Optimized Flowsheet for the Dissolution of Uranium Metal

Tracy Rudisill and Gene Daniel

2018 Mo-99 Topical Meeting
September 26, 2018
Problem Statement

• Single-use target was under development by the General Atomics, MURR, and Nordion cooperative agreement team for the production of Mo-99

• Plans were to irradiate a uranium dioxide (UO₂) target at MURR and transfer to a hot cell for Mo-99 recovery

• UO₂ targets were to be fabricated by a private company using U metal enriched to 19.75% U-235

• U metal must be initially dissolved to produce a pure uranyl nitrate (UO₂(NO₃)₂) solution

• Dissolution rate of the metal using the current flowsheet was slow and was not acceptable for the production process

• SRNL was asked to develop an improved flowsheet with an optimized U metal dissolution rate
Preparation of UO$_2$ for Target Fabrication

- Dissolution of U metal in nitric acid (HNO$_3$) required to produce pure UO$_2$(NO$_3$)$_2$ solution
  - Addition of fluoride to catalyze the dissolution would introduce an impurity
- Ammonium diuranate (ADU) precipitation used to convert U solution to a solid phase
- ADU is initially converted to uranium trioxide (UO$_3$) by heating in air at 500 °C
- UO$_2$ for target fabrication is prepared by heating UO$_3$ powder in the presence of H$_2$

\[
2\text{UO}_2(\text{NO}_3)_2 + 6\text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{U}_2\text{O}_7 + 4\text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}
\]
Strategy to Improve U Metal Dissolution Rate

• Dissolution of U metal in HNO₃ is quite complex, with the acid reduction products varying from nitrogen dioxide (NO₂) to elemental nitrogen (N₂)
  – In general, dissolutions performed using 8 M HNO₃ or less generate nitric oxide (NO) as the principal gaseous product; those carried out at higher acidities produce NO₂ as the principal product
    \[
    \begin{align*}
    U + 4\text{HNO}_3 & \rightarrow UO_2(\text{NO}_3)_2 + 2\text{NO} + 2\text{H}_2\text{O} \\
    U + 8\text{HNO}_3 & \rightarrow UO_2(\text{NO}_3)_2 + 6\text{NO}_2 + 4\text{H}_2\text{O}
    \end{align*}
    \]
    \[
    \text{HNO}_3 < 8 \text{ M} \hspace{1cm} \text{HNO}_3 > 8 \text{ M}
    \]
• Factors which influence the dissolution rate of large pieces of U metal
  – Factors inherent in the material being dissolved – impurities, metallurgical treatment, grain size, shape, and surface area
  – Factors easily varied during dissolution – acid concentration, temperature, circumstances influencing concentrations of reaction products
• Dissolution of U metal is autocatalytic – increases in the concentration of reaction products increases the dissolution rate
  – Dissolution rate of U metal can be increased considerably by the addition of nitrite to the HNO₃
  – NO₂ gas can be used to produce nitrous acid (HNO₂) which decomposes to NO and HNO₃
    \[
    \begin{align*}
    2\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{HNO}_3 + \text{HNO}_2 \\
    3\text{HNO}_2 & \rightarrow \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}
    \end{align*}
    \]
LEU metal used in dissolution experiments was produced by electrometallurgical processing at INL
  - Molten metal was vacuum cast into sample rods
  - Impurity concentration was less than 1000 ppm (99.9% U)

Dissolution experiments were performed in laboratory glassware fabricated by SRNL Glass Shop
  - Approximate 3 g U samples dissolved in 120-130 mL of solution
  - Sample held by a glass basket supported by glass rod; compression fitting used to raise and lower the metal into solution
  - Solution temperature was controlled by an external thermocouple monitored by the hot plate/stirrer
  - Raman spectrometer available to measure non-condensable gases (H₂, N₂, O₂, Ar, NO, N₂O and NO₂)

U metal was periodically removed from solution to measure mass and dimensions
  - Rate calculated from rate of change of mass to surface area ratio

Experiments performed to evaluate the effect of HNO₃ concentration and temperature and catalytic effects of fluoride and nitric oxide (NO) gas on the dissolution rate
Effect of Nitric Acid Concentration on U Metal Dissolution Rate

- Dissolution experiments performed at the boiling point of 10, 8, 6, and 4 M HNO₃; data at 7 M from previous work
  - Linear portion of curve used to calculate dissolution rate
  - Induction period observed, especially at lower acidities; due to oxide dissolution
  - Apparent rate often slows near complete dissolution of U; likely due to difficulty in accurately calculating surface area

- U metal dissolution rate increases with increasing HNO₃ concentration
  - Data are consistent with published literature
  - Expect the rate to begin to decrease between 13-14 M due to highly oxidizing solution

- Optimum HNO₃ concentration depends upon desired cycle time and acid concentration required for downstream processing

Temperature Effects during U Metal Dissolution

- Dissolution experiments were performed using 8 M HNO₃ at the boiling point (110 °C) of the solution and at 100 °C and 90 °C
  - Linear portion of curve used to calculate dissolution rate
  - Induction period was more pronounced at lower temperatures
- Dissolution rate increased with increasing temperature as expected; although, not an extremely strong function of temperature
  - Approximate 50% drop in rate when the temperature is reduced from boiling to 100 °C
  - Only 10% drop in rate with a reduction from 100 to 90 °C
- Unless there is a reason to use a temperature less than the boiling point of the solution (e.g., safety), performing the dissolution at the boiling point is recommended
Catalytic Effect of Fluoride during U Metal Dissolution

- General Atomics requested that we evaluate the use of fluoride as a catalyst during U metal dissolution
  - One dissolution experiment was added in which three concentrations of fluoride (0.01, 0.05, and 0.1 M) were sequentially added to the solution

- Addition of fluoride to the dissolving solution adds an impurity which must be removed during the ADU precipitation process
  - Precipitation processes do not result in high decontamination factors without large cake wash volumes (generates more liquid waste)
  - Residual fluoride will cause downstream corrosion

- A significant increase in dissolution rate was not observed until the fluoride concentration was increased to 0.05 M
  - Complexation of the fluoride at low concentration by U reduces the catalytic activity

- Use of fluoride to catalyze U metal dissolution must be balanced against the potential for corrosion of downstream equipment and the addition of corrosion products to the U stream
Catalytic Effect of Nitric Oxide Gas During U Metal Dissolution

- Two dissolution experiments were performed in which nitric oxide (NO) gas was sparged into a solution containing 8 M HNO₃ at 100 °C
  - Dissolution rate of U metal significantly increases with the addition of nitrite to the HNO₃ solution
  - Since HNO₂ acid is in equilibrium with the gas reaction products (i.e., NO and NO₂) produced during U metal dissolution, it follows that the reaction is autocatalytic
- NO flowrates of 35 and 50 cm³/min were tested; residence times of 3.4 and 2.4 min in 120 mL of solution following saturation
  - NO addition resulted in significant increases in U metal dissolution rate (> 300% increase) compared to dissolution experiment with no purge at same conditions
  - Dissolution rate at 35 cm³/min (25 mg/min·cm²) was greater than the rate at 50 cm³/min (8.2 mg/min·cm²) due to high gas velocity; mass transfer limitation for access of HNO₃ to metal surface
- Use of NO gas to catalyze U metal dissolution is a viable option and is recommend for applications where high purity UO₂(NO₃)₂ is required
  - Flowrate required should be selected based on dissolver size and volume; saturate the solution with NO
  - Purge should not impinge directly upon the U metal
Characterization of Offgas from LEU Dissolution Experiments

- Data shown are from the development of a dissolution flowsheet for LEU ingots from Experimental Breeder Reactor-II fuel
  - Flowsheet sequence includes dissolution of five charges of U-Al alloy research reactor fuels (targeting 1.6 M Al in an H-Canyon dissolver)
  - Dissolution of LEU ingots would follow research reactor fuels with more HNO₃ added to dissolver as necessary
    - LEU ingots loaded in dissolver using carbon steel cans

- Little offgas generation (including hydrogen) compared to dissolution of Al 1100 alloy (used to model the U-Al alloy fuel)
Conclusions and Recommendations

• Optimum HNO₃ concentration used for U metal dissolution depends upon desired cycle time and acid concentration required for downstream processing

• Unless there is a reason to use a temperature less than the boiling point of the solution (e.g., safety), performing the dissolution at the boiling point is recommended

• Use of fluoride to catalyze U metal dissolution must be balanced against the potential for corrosion of downstream equipment and the addition of corrosion products to the U stream

• Use of NO gas to catalyze U metal dissolution is a viable option and is recommend for applications where high purity \( \text{UO}_2(\text{NO}_3)_2 \) is required

• Generation of \( \text{H}_2 \) during U metal dissolution in not a processing concern