ONLINE DIVERSION DETECTION IN CYCLUS

BY

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THESIS

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ABSTRACT

Abstract

dedication

ACKNOWLEDGMENTS

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INTRODUCTION

The diversion of significant quantities of Special Nuclear Material (SNM) from the nuclear fuel cycle is major non-proliferation concern [1]. These diversions must be detected in a timely manner using signatures and observables in order to properly safegaurd the fuel cycle. Timely detection is critical in non-proliferation to discover these shadow fuel cycles before diverted material is further processed. Pyroprocessing is a used nuclear fuel separations technology for advanced reactors. Signatures and observables are used to detect diversion of nuclear material. The goal of this research is to identify potential signs of material diversion in a pyroprocessing facility and implement models of these processes into a detailed pyroprocessing facility archetype to the modular, agent-based, fuel cycle simulator, Cyclus [2]. This facility archetype will equip users of the Cyclus fuel cycle simulator to investigate detection timeliness enabled by measuring signatures and observables in various fuel cycle scenarios.

1.1 Motivation

1.1.1 Safeguards

Currently there are no commercially operated pyroprocessing plants, however various research designs exist in national labs. Notably Argonne National Lab, Idaho National Lab and, in South Korea, KAERI [3, 4, 5]. Therefore, prior to construction of any design we want to implement safeguards by design. Similar to security by design in next generation reactors, the goal is to include key measurement points and access points to the design of the facility. Rather than learn from mistakes, in the future we aim to incorporate safety into the design.

1.1.2 Pyroprocessing

For other fuel cycle facilities, we have plenty of operating experience to inform on safeguard construction. For example, with aqueous reprocessing the IAEA provides detailed flowsheets of example facilities [6]. To combat this, multiple modeling tools have been developed for electrochemical processes such as SSPM and AMPYRE []. These tools take a high fidelity approach to model the chemistry taking place within each chamber. In order to run these tools, the user must have intimate knowlege of the specific facility the flowsheets have been designed for. There is a gap, however, in the medium fidelity models that can inform on broader fuel cycle applications. A generic facility capable of modeling changes in operational settings and various layouts has not yet been implemented to a fuel cycle simulator [7].

1.1.3 Future Fuel Cycles

As the world begins to consider cleaner forms of energy in response to climate change, nuclear energy has regained traction. A main concern with nuclear power is the pileup of UNF as a result of the once through fuel cycle. In turn, one suggested solution is converting to a closed fuel cycle [16]. There are many approaches to transitioning from our current fuel cycle to a new or closed cycle. Of these evaluation groups, EGs, those involving sodium fast reactors are of interest. Pyroprocessing can transition between current fuel cycle scenarios with light water reactors and SFRs and other metallic fuel. Therefore, pyroprocessing is under consideration as a means of processing the fuel required to start up new breeder reactors for the EG01-EG24 transition scenario.

1.2 Background

1.2.1 Pyroprocessing

Pyroprocessing is an electrochemical separation method used primarily for metallic fast reactor fuel. This reprocessing technique uses molten salt, which differs depending on the facility, to provide a medium for current to travel

across. Molten salt such as LiCl-KCl has a broader stability range comparative to water, allowing high potentials to be used for separation. Traditionally, separation would be conducted in a nitric acid which uses water as its medium. Water, however, has a significantly lower stability compared to molten salt. This becomes a problem when considering higher elements such as lanthanides and actinides. Controlling the oxidation states of these elements often requires potentials outside the stability of water. Hence, Pyroprocessing was born to improve nonproliferation and reprocessing capabilities.

In addition to the additional redox control of higher elements, we also co-extract materials of interest such that they cannot easily be refined for weapons. This is done through the electrorefining and electrowinning stages by separating a pure Uranium stream as well as a Uranium/Transuranic mix stream. The U/TRU can then be readily used for fuel fabrication while maintaining proliferation resistance.

Electrochemical Separations

Electrochemical separation is the driving force behind pyroprocessing. Electrochemistry relies on the use of Gibbs free energy to determine the required amount of energy to drive a reaction forward.
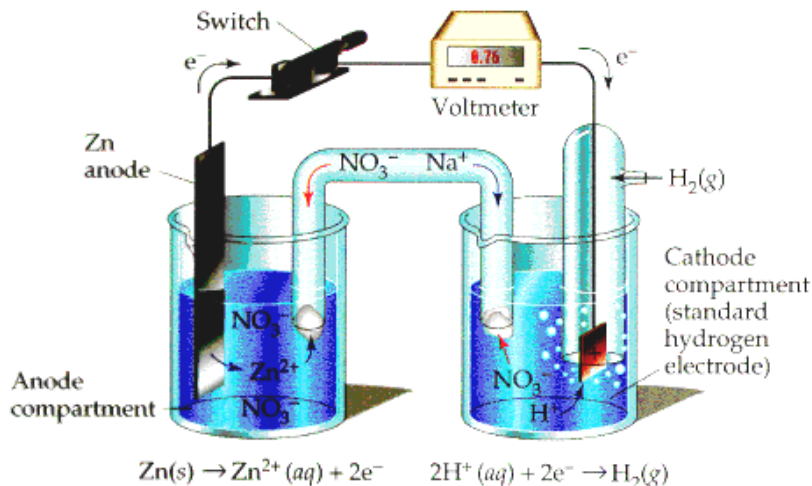

Figure 1.1: Basic example of movement of ion within galvanic cell [8].

Figure 1.1 demonstrates an electrochemical process that generates elec-

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tricity as a basic example. The processes described here follow the same principles, however, require energy to run. In both cases, ions are exchanged between the anode and cathode in an attempt to balance the potential difference. In the case of pyroprocessing, the potential difference is artificially applied. A number of different anodes and cathodes are used to force the desired ions to deliver charge from one end of the cell to the other. These ions that collect on the surface of the cathode can then be removed from the liquid and separated from the rest of the solution. By controlling the voltage of the solution as well as the composition of the anode, cathode, and electrolyte we can ensure the removal of unwanted elements/isotopes.

Voloxidation

Voloxidation is used following the chopping and decladding of the spent fuel. The process is very similar to annealing in regards to materials. The Uranium dioxide is heated to temperatures around 700-1000$°C$ which allows gases and some fission products to escape the fuel pellet. UO_2 is converted to U_3O_8 in this process as well[9]. Voloxidation, in most cases, takes place in air which provides plenty of oxygen for oxidization of solid UO_2 [10]:

$$3UO_2 + O_2 \rightarrow U_3O_8$$
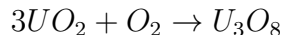
The above reaction is possible because of the expansion of uranium at elevated temperatures. A positive feedback is also established as the Uranium dioxide converts to yellowcake powder, the fuel element expands exposing more Uranium dioxide to oxygen. The rate of this reaction/conversion is dependent on the temperature and gas used. Higher temperatures will yield a faster reaction rate, however, even 500 $°C$ is sufficient for 99% reduction in 4 hours.

An added benefit of running a pyroprocessing voloxidation sub-process at the temperatures previously mentioned, 700-1000$°C$, is the removal of some fission products. The PRIDE facility at KAERI takes it a step further and voloxidates at 1250$°C$ to remove troublesome fission products at the beginning of the cycle[9]:

Voloxidation temperature	H-3	C-14	Kr-85	I-129	Cs	Tc	Ru	Rh	Te	Mo
1 250ºC	100	100	100	100	98	100	100	80	90	80

As shown in the table above, a majority of high activity isotopes are removed from the system at the beginning of pyroprocessing. This protects equipment and workers down the line. These gases are sent to the off-gas treatment facility that makes use of various scrubbing techniques such as liquid scrubbing, cyrogenic distillation (for the krypton), caustic scrubbing, etc [10].

Electroreduction

Following off-gassing and conversion to yellowcake, the non-metallic fuel must be converted and reduced to molten salt mixture. Most cases this is done with a LiCl-KCl salt eutectic combined with Li_2O catalyst. The electrolytic reduction phase consists of three main parts: UO_2 recovery, reduction, and RE removal.
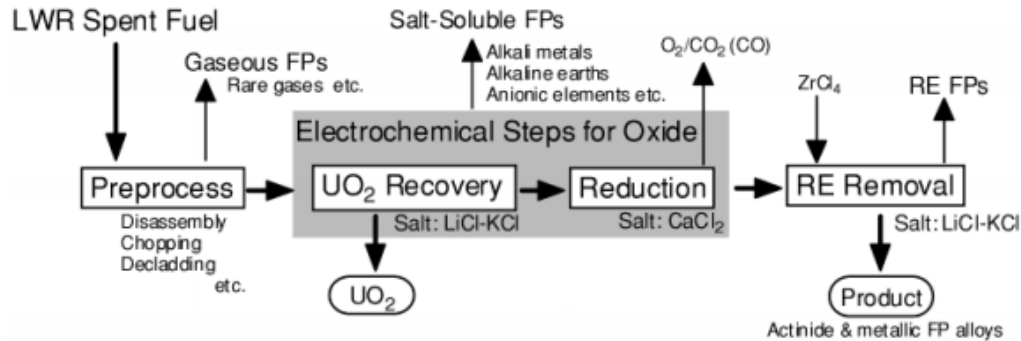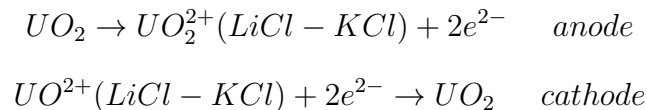

Figure 1.2: Electroreduction flow sheet [11].
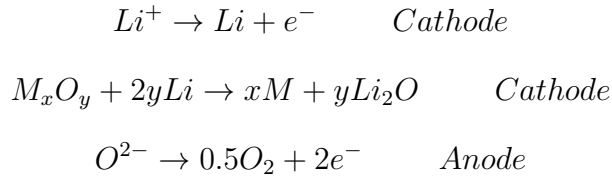
First step in electrolytic reduction is the recovery of UO_2 before reducing the remaining material. The following equations dictate the transfer of Uranium from the anode to the cathode.

$$UO_2 \rightarrow UO_2^{2+}(LiCl - KCl) + 2e^{2-} \quad anode$$

$$UO^{2+}(LiCl - KCl) + 2e^{2-} \rightarrow UO_2 \quad cathode$$

As in other separations technologies, noble metals can often follow the uranium through the rest of the process. The lurking noble metal fission products cause an increase in radioactivity of the UO_2 stream. Therefore, the weight percent dissolution of Uranium is critical in reducing the amount of waste that follows to the product stream. Lithium Oxide can also be used as a catalyst to draw Uranium to the cathode while leaving the noble metal fission products in the salt. This is done with 1-3wt% Li_2O in the following equations [12]:

$$Li_2O \rightarrow 2Li^+ + O^{2-}$$

$$UO_{x/2} + xLi \rightarrow U + xLi_2O$$
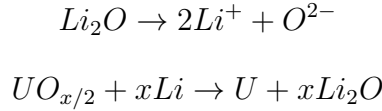
These equations make a continuously driven loop dragging Uranium (either UO_2 or U_3O_8) from the anode to the cathode. Disproportionated Lithium ions from the first equation break apart the Uranium and Oxide, with help from the electric potential. The U will collect on the cathode while the Li_2O is recycled and drives the first equation to the right again. Reduction then occurs on the cathode where the U, TRU, rare earths and noble metals have collected. This is achieved by evolving oxygen gas along the anode using the following reactions[12, 9]:

$$Li^+ \rightarrow Li + e^- \qquad Cathode$$

$$M_xO_y + 2yLi \rightarrow xM + yLi_2O \qquad Cathode$$

$$O^{2-} \rightarrow 0.5O_2 + 2e^- \qquad Anode$$

Electrochemical reduction results in an alloy of reduced U/TRU/RE/NM, however, we want to minimize the amount of RE and NM in the product. We've touched already on how to reduce the quantity of NM and for the final step the RE must be removed. The RE FPs can be removed from the alloy by substituting another chloride into the LiCl-KCl eutectic. In the case of Ohta et al. $ZrCl_4$ was considered [11]:

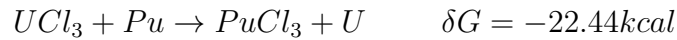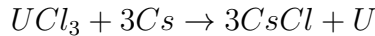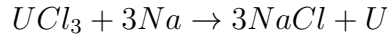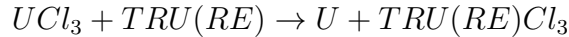$$3ZrCl_4(LiCl - KCl + RE \rightarrow 3Zr + 4RECl_3(LiCl - KCl)$$
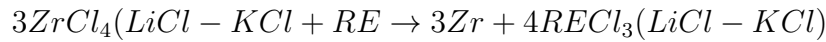
This process is shown to have a decontamination factor of 10 in regards to separating REs from actinides [13]. Additionally, by using Zirconium as the

metal substitute, it is compatible with fuel fabrication later [11].

Electrorefining

Electrorefining is the primary process in pyroprocessing, and is the feed point for fast reactor fuel, since it does not require reduction or chopping. Being the most important process, it is also the most complex with a multitude of input parameters and outputs. The goal of the refining process is to separate the Uranium and TRU from the alloy ingot formed in the reduction phase. Two streams will be formed for the fabrication of fuel. One stream that is a mix of U/TRU at the desired ratio, and the other a pure stream of Uranium. The refining step's efficiency relies on temperature and current primarily, however, advanced methods are being developed. KAERI for example has conducted work on adding a central stirrer, vacuum pressure, and rotating the anode [4]. The rotation aims to mix the Uranium in the salt such that none gets stuck on the bottom or edges of the vessel. Stirring too vigorously, however, can lead to the removal of uranium dendrites from the cathode thereby decreasing efficiency.

The governing reactions that allow this process to work are based on the stability constants and oxidization potential of the remaining fission products. The voltage used is such that Uranium is unstable in the chloride form, 0.5 1V [9], while transuranics have a higher stability. This leads to TRU remaining in chloride form, along with some Uranium, and pure Uranium accumulating on the cathode. The chloride reaction follows the below equation, and will run to the right as long as there is Uranium within the salt [9].

$$UCl_3 + TRU(RE) \rightarrow U + TRU(RE)Cl_3$$

$$UCl_3 + 3Na \rightarrow 3NaCl + U$$

$$UCl_3 + 3Cs \rightarrow 3CsCl + U$$

$$UCl_3 + Pu \rightarrow PuCl_3 + U \qquad \delta G = -22.44 kcal$$

$$4UCl_3 + 3Zr \rightarrow 3ZrCl_4 + 5U \qquad \delta G = 31.123 kcal$$

As shown by the reactions above, the TRU have a favorable gibbs free energy value for spontaneous reaction while the transition metals do not [14]. This leads to the transition metals remaining in anode basket while the TRU are drawn into the liquid cadmium cathode [15].

Electrowinning

The Electrorefiner accumulates TRUs and rare earth fission products within the salt. These isotopes build up and require separation and disposal, therefore the salt from the refiner is sent to the electrowinner. This stage further purifies the salt by targeting the electric potential of TRUs, RE and Uranium again [15, 9]. Placed in liquid cadmium once again, the three groups have overlapping electric potentials. Therefore, the three groups will all deposit in the cadmium [15]. While the refiner's role is to generate a stream of pure Uranium, the electrowinner performs co-extraction of Uranium and TRUs. This inherit proliferation resistance is a main draw of the pyroprocessing technique. Rare earths are still present on the cadmium therefore further separations must be conducted. These elements are removed through the addition of $CdCl_2$ which oxidizes the rare earths while the uranium and TRUs are unaffected. These oxidized elements fall back into the salt, leaving the purified U/TRU stream on the electrowinner.

Although the facility is great in terms of safeguards, pyroprocessing has its share of drawbacks as well. Currently, pyroprocessing can only be performed as a batch process, which signficantly limits throughput compared to a continuous facility. Additionally, the safety and economical concerns of running a molten salt plant are much greater than a nitric acid one. Despite these downsides, pyroprocessing is an efficient use of electrochemical separation and leader in proliferation resistant separations.

There are multiple different designs for a pyroprocessing facility, the most prominent being from ANL, INL, and KAERI. In order to encompass them all, we must take a generic approach. This is accomplished by including the following sub-processes: Voloxidation, Electroreduction, Electrorefining, and Electrowinning. While Electrorefining is the process of primary concern, each of the processes has an important in role in various processing plants.

1.3   Goals

The goals of this work are to appropriately model a generic pyroprocessing facility with medium fidelity capable of diversion. With this model in CYCLUS we wish to explore the capability of modeling sub-facilities and diversion. In addition, we will use this higher fidelity model to verify transition scenarios such as EG01-EG24 within CYCLUS [16]. Finally we wish to evaluate optimum detector placement and measurement points for various facility layouts through sensitivity analysis.

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