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**OPTIMIZATION AND SCALE-UP OF A NITRIC-ACID DISSOLVER
SYSTEM FOR LEU-FOIL TARGETS FOR ⁹⁹Mo PRODUCTION**

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ABSTRACT

One of the methods for producing Mo-99 (parent nuclide of the medical isotope Tc-99m) currently being investigated is the irradiation of U-235 in low enriched uranium (LEU) foil targets. Four key steps in producing Mo-99 from irradiated LEU-foil targets are: (1) removal of the foil from its cladding, (2) rapid dissolution of the foil, (3) chemical separation of Mo-99 from other fission products, and (4) purification of Mo-99 to pharmaceutical standards. This paper presents results from on-going research at Argonne focused on the optimization of step (2) in the LEU-Modified Cintichem Process (LMCP) for Mo-99 production. A primary focus of this research is to provide a technical basis for scaling-up the nitric-acid dissolver system used in the LMCP to facilitate greater throughput for large-scale production. A key technical challenge is designing a gas trap capable of handling the increased amounts of acid, nitrogen oxides, and fission product gases produced when greater amounts of irradiated LEU foil are dissolved. Specifically, this paper presents results from experiments and thermodynamic modeling that provide a preliminary predictive understanding of the chemistry of key gaseous species within the dissolver and an associated cryogenic gas trap filled with adsorbents. Establishing this predictive capacity will facilitate the safe and efficient scale-up of the dissolver/gas-trap system used in the LEU-Modified Cintichem Process.

1. Introduction

In the LEU-Modified Cintichem process, the first processing step in extracting ⁹⁹Mo is dissolving the irradiated uranium foil in nitric acid. A pilot-scale dissolver system, designed at Argonne [1] and demonstrated at the Missouri University Research Reactor facility (MURR) is currently being used to collect data needed to design a production-scale dissolver capable of dissolving up to 250 g of irradiated uranium and the accompanying nickel fission-recoil barrier. The key technical challenge involved in scaling-up the dissolver system is ensuring that the off gas produced during the dissolution (NO_x, and fission-products gases) can be removed from the dissolver vessel and trapped in a separate volume. Our approach to meeting this challenge is to perform experiments and thermodynamic modeling to develop a predictive understanding of the chemistry of the dissolver solution and gas phase. It is particularly important to quantify the volume and speciation of the off gas so that an efficient gas trap can be designed and optimized.

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2. Dissolver and Cryogenic Gas Trap

The pilot-scale dissolver (Figure 1) is constructed of 304 Stainless Steel with a volume of 360 cm³. Based on uranyl-nitrate solubility, this size vessel could dissolve up to 120 g of irradiated foil per batch. It consists of a cylindrical body and a separate lid assembly. The lid is a flanged lid with an o-ring seal, and a “cross” fitting with a pressure gauge, a plug valve attached to a quick-connect plug, a plug valve attached to a septum, and a pressure relief valve. Hydrostatic pressure tests have established the dissolver vessel pressure rating at > 800 psig at 25°C; however, the individual components of the dissolver can theoretically withstand over 1000 psig. The dissolver is supported within a cylindrical steel sleeve with an open base and a flange at the top. This allows the dissolver to remain vertical during dissolution. An electric heat gun blows hot air into the support sleeve to increase and maintain the temperature. The heat gun (heater turned off) also provides the air for cooling upon shutdown. The temperature of the dissolver is monitored by two thermocouples (one to indicate temperature, and one for temperature over-run).

The gas trap consists of a seamless, type-L copper tube that is soldered with a copper cap at one end and with a series of copper and brass fittings at the other. Prior to and during use this gas trap rests in a vertical position, within a Dewar of liquid nitrogen (Figure 1). This cryogenic gas trap is attached to the dissolver once the dissolution is complete and the dissolver has cooled to near ambient temperature. The gas trap is immersed in liquid nitrogen throughout the dissolution; therefore, once the valves are opened, the off gas from the dissolver is cryo-pumped into the adsorbent-filled gas trap and thus removed from the headspace of the dissolver.

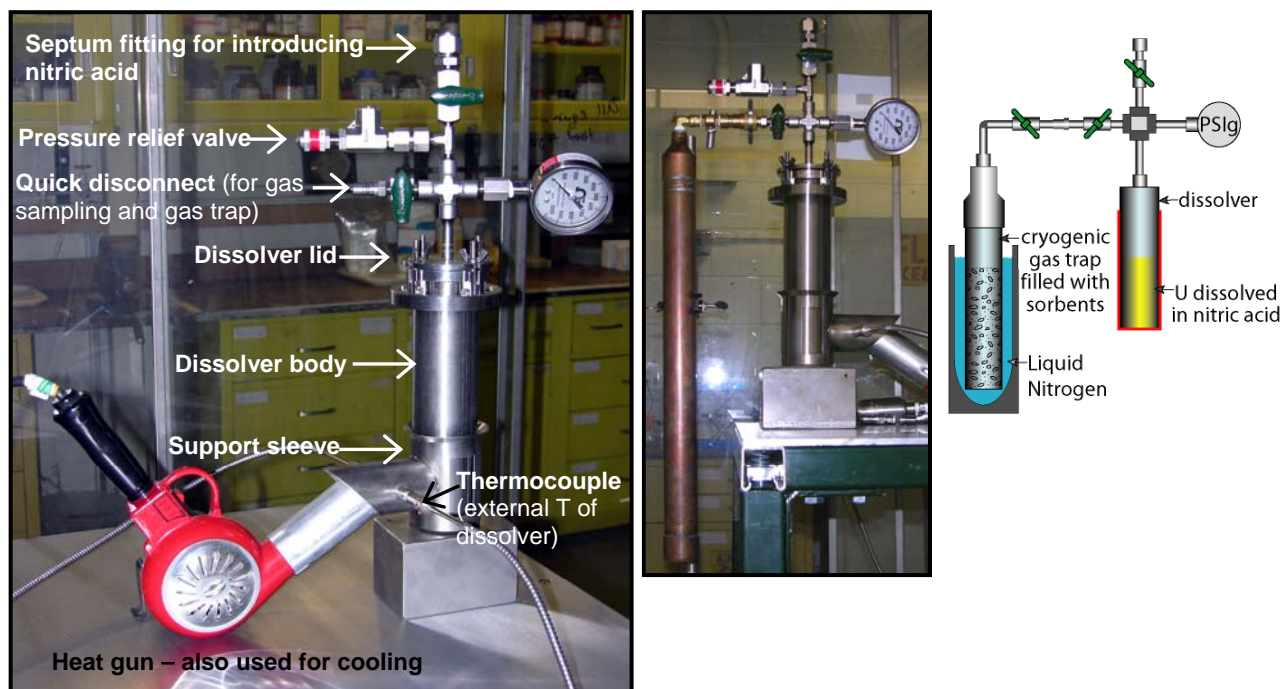


Figure 1. Photograph of dissolver (left), dissolver with copper gas trap attached (middle), and schematic drawing of the dissolver set-up showing the cryogenic gas trap (right).

Within the cryogenic gas trap, water, fission product gases (e.g. xenon, krypton) and nitrogen oxide (NO_x) gases (e.g., HNO₃, HNO₂, NO, N₂O, N₂O₄, NO₂) may be adsorbed by 13X molecular sieve, which is a microporous alkali aluminosilicate. Water vapor is also adsorbed by a calcium sulfate desiccant and acid gases (e.g., HNO₃, HNO₂) are adsorbed by calcium oxide. The NO_x gases also react with the calcium oxide; however, the details of this interaction are not known and will be the subject of future research. This future work will involve measuring the adsorption capacities for the gas sorbents so that the dimensions of the cryogenic trap and the mass of the gas adsorbents can be scaled up to accommodate the larger amounts of gas generated by larger uranium through put.

3. Thermodynamic Modeling Results and Implications for Cold Trap Design

In an effort to develop a predictive understanding of how the chemistry of the dissolver solution and gas phase will change as increasing masses of uranium are dissolved, the thermodynamic code OLI-ESP was used to simulate the chemistry of the dissolver for different conditions. The models assume that the system is in equilibrium at the end of dissolution. The modeling results are shown in Tables 1 and 2.

For efficient separation of molybdenum using the LEU-Modified Cintichem process, the final the nitric-acid concentration and oxidation/reduction potential (ORP) of the dissolver solution should be around 1 molar and approximately 1.0 volts (or greater) respectively. The requirement that the final nitric acid concentration be around 1.0 molar determines the starting acid concentration for a give volume of nitric acid. The volume of nitric acid is minimized for the purpose of waste minimization. This concentration is determined by assuming that 4 moles of HNO₃ are consumed for every mole of U_{metal} dissolved, as suggested by reaction (1).



Our experimental results have confirmed that reaction 1 is valid for calculating nitric acid consumption; however, the actual stoichiometry of reaction is more complex (see section 4).

The model results show the initial acid volumes and concentrations required to end with a 1 molar nitric acid product after dissolving different amounts of uranium metal. Assuming that the dissolver temperature is held (through an active heating/cooling system) at 200°C during the dissolution, then the dominant NO_x gas species are predicted to be NO and NO₂ in nearly equal proportions (note: in actual dissolutions the temperature is less than 150°C; 200°C was chosen as an upper extreme value for the calculations). The total pressure in the dissolver at this temperature is dominated by the water-vapor pressure. The speciation of the generated gas is predicted to change when the dissolver is allowed cool to 25°C (Table 2). In this case, the dominant NO_x species is predicted to be NO and the amount of gas produced for dissolving 250 grams of uranium metal in 500 mL of 9.4 molar nitric acid is predicted to be 2.1 moles (dominantly NO). This amount of gas will determine the final pressure in the dissolver, as well as the dimension and contents of the cryogenic gas trap. The model also predicts the solubility of gases in the dissolver solution. For the 200°C case it predicts that the dissolved concentration of NO is 1.8x10⁻³ molar and NO₂ is 0.01 molar. For the 25°C case, the model predicts that the dissolved concentration of NO is 2.1x10⁻³ molar and NO₂ is 7.0x10⁻³ molar. Future work will

investigate methods to remove the dissolved gas from the dissolver solution, as they can complicate down-stream processing steps.

Table 1. Thermodynamic modeling results simulating the off gas composition for the dissolution of uranium metal at a steady state temperature of 200°C (this temperature is an upper extreme, most dissolutions will be done at <150°C). The volumes and molarities of nitric acid were chosen so that the final concentration for a given run is 1.0 molar.

U metal (g)	Acid Vol. (mL)	Initial Con. (molar)	ORP (volts)	H ₂ O (moles)	NO (moles)	NO ₂ (moles)	HNO ₃ (moles)	HNO ₂ (moles)	Vapor (moles)
5	40	3.1	1.030	0.372	0.032	0.019	2.6E-03	0.006	0.431
10	40	5.2	0.975	0.531	0.065	0.035	6.2E-03	0.011	0.648
20	40	9.4	0.996	0.751	0.112	0.118	2.7E-02	0.024	1.032
25	50	9.4	0.996	0.938	0.140	0.148	3.4E-02	0.030	1.290
50	100	9.4	0.996	1.877	0.281	0.296	6.8E-02	0.060	2.582
75	150	9.4	0.996	2.816	0.421	0.444	1.0E-01	0.090	3.872
100	200	9.4	0.996	3.754	0.561	0.592	1.4E-01	0.120	5.162
125	250	9.4	0.996	4.692	0.701	0.740	1.7E-01	0.150	6.453
150	300	9.4	0.996	5.631	0.842	0.888	2.0E-01	0.180	7.744
175	350	9.4	0.996	6.569	0.982	1.036	2.4E-01	0.210	9.035
200	400	9.4	0.996	7.508	1.122	1.184	2.7E-01	0.240	10.325
225	450	9.4	0.996	8.447	1.262	1.332	3.1E-01	0.270	11.616
250	500	9.4	0.996	9.385	1.403	1.480	3.4E-01	0.300	12.907

ORP: oxidation/reduction potential relative to the standard hydrogen electrode.

Initial con. refers to the initial concentration of nitric acid.

Table 2. Thermodynamic modeling results simulating the off gas composition for the dissolution of uranium metal after the dissolver has cooled to a temperature of 25°C . The ORP, volume and initial concentration of nitric acid for these simulations are shown in Table 1.

U metal (g)	H ₂ O (moles)	NO (moles)	NO ₂ (moles)	HNO ₃ (moles)	HNO ₂ (moles)	Vapor (moles)
5	1.2E-03	0.0404	3.5E-05	3E-08	2.2E-04	0.0418
10	2.3E-03	0.0816	1.4E-04	2E-07	6.0E-04	0.0847
20	3.8E-03	0.1632	9.8E-04	2E-06	2.0E-03	0.17
25	4.7E-03	0.2041	1.2E-03	2E-06	2.5E-03	0.2125
50	9.4E-03	0.4083	2.4E-03	5E-06	5.0E-03	0.4252
75	0.0141	0.6124	3.7E-03	7E-06	7.6E-03	0.6377
100	0.0188	0.8164	4.9E-03	9E-06	0.0101	0.8502
125	0.0235	1.0205	6.1E-03	1E-05	0.0126	1.0628
150	0.0283	1.2248	7.3E-03	1E-05	0.0151	1.2755
175	0.033	1.4288	8.5E-03	2E-05	0.0176	1.488
200	0.0377	1.6329	9.8E-03	2E-05	0.0201	1.7005
225	0.0424	1.8372	0.011	2E-05	0.0227	1.9132
250	0.0471	2.0412	0.0122	2E-05	0.0252	2.1257

4. Results from Argonne Dissolver Experiments using Depleted Uranium Foils

Two dissolution experiments using depleted uranium were performed at Argonne: (1) dissolution of 2.0 grams of uranium metal foil in 40 mL of 3.0 molar nitric acid and (2) dissolution of 5.58 grams of uranium metal foil in 40mL of 3.3 molar nitric acid. The experimental procedure involved first placing the uranium metal foil samples in the dissolver, sealing the lid, evacuating the dissolver using a diaphragm vacuum pump (pump down for 15 minutes) and then adding the acid to the dissolver using a needle and syringe through the septum fitting. The pressure in the dissolver is around 0.05 atmospheres (based on the limit of the pump), therefore, there will be some residual nitrogen and oxygen (from air) in the dissolver during the formation of the NO_x . The nitric acid consumed during the dissolution was determined for experiment (2) by titrating the final solution using a potassium oxalate method [3]. For experiment (1) the off gas was sampled while the dissolver was still hot and for experiment (2) the off gas was sampled once the dissolver had cooled down to near ambient temperatures. The composition of the off gas was determined by gas chromatography (GC). The pressure and external vessel temperature profiles from experiment (2) are shown in Figure 2.

The initial concentration of nitric acid used for the dissolution of 5.58 grams of uranium was 3.3 molar. This concentration was chosen so that the final concentration (after complete dissolution) will be 1 molar [as determined by reaction (1)]. The final acid concentration following the complete dissolution of uranium in experiment 2 was 1.13 molar (as determined by titration [3]). This indicates that using reaction (1) to determine the starting acid concentration is valid, although the actual stoichiometry of the dissolution is more complicated than implied by the reaction (i.e. NO gas product). The GC results (Figure 3) indicate that the off gas from experiment (2) contains large amounts of N_2 , and NO_2 , a small amount of O_2 and trace N_2O and CO_2 (not shown). Therefore, the GC data do not agree with the modeling results (Tables 1 and 2), which predict NO to be a dominant gas species. The lack of NO in the sample from experiment (2) is believed to be due to the presence of oxygen (from air) in the dissolver during the dissolution (NO converts rapidly to NO_2 in the presence of O_2). This hypothesis, which is supported by the large amount of N_2 in the sample, will be tested in future experiments.

5. Summary and Future Work

Our models predict that 2.1 moles of NO_x gas will be produced when 250 grams of uranium metal foil is dissolved in 500mL of 9.4 molar nitric acid. The thermodynamic simulations suggest that the dominant NO_x species will be NO ; however, our experimental results (off gas composition from pilot-scale demonstrations at Argonne) do not agree with this prediction. This discrepancy appears to be due to the presence of oxygen (from air) during dissolution (NO converted to NO_2). Our experiments do confirm; however, that our method of calculating the initial concentration of nitric acid needed to produce a 1 molar feed for the LEU-Modified Cintichem process is valid.

Future work will involve more dissolution experiments and testing of the cryogenic gas trap as well as the development of more quantitative techniques to determine the composition of off gas from the dissolver. The experiments with the gas trap will determine the adsorption capacity of the NO_x adsorbents currently being used and alternative (possibly higher capacity) adsorbents

will be tested. The goal of this work is to develop a predictive understanding that will allow us to design a production scale uranium/nickel metal foil dissolver.

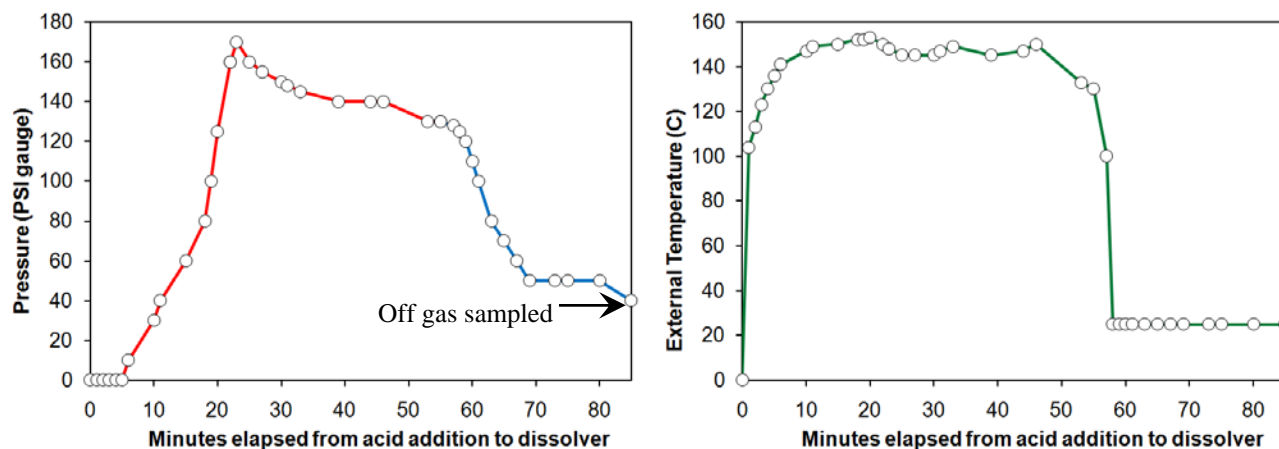


Figure 2. Pressure profile (left) and the external temperature profile (right) for experiment (1) which involved the dissolution of 5.58 grams of uranium metal in 40 mL of 3.3 molar nitric acid. The temperature controller set point thermocouple was set at 175°C for this dissolution.

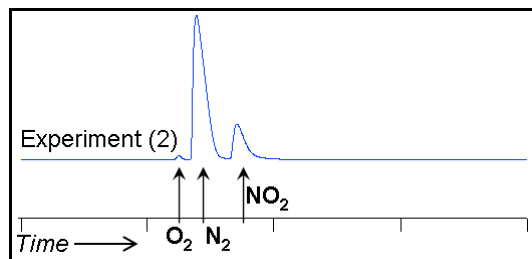


Figure 3. Off gas composition from experiment (2). The peaks are identified relative to a standard gas mixture containing known concentrations of O₂, N₂, NO₂, N₂O.

6. Acknowledgments

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7. References

- [1] Allen Bakel, Argentina Leyva, Thomas Wiencek, Andrew Hebden, Kevin Quigley, John Falkenberg, Lohman Hafenrichter, and George Vandegrift, "Overview of Progress Related to Implementation of the LEU-Modified Cintichem Process," Proceedings of the RERTR 2008 International Meeting, Washington D.C, October 5-9, 2008.
- [2] Hofstetter, K. J., Bowers, D. L., & Kemmerlin, R. P. "Determination of the Acidity of Aqueous Solutions Containing Hydrolyzable Metal Ions Using Oxalate Complexation." Barnwell Nuclear Fuel Plant, Barnwell, South Carolina, June, 1978.