Review of Wilson data and synthesis tests

Presented to:
DOE-CEA Technical Exchange Meeting

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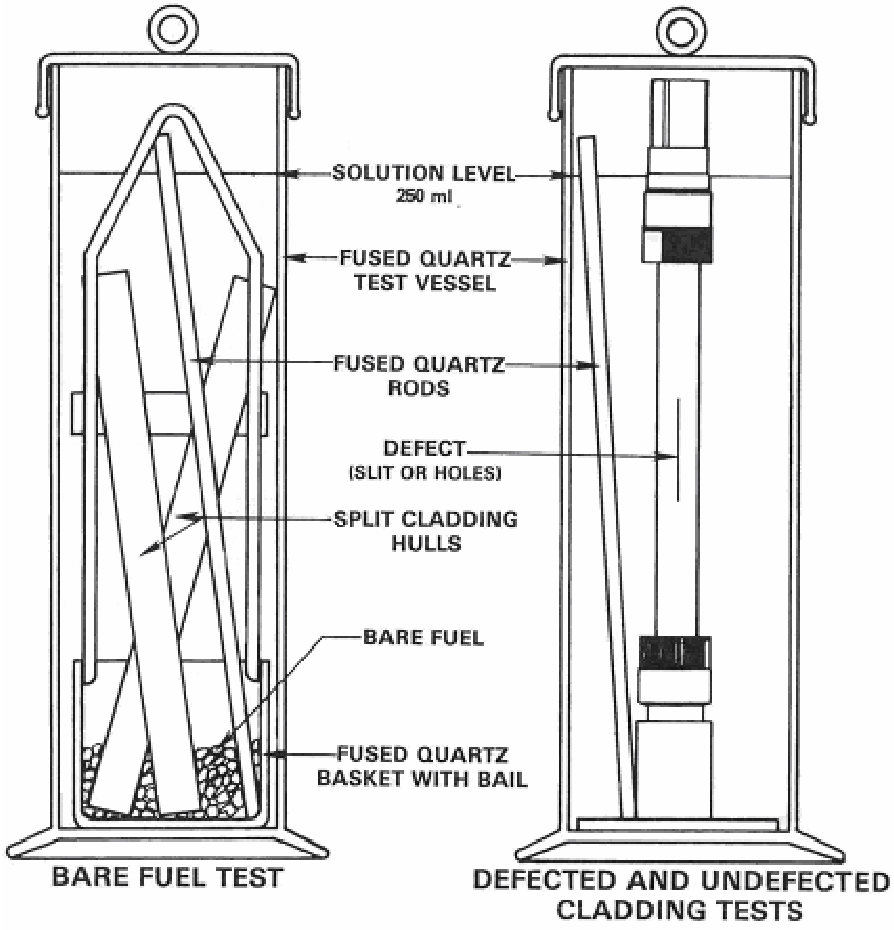
“Wilson Tests” Outline

- Description of “Wilson Tests”
  - Series 1
    - De-ionized water at room temperature
  - Series 2
    - J-13 water at room temperature
  - Series 3
    - J-13 water at 85°C and 25°C
- Radionuclide release limitation
  - Synthesis tests

“Wilson Tests”

- **Goal**
  - **Measure radionuclide release from SNF with various defects in the cladding**
- **Cladding defects tested:**
  - **Bare fuel**
  - **150μm wide slit 2 cm long**
  - **Two laser drilled holes ≈200 μm diameter**
  - **One laser drilled hole ≈200 μm diameter**
- **Sampling interval:**
  - **1, 5, 15, 30, 60, 90, 120, 180, 240 days**



“Wilson Tests” Series 1

- **Total Measured Release as a Fraction of Inventory (10^{-5})**

Component	Bare Fuel	Slit Defect	Holes Defect	Undefected
Uranium	28.0	0.078	<0.041	<0.018
$^{239}Pu+^{240}Pu$	28.0	0.341	0.069	0.027
^{241}Am	21.7	0.208	<0.030	<0.011
^{244}Cm	30.0	0.76	0.039	0.008
^{237}Np	54	2.2	--	--
^{137}Cs	300	142.1	85.6	0.041
^{99}Tc	230	12.1	<6.7	--

"Wilson Tests" Series 1

- **Conclusions**
  - U, Pu, Am, Cm release congruently under all conditions
  - ^{237}Np data was not good enough to determine congruent release
  - Cs was rapidly released, with additional release from the grain boundary inventory
  - ^{99}Tc released was one order of magnitude greater than the actinides in bare fuel tests
    - Three orders of magnitude in defected cladding tests

"Wilson Tests" Series 1 con't

- **Uranium saturation occurred at 1 ppb**
  - **18Å filtration removed U, Am and Cm from "solution"**
- **Grain boundary dissolution is the major source of release for ^{99}Tc**
- **Leaching behavior is influenced by mircostructural phenomena**
  - **Irradiation time**
  - **Temperature**
  - **Fission gas release**

“Wilson Tests” Series 2

- 5 cycles
  - Test vessel emptied, acid striped before original fuel returned and test started again with fresh J-13 water
- Conclusions
  - Actinide concentrations reached steady-state rapidly in each cycle
  - Pu, Am and Cm concentrations are dependent on filtration

“Wilson Tests” Series 2

- Approximate actinide steady-state concentrations are:
  - U 4E-6 to 8E-6 M
  - Pu 8.8E-10 to 4.4E-9 M
  - Am 1.5E-10 M
  - Cm 2.6E-12 M
  - Np 2.4E-9 M
- Fission produced nuclides did not reach saturation
- Calcite and haiweeite were two secondary phases observed by XRD in the tests

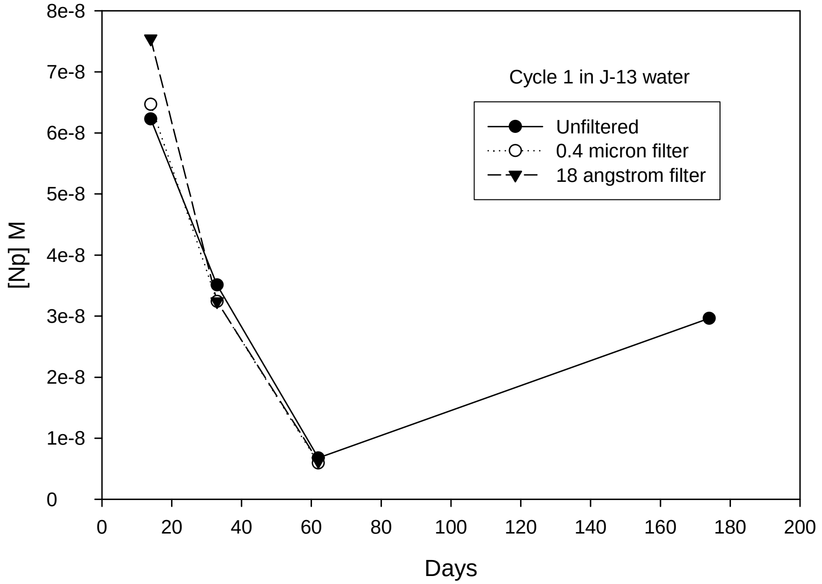
“Wilson Tests” Series 3

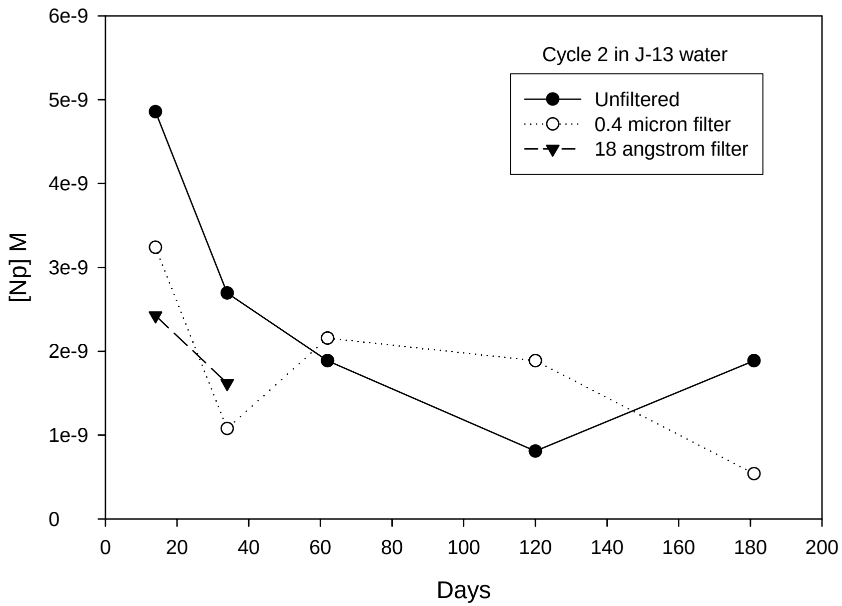
- Three cycles at 85°C and 25°C
- Conclusions
  - Actinide concentrations reached steady-state levels in all cycles
    - Attributed to a steady-state between fuel dissolution and secondary-phase formation
  - Uranium-bearing secondary phases were found in significant amounts
    - Uranophane, haiweeite, soddyite
  - Lower actinide concentration in 85C tests attributed to faster kinetics for the formation of solubility-limiting secondary phases

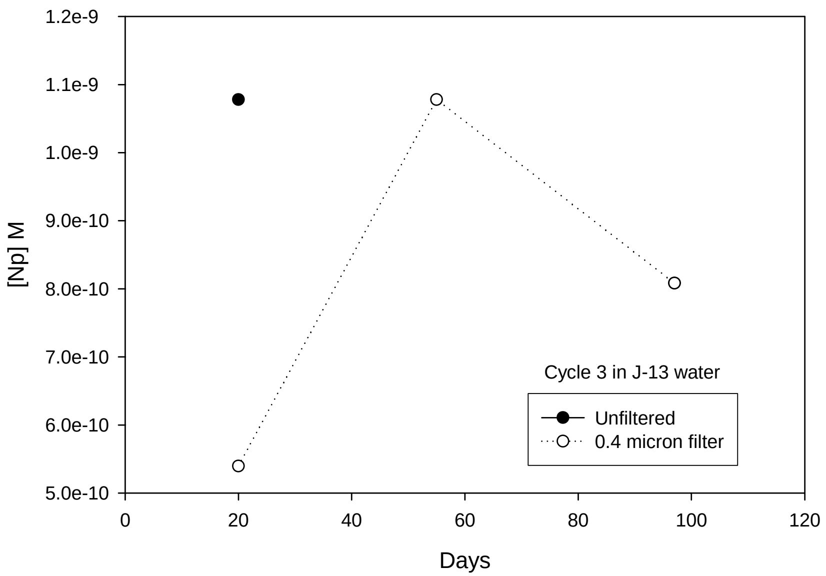
“Wilson Tests” Series 3

- Pu, Am and Cm were filter dependent, Np was independent of filtration technique
- Fission products were continuously released, with ^{90}Sr the only nuclide measured that indicated its concentration was limited by solubility
- Test vessel corrosion occurred at 85C.
  - Uranium concentration dropped
  - Tc below detectable levels

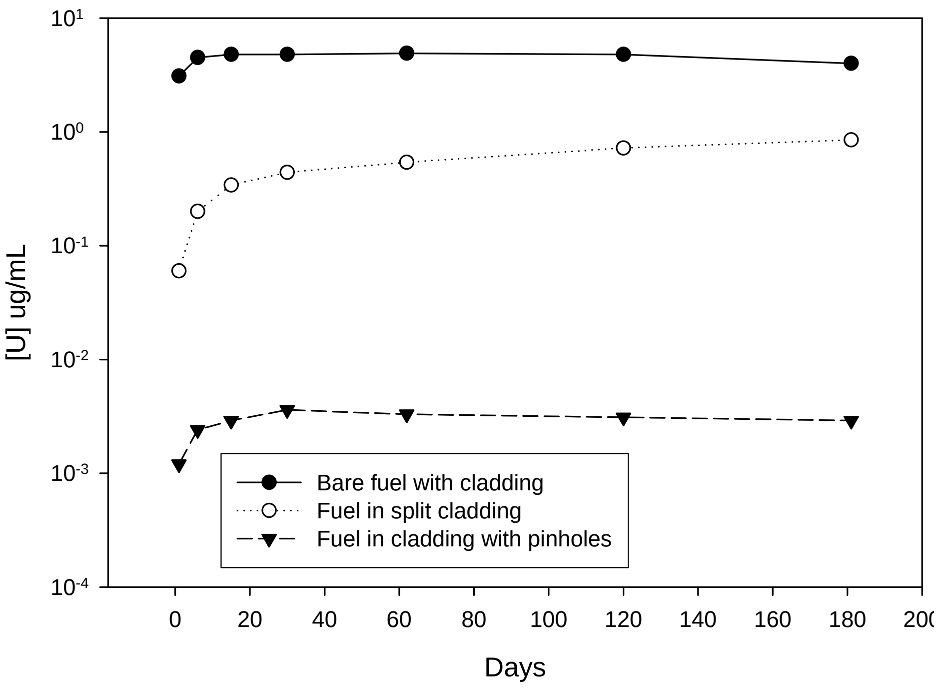
Cycle behavior



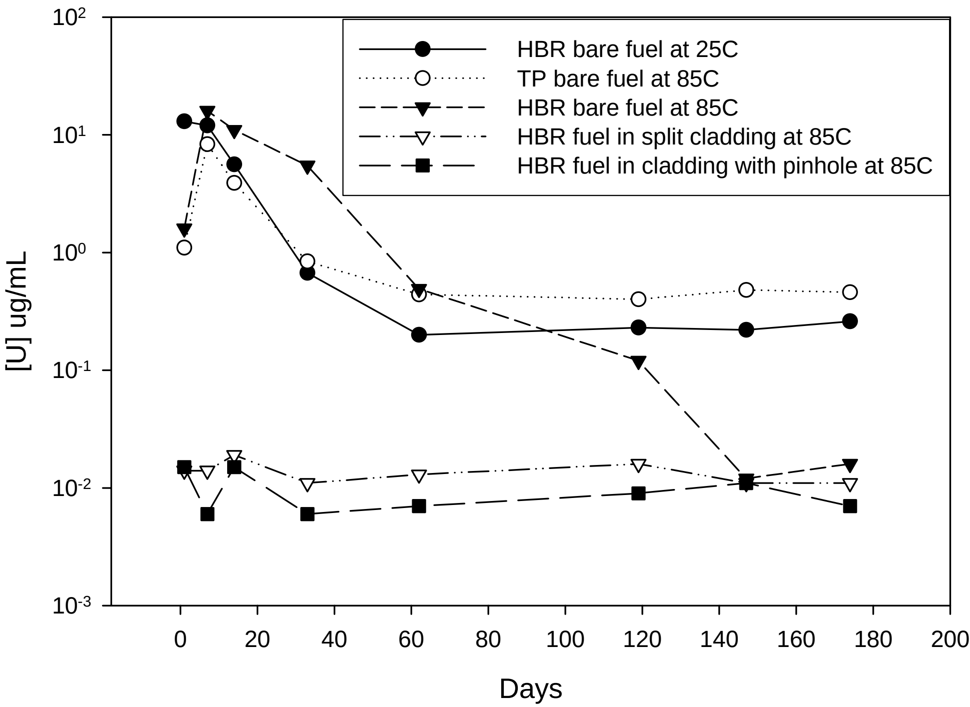




Uranium Release from "Wilson Tests"

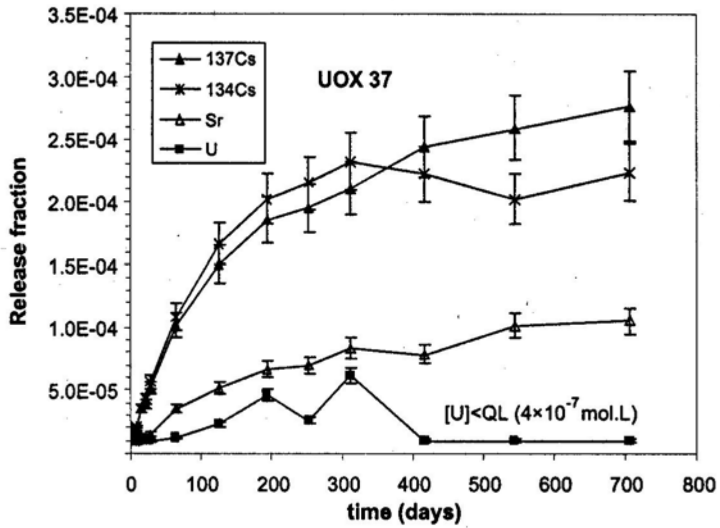


Uranium Release from Series 2 Tests

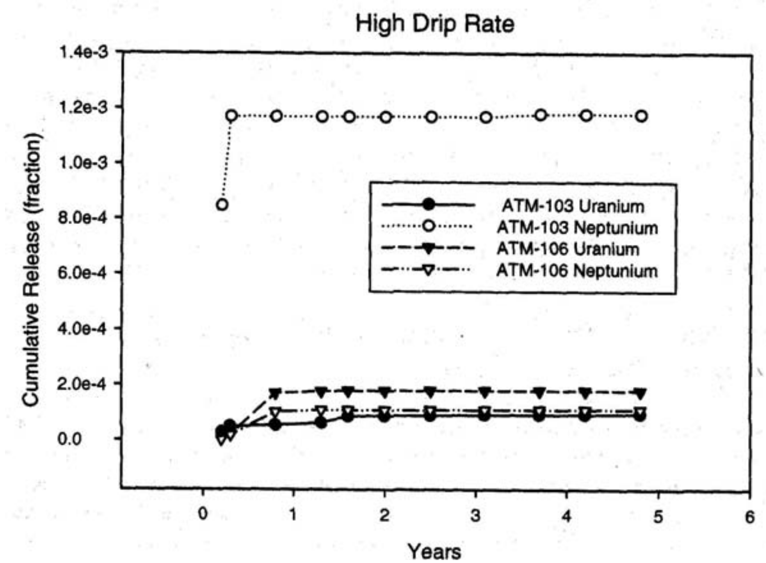


Uranium Release from Series 3 Tests

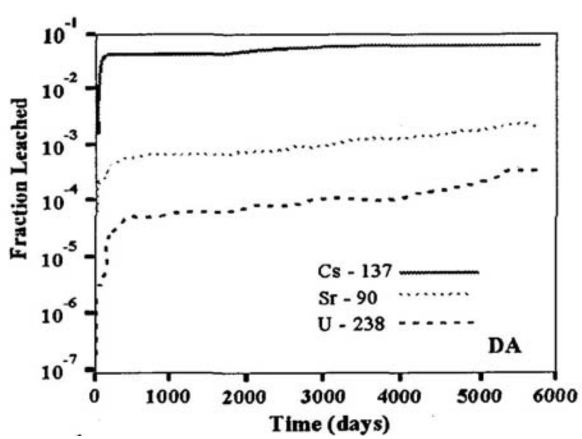
Other SNF data

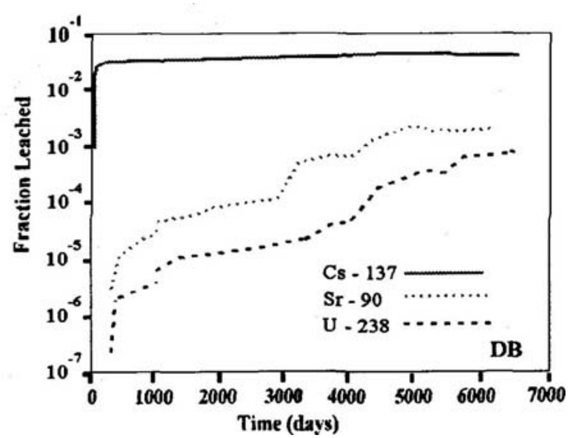


Jegou et. al. JNM 326(2004) -Static



ANL drip test

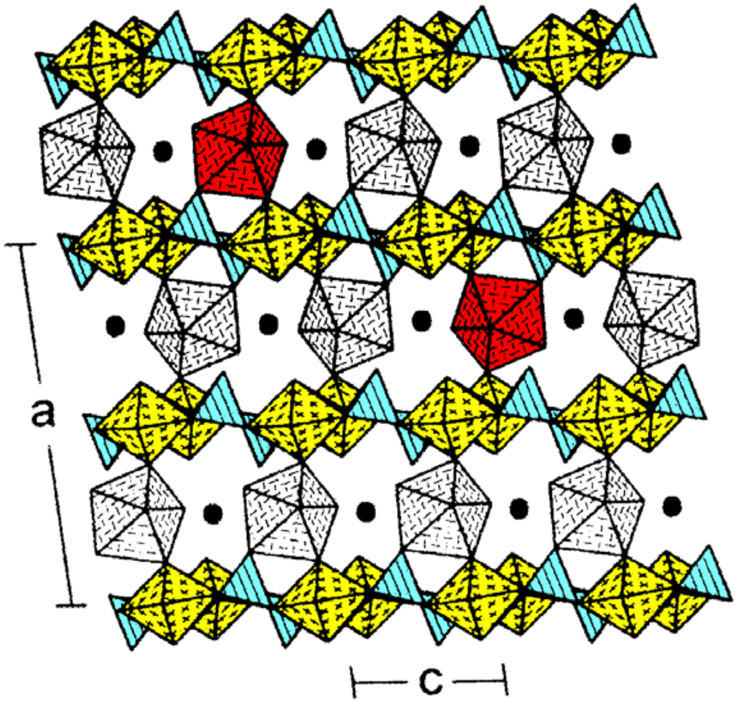




19-yr static tests from Stroes-Gascoyne et. al. MRS(465) 1997.

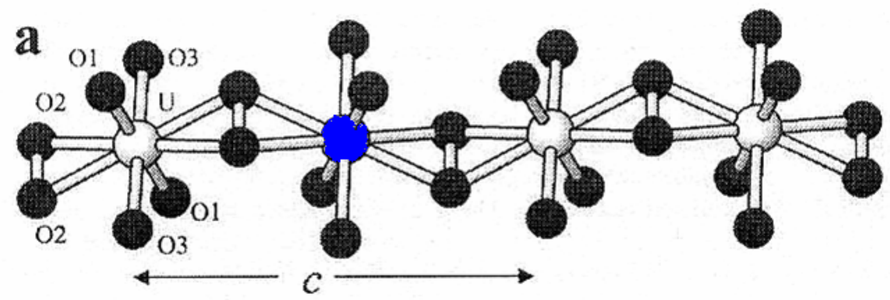
Radionuclide incorporation into uranyl alteration phases

Isomorphous replacement by a foreign constituent in the structure of a U(VI) phase



Adapted from Burns, P.C. (1999).

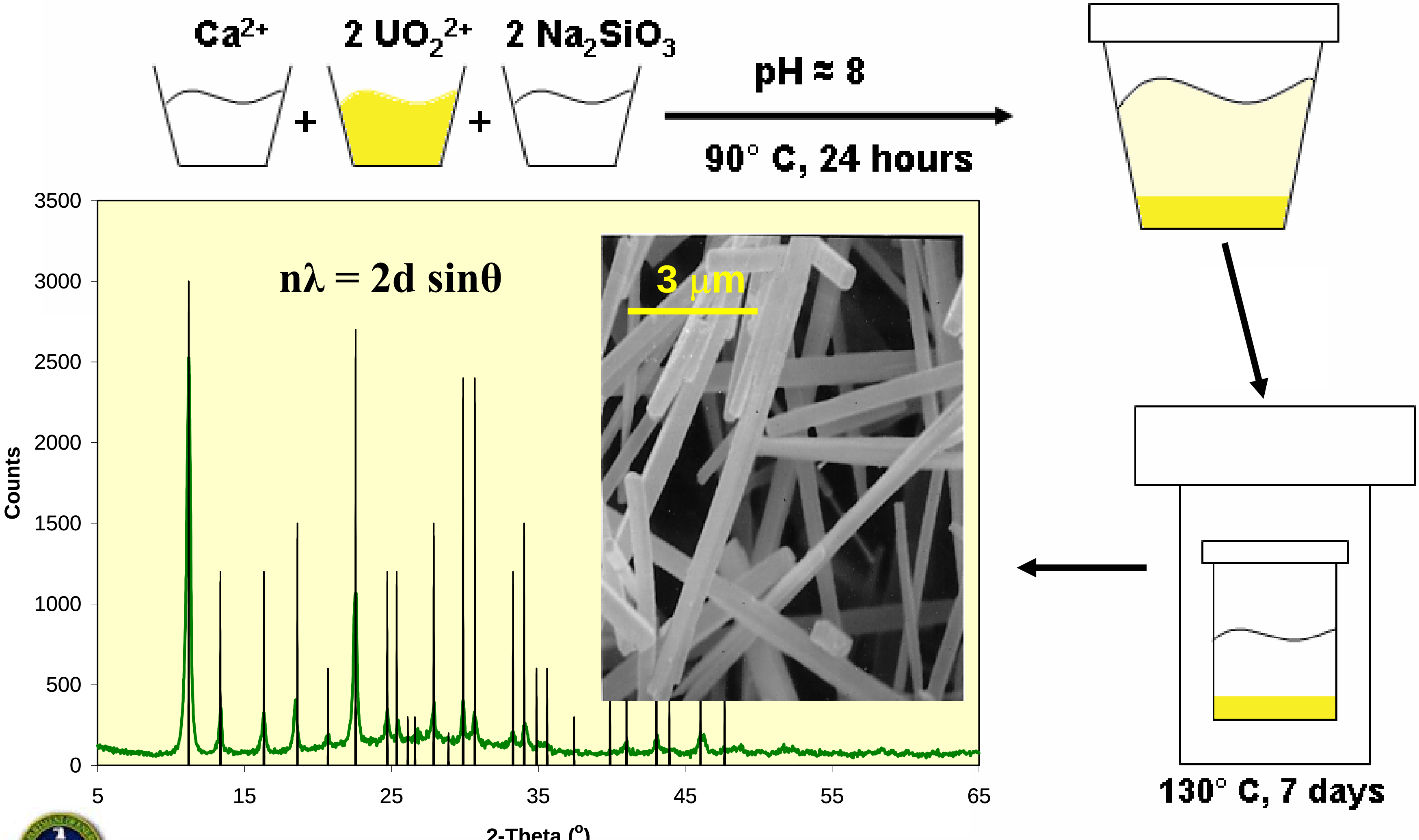
- Solubility of metal ions in solid solutions is expected to be reduced compared to pure phases of the minor ion



Adapted from Burns, P.C. et al. (2003).

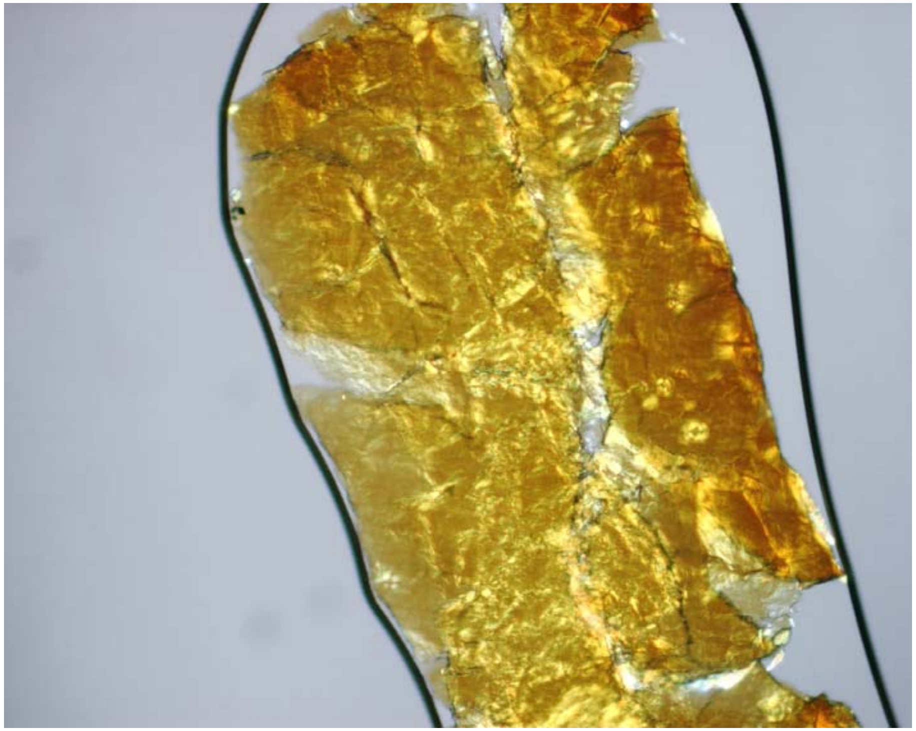
Synthesis of α-uranophane

Preparation from Nguyen et al., *J. Chem. Thermodynamics,* **24**, 359-376 (1992)

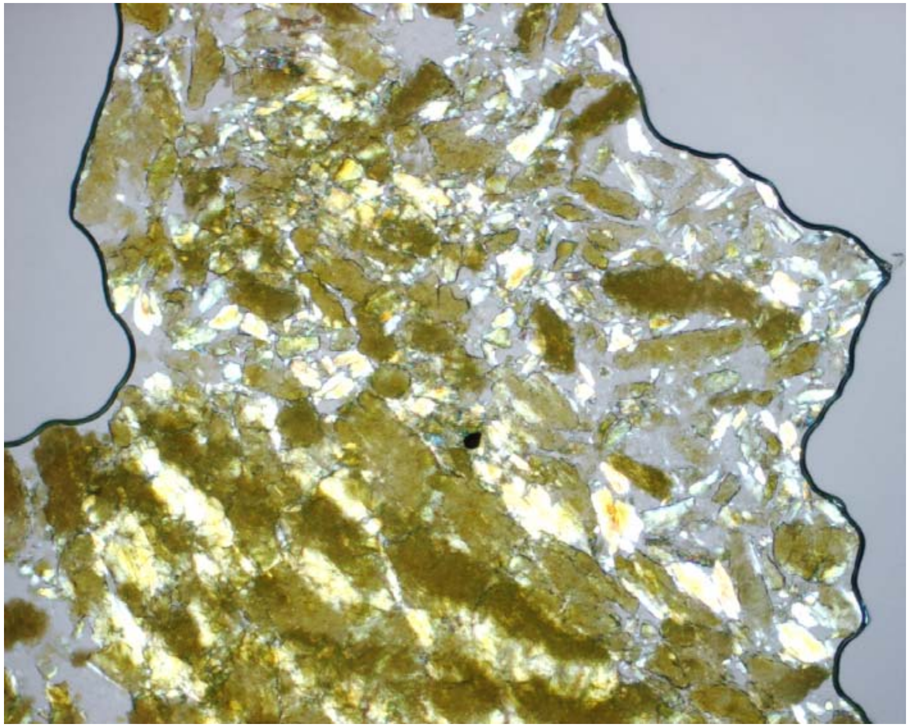


Neptunium effect on color. . .

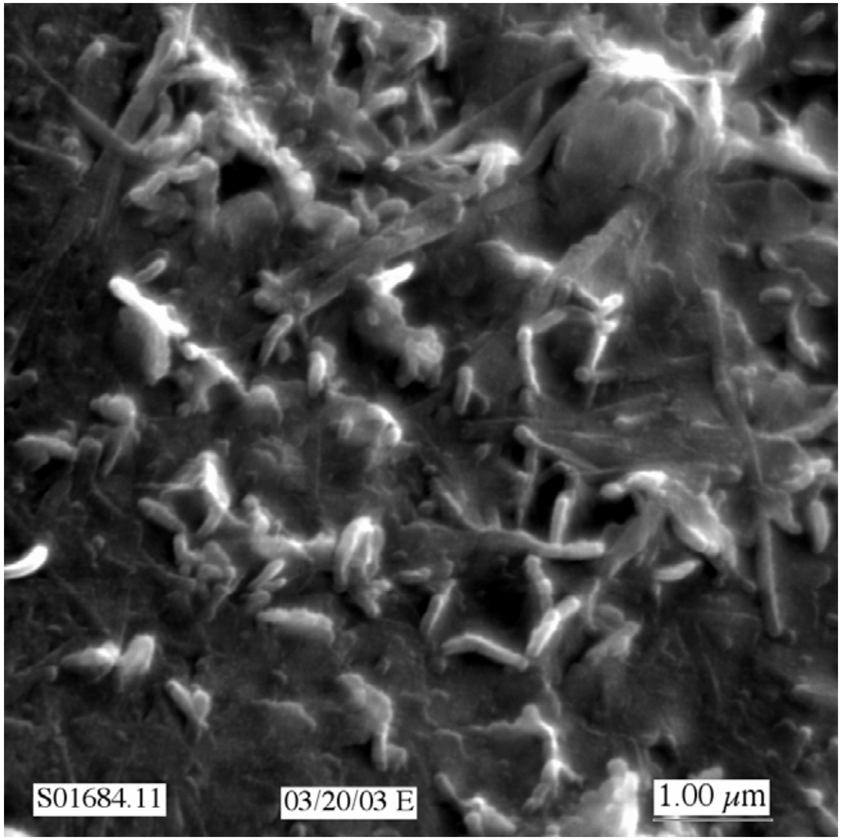
U(VI) silicate, 3000 μg/g Np

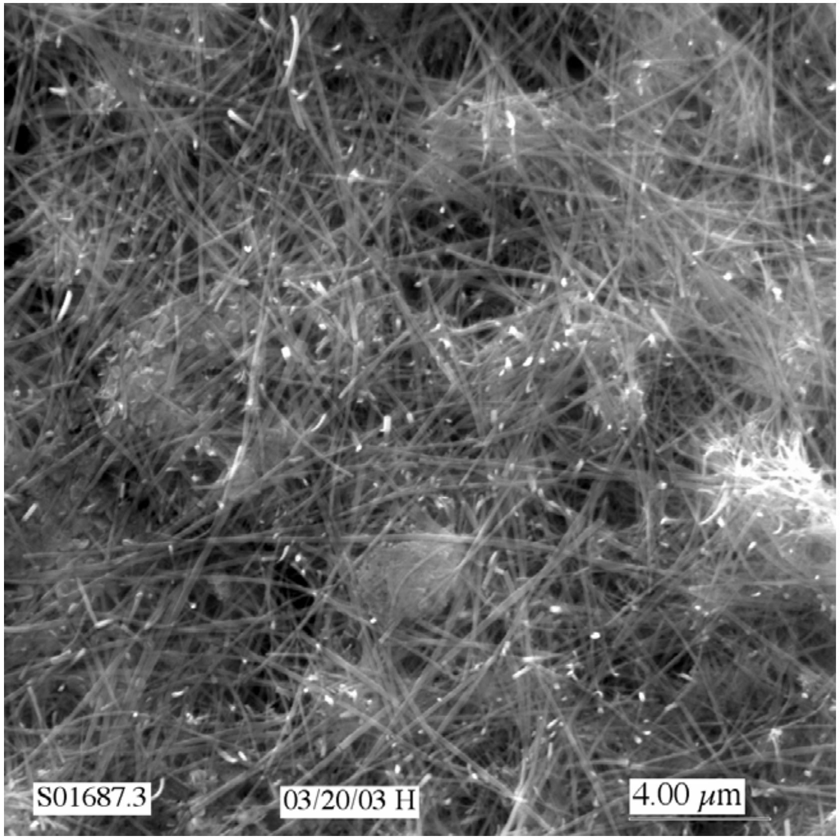


U(VI) silicate, No Np



Morphologies of solids by SEM



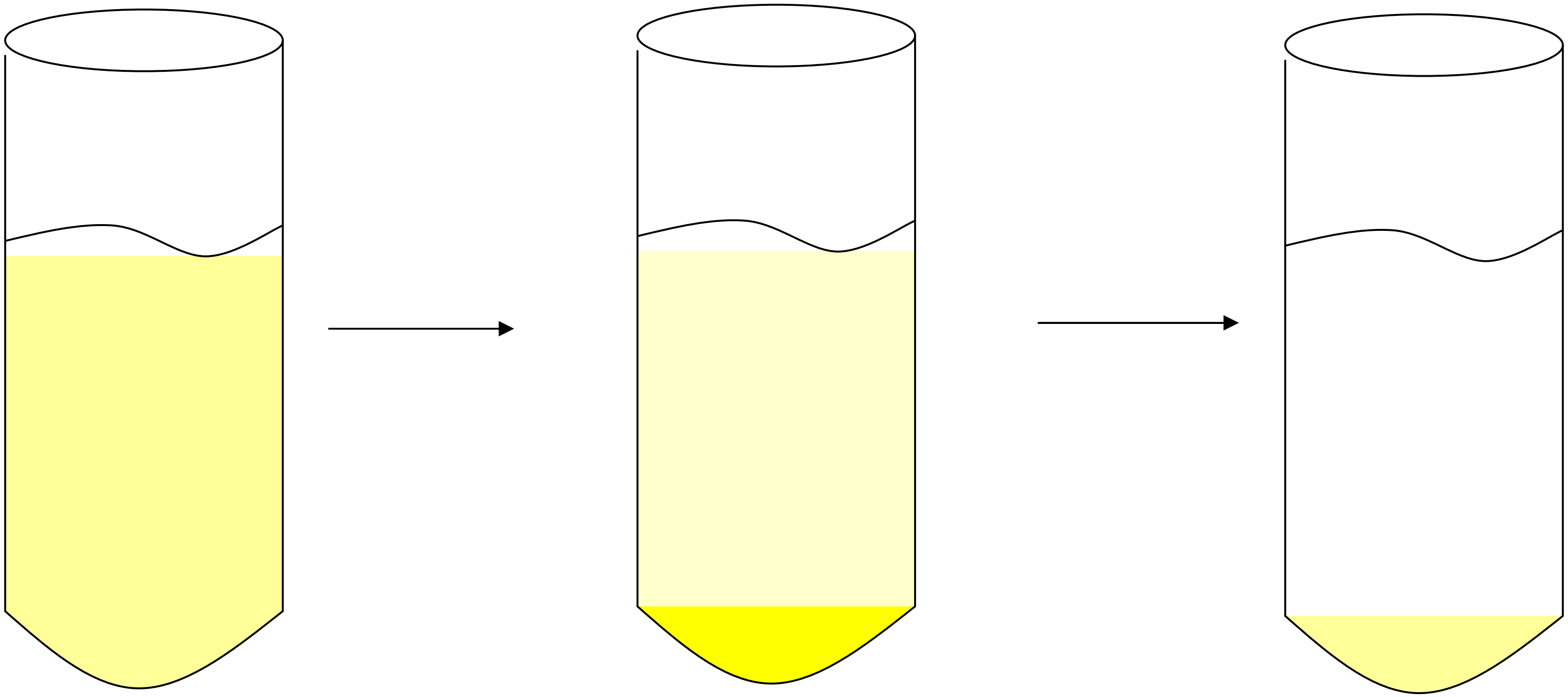


Solution Np:U = 0.02,

6300 μg/g Np in solid

No Np in synthesis

Neptunium in U(VI)-peroxides



$0.01\ M\ UO_2^{2+}$

2 mol % Np

pH 3.6

pH 5.5 w/ NaOH

metaschoepite

$[(UO_2)_8O_2(OH)_{12}](H_2O)_{10}$

(<10 ppm Np)

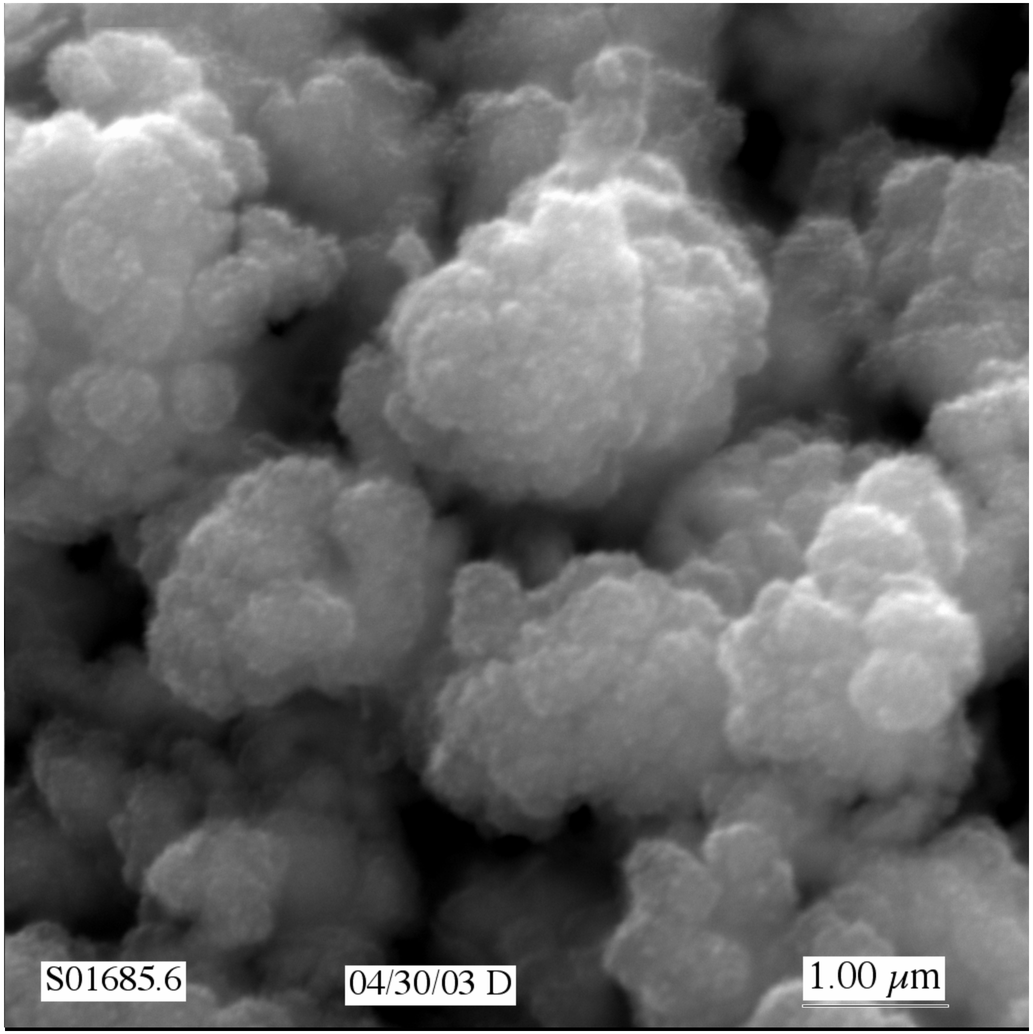
30 % H_2O_2, pH ---> 4.6

studtite

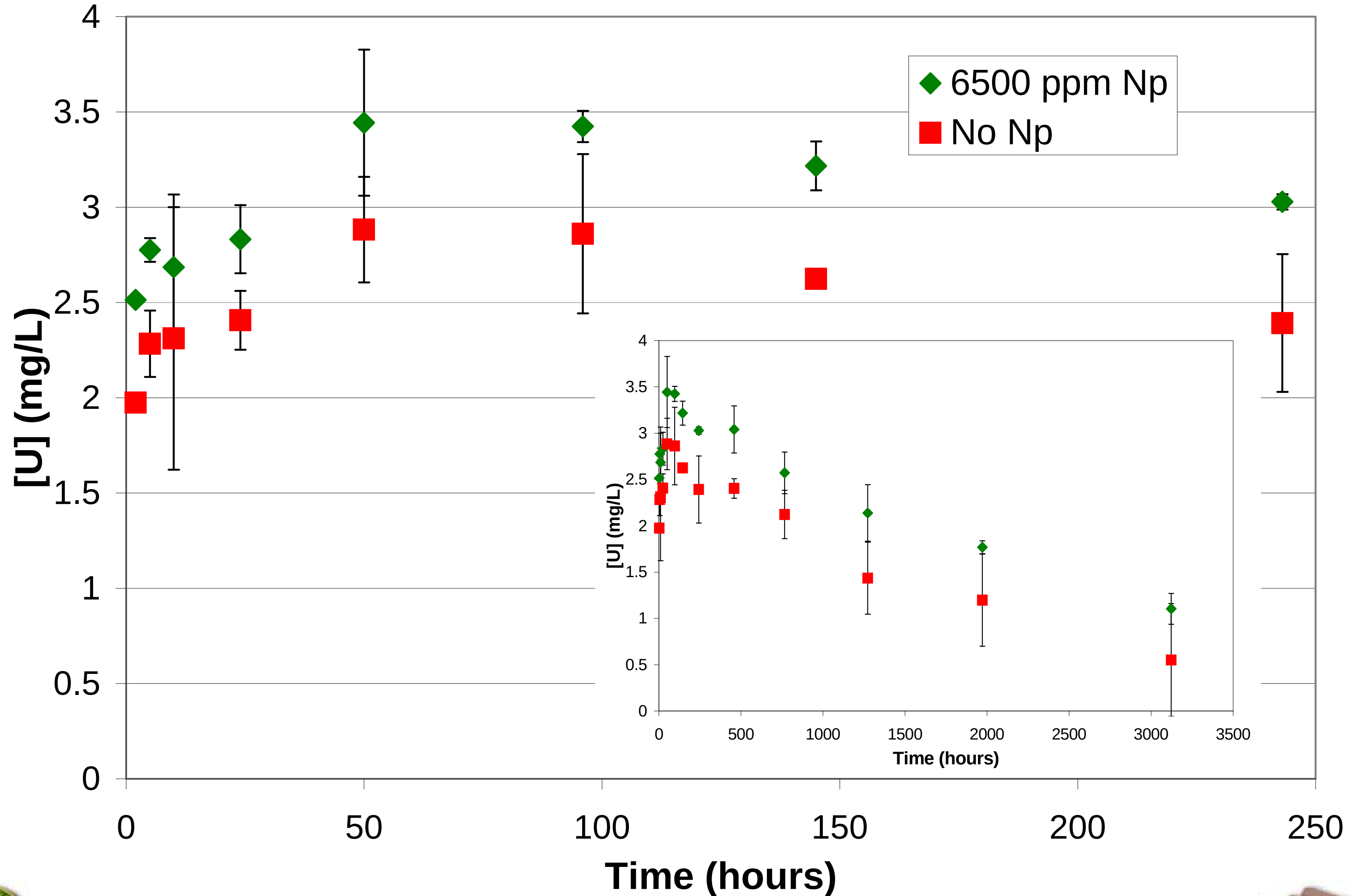
$[(UO_2)O_2(H_2O)_4]$

(6,500 ppm Np)

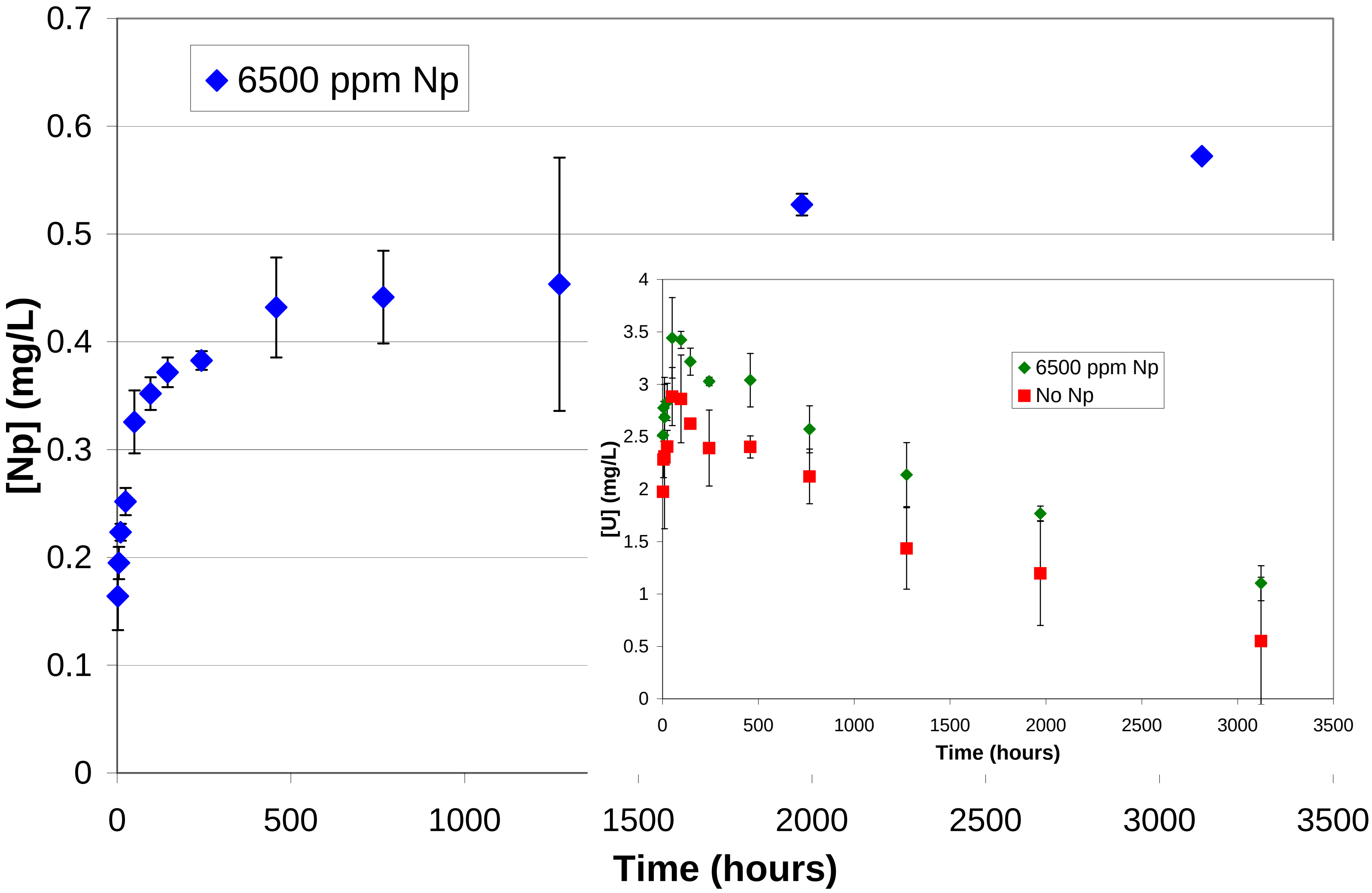
Studtite: 6500 μg/g Np



Metastudtite: Dissolved U



Metastudtite: Dissolved Np



Summary

- Release of Np exceeds congruent dissolution of U
- Heterogeneity/particle-size of solids likely influence dissolution behavior
- Np does not appear to associate with the re-precipitated phase
- Uranyl peroxides appear to be stable in batch systems, without a H_2O_2 source
- While there is some evidence consistent with solid solution formation, other factors including poor crystallinity and amorphous phases may not reduce dissolved concentrations as expected

Acknowledgments

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