The Impact of Chemistry in Criticality Safety Analysis

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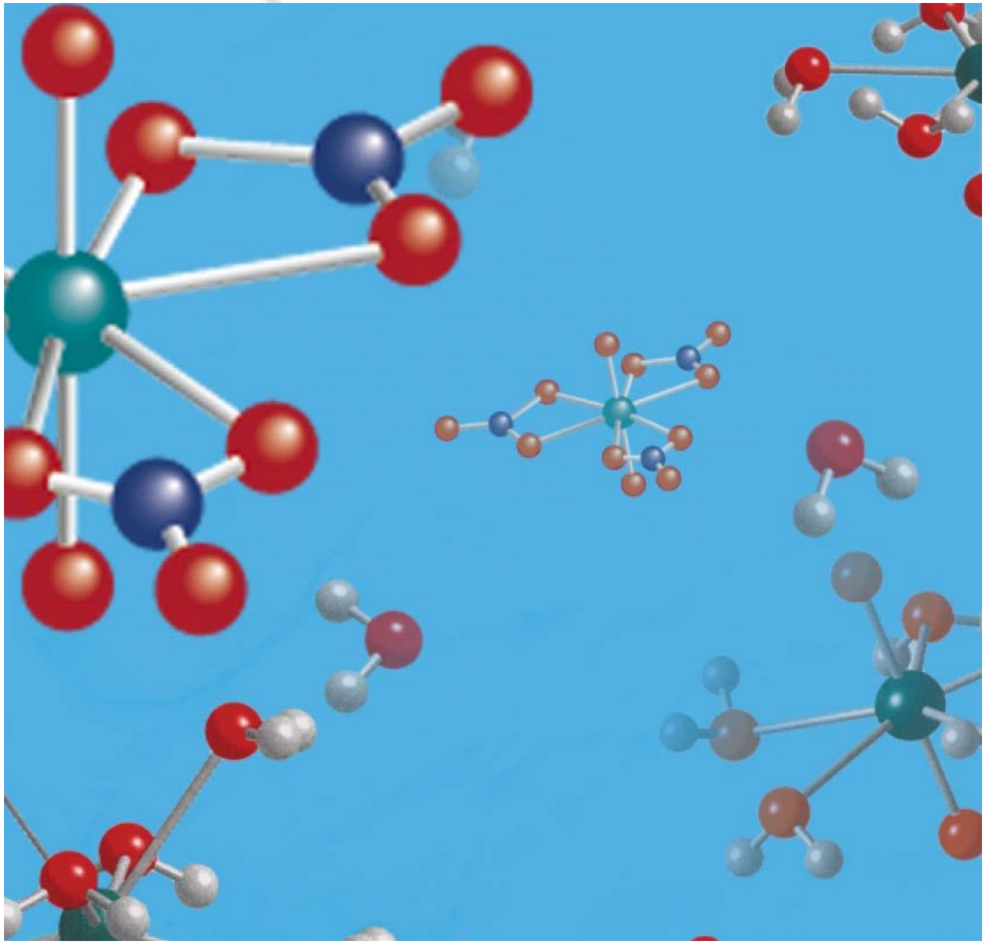
Impact of Pu Chemistry in Analysis

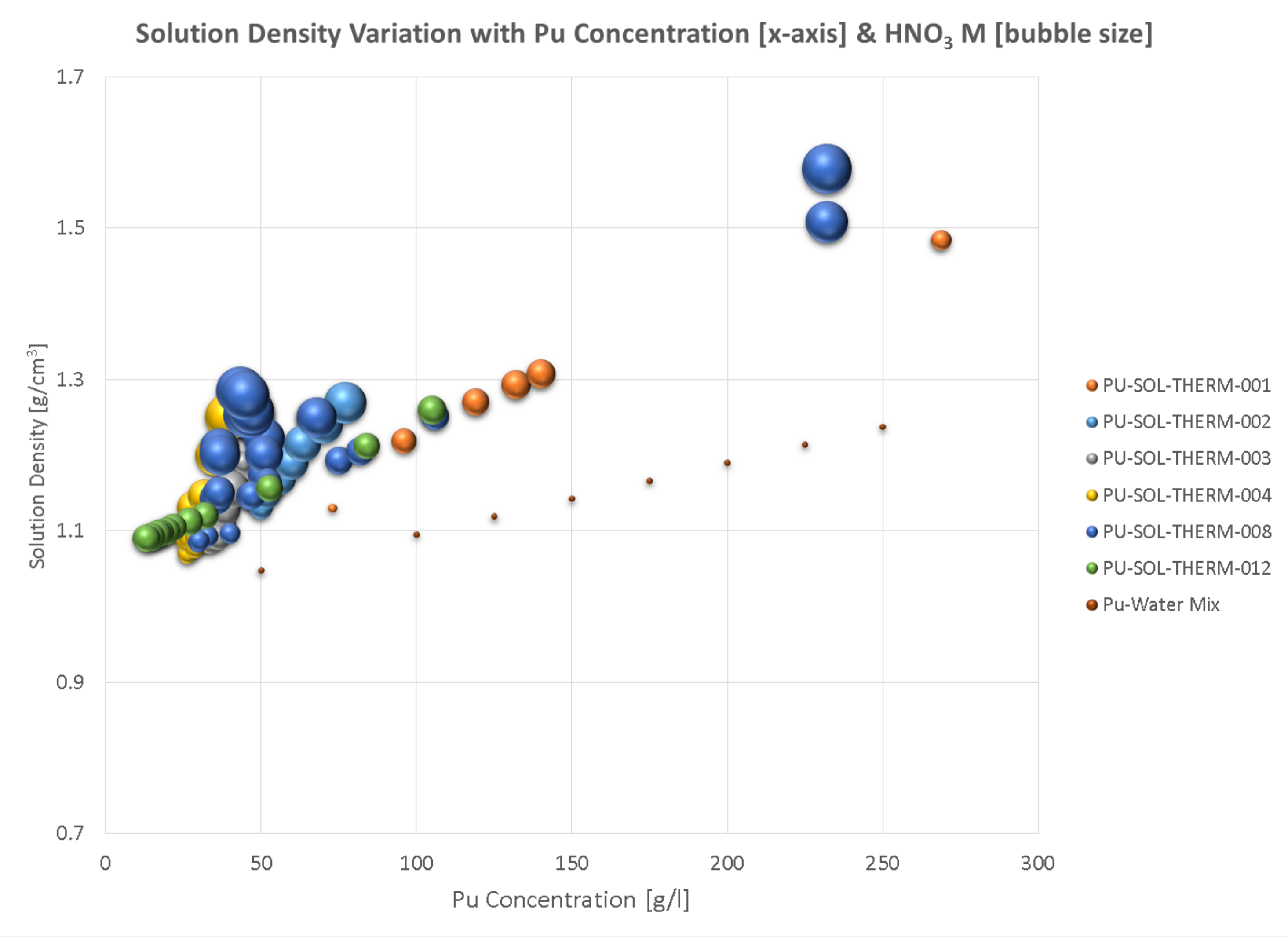
- Density of Solution
- Oxidation State
  - Common in processing
  - Changes
    - Radiolysis
    - Temperature
- Speciation
- Common ligands
  - Neutronics
  - Validation tools



Clark, D. L., *The Chemical Complexities of Plutonium*. Los Alamos Science Number 26. 2000.

Impact of Pu Chemistry in Analysis Density

- Predictive capability improvements
  - Isopiestic Density Law of Nitrates [1]
  - Pitzer Method[2]
- H density of metal-water mixture vs. actual solution density



1. Leclaire, N. P., J. A. Anno, and G. Courtois. Criticality Calculations Using the Isopiestic Density Law of Actinide Nitrates. *Nuclear Technology*. 144. 2003.

2. Weber, C. F., and C. M. Hopper. Application of the Pitzer Method for Modeling Densities of Actinide Solutions in the Scale Code System. *Nuclear Technology*. 53. 2006.

Impact of Pu Chemistry in Analysis Oxidation States for Pu Nitrate

- Pu forms Pu(III), Pu(IV), Pu(V), Pu(VI) and Pu(VII) in solution
- In acid solution
  - Pu(III), Pu(IV), Pu(V), Pu(VI) can exist simultaneously
  - III, IV, and VI are most common
- Oxidants/Reductants
  - change/stabilize oxidation states

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Impact of Pu Chemistry in Analysis

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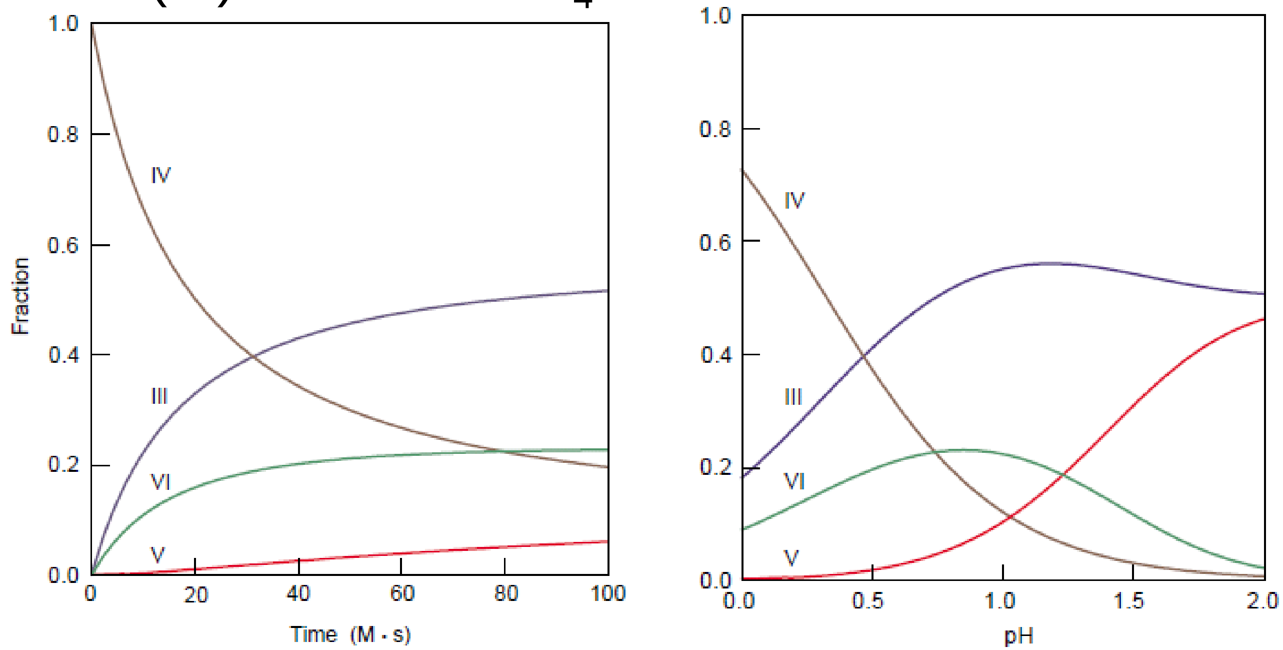
- Pu(IV) nitrate disproportionation
  - Pu self-oxidation/reduction

$$2Pu^{4+} + 2H_2O \rightleftharpoons Pu^{3+} + PuO_2^{+} + 4H^{+}$$
$$Pu^{4+} + PuO_2^{+} \rightleftharpoons Pu^{3+} + PuO_2^{2+}$$
$$2PuO_2^{+} + 4H^{+} \rightleftharpoons Pu^{4+} + PuO_2^{2+} + 2H_2O$$

- 8M nitric acid Pu(IV) stabilized
- Dilute acid
  - Mix III, IV, VI
  - Irreversible
  - Unavoidable

Pu(IV) in 1 M $NaClO_4$:



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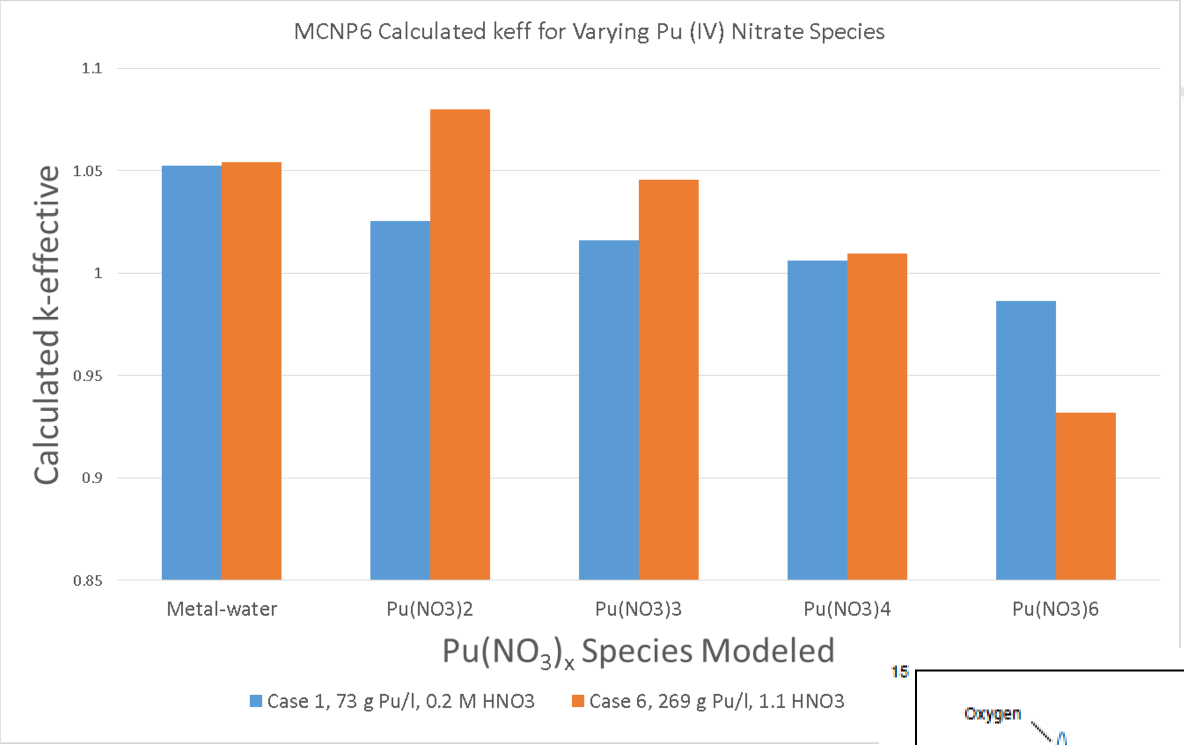
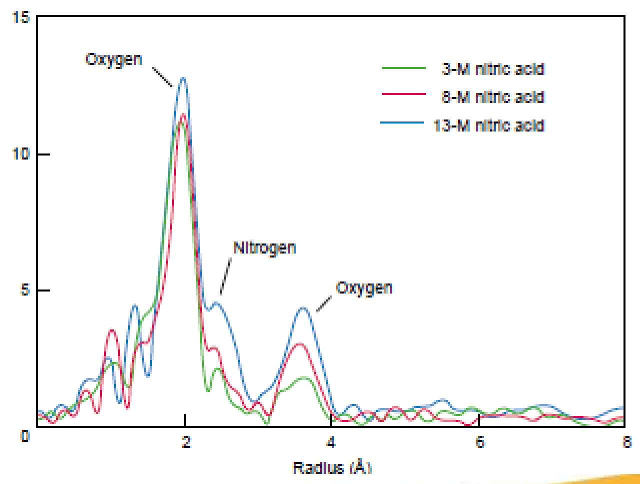
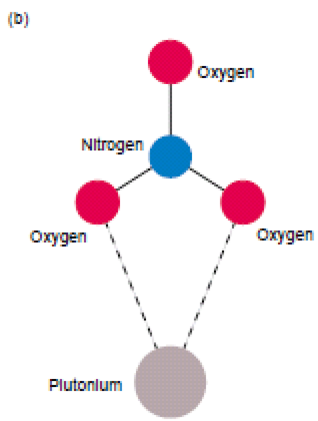
Impact of Pu Chemistry in Analysis Oxidation State Changes

- Pu(IV) Nitrate
- Radiolysis
  - Alpha emissions from Pu can alter oxidation state
  - Example: PuO_2^{2+} reduced to Pu^{4+} ~ 1.5% per day
- Temperature
  - Changes in temperature can alter oxidation state

Impact of Pu Chemistry in Analysis







Marsh S.F., D. K. Veirs, G. D. Jarvinen, M. E. Barr, and E. W. Moody., *Molecularly Engineered Resins for Plutonium Recovery*. Los Alamos Science Number 26. 2000.

Impact of Pu Chemistry in Analysis
Pu(IV) Nitrate

- Pu(IV) forms various species
  - Depends on free nitric acid present
  - $Pu(NO_3)_2^{2+}$
    - highest concentration in 2 M nitric acid
  - $Pu(NO_3)_4$ and $Pu(NO_3)_6^{2-}$
    - present in ~equal concentrations in 7 M nitric acid
  - $Pu(NO_3)_6^{2-}$
    - major species in 13 M nitric acid

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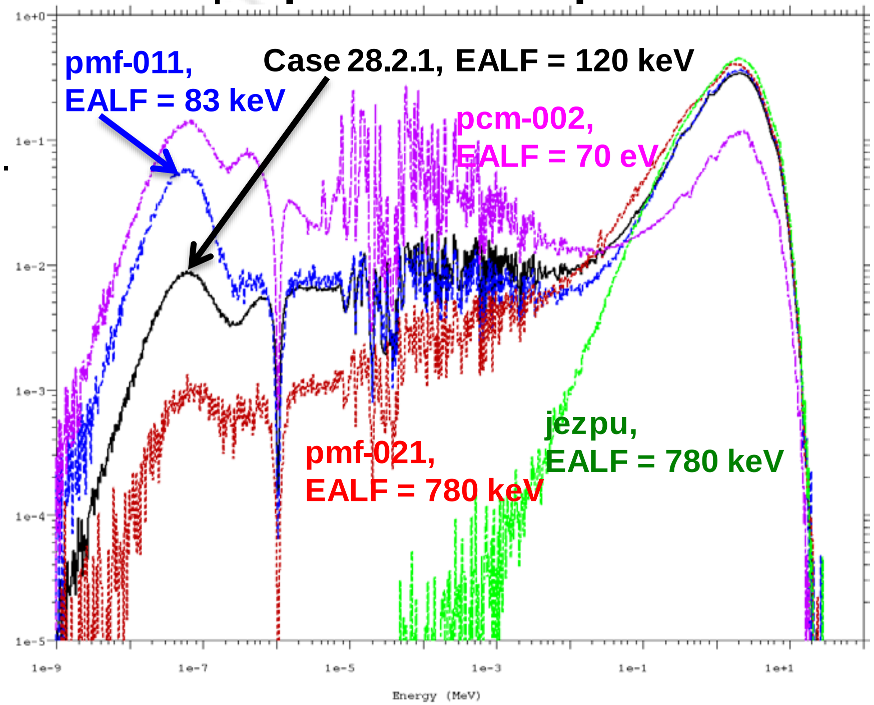
Impact of Pu Chemistry in Analysis

Whisper with MCNP6

- Nuclear Criticality Safety analysis requires validation of computational methods
- Neutron spectra are complex functions of geometry, materials, nuclear cross-section, etc.
- **MCNP-WHISPER Methodology:**
- MCNP determines sensitivity profiles to characterize neutronics of an application or benchmark, S(energy, reaction, isotope) $S=(dk/k)/(d\sigma/\sigma)$
- **WHISPER uses:**
  - Sensitivity profile data for application
  - Covariance files for nuclear data
- To determine
  - Baseline upper subcritical limit (USL) with bias, bias uncertainty, margin of subcriticality
  - Similar benchmarks from library of 1100+ ICSBEP experiments
- Can support traditional validation and help determine or support validation weaknesses

$\nu\Sigma_F\Phi$ production spectrum



Brown, F. E., M. Rising, and J. L. Alwin., *MCNP-WHISPER Methodology for Nuclear Criticality Safety Validation*. LA-UR-16-23757

Impact of Pu Chemistry in Analysis

- Pu chloride solutions similarity to Pu nitrate solutions
- Whisper & MCNP6

	Chloride	Nitrate
EALF (MeV)	9.04e-08	8.65e-08
ANECF (MeV)	1.33e-02	1.29e-02