. 1977). The captured material is collected from the filters and returned to the hydrofluorination process.

The remaining gases are treated through venturi water scrubbers that condense the HF into dilute hydrofluoric acid (DHF). The DHF can be recycled for use within the aqueous separations operation that converts scrap uranium to UO_2. Excess DHF is neutralized with lime producing CaF_2 and disposed according to environmental regulations. The nitrogen gas containing residual HF gas is passed through a potassium hydroxide (KOH) venturi scrubber as well as a KOH solution in a packed tower before being released from the facility. A flowsheet of the off-gas system is given in Figure 5.

2.6 FACILITY DESCRIPTION

The facility required for the baseline conversion process consists of two areas, the laboratory area and the basement. A schematic of the laboratory area is shown in Figure 6. The approximate size of the nonaqueous process area shown in Figure 6 is 2000 ft^2, or 40 ft × 50 ft (i.e., omitting the aqueous uranium recovery, waste packaging, and offices). A brief description of the process areas follows.

2.6.1 Laboratory Area

Four separate laboratory areas are required in the facility. The first laboratory contains the aqueous separations area, which accepts the uranium scrap from the carrier bay and converts the material into UO_2. The second area, the hydrofluorination laboratory, contains the bed reactors and serves as a housing unit for both the UO_2 and UF_4 material hoppers. Adjacent to this

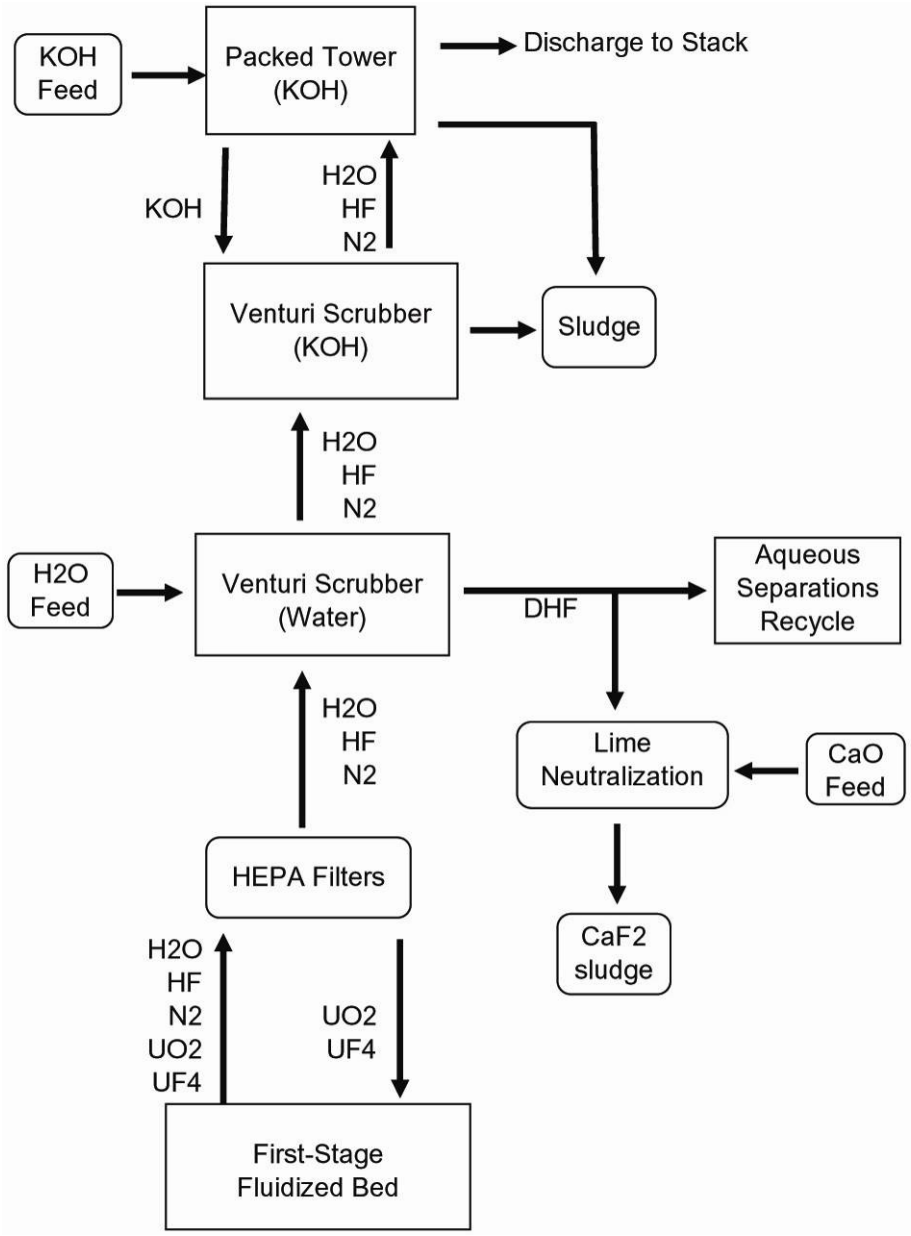

FIGURE 5 Off-gas Treatment (Source: Perkins 1982)

laboratory is the reduction lab that contains a glovebox, an inert atmosphere purification system, an induction furnace controller, and intermediate storage for the raw and final products. The fourth and final laboratory serves as the uranium and solid waste packaging area. This laboratory would organize the waste streams and direct the materials to the final storage or recycle locations within the facility. All four of these areas would be fitted with overhead bridge cranes equipped to handle both equipment installations and product transfers.

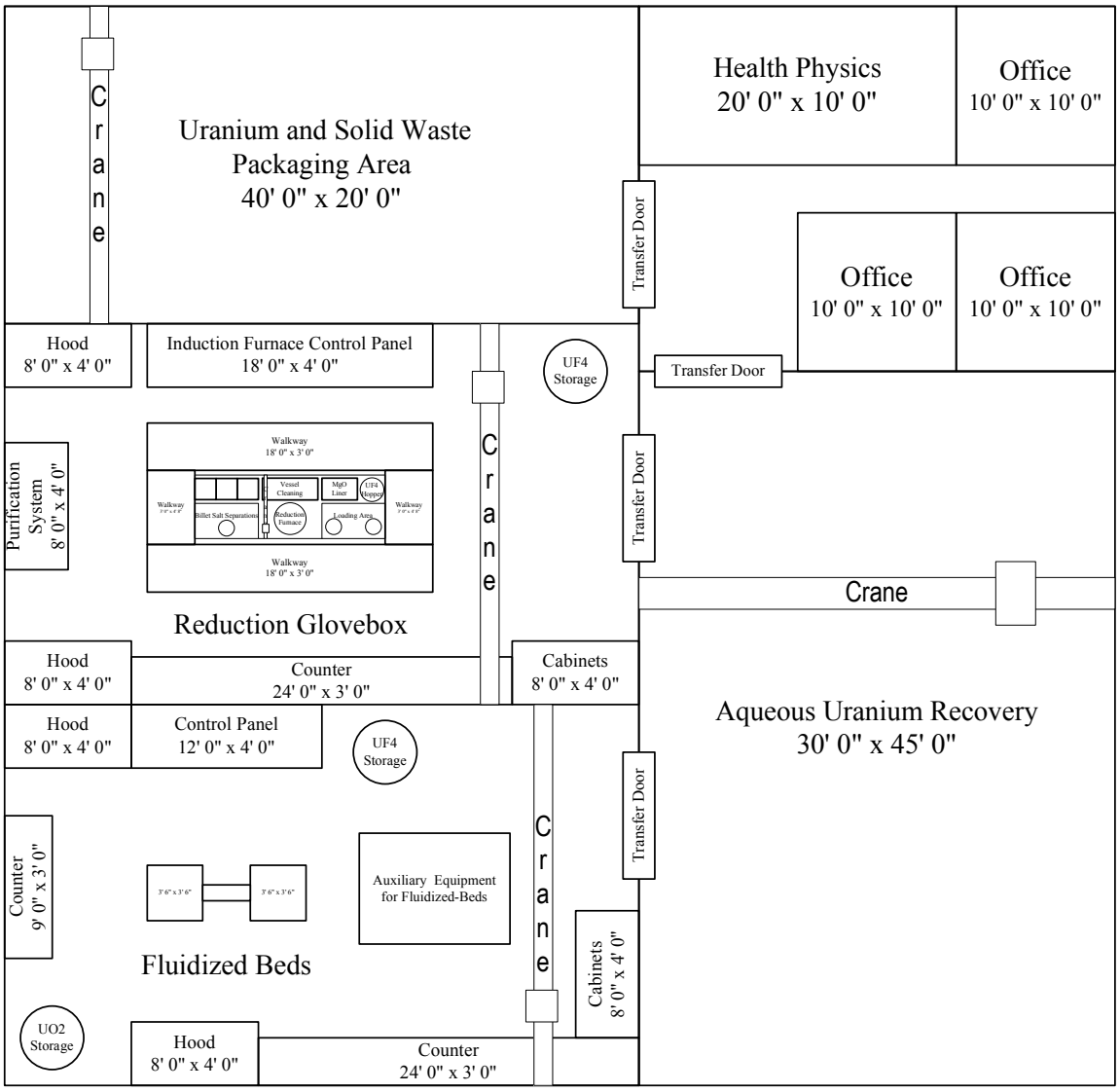

FIGURE 6 Baseline Facility Layout

2.6.2 Basement Area

In order to limit the footprint of the controlled area around the radioactive operations, the basement would be used whenever possible to house supporting equipment. The types of equipment found include air compressors, water chillers, pumping stations, gas cylinder racks for the reduction glovebox, the HF vaporizer, and the off-gas treatment equipment.

Hydrogen fluoride gas is generated by vaporizing the anhydrous HF feed. The vaporization equipment includes electrical heat exchangers to raise the temperature of the gas stream to 425°C.

The material hoppers can be constructed of steel but would maintain a nitrogen atmosphere in order to prevent side reactions with moisture to reduce corrosion. The UO_2 feed hopper would be fitted with heaters to preheat the feed material prior to entering the hydrofluorination furnace. The UF_4 hopper is the primary storage station for the fluorinated product. The UF_4 would be stored until the material was transferred into the reduction glovebox and prepared for use in the reduction vessel. Both hoppers would be sized to hold up to 50 kg.

2.7 COST ESTIMATE

An estimated equipment cost for the baseline process is shown in Table 1. The hydrofluorination beds, the HF vaporizer, the glovebox purification system, and the induction furnace are all commercially available pieces of equipment and require few modifications for this implementation. The total baseline facility cost (process equipment + glovebox) is estimated to be $1655k. No cost estimate is provided for the aqueous separations required for treating ~1800 kg of calcium fluoride salt and the 1375 kg of ceramic crucibles.

TABLE 1 Baseline Equipment Costs

Reduction Glovebox	Cost ($k)
Glovebox 12' × 4' × 8' with Small Crane	1155
Purification System	155
Total Glovebox Cost	1310
Experimental Equipment	
Fluidized Beds	150
HF Vaporizer	25
Uranium Storage System	20
Induction Furnace	50
Off-gas Treatment	100
Total Equipment Cost	345
Total Facility Cost	1655

3 ALTERNATIVE PROCESS

An alternative conversion method is available for the conversion of UO_2 to uranium. The method consists of the electrochemical reduction of uranium dioxide to yield uranium followed by a salt-metal separation process (Gourishankar et al. 2002; Westphal et al. 2002). The electrochemical (or electrolytic) reduction process comprises loading the UO_2 from the aqueous purification process into a basket that functions as the cathode in the electrochemical cell. The basket with the dioxide is then immersed in molten LiCl that contains 1 wt% Li_2O. As current is passed between the cathode and anode of the cell, uranium ions in the UO_2 are reduced to uranium metal and oxide ions are liberated to the salt phase. Simultaneously, oxide ions are oxidized at an inert anode to produce oxygen gas that is swept from the cell. The resulting metallic product is removed from the cathode and treated in a furnace to remove the salt adhering to the metal and, ultimately, melt the uranium into a billet.

The advantages of the electrolytic reduction process as compared to hydrofluorination and calciothermic reduction include limited need for chemical reagents because the process uses electrons for the oxide-to-metal conversion; reduced process waste since no HF, no reductant metal, or one-time-use liners are needed; enhanced process safety due to no HF or steam handling requirements; and reduced process footprint.

A flowsheet for the conversion process and mass balance is presented in the next section of this report. A brief description of the proposed conversion equipment and facility follows the mass balance information.

3.1 MASS BALANCE

As described for the baseline process, the GTRI has estimated that the proposed manufacturing process for fuel conversion will require 4759 kg of LEU annually (Wachs 2008). Using the overall efficiency factor of 56%, approximately 2094 kg of uranium scrap will be generated annually. The scrap uranium conversion facility is designed to treat 2500 kg annually, giving approximately 15% excess capacity. The current facility would be required to operate for 250 days per year with an average daily processing amount of 10 kg of U. A detailed criticality safety analysis was not part of this study. The other assumptions used in developing the mass balance flowsheet are given below.

3.1.1 General Assumptions

1. Annual amount of uranium scrap is 2094 kg
2. Facility designed for 2500 kg/yr
3. Aqueous separations provide feed material in the form of UO_2

3.1.2 Electrolytic Reduction

1. Reduction process efficiency is 100%
2. Complete recovery of uranium metal from cathode basket
3. 15 wt% carryover of molten salt with product metal to cathode processor
4. Cathode baskets reused 25 times before disposal as waste

3.1.3 Cathode Processing

1. Salt/metal separation efficiency is 100%
2. Crucibles reused 25 times before recycle
3. Salt collected in distillation process recycled to electrolytic reduction system

3.1.4 Waste Treatment

1. Cathode baskets treated by aqueous separations to remove adhering salt and discharged as waste
2. Crucibles from cathode processing treated by aqueous separations to remove adhering salt and material is recycled

A simplified schematic of the conversion process and mass balance is shown in Figure 7. The mass balance flowsheet assumes 100% efficiency for conversion of UO_2 to uranium metal.

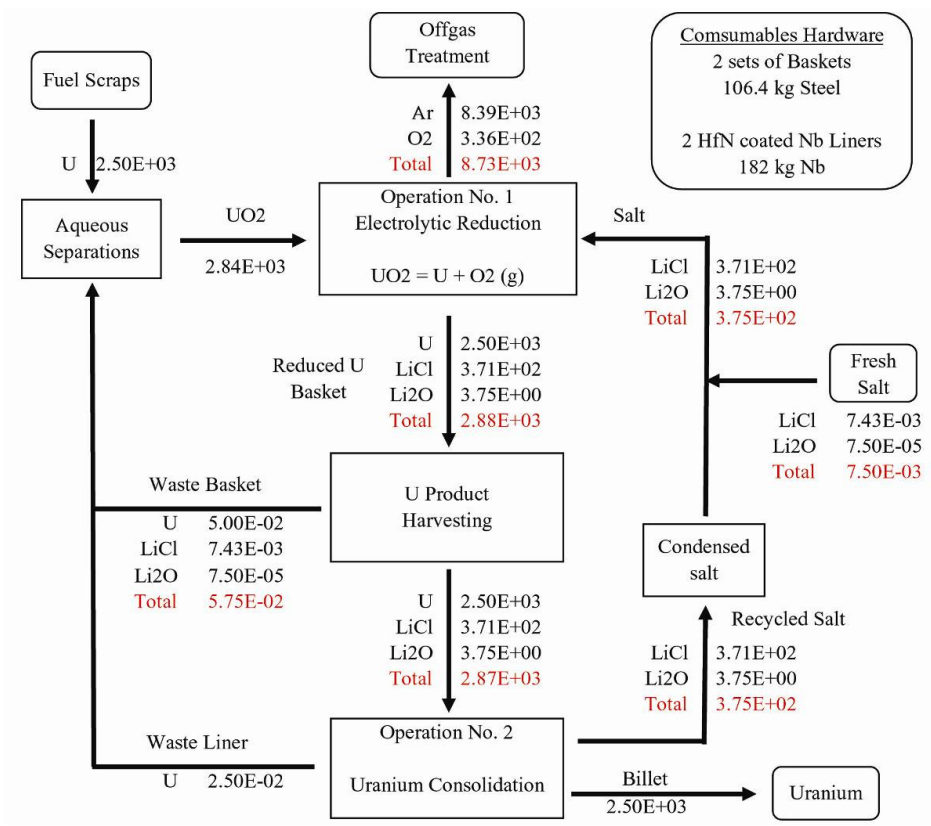

FIGURE 7 Alternative Facility Mass Balance Flowsheet

The waste from the process is composed of cathode baskets from the electrolytic reduction system and crucibles from cathode processing. However, the amount of waste is small—106.4 kg of steel from the reduction system and 182 kg of niobium from the cathode processer, which may recycled to the crucible manufacturer. Other process waste from the system is very small. The $LiCl$-Li_2O molten salt is recycled from the cathode processor to the electrolytic reduction process. Small additions of $LiCl$ or Li_2O will be required to offset the small amount of material sent to aqueous separations.

3.2 ELECTROLYTIC REDUCTION

Electrolytic reduction was originally conceived for the treatment of spent oxide nuclear fuel from light water and fast neutron spectrum reactors. Gourishankar et al. (2002) demonstrated the electrolytic reduction of uranium dioxide as part of the technology development activities for the treatment of spent nuclear fuel. Since that study, other researchers have confirmed the viability of using the process for converting uranium and spent fuel oxides to metal (Barnes and Willit 2007; Barnes 2008; Li et al. 2006; Sakamura et al. 2006). Barnes has demonstrated the complete conversion of UO_2 and U_3O_8 to uranium by electrolytic reduction. Current development activities focus on scale-up and optimization of the technology. Implementation of this technology for uranium oxide conversion is straightforward.

In the process, the uranium dioxide functions as the cathode of the electrolytic cell. The half-reaction describing the reduction process is

$$UO_2(s) + 4e^- = U(s) + 2O^{2-}. \tag{3}$$

The anode process consists of the oxidation of the oxide ions and evolution of oxygen gas. The half-reaction describing this process is

$$2O^{2-} = O_2(g) + 4e^-. \tag{4}$$

Platinum or another similar inert conductive material functions as the cell anode. Lithium chloride molten salt that contains 1 wt% lithium oxide is used as the electrolyte in the cell. The normal operating temperature for the cell is 650°C. The cell is operated at approximately 3 volts to reduce the uranium ions but not degrade the LiCl electrolyte. Cell currents depend on the size of the cathode system, but can range from tens to thousands of amps.

The electrolytic reduction process is completed in a furnace well attached to an inert atmosphere glovebox. The reduction process is sized to be filled with 56.7 kg of UO_2 (50 kg U) per loading. A process schedule that would meet the throughput requirements of 10 kg per day is one day for UO_2 basket loading, two days for reduction of the dioxide, one day for U product removal, and one day for cell clean-up. The uranium that is recovered from the basket is expected to contain approximately 15 wt% salt.

The cathode baskets would be constructed of stainless steel and are sized to contain approximately 23 L of material, assuming a conservative bulk density of 2.5 kg/L. A set of

six baskets that are 24 in. wide × 1 in. thick × 10 in. tall would appropriately accommodate this material. The basket dimensions are limited to 10 in. tall to simplify the product loading and harvesting process. The six-basket set has an estimated empty mass of 53.2 kg and 109.9 kg when fully loaded with UO_2. It is estimated that the baskets can be reused 25 times before replacement. The overall basket assembly footprint would be approximately 2 ft × 2 ft and fit within the reduction vessel opening sized to be 3 ft × 3 ft.

3.3 URANIUM CATHODE PROCESSING

Uranium cathode processing is required to remove residual salt that adheres to the metal and to consolidate the uranium into an ingot (Westphal et al. 2002; Brunsvold et al. 2000). In practice, the uranium metal covered with residual salt is recovered from the cathode of the reduction cell and placed into a crucible that is installed 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 from the uranium and then heated to 1200°C to melt the uranium to allow formation of an ingot. Salt is collected in a condenser and eventually recycled to the reduction system. After cool-down, the uranium ingot is removed from the crucible and recycled to fuel fabrication or prepared for storage.

The principal components of the cathode processor are the stainless steel vessel, the loading/unloading trolley, the induction furnace, vacuum pumps, and the condenser assembly. The equipment is sized to process 50 kg of U per loading. The main crucible is constructed of a hafnium nitride-coated niobium that is estimated to be reused 25 times. The crucible has an empty mass of 91 kg. Many of these components are commercially available and require few modifications before installation. The overall footprint of the cathode processor is approximately 8 ft by 16 ft. Due to the large footprint and the desire to reduce the glovebox manufacturing costs, only the loading and unloading of the cathode processor would be performed in the inert glovebox. The trolley rail system would be designed to deliver the crucible to the consolidation vessel while maintaining an inert atmosphere. The consolidation vessel is located next to the glovebox to minimize the distance that the crucible must travel.

3.4 FACILITY DESCRIPTION

Both processes are performed within an inert argon glovebox that is maintained with oxygen, water, and nitrogen purification systems. Additional equipment requirements include: UO_2 and U hoppers, power supplies, a heated reduction furnace well, an oxygen gas collector system, an induction furnace, and an overhead glovebox crane.

3.4.1 Electrolytic Reduction Glovebox

The inert atmosphere glovebox shown in Figure 8 is 16 ft long by 8 ft wide and contains two distinct areas: (1) electrolytic reduction, and (2) consolidation. The electrolytic reduction area requires five separate window stations each 4 ft by 4 ft wide. These stations are the heated salt well, salt and basket storage, basket loading, basket cleaning, and uranium harvesting. The

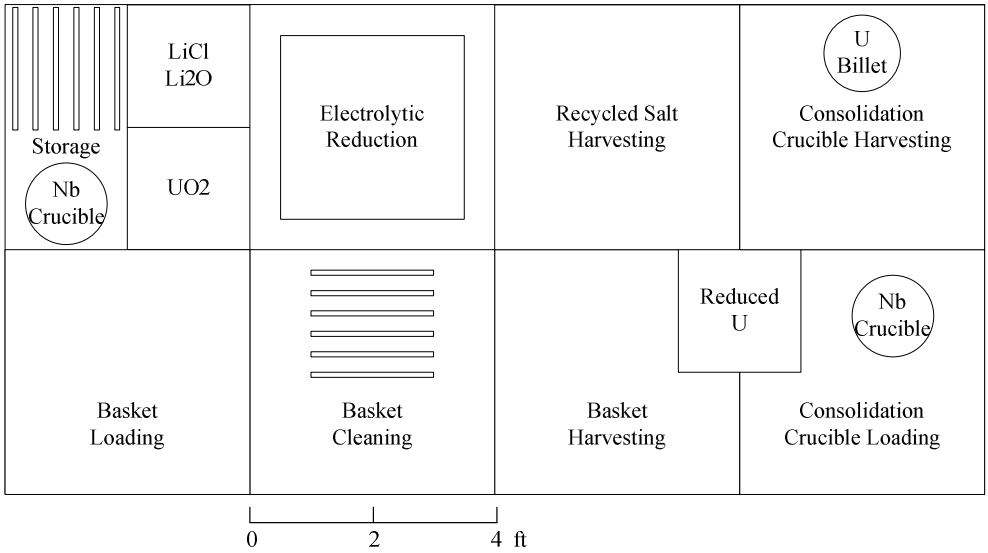

FIGURE 8 Reduction Glovebox Diagram with Crucible Loading/Unloading Station

consolidation area is made up of the remaining three stations. These stations are used for the crucible loading, uranium removal from the crucible, and salt recovery. The crucible loading and uranium harvesting stations are located next to each other and share a storage location. The uranium billets formed in the cathode processor are stored in a well within the station for uranium recovery from the crucible.

3.4.2 Cathode Processor

The cathode processor trolley would take the loaded crucible to the induction heater equipment located next to the glovebox and return the uranium ingot and salt after the cycle is completed. Figure 9 shows the overall layout with the cathode processor next to the glovebox. The glovebox pressure should be maintained negative to the facility to protect workers from possible uranium dust releases. The glovebox argon atmosphere would be maintained at low (ppm) O_2, H_2O, and N_2 levels using a dedicated purification system.

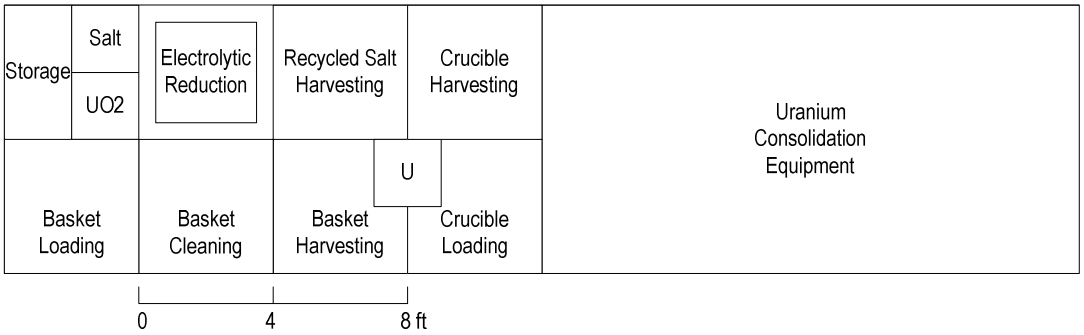

FIGURE 9 Reduction Glovebox Diagram and Uranium Consolidation

3.4.3 Laboratory Area

Three separate laboratory areas are required to make up the facility. The first laboratory contains the aqueous separations area, which accepts the uranium scrap from the carrier bay and converts the material into purified UO_2. The second area, the glovebox laboratory, contains the electrolytic reduction glovebox and the uranium consolidation equipment. This area also contains the inert atmosphere purification system, an induction furnace controller, and intermediate storage for the feed and final product. The third and final laboratory serves as the uranium and solid waste packaging area. Each of these areas would be fitted with overhead bridge cranes equipped to handle both equipment installation and product transfer. The approximate size of the nonaqueous process area (Figure 10) is 1350 ft^2, or 30 ft by 45 ft (i.e., excluding aqueous uranium recovery, waste packaging, and offices).

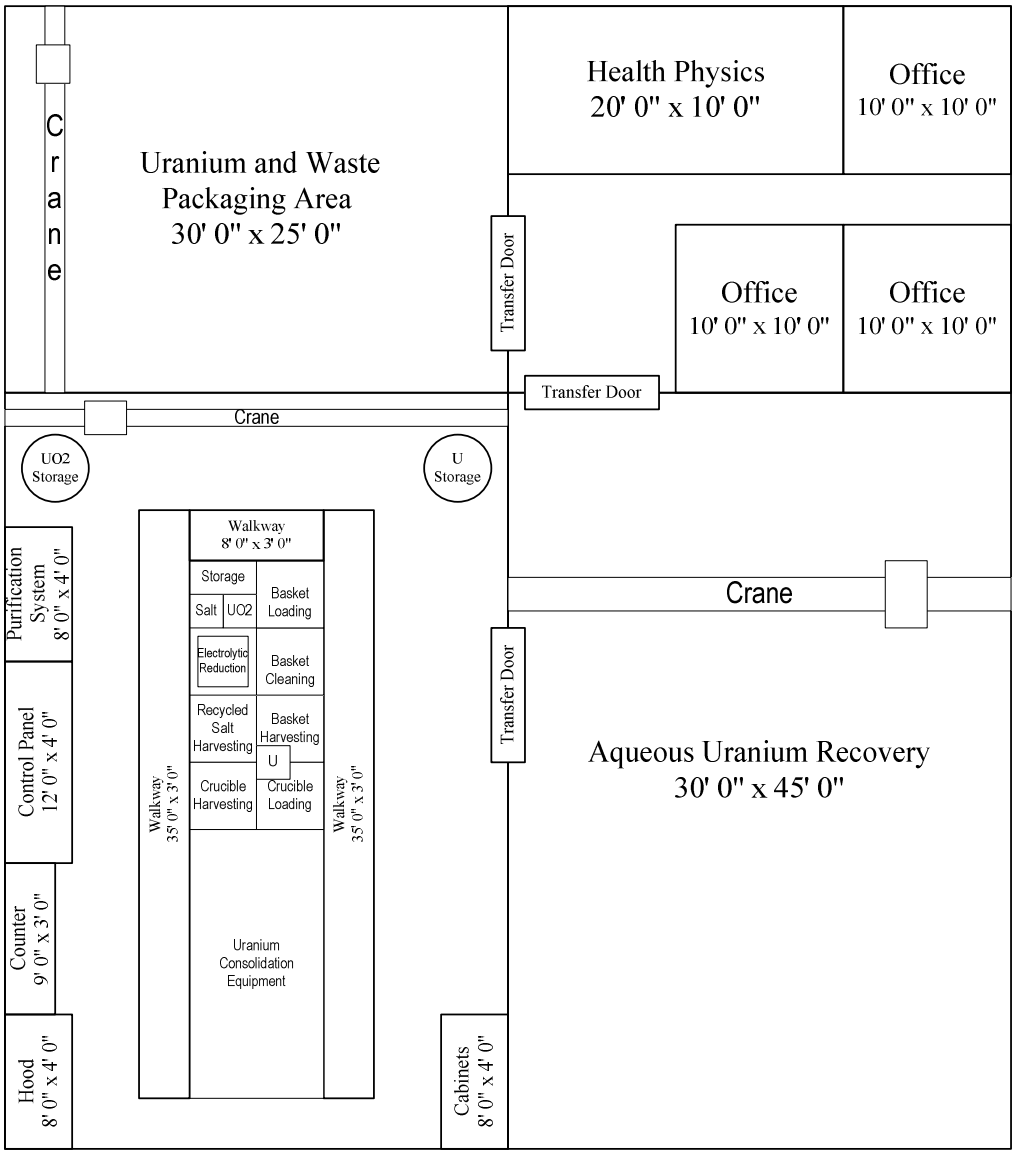

FIGURE 10 Alternative Facility Layout

3.5 COST ESTIMATE

An estimated equipment cost for the alternative process is shown in Table 2. The electrolytic reduction furnace well, the glovebox purification system, and the induction furnace are all commercially available pieces of equipment and require few modifications. The electrolytic reduction system would be designed based on current knowledge. Design improvements would be implemented as the technology is matured. The overall equipment cost for the alternative process is estimated to be $2220k.

TABLE 2 Alternative Equipment Costs

Reduction Glovebox	Cost ($k)
Glovebox 16' × 8' × 8' with Crane	1560
Purification System	155
Total Glovebox Cost	1715
Experimental Equipment	
Electrolytic Reduction	150
Cathode Processor	275
Uranium Storage System	20
Induction Furnace	40
Off-gas Treatment	20
Total Equipment Cost	505
Total Facility Cost	2220

4 SUMMARY

The facility envisioned for manufacturing the LEU fuel from HEU feedstock would create more than 2000 kg of LEU to be recycled annually. Two processes were proposed to treat the uranium dioxide produced by the aqueous purification process, which would remove the impurities from the recycle uranium. The baseline process consisting of hydrofluorination and calciothermic reduction is well established and yields high quality metallic product. The alternative process comprised of electrolytic reduction and cathode processing has been developed on the engineering scale, but requires demonstration at the scale proposed by this study. Although this alternative process has been shown to yield high purity uranium metal, it needs to be demonstrated a statistically significant number of times before comparison with the baseline process is meaningful.

The waste created in both processes is sent to the aqueous purification step to recover the uranium and stabilize the waste material into a suitable disposal form. The baseline process produces approximately 1800 kg of salt and 1400 kg of ceramic waste per year. In contrast, the alternative process is expected to produce an insignificant amount of salt waste (<1 kg), 106 kg of steel waste, and 186 kg of niobium for recycle. Significant annual savings in waste disposal and associated waste processing cost are anticipated for the alternative process.

Implementation of the baseline process is the lowest technical risk option for conversion of uranium dioxide to metal. However, this process produces substantially more waste than the alternative, which could lead to higher operational costs. Investment in a modest program to verify product quality for the alternative process would lower the technical risk associated with that approach and also provide additional confidence in the waste estimates for the large conversion facility.

A conceptual facility layout was developed for the baseline and alternative conversion processes. The nonaqueous processing area was 2000 ft^2 for the baseline process, while the alternative process would only require 1350 ft^2. Refinement of equipment design and layout would lead to optimization of laboratory space and perhaps yield a reduced space requirement for the baseline process. Nonetheless, the alternative requires a significantly less facility footprint.

The capital costs for baseline process equipment to convert uranium dioxide to uranium metal were estimated to be $1655k, while those for the alternative process were estimated to be $2220k. Although the capital cost for the alternative process is higher, savings are anticipated in operating and waste disposal cost for the alternative process. In a few years of operation, these savings could off-set the slightly higher capital cost for the alternative.

A follow-on design study to optimize the facility layout and yield more detailed equipment design information including a criticality safety analysis would provide additional confidence in the estimated facility requirements for each system. This design information would also allow for an improved bottoms-up cost estimate based on the newly generated data. Estimates of operating and waste management costs could also be derived as part of the design study and would provide additional insight into the selection of a preferred approach.

5 REFERENCES

Baker, R.D., et al., 1945, *Chemical and Metallurgical Operations Involved in the Fabrication of Uranium 235 for use in nuclear weapons: Part III. Reduction of Uranium Tetrafluoride to Metal,* LA-412, March

Banker, J.G., et al., 1981, *Method for Cleaning Bomb-Reduced Uranium Derbies*, United States Patent 4252564, February.

Barnes, L., and J.L. Willit, 2007, "*Direct Electrolytic Reduction of UO_2 vs U_3O_8*," Global 07 – Advanced Nuclear Fuel Cycles and System, Boise Idaho, 763-65.

Barnes, L., 2008, private communication.

Bonini, I., et al., 1998, "Nuclear Fuel Cycle Head-End Enriched Uranium Purification and Conversion into Metal," 1998 International Reduced Enrichment for Test Reactor Conference, Sao Paulo, Brazil, October.

Brunsvold, A., P. Roach, and B. Westphal, 2000, "Design and Development of a Cathode Processor for Electrometallurgical Treatment of Spent Nuclear Fuel," *Proceedings of ICONE 8: 8th International Conference on Nuclear Engineering*, Baltimore, MD.

Dussoubsa, B., J. Jourdeb, F. Patissona, J.-L. Houzelotc, and D. Ablitzera, 2002, "Mathematical modeling of uranium dioxide conversion in a moving bed furnace," Powder Technology 128:168–177.

Dussoubsa, B., J. Jourdeb, F. Patissona, J.-L. Houzelotc, and D. Ablitzera, 2003a, "Modelling of a moving bed furnace for the production of uranium tetrafluoride. Part 1: formulation of the model," Chemical Engineering Science 58:2617–2627.

Dussoubsa, B., J. Jourdeb, F. Patissona, J.-L. Houzelotc, and D. Ablitzera, 2003b, "Modelling of a moving bed furnace for the production of uranium tetrafluoride. Part 2: Application of the model," Chemical Engineering Science 58:2629–2642.

Edwards, C.R., and A.J. Oliver, 2000, "Uranium Processing: A Review of Current Methods and Technology," *JOM*, 52 (9):12–20.

Goorevich, R., 1998, *Handbook for Notification of Exports to Iraq: Annex 3*, *DOE Chapter 6, Plants and Equipment for the Conversion of Uranium*, SARC - 001/98, April.

Gourishankar, K., L. Redey, and M. Williamson, 2002, "Electrochemical reduction of metal oxides in molten salts," TMS 2002: 131st TMS Annual Meeting and Exhibition, Seattle, WA (US), in Light Metals 2002, Schneider, W.A., ed. Minerals, Metals & Materials Soc: Warrendale, 1075-82.

IAEA (International Atomic Energy Agency), 1999, *Potential Vulnerabilities of Nuclear Fuel Cycle Facilities to the Year 2000 (Y2K) Issue and Measures to Address Them*, IAEA-TECDOC-1087, May.

Li, S.X., M.F. Simpson, and S.D. Herrmann, 2006, "Oxygen Ion Oxidation Process on a Platinum Electrode in LiCl-Li_2O at 650°C," Molten Salt XIV, Proc. Fourteenth Int. Symp. Molten Salts.

Patisson, F., and D. Ablitzer, 2002, "Physicochemical and thermal modelling of the reaction between a porous pellet and a gas," *Powder Technology* 128:300– 305.

Perkins, B.L., 1982, *Evaluation of Environmental Control Technologies for Commercial Nuclear Fuel Conversion (UF_6) Facilities,* LA-9397-MS, UC-70, October.

Roddy, J.W., R.E. Blanco, and B.C. Finney, 1977, *Correlation of Radioactive Waste Treatment Costs and the Environmental Impact of Waste Effluents in the Nuclear Fuel Cycle – Conversion of Recycle Uranium to UF_4*, ORNL/NUREG/TM-37, April.

Sakamura, Y., M. Kurata, and T. Inoue, 2006, "Electrochemical Reduction of UO_2 in Molten $CaCl_2$ or LiCl," *J. Electrochem. Soc.,* 153(3):D31–D39.

Sheller, O.P., 1961, *Method for Reducing Uranium Tetrafluoride to Metallic Uranium*, United States Patent 3850623, January.

Wachs, D.M., C.R. Clark, and R.J. Dunavent, 2008, *Conceptual Process Description for the Manufacture of Low-Enriched Uranium-Molybdenum Fuel,* INL/EXT-08-1340, February.

Westphal, B.R., J.R. Krsul, and D.W. Maddison, 2002, "Molten Salt Separation form Uranium During the Processing of Spent Nuclear Fuel," TMS 2002: 131st Annual Meeting and Exhibition, Seattle, WA (U.S.), in Light Metals 2002, Schneider, W.A., ed., Minerals, Metals & Materials Soc: Warrendale, 57-62.

Chemical Science and Engineering Division
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 205
Argonne, IL 60439-4837

www.anl.gov

Argonne National Laboratory is a U.S. Department of Energy
laboratory managed by UChicago Argonne, LLC