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Optimized Flowsheet for the Dissolution of Uranium Metal

Tracy Rudisill and Gene Daniel

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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 (UO_2) target at MURR and transfer to a hot cell for Mo-99 recovery
- UO_2 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 ($UO_2(NO_3)_2$) 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

$$2UO_2(NO_3)_2 + 6NH_4OH \rightarrow (NH_4)_2U_2O_7 + 4NH_4NO_3 + 3H_2O$$

- 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

Strategy to Improve U Metal Dissolution Rate

- Dissolution of U metal in HNO_3 is quite complex, with the acid reduction products varying from nitrogen dioxide (NO_2) to elemental nitrogen (N_2)
  - In general, dissolutions performed using 8 M HNO_3 or less generate nitric oxide (NO) as the principal gaseous product; those carried out at higher acidities produce NO_2 as the principal product

$$U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO + 2H_2O$$

$HNO_3 < 8$ M

$$U + 8HNO_3 \rightarrow UO_2(NO_3)_2 + 6NO_2 + 4H_2O$$

$HNO_3 > 8$ M

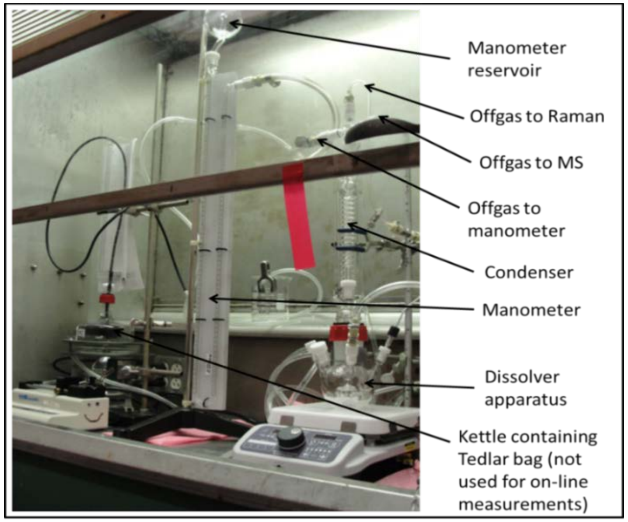
- Factors which influence the dissolution rate of large pieces of U metal
  - Factors inherent in the material being dissolved – impurities, metallurgical treatment, grain size, shape, and surface area
  - Factors easily varied during dissolution – acid concentration, temperature, circumstances influencing 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 HNO_3
  - NO_2 gas can be used to produce nitrous acid (HNO_2) which decomposes to NO and HNO_3

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

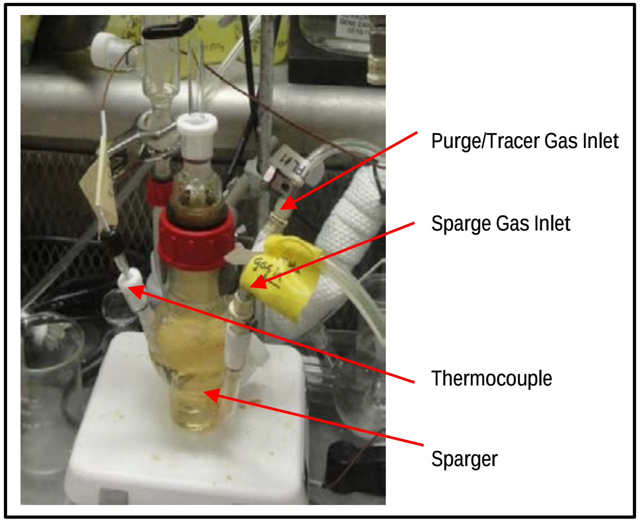
$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

Experimental Overview

- 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 (H_2, N_2, O_2, Ar, NO, N_2O and NO_2)
- 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 HNO_3 concentration and temperature and catalytic effects of fluoride and nitric oxide (NO) gas on the dissolution rate



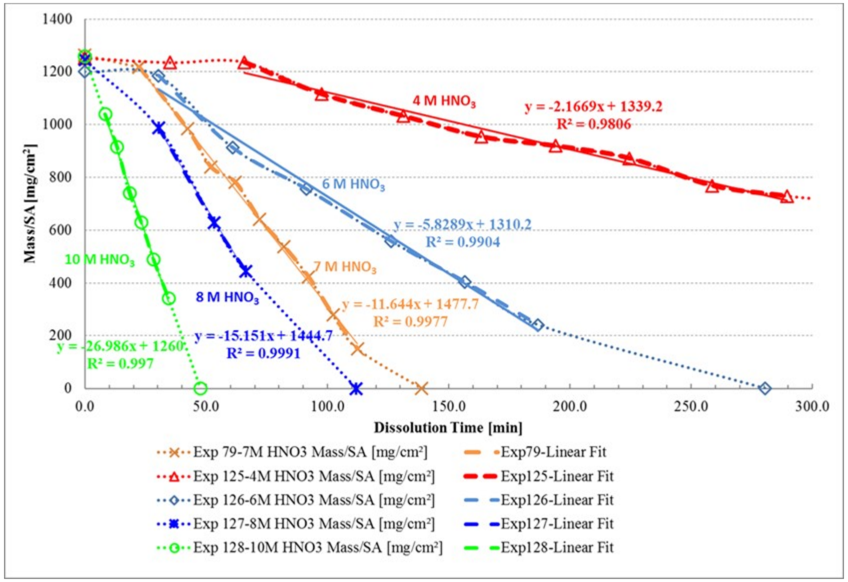
U Metal Dissolution Equipment

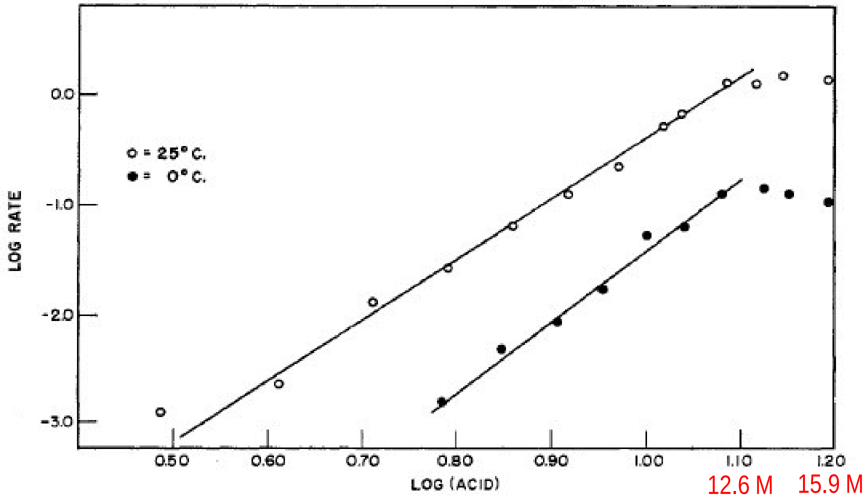


Dissolution Vessel with Nitric Oxide Sparge

Effect of Nitric Acid Concentration on U Metal Dissolution Rate

- Dissolution experiments performed at the boiling point of 10, 8, 6, and 4 M HNO_3; 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



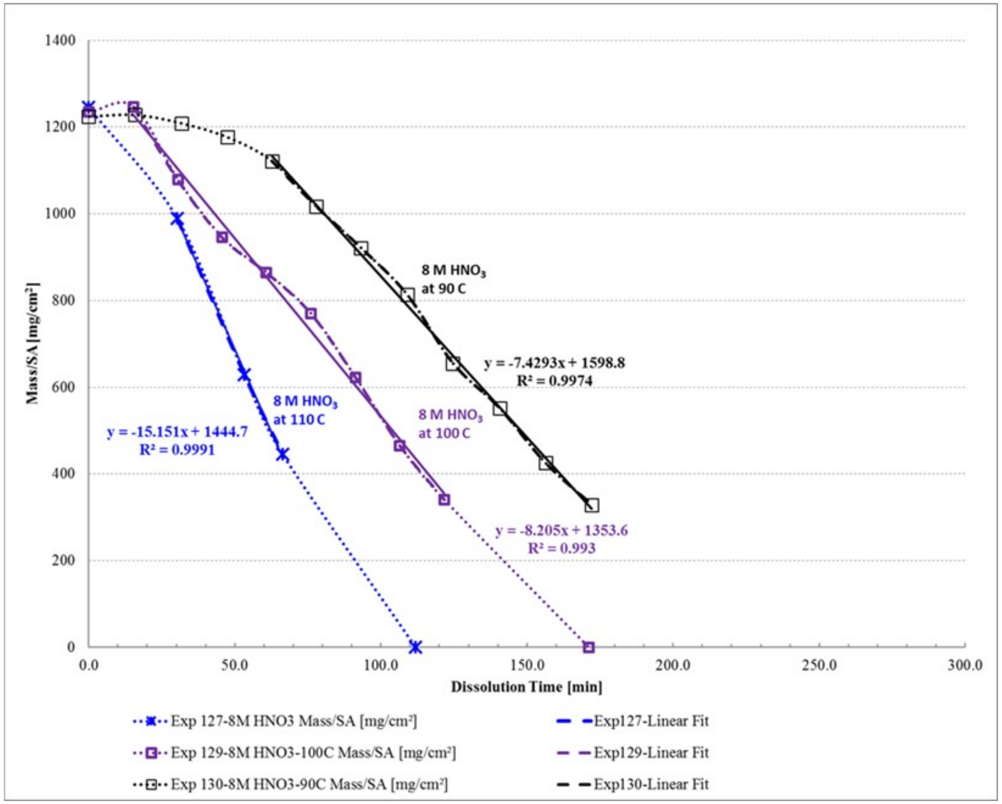


J. R. Lacher, et al., Ind Eng Chem, 53, 282-284 (1961)

- U metal dissolution rate increases with increasing HNO_3 concentration
  - Data are consistent with published literature
  - Expect the rate to begin to decrease between 13-14 M due to highly oxidizing solution
- Optimum HNO_3 concentration depends upon desired cycle time and acid concentration required for downstream processing

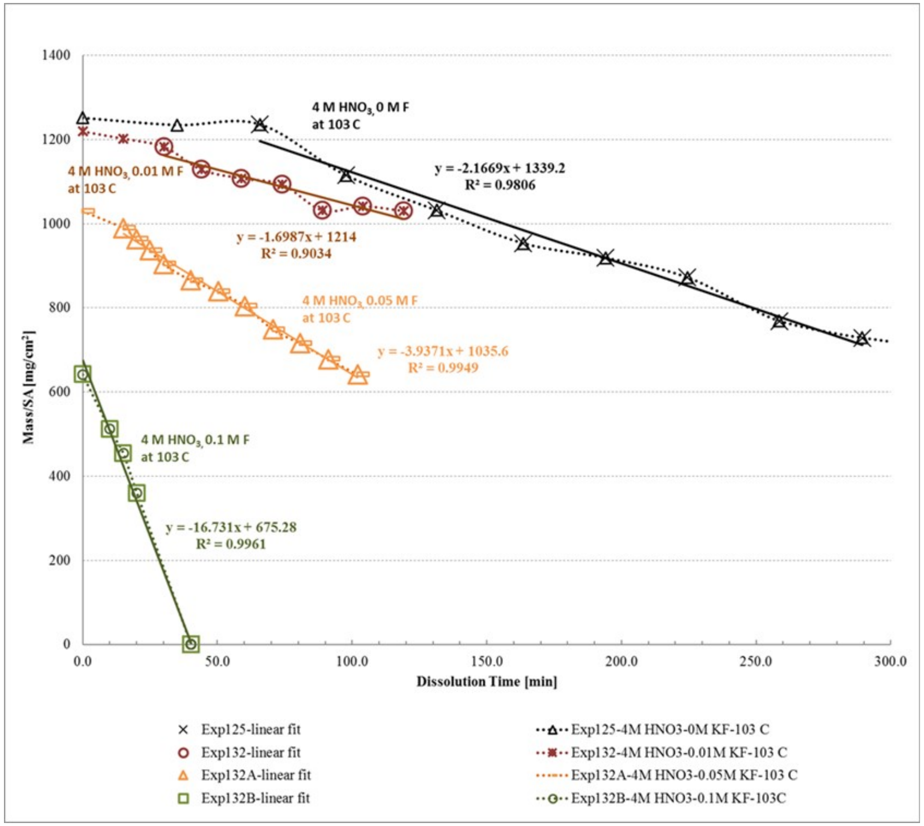
Temperature Effects during U Metal Dissolution

- Dissolution experiments were performed using 8 M HNO_3 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



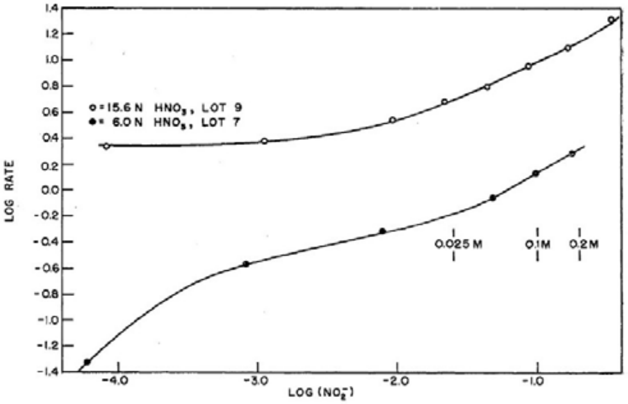
Catalytic Effect of Fluoride during U Metal Dissolution

- 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 HNO_3 at 100 °C
  - Dissolution rate of U metal significantly increases with the addition of nitrite to the HNO_3 solution
  - Since HNO_2 acid is in equilibrium with the gas reaction products (i.e., NO and NO_2) produced during U metal dissolution, it follows that the reaction is autocatalytic
- NO flowrates of 35 and 50 cm^3/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 cm^3/min (25 mg/min·cm^2) was greater than the rate at 50 cm^3/min (8.2 mg/min·cm^2) due to high gas velocity; mass transfer limitation for access of HNO_3 to metal surface
- Use of NO gas to catalyze U metal dissolution is a viable option and is recommend for applications where high purity $UO_2(NO_3)_2$ 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



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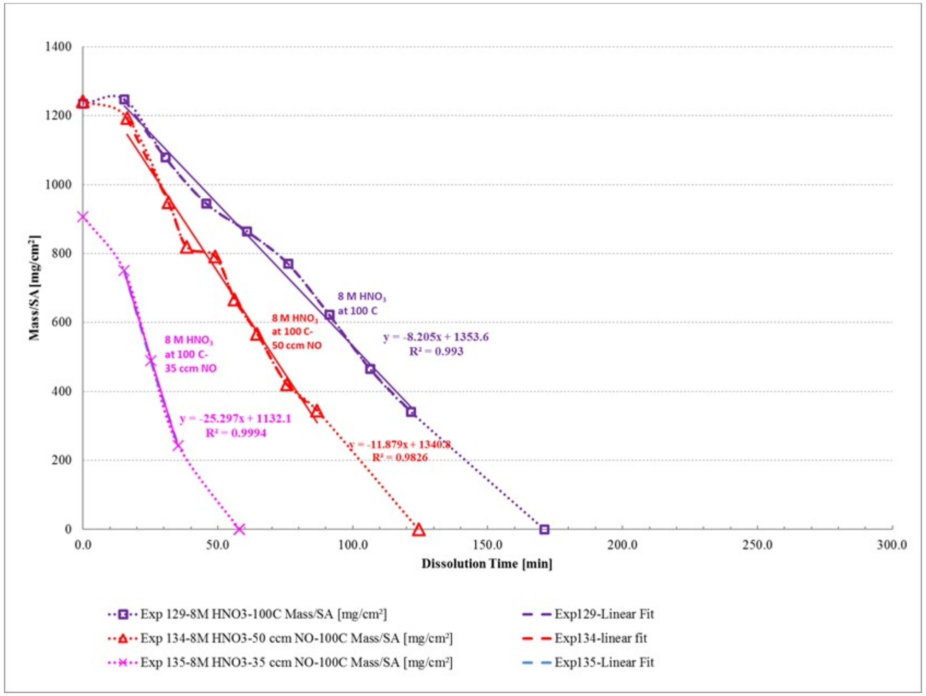
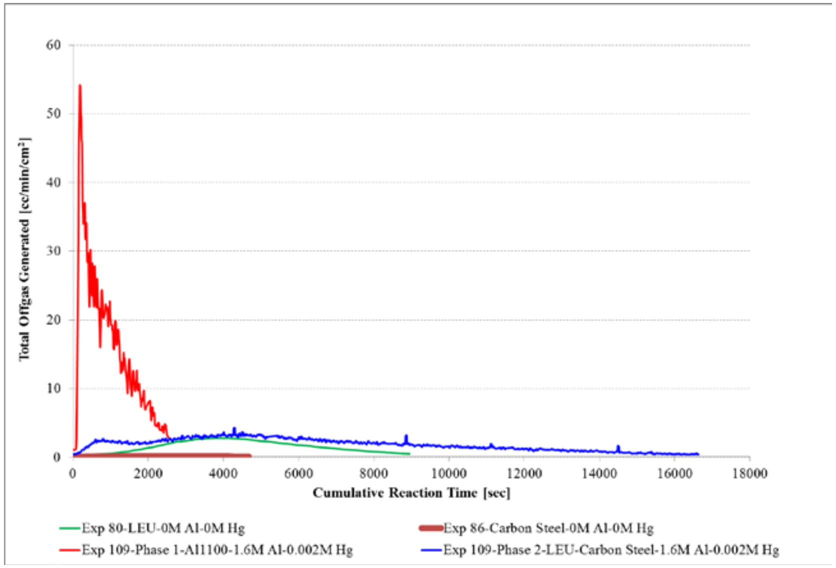
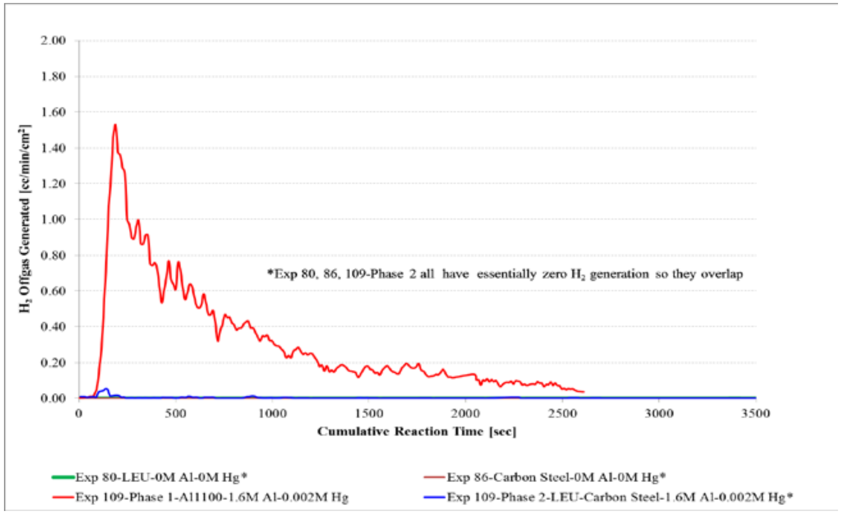


Characterization of Offgas from LEU Dissolution Experiments

- 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 HNO_3 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 HNO_3 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 $UO_2(NO_3)_2$ is required
- Generation of H_2 during U metal dissolution in not a processing concern