

**ANL Progress in Minimizing Effects of LEU Conversion on Calcination of
Fission-Product ⁹⁹Mo Acid Waste Solution**

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ABSTRACT

The goal of the Reduced Enrichment for Research and Test Reactors (RERTR) Program is to limit the use of high-enriched uranium (HEU) in research and test reactors by substituting low-enriched uranium (LEU) wherever possible. The work reported here documents technical progress in our partnership with MDS Nordion (MSDN), Atomic Energy Canada Limited (AECL) and SGN of France to convert the ^{99}Mo production in the MAPLE reactors and the New Processing Facility at AECL's Chalk River Laboratories from the use of HEU targets to LEU targets. The role of Argonne National Laboratory and the Chemical Engineering Division in the program is to work with MSDN to minimize the impact of conversion on the efficiency and reliability of their production effort.

The primary concern with the conversion to LEU from HEU targets is that it would result in a five fold increase in the total uranium. This increase is likely to result in more liquid waste from the process. We have been working with MSDN/AECL/SGN to minimize liquid waste volume and the effects of 5 times more uranium on waste treatment and storage. The planned process for solidifying high level fissile waste from the processing of HEU targets in the New Processing Facility will use calcination of the uranium waste solution. This method generates NO_2 gas and UO_3 solid.

We have studied two processes for treating the uranium-rich liquid waste from a LEU-based process for MSDN: (1) an optimized direct calcination process that is similar to the planned process, and (2), a calcination of uranyl oxalate precipitate. The specific goal of the work reported here was to characterize the chemical reactions that occur during these two processes. In particular, the compositions of the gaseous and solid products were of interest. A series of experiments was carried out to show the effects of temperature and the redox potential of the reaction atmosphere. The primary products of the direct calcination process were mixtures of U_3O_8 and UO_3 solids and NO_2 gas. The primary products of the uranyl oxalate precipitate process were mixtures of U_3O_8 and UO_2 solid and CO_2 gas. Higher temperature and a reducing atmosphere tended to favor quadravalent uranium over hexavalent uranium in the solid product. These data will help to plan for pilot plant testing. In addition, the data provides information for the design of the off gas systems for pilot and production facilities.

I. Introduction

A. Background

To reduce nuclear proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) Program is working to reduce the use of high-enriched uranium (HEU) in research and test reactors by substituting low-enriched uranium (LEU) fuel and targets. Radioactive decay of ^{99}Mo produces $^{99\text{m}}\text{Tc}$ (half-life of 2.75 days), which is used in large quantities in nuclear medicine. Thermal neutron fission of ^{235}U generates ^{99}Mo ; the ^{235}U is generally in the form of HEU (93% enriched ^{235}U) targets. Because LEU contains <20% ^{235}U , a five fold increase in the total amount of uranium is needed to produce an equivalent amount of ^{99}Mo . Such an increase in total uranium would lead to an increase in the amount of waste, and possibly, a reduction in

facility throughput. ANL's role is to help each producer minimize the negative impact of LEU conversion on their process.

Currently, we are working with MDS Nordion in cooperation with Atomic Energy Canada Limited (AECL) and SGN (France) to convert the ^{99}Mo production in the MAPLE reactors and the New Processing Facility at AECL's Chalk River Laboratories from HEU to LEU targets. The baseline HEU process utilizes HNO_3 to dissolve irradiated uranium oxide from the targets, and ^{99}Mo is separated from the dissolver solution using ion exchange. The effluent from the initial ion-exchange column contains most of the fission products with the uranium in nitric acid. This waste solution is directly calcined in order to form a stable uranium oxide waste storage form. The concentration of uranium in the ion-exchange effluent and perhaps, its volume 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 and reliability of ^{99}Mo production. This work is an extension of earlier reported progress [1-3]

Our studies of the direct calcination and calcination of oxalate precipitate from the uranium waste solution investigated the composition of the gaseous and solid products generated under various process conditions. These studies are aimed at providing data to design off-gas, waste treatment, and waste storage facilities to deal with LEU conversion.

B. Goals

This project aims to assist MDSN in their effort to convert their ^{99}Mo production from HEU to LEU targets. The specific goals of this work were to identify the gaseous and solid products of uranyl nitrate/nitric acid and uranyl nitrate/nitric acid/oxalic acid slurries. These data are needed for the design of a pilot-scale calcination facility, and to interpret results from pilot scale testing.

II. Experimental

A. Test matrix

The calcination experiments were performed in a steel calciner apparatus to allow for operation at temperatures up to 1000°C . The calciner consisted of a steel cup that was screwed into the calciner head and was removed after each experiment for collection of the solid products. The calciner was designed to allow collection of gas samples during the experiment.

Samples of solid uranyl nitrate hexahydrate (UNH) or uranyl oxalate derived from evaporating simulated uranium waste solutions were placed in a 10 mL beaker that was inside the steel cup. The cup was then sealed in place on the calciner head. The sweep gas was started and the furnace was set to the desired temperature. Gas samples were collected throughout the experiment. The final temperature was held for 2 hours to

assure that the reactions were complete. Samples of the solid products were collected after the system had cooled overnight.

Experiments were conducted at two different temperatures (400 and 600°C), and with two different sweep gasses (air, and 4% H₂ / 96% He) with UNH and uranyl oxalate. This results of these tests were interpreted in terms of temperature and oxidation potential of the atmosphere. The air sweep gas ensures that the atmosphere is oxidizing, and the H₂/He ensures that the atmosphere is reducing.

B. Gas analysis

The gas samples collected during the calcination experiments were analyzed using a mass spectrometer designed specifically for gas analysis. The gas samples were introduced through a capillary tube into the ionization source. The fragments were separated using a quadrupole. The fragments were assigned as follows: CO + N₂, m/z = 28 (m/z is the value of a fragment's mass divided by its charge), therefore, CO cannot be determined in the samples collected with air as the sparge gas; NO, m/z = 30; O₂, m/z = 32; CO₂ + N₂O, m/z = 44; and NO₂, m/z = 46. The m/z = 44 peak was assigned to N₂O in the UNH tests, and to CO₂ in the oxalate tests.

C. Thermogravimetric analysis.

Samples (UNH and uranyl oxalate solids) collected from the evaporation/precipitation steps were analyzed using thermogravimetric analysis (TGA). These analyses characterize the thermal decomposition of solid phases during a heating from ambient to 900°C over the course of 90 minutes. Mass loss was monitored, and the evolved gas was identified using infrared absorption line energies. These data were used to assist in the identification of the gaseous products of the calcination of UNH and uranyl oxalate.

III. Results and Discussion

A. UNH, Direct Calcination

1. Solid Products

The solid products of the calcinations in air at both 400 and 600°C (Table 1) had a yellow color typical of UO₃. X-ray diffraction patterns showed that these samples are composed primarily of UO₃, but also contain some U₃O₈.

The solids from the calcination in 4% H₂/96% He at 400°C has a greenish-black color typical of U₃O₈, while the material calcined at 600°C has a black color typical of UO₂. X-ray diffraction patterns show that the material calcined at 400°C is composed primarily of UO₃, and contains a small amount of U₃O₈. X-ray diffraction patterns show that the material calcined at 600°C is composed entirely of UO₂.

Table 1. Characteristics of the products of UNH calcinations

Atmosphere	Temperature	Appearance	Identification by XRD
Air	400°C	Yellow	U ₃ O ₈ /UO ₃ (28/72)
Air	600°C	Yellow	U ₃ O ₈ /UO ₃ (24/76)
4% H ₂ /96% He	400°C	Greenish-black	U ₃ O ₈ /UO ₃ (30/70)
4% H ₂ /96% He	600°C	Black	UO ₂

2. Gaseous Products

Gases were collected during the calcination experiments with UNH. The samples were analyzed with mass spectrometry to determine their compositions (Table 2). The experiment performed in air generated NO₂, and smaller amounts of NO and CO₂ + N₂O (assumed to be N₂O in this case). The highest concentrations of these gases were observed in the samples collected at about 25 minutes.

The experiment performed in 4% H₂/96% He generated NO₂, and smaller amounts of NO and N₂O (Table 2). The highest concentrations of these gases were observed in the sample collected at 25 minutes after the beginning of the experiment. The predominance of NO₂ in the generated gas suggests that denitration of the UNH occurred during the calcination experiments regardless of the sweep gas.

TGA analysis was conducted with UNH to confirm the identity of gas. Because the TGA was run with an air purge gas, the results should compare to our calcination results in air. The data in Figure 1 show that the major decomposition products of the TGA were water evolved at 120-250°C, and NO₂ evolved at 250-830°C. The water detected during TGA experiments would not be detected in our calcinations because any water evolved would be condensed. The major gaseous product of our calcinations of UNH in air sweep gas was NO₂ (Table 2). Therefore, the results from TGA are consistent with the results from calcination experiments. Specifically, NO₂ is the major gases generated during the calcination of UNH in air.

Table 2. Concentrations (mol%) of gases collected from calcinations of UNH solids.

Atmosphere	Temperature	Time ^a	NO ₂ m/z = 46	NO m/z = 30	N ₂ O ^b m/z = 44
Air	400°C	15	<0.01	<0.01	<0.01
Air	400°C	21	0.10	0.01	0.08
Air	400°C	26	1.62	0.33	0.12
Air	400°C	36	<0.01	0.04	0.05
Air	400°C	46	<0.01	0.09	0.03
Air	400°C	56	0.03	<0.01	0.07
Air	600°C	15	<0.01	<0.01	<0.01
Air	600°C	25	1.67	0.37	0.14
Air	600°C	35	0.22	0.11	0.04
Air	600°C	45	<0.01	0.02	<0.01
H ₂ / 96% He	400°C	15	0.27	<0.01	<0.01
H ₂ / 96% He	400°C	25	2.75	0.48	0.34
H ₂ / 96% He	400°C	30	0.24	<0.01	0.03
H ₂ / 96% He	400°C	40	0.09	<0.01	0.01
H ₂ / 96% He	600°C	15	0.26	0.08	0.07
H ₂ / 96% He	600°C	18	0.88	0.13	0.29
H ₂ / 96% He	600°C	23	0.64	0.13	0.18
H ₂ / 96% He	600°C	27	0.01	<0.01	<0.01

a. -time (number of minutes after furnace was turned on) when sample was collected.

b. -because no carbon was in these samples, all of the m/z=44 peak is assumed to be N₂O.

3. Reactions

The calcination of UNH under these experimental conditions is a combination of several complex reactions. The present data do not allow us to rigorously determine all of the reactions, or the stoichiometry of the overall reaction. However, the products observed, and their relative abundances allow us to propose some reactions that occur during the calcinations.

Heating uranyl nitrate hexahydrate leads to two-step dehydration (reactions 1 and 2). Calcination of UNH in air at 400 and 600°C yielded UO₃, a small amount of U₃O₈, and NO₂ gas. Therefore, we propose that reaction (3) was dominant, with a small contribution from the higher temperature reaction (4). Calcination of UNH in 4% H₂/96% He at 400°C yielded U₃O₈, and UO₃, and NO₂ gas. These products indicate that reactions (3), and (5) occurred. Calcination of UNH in 4% H₂/96% He at 600°C yielded UO₂, and NO₂ gas. Reaction (6) is proposed as the dominant reaction in the higher temperature experiment in a reducing atmosphere.

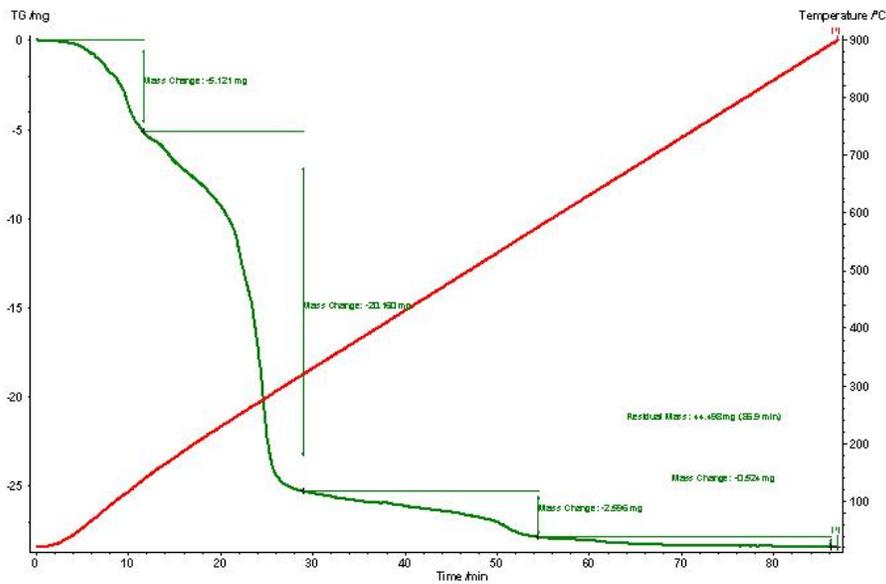
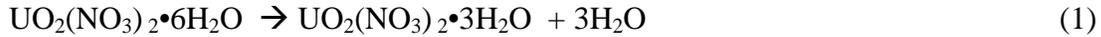


Figure 1. TGA results from the analysis of UNH.

4. Summary

The primary reaction that occurs during the calcination reactions is the denitration of UNH. Solid products produced during calcinations in air were mixtures of UO_3 and U_3O_8 . When the calcination was carried out in a reducing atmosphere (H_2/He sweep gas), a mixture of UO_3 and U_3O_8 was produced at 400°C , and only UO_2 was produced at 600°C .

The gaseous reaction products produced during calcinations were identified. The primary off gas from the calcinations of UNH was NO_2 , regardless of the experimental

conditions. This shows that denitration of UNH is the dominant reaction during the calcination step.

B. Uranyl Oxalate Precipitate Process

An alternative process was needed because of concerns about the splattering of uranium oxide calcinations product, leading to equipment contamination and the generation of NO_x gases, leading to regulatory problems. Facilitated calcination by precipitation of uranyl oxalate in laboratory tests was promising as an alternative to direct calcinations as a treatment process for the UNH/ HNO_3 waste solutions expected in the process with LEU.

Uranyl oxalate trihydrate [$\text{UO}_2(\text{C}_2\text{O}_4)\cdot 3\text{H}_2\text{O}$] 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 typically found in these wastes [4]. The solubility is about 5 times higher at 100°C [5]. The precipitation is optimized (i.e., the solubility is lowest) when there is a small excess of oxalic acid present [4].

1. Calcinations

A set of experiments was performed in the steel calciner to decompose (at 400 and 600°C) uranyl oxalate. Samples of uranyl oxalate were calcined in oxidizing air and in reducing H_2/He sweep gasses. Gaseous products were collected throughout the calcinations. The experiment was held at the final temperature for at least 2 hours to ensure complete reaction. The calcinations were expected to generate solid uranium oxides and carbon oxide gases. The identification and proportions of these products will allow us to describe the reactions that occur during the calcination process.

2. Solid Products

Solids collected from the calcinations of uranyl oxalate (Table 3) were collected and analyzed with x-ray diffraction to determine their compositions. The material calcined in air at 400°C showed both the black color typical of UO_2 and the orange color typical of UO_3 . However, the x-ray diffraction pattern showed that this material was primarily U_3O_8 . The material calcined in air at 600°C was black, and the x-ray pattern showed that the primary component of the calcined solid was again, U_3O_8 . The materials calcined in 4% $\text{H}_2/96\%$ He were both black. The x-ray diffraction analysis showed that the material calcined in 4% $\text{H}_2/96\%$ He at 400°C was a mixture of UO_2 and U_3O_8 . The material calcined in 4% $\text{H}_2/96\%$ He at 600°C was composed primarily of UO_2

Table 3. Characteristics of the solid products of uranyl oxalate calcinations.

Atmosphere	Temperature	Appearance	Identification
Air	400°C	Black/orange	U ₃ O ₈
Air	600°C	black	U ₃ O ₈
4% H ₂ /96% He	400°C	black	U ₃ O ₈ /UO ₂ (89/11)
4% H ₂ /96% He	600°C	black	UO ₂

3. Gaseous Products

Gases were collected during the calcinations of uranyl oxalate, and analyzed with mass spectrometry (Table 4) to determine their compositions. Gas samples from the calcination experiments performed in air contain CO₂ + N₂O, less NO, and small amounts of NO₂. Gas samples from the experiments performed in 4% H₂/96% He contain small amounts of CO₂ + N₂O (assumed to be CO₂ in this case), and NO, and less NO₂.

TGA analysis was conducted on solid uranyl oxalate samples. Because the TGA was run with an air purge gas, the results should compare to our calcination results with air sweep gas. The data in Figure 2 show that the major products of the TGA experiment were water (evolved at 130-330°C), CO and CO₂ (evolved at 330-430°C). The water detected during TGA experiments would not be detected in the gasses collected during our calcinations because any water evolved would be condensed. The major gaseous product of our calcinations of uranyl oxalate in air sweep gas was CO₂ (Table 4). Note that CO generates the same molecular fragment as N₂, and thus was not detected using mass spectrometry in the presence of air. Therefore, the results from TGA are consistent with the results from calcination experiments. Specifically, CO and CO₂ are the major gases generated during the calcination of uranyl oxalate in air.

4. Reactions

Heating uranyl oxalate trihydrate leads to dehydration (7) Calcination of uranyl oxalate in air at both 400°C and 600°C yielded U₃O₈ and CO₂ gas. Therefore, we propose that reaction (8) was dominant under oxidizing conditions. The TGA results show that CO is also generated during the calcination of uranyl oxalate. Equation (9) shows the degradation of any residual oxalic acid to generate CO, and reaction 10 shows the reduction of CO₂ by H₂ to form CO. Calcination of uranyl oxalate in 4% H₂/96% He at 400°C yielded a mixture of UO₂ and U₃O₈, and CO₂ gas. A combination of reactions (8) and (11) is suggested. Calcination of uranyl oxalate in 4% H₂/96% He at 600°C yielded UO₂, and CO₂ gas. These products are consistent with reaction (11).



Table 4. Concentrations (mol%) of gases collected from calcinations of uranyl oxalate solids.

Atmosphere	Temperature	Time ^a	NO m/z = 30	O ₂ m/z = 32	CO ₂ ^b m/z = 44	NO ₂ m/z = 46
Air	400°C	18	0.15	<0.01	0.12	<0.01
Air	400°C	26	0.25	<0.01	0.32	<0.01
Air	400°C	31	<0.01	<0.01	0.33	0.03
Air	400°C	41	<0.01	<0.01	0.29	<0.01
Air	400°C	51	<0.01	<0.01	0.15	<0.01
Air	600°C	10	0.01	<0.01	0.03	0.01
Air	600°C	16	0.11	<0.01	0.36	0.03
Air	600°C	22	0.06	<0.01	1.38	0.08
Air	600°C	33	0.15	<0.01	0.12	<0.01
Air	600°C	44	0.07	<0.01	0.06	<0.01
Air	600°C	54	<0.01	<0.01	0.03	0.06
4% H ₂ /96%	400°C	15	0.08	<0.01	0.06	0.01
4% H ₂ /96%	400°C	24	0.11	<0.01	0.28	0.03
4% H ₂ /96%	400°C	35	<0.01	<0.01	0.05	<0.01
4% H ₂ /96%	400°C	45	0.01	<0.01	0.01	<0.01
4% H ₂ /96%	600°C	15	0.14	<0.01	0.06	<0.01
4% H ₂ /96%	600°C	20	0.15	<0.01	0.15	<0.01
4% H ₂ /96%	600°C	30	0.32	<0.01	0.13	0.11
4% H ₂ /96%	600°C	40	0.53	<0.01	0.16	0.03
4% H ₂ /96%	600°C	50	<0.01	<0.01	0.01	0.03
4% H ₂ /96%	600°C	60	0.01	<0.01	<0.01	0.01

a. time (number of minutes after furnace was turned on) when sample was collected.

b. because no carbon was in these samples, all of the m/z=44 peak is assumed to be N₂O.

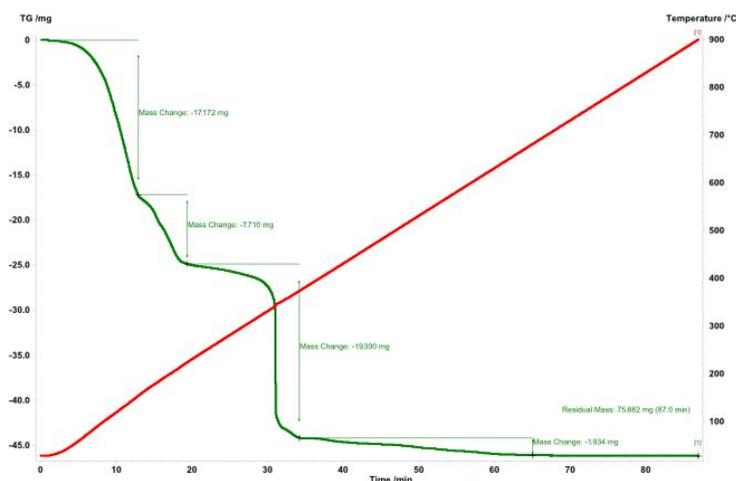


Figure 2. TGA results from the analysis of uranyl oxalate.

5. Summary

The work reported here focused on the calcination of uranyl oxalate. The primary reaction that occurs during the calcination step is the degradation of uranyl oxalate to UO_2 , U_3O_8 , CO , and CO_2 .

The solid products of each step were identified in order to determine the reactions and to support the design of a waste storage system for a pilot or production scale facility. Solid products produced during calcinations in air were primarily U_3O_8 . Calcinations carried out in a reducing atmosphere (4% H_2 /96% He) at 400°C generated a mixture of U_3O_8 and UO_2 , and at 600°C generated UO_2 . These results suggest that higher temperature and a reducing atmosphere favor reduction of uranium.

The gaseous reaction products of each step were identified in order to support the design of off gas systems for a pilot or production scale facility. The primary off gasses from the calcination step are CO , and CO_2 . The decomposition of oxalate is the primary source of this gas. Based on gas and solids compositions, we have suggested possible chemical reactions that occur during the process.

C. Comparison of the two processes

The data presented here can be used to compare the direct calcination process to the calcination of oxalate precipitate for treatment of the UNH/ HNO_3 waste solutions expected from LEU-based ^{99}Mo production. A decision will be made based on safety, cost, and reliability.

Earlier studies showed that the direct calcination process yields a higher density product than the uranyl oxalate process. Therefore, without a compaction step, the

oxalate process would allow for less uranium in each calciner cup. If a solid compaction step is not added, the additional cups needed for implementation of the oxalate process may impact the solid waste treatment and storage facilities. On the other hand, no splattering was observed during the calcination of oxalate precipitate, while splattering was a significant problem during the direct calcinations process. The observed splattering might lead to contamination of the calciner equipment, which might impact the safety and downtime of the operation.

Table 5. Primary products of calcinations reactions

Form	Atmosphere	Temperature	UNH	Oxalate
Solid	Air	400°	UO ₃ /U ₃ O ₈	U ₃ O ₈
Solid	Air	600°	UO ₃ /U ₃ O ₈	U ₃ O ₈
Gas	Air	400°	NO ₂	CO ₂
Gas	Air	600°	NO ₂	CO ₂
Solid	4% H ₂ / 96% He	400°	UO ₃ /U ₃ O ₈	U ₃ O ₈ /UO ₂
Solid	4% H ₂ / 96% He	600°	UO ₂	UO ₂
Gas	4% H ₂ / 96% He	400°	NO ₂	CO ₂
Gas	4% H ₂ / 96% He	600°	NO ₂	NO

A comparison of the solid and gaseous products from the calcinations of the UNH and oxalate processes is shown in Table 5. Under most conditions, calcination of the UNH yields a mixture of UO₃ and U₃O₈, and calcination of uranyl oxalate yields a mixture of U₃O₈ and UO₂. The primary off gas from calcination of UNH in this study is NO₂, and the primary off gas from calcination of uranyl oxalate is CO and CO₂. Therefore, these two processes present two alternatives, and are different operationally, and with respect to their products. These data can help form the basis of a decision between the two processes.

IV Summary and Conclusions

Two processes were investigated for treating UHN/HNO₃ waste expected in the ⁹⁹Mo production in the MAPLE reactors and the New Processing Facility at AECL's Chalk River Laboratories: direct calcination of the UNH/HNO₃ solution, and oxalate precipitation followed by calcination of the uranyl oxalate precipitate. A series of experiments was conducted to characterize the chemical reactions that occur during the calcination steps for both processes. Different sparge gases were used to show the effect of redox potential of the atmosphere on the reaction products. Calcinations were carried out at both 400°C and 600°C to show the effects of temperature on the reaction products.

The direct calcination process yielded a mixture of UO₃ and U₃O₈ under most of the conditions used in this study. The solid product was observed to splatter and has a density of about 3.0 g U/mL. The primary gaseous product of this reaction under all conditions was NO₂. Calcination of uranyl oxalate yielded a mixture of U₃O₈ and UO₂ under most of the conditions used in this study. Calcination at 600°C in a reducing

atmosphere yielded UO_2 . The solid products did not splatter but formed a friable, compressible powder with a density of about 1.3 g U/mL. The primary gaseous products of this reaction in most of our experiments were CO and CO_2 . Data presented here show that both processes are feasible.

V. Literature Cited

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