ARGONNE NATIONAL LABORATORY (ANL) PROGRESS IN MINIMIZING EFFECTS OF LEU CONVERSION ON CALCINATION OF FISSION PRODUCT ^{99}Mo ACID WASTE SOLUTION.

A. J. Bakel, K. J. Quigley, and G. F. Vandegrift

Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL

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ABSTRACT

A partnership between Argonne National Laboratory (ANL), MDS Nordion (MDSN), Atomic Energy Canada Limited (AECL) and SGN (France) has addressed the conversion of the MAPLE Reactor ^{99}Mo production process from high-enriched uranium (HEU) targets to low-enriched uranium (LEU) targets. One effect of the conversion would be to increase the amount of solid uranium waste five-fold; we have worked to minimize the effect of the additional waste on the overall production process and, in particular, solid waste storage. Two processes were investigated for the treatment of the uranium-rich acidic waste solution: direct calcination, and oxalate precipitation as a prelude to calcination. Direct calcination generates a dense UO_3 solid that should allow a significantly greater amount of uranium in one waste container than is planned for the HEU process, but doing so results in undesirable sputtering. These results suggest that direct calcination could be adapted for use with LEU targets without a large effect on the uranium waste treatment procedures. The oxalate-calcination generates a lower-density granular U_3O_8 product; sputtering is not significant during calcination of the uranyl oxalate precipitate. A physical means to densify the product would need to be developed to increase the amount of uranium in each waste container. Future work will focus on the specific chemical reactions that occur during the direct and oxalate calcination processes.

INTRODUCTION

To reduce nuclear-proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) Program is working to limit the use of high-enriched uranium (HEU) by substituting low-enriched uranium (LEU) fuel and targets. Production of medical-grade ^{99}Mo by irradiation of HEU targets is a significant fraction of U.S. HEU exports. Technetium-99m, the daughter of ^{99}Mo, is the most commonly used medical radioisotope. Molybdenum-99 is produced by the thermal neutron fission of ^{235}U, generally in HEU targets. Because LEU contains <20% ^{235}U, an approximately five-fold increase in the total amount of uranium is needed to produce an equivalent amount of ^{99}Mo.

Currently, we are working with MDS Nordion (MDSN) in cooperation with Atomic Energy Canada Limited (AECL) and Société Générale pour les techniques Nouvelles (SGN, France) to convert their ^{99}Mo production from HEU to LEU targets [1, 2]. The MDSN/AECL/SGN process utilizes HNO_3 to dissolve the irradiated uranium from the targets,

and ^{99}Mo is separated and purified using ion exchange procedures. The waste uranium stream is the effluent from the initial ion-exchange column and contains most of the fission products with the uranium in nitric acid. The concentration of uranium in this stream and perhaps the volume of this waste stream will increase when the process is converted to LEU. The main objective of this partnership is to minimize the impact of the LEU uranium-waste solution on the efficiency of ^{99}Mo production.

Our studies of the direct calcination process address three issues: (1) the density (volume) of the final calcine product, (2) the reaction sequence of this process, and (3) the off-gas and solid products generated under various conditions. Initial work concentrated on increasing the density of the solid generated from direct calcination of the uranium waste solutions. We worked on optimizing the direct calcination process in our laboratory-scale calciner. Experiments were conducted to allow for direct observation of the reactions occurring during the process. Current and future work investigates the stoichiometry of the reactions, and the products of the reactions under various experimental conditions. These studies are aimed at providing data to evaluate the effectiveness of current off-gas, waste treatment, and waste storage facilities to deal with LEU conversion.

Our studies of the oxalate-precipitation process confirmed the feasibility of the process for the treatment of uranium-rich waste solutions, and investigated the sequence of reactions in the process. Future work will investigate the stoichiometry of the reactions, and the products of the reactions under various experimental conditions.

EXPERIMENTAL

The calciner/evaporator used in this study is shown schematically in Figure I. The calciner head is permanently attached to the furnace and is connected to a water-cooled condenser. The calciner cup was fabricated from 2-inch pipe and has a volume of 250 mL. It is screwed into the calciner head and can be removed after each experiment for inspection. Condensed liquid is collected in gradated cylinders, and the vapor is routed through two alkali scrubbers to trap NO_x.   All solutions tested were unirradiated depleted uranium nitrate hexahydrate (UNH) dissolved in 1 M HNO_3.

To begin a run, a portion of the UNH/HNO_3 solution was fed into the calciner cup. The furnace was then set to the appropriate temperature and turned on. When condensate appeared in the condenser, the feed pump was switched on. The pump speed was adjusted so that the feed rate approximately matched the condensation rate. Samples of the condensate were taken at various times throughout the experiment and titrated to determine the concentration of nitric acid in each fraction.   The feed rate and condensation rate, as well as the vapor and liquid temperatures in the calciner cup were monitored and recorded throughout the experiment. When all of the UNH/HNO_3 solution had been fed into the system and the water and HNO_3 had evaporated, the temperature in the cup increased. The experiment continued for an additional 2 hours to allow for complete calcination.

A similar glass calciner/evaporator (Figure II) was assembled to allow us to observe and collect samples from the direct calcination and oxalate processes. The procedure was similar to that described above for the stainless steel calciner. During runs, we observed the reactions and collected samples of gaseous products, condensates, and contents of the reaction vessel. Mass balance calculations are being done to determine the stoichiometry of the reactions that occur during each process.

RESULTS AND DISCUSSION

Early studies were concerned with optimizing the direct calcination process, and in particular, maximizing the density of the uranium-bearing solid product. Current studies are concerned with describing the reactions that occur during the direct calcination and oxalate processes. Future studies will be concerned with the effects of several variables on the products generated during each process.

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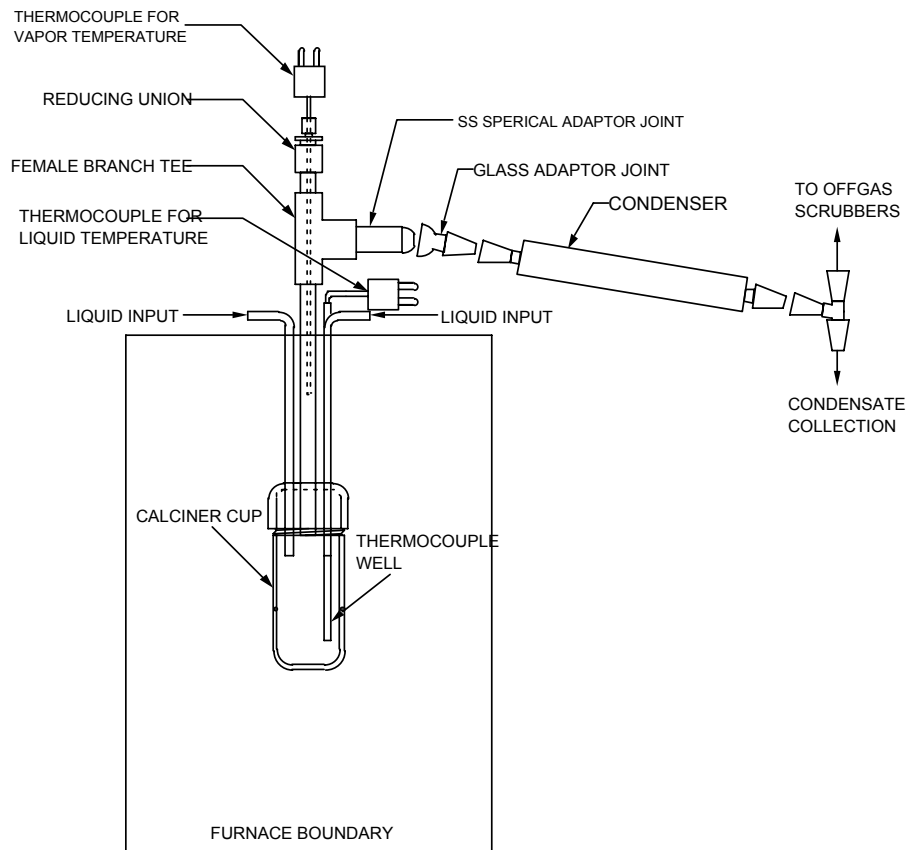CALCINER CUP

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Figure I. Schematic diagram of the stainless-steel calciner apparatus built in our laboratory to study the direct calcination of UNH/nitric acid solution.
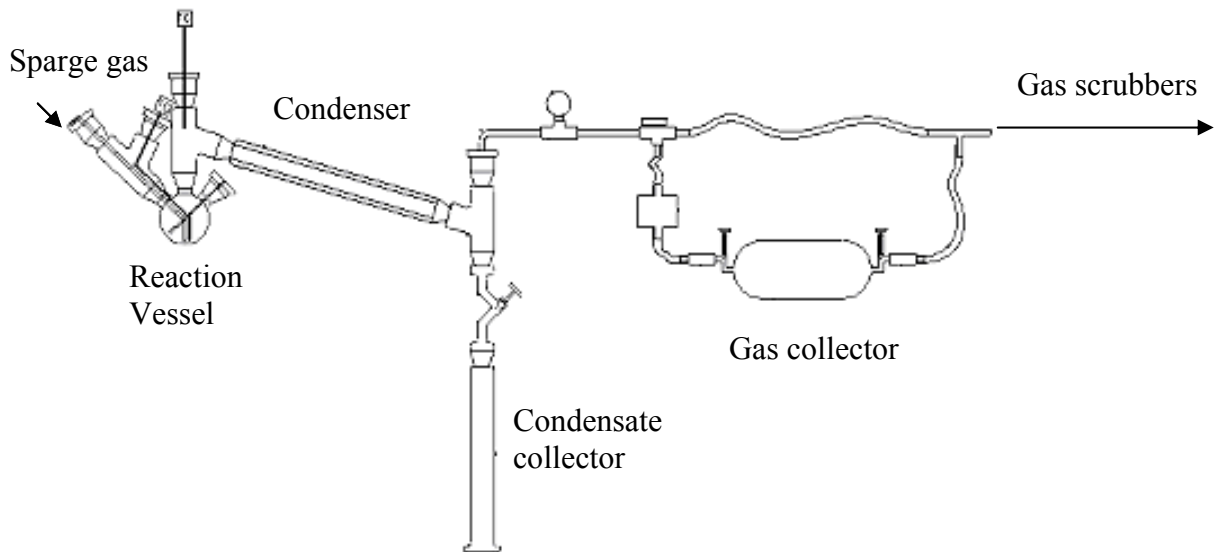
Figure II. Schematic diagram of the glass calciner apparatus built in our laboratory to study the reactions in the direct calcination and oxalate processes.

Direct Calcination Studies

Converting from HEU targets to LEU targets will require that approximately five times more uranium be placed in each calciner cup if the number of cups is to remain constant. An experiment was conducted to determine how much uranium could be placed into one calciner cup. We were able to place 675 g of U into a calciner cup. The in-cup density was about 3.0 g U/mL. The cup was about 90% full at the end of the experiment (Figures III and IV), and solid was splattered up the sides of the cup as well as onto the calciner head. This splattering is a concern because of possible equipment contamination in a production facility. An experiment was performed in the glass calciner apparatus (Figure II) to describe the reactions that occur during the direct calcination process. In particular, the splattering during the final stages of the process was of interest.

As the UNH/HNO_3 solution was fed into the calciner, a highly viscous, concentrated solution formed. After the feed was stopped, the solution boiled to dryness, leaving a porous yellow residue (Figure V). As the solid formed, a great deal of brown gas, presumably NO_2, was evolved, and finally a yellow solid remained at the bottom of the reaction vessel. Results from x-ray diffraction analysis show that this yellow solid was composed primarily of UO_3.

$$UO_2(NO_3)_2 \rightarrow UO_3 + 2NO_2 + 1/2O_2 \tag{1}$$
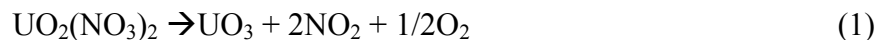
Sputtering was observed in the final stage of the process as the brown gas violently bubbled out of the concentrated solution. Figure VI shows the solids splattered on the sides of the reaction vessel during the final stages of the process. This is consistent with the solids observed on the side of the cup during operation of the stainless steel calciner (Figures III and IV).

Figure III. Photograph of the calciner cup after feed of 675 g U (1420 g UNH) in 6.68 L of 1 M nitric acid solution was completed.

Figure IV. Photograph of the calciner cup calcination (600°C for 2 hours) of the material shown in Figure III.

The direct calcination process has been shown to be feasible for the treatment of UNH/HNO$_3$ solutions in our laboratory-scale calciner. Chemical reactions during the process include evaporation, and denitration of UNH to UO$_3$. A relatively large amount of uranium can be placed into a cup by this process, however, sputtering was observed that could lead to equipment contamination. If splattering can be mitigated by the splatter guard already in the calciner, then the direct calcination process could be used for the UNH/HNO$_3$ waste from processing LEU targets in the MDSN/AECL/SGN process.

Oxalate Precipitation Studies

Uranyl oxalate trihydrate [UO$_2$(C$_2$O$_4$)•3H$_2$O] readily precipitates from uranyl salt solutions upon addition of oxalic acid. The precipitation is nearly complete; uranyl oxalate is less than 1 wt. % soluble (at 25°C) in the 1M HNO$_3$ solution [3] typically found in these wastes. The solubility is about five times higher at 100°C [4]. The precipitation is optimized when there is a small excess of oxalic acid present [3].

Thermal decomposition of precipitated uranyl oxalate can yield either UO$_2$ or UO$_3$. The dioxide is formed when oxalate is oxidized and uranium is reduced from U(VI) [(UO$_2$)$^{+2}$] to U(IV) (UO$_2$). The trioxide is formed when oxalate is oxidized and nitrogen is reduced from N(V) [(NO$_3$)$^-$] to N(IV) (NO$_2$).

Figure V. Photograph of the reaction flask after feed was stopped and all of the liquid was boiled away. The lighting was arranged to highlight the porous, yellow solid in the bottom of the vessel.

Figure VI. Photograph of the reaction flask after feed was stopped and all of the liquid was boiled away. The lighting was arranged to highlight the splatter on the side of the vessel.

An initial study was done to test the feasibility of the oxalate precipitation process for treatment of uranium rich acidic wastes in the MDSN/AECL/SGN process. The uranyl oxalate was precipitated outside the calciner at room temperature, and separated from the supernatant by decanting or filtering. This process generated two feeds for the calciner: (1) a dilute supernatant that could be rapidly evaporated in the calciner, and (2) a uranium-rich solid that could be placed directly into the calciner cup and decomposed to oxides.

The precipitate/supernatant slurry rapidly filtered through a 0.45 μm membrane vacuum filter, and produced a dense filter cake. The supernatant was analyzed with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and found to contain about 3.8 g U / L. Based on the results of these initial experiments, we determined that the oxalate precipitation process was promising.

Further studies were done to investigate the feasibility of the oxalate precipitation process in our laboratory-scale calciner. In this process, uranyl oxalate precipitated when the UNH/HNO$_3$ solution was mixed with solid oxalic acid in the heated calciner cup. After feed was stopped and evaporation was complete, the temperature inside the calciner cup increased. At this higher temperature, uranyl oxalate decomposed to a mixture of uranium oxides. The decomposition product in each experiment, regardless of the amount of oxalic acid used, was the mixed-valence U$_3$O$_8$ in a granular form with an in-cup density of about 1.3 g U/mL. With no physical compaction, this process would allow about 260 g U in a calciner cup. Physical compaction of this material to approximately 2.8 g U /mL is easily performed in the laboratory but would be a design challenge for hot-cell processing. Sputtering was not observed during this process, and most of the U$_3$O$_8$ was in the bottom of the cup. While these experiments demonstrated the feasibility of the uranyl oxalate precipitation process, the sequence of reactions during this process was not well known.

The reaction sequence was further investigated by performing the process in the glass calciner apparatus (Figure II). Oxalic acid dihydrate (0.2 moles) was placed in the reaction vessel, and 200 mL of a UNH/HNO_3 solution (0.08 moles of U) was added. A small amount of yellow solid, presumably uranyl oxalate, and a larger amount of white solid, presumably oxalic acid, was observed prior to heating. The mixture was then heated to boiling, resulting in the suspension of the solids. As the reaction proceeded, an increasing amount of brown gas was observed. The brown gas, presumably NO_2, was probably formed by the reduction of NO_3^- by oxalic acid. Therefore, the oxalic acid acts as a precipitation agent for uranium, as well as a reducing agent for nitrate during this process. Once all of the liquid had evaporated, the contained solids were primarily yellow with some orange and white (Figure VII). We expect that the yellow solid was uranyl oxalate and/or uranyl nitrate, the orange solid was UO_3, and the white solid was unreacted oxalic acid. As the temperature of the reaction vessel increased, up to about 450°C, the solid was increasingly black (Figure VIII) as the uranyl oxalate and UO_3 were reduced to U_3O_8. No sputtering was observed during the decomposition of uranyl oxalate to U_3O_8, and most of the black solid was at the bottom of the reaction flask (Figure VIII).

The oxalate precipitation process has been shown to be feasible for the treatment of UNH/HNO_3 solutions in our laboratory-scale calciner. Chemical reactions during the process include precipitation of uranyl oxalate, reduction of nitrate, and reduction of uranyl oxalate and UO_3 to U_3O_8. Relative to the direct calcination process, the oxalate precipitation process yields a lower-density product and, without a compaction step, would allow for less uranium in each calciner cup. On the other hand, no sputtering was observed during the oxalate precipitation process and physical compaction is a possibility for increasing the density of the final product.

Figure VII. Photograph of reaction flask immediately after all of the liquid was evaporated.

Figure VIII. Photograph of the reaction vessel some time after all of the liquid was evaporated. The temperature of the system was about 450°C.

FUTURE WORK

The focus of future work will be to describe the specific chemical reactions that occur during the treatment of UHN/HNO$_3$ waste solutions by the oxalate precipitation process. A quantitative understanding of the chemical reactions that occur during this process is needed in order to predict the compositions and volumes of products. Such predictions are needed to validate the ability of the current off-gas system for a production facility to handle this process. Similar predictions are needed to assure capability of in-place systems for handling and disposing of the solid and condensate waste products.

The matrix for these planned tests is shown in Table 1. The variables to be tested are oxalic acid to uranium molar ratio (OA:U), sparge-gas composition, and calcination temperature. Evaporation/precipitation experiments will be carried out with different OA:U ratios and different sparge gases. For example, test 1 (Table 1) will be an evaporation/precipitation experiment with an OA:U ratio of 0.75 performed with He as a sparge gas. Calcinations of the solid product from the evaporation/precipitation in test 1 will be done at different temperatures and different sweep gases. The solids from test 1 will be divided into six portions. Five of the portions will be calcined in He (1a-1e in Table 1) at the indicated temperatures, and the sixth will be analyzed using x-ray diffraction.

Samples of gaseous products, condensates and solids will be collected from each of these experiments and analyzed. Results of these products will allow us to determine which reactions occur during this process and the effect that each of the tested variables has on those reactions. This understanding will lead to predictive models for the products of the uranyl oxalate process.

CONCLUSIONS

The aim of this work is to assist MDSN/AECL/SGN to address the challenges presented by conversion from HEU to LEU targets for [99]Mo production. Conversion would increase the amount of solid uranium waste by approximately five times. Therefore, a top priority was a means to optimize treatment of the uranium-rich acidic waste solutions to minimize the effects of conversion. Specifically, strategies to improve concentration and calcination to accept a five-fold increase in uranium mass were investigated.

The direct calcination process was shown to be feasible for the treatment of UNH/HNO$_3$ solutions in our laboratory-scale calciner. However, sputtering was observed that could result in equipment contamination. If these results can be achieved in a production facility, then the direct calcination process could be used for the UNH/HNO$_3$ waste from processing LEU targets. Chemical reactions during the process include evaporation of water and HNO$_3$, and denitration of UNH to UO$_3$.

The oxalate precipitation process was also shown to be feasible for the treatment of UNH/HNO$_3$ solutions in bench-scale tests and in our laboratory-scale calciner. Chemical reactions during the process include precipitation of uranyl oxalate, reduction of nitrate by oxalate, and decomposition of uranyl oxalate and UO$_3$ to U$_3$O$_8$. Relative to the direct calcination

process, the uranyl precipitation process would allow for less uranium in each calciner cup with no compaction step. No sputtering was observed during the oxalate precipitation process.

The focus of future work will be to describe the specific chemical reactions that occur during the treatment of UHN/HNO$_3$ waste solutions by the oxalate precipitation process. Detailed knowledge of the chemical reactions will allow predictive models for the products of the uranyl oxalate process.

Table 1. Test matrix for the study of the oxalate precipitation process

OA:U	Calcine Temperature	Test vs. Sparge Gas		
mole/mole	°C	He	Air	4% H$_2$ / 96% He
0.75		Test 1	Test 4	Test 7
	400	1a	4a	7a
	500	1b	4b	7b
	600	1c	4c	7c
	700	1d	4d	7d
	800	1e	4e	7e
1.0		Test 2	Test 5	Test 8
	400	2a	5a	8a
	500	2b	5b	8b
	600	2c	5c	8c
	700	2d	5d	8d
	800	2e	5e	8e
1.25		Test 3	Test 6	Test 9
	400	3a	6a	9a
	500	3b	6b	9b
	600	3c	6c	9c
	700	3d	6d	9d
	800	3e	6e	9e

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