U.S. Department of Energy
Office of Civilian Radioactive Waste Management

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Impact of Uranyl Alteration Phases of Spent Fuel on Mobility of Np

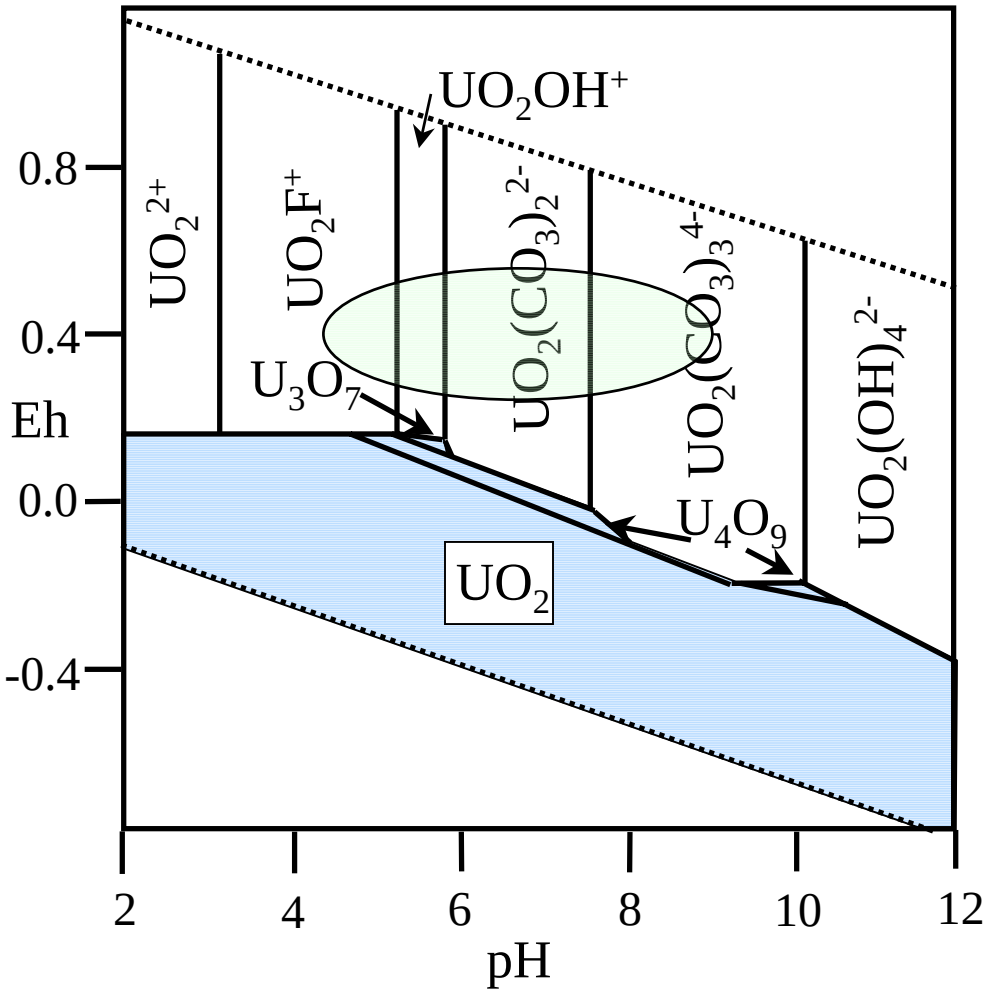
Presented to:
DOE-CEA Technical Exchange Meeting

Presented by:
Peter C. Burns
Professor, University of Notre Dame

Wednesday, February 9, 2005
Las Vegas, Nevada

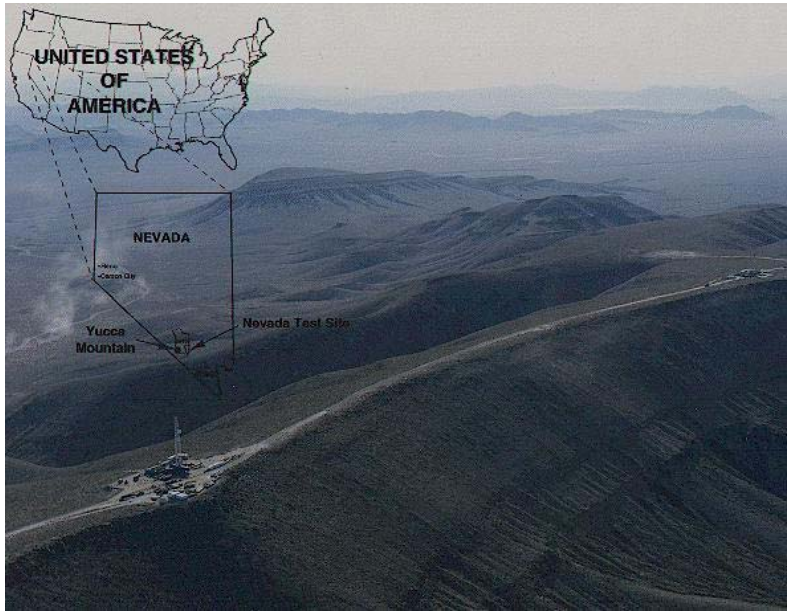
Oxidation of Spent Nuclear Fuel

Johnson & Werme (1994)

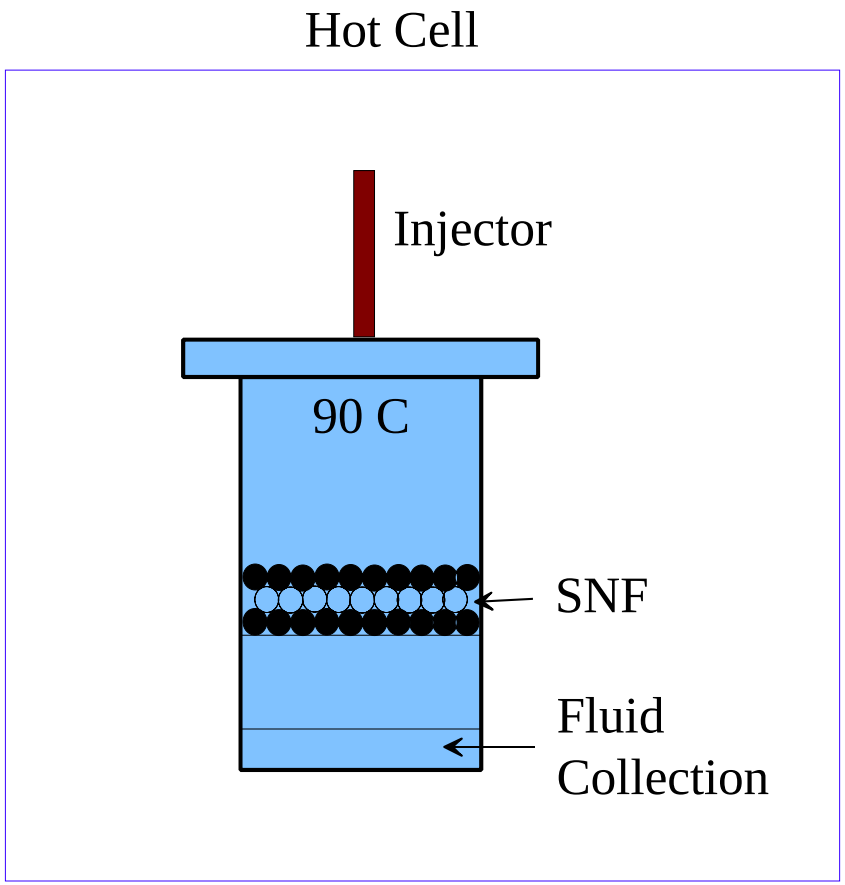


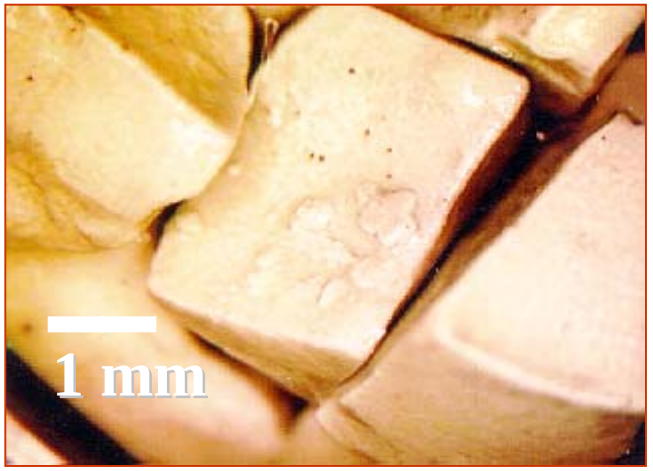
For uranium in synthetic groundwater at 25ºC

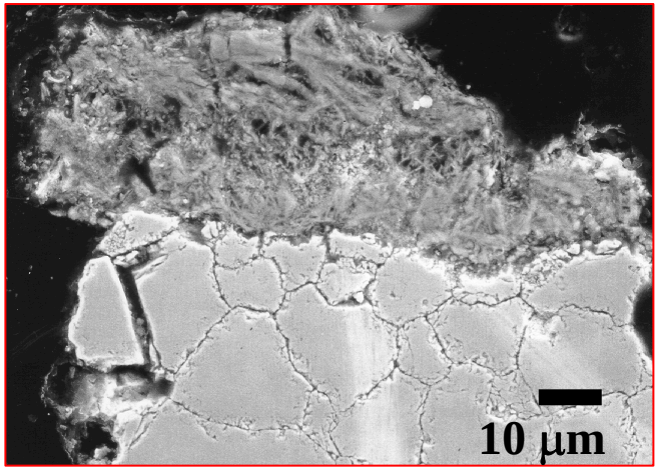
Yucca Mountain



Laboratory Studies: Argonne National Labs



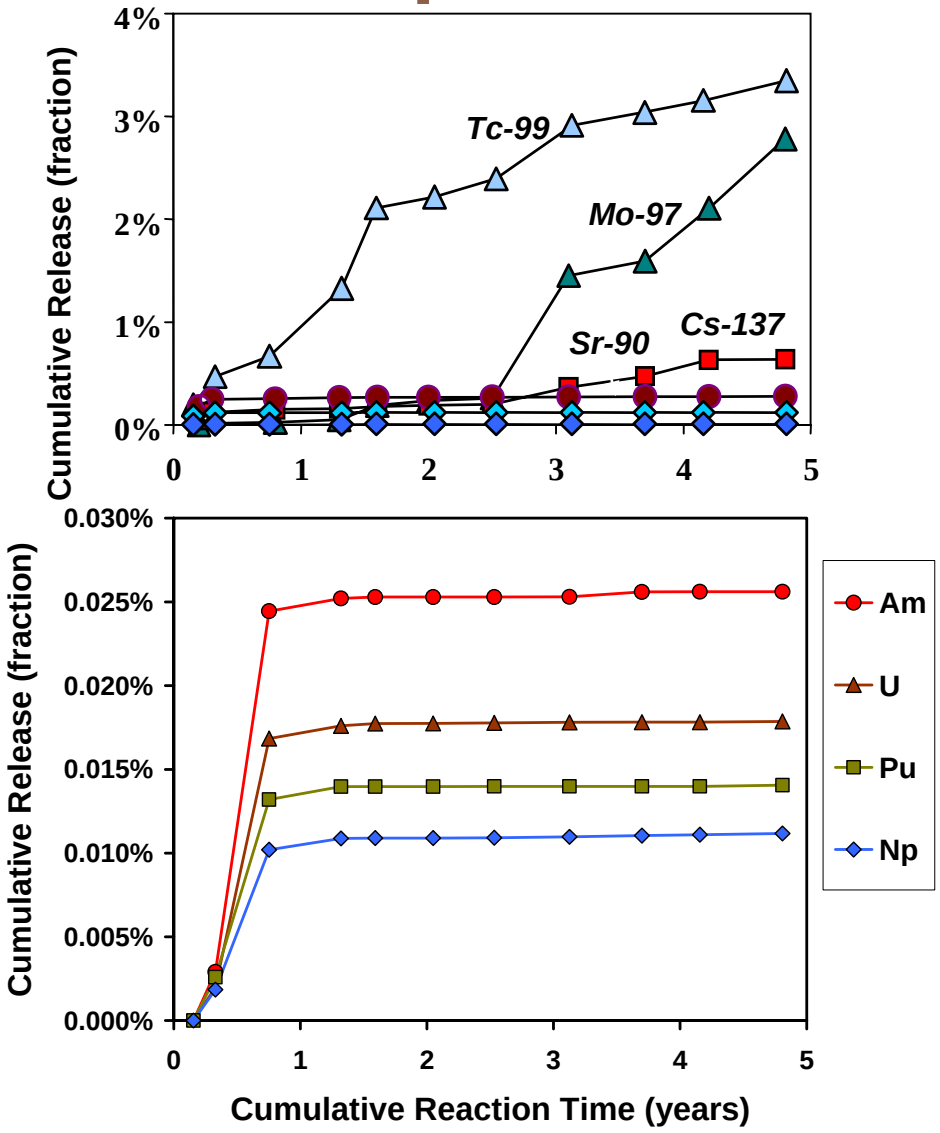




Finn, Hoh, Wolf, Slater & Bates (1996): JNM
Buck, Wronkiewicz, Finn & Bates (1997): JNM
Finch, Buck, Finn & Bates (1999): MRS Proc.

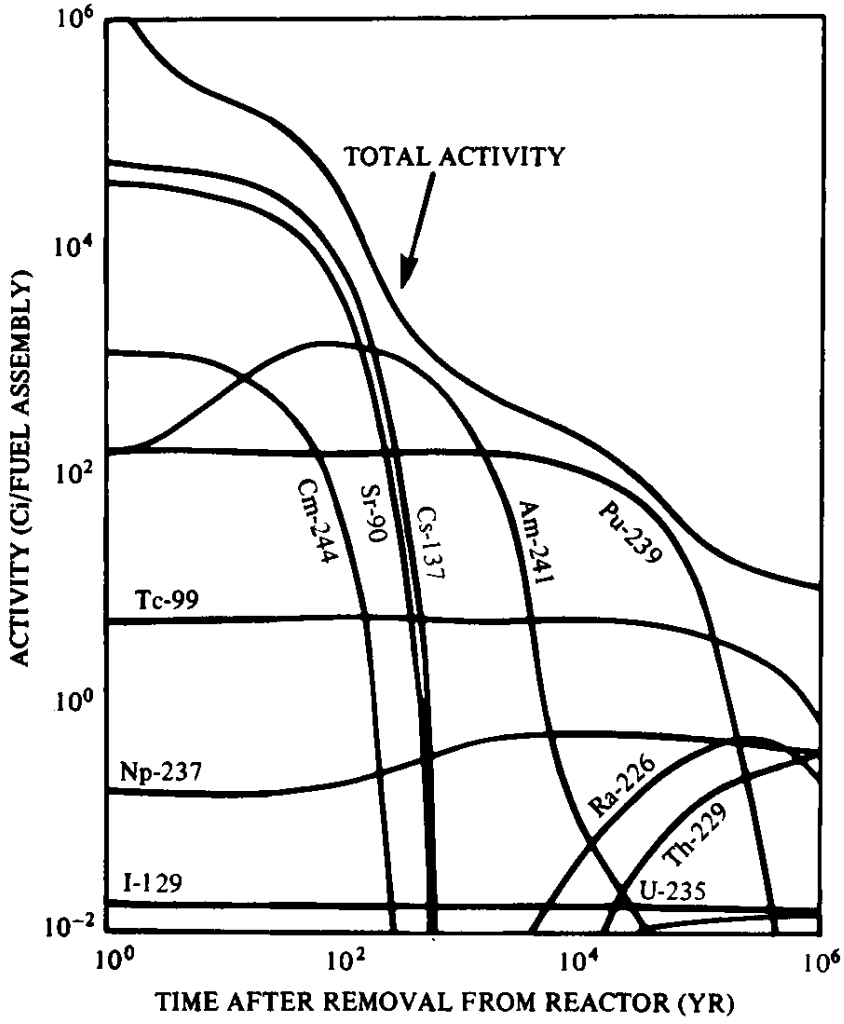
Boltwoodite: $(K,Na)[(UO_2)(SiO_3OH)](H_2O)_{1.5}$
Uranophane: $Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$

Neptunium at Yucca Mountain



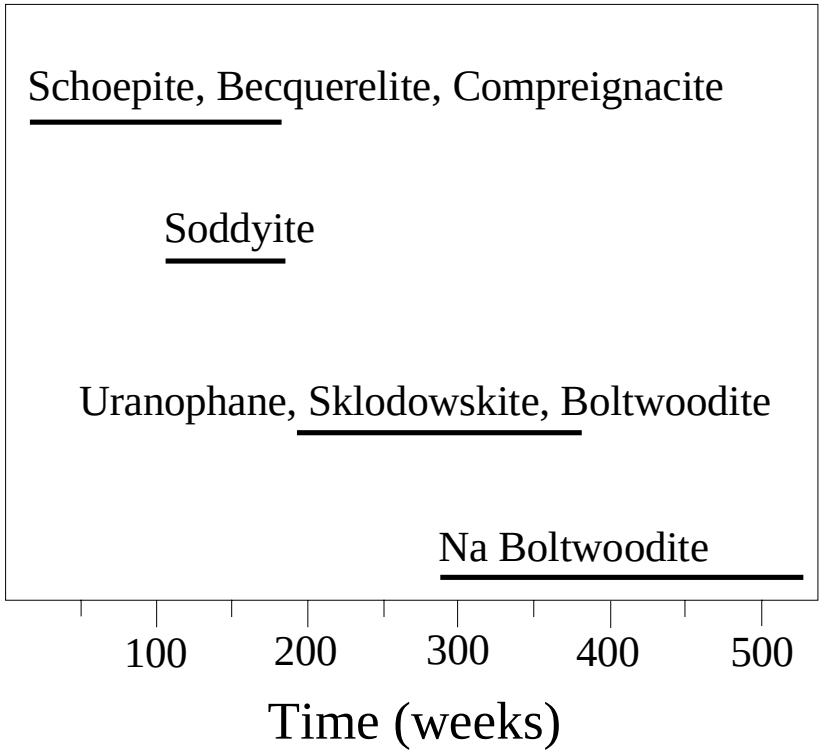
Provided by Robert Finch

PWR SNF



Brookings 1984

Paragenesis of Uranyl Minerals: Spent Fuel

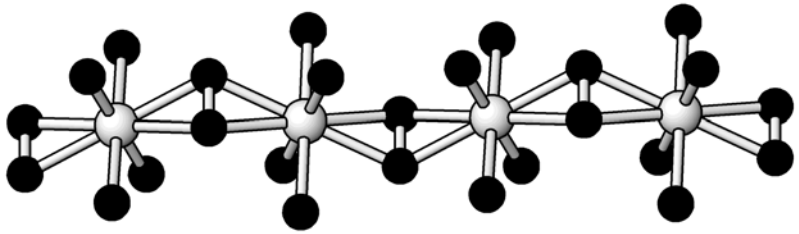


Wronkiewicz, Bates, Gerding, Veleckis & Tani (1992): JNM
Wronkiewicz, Bates, Wolf, & Buck (1996): JNM
Finch, Buck, Finn, Bates (1999): MRS Proc.

Uranyl Peroxides

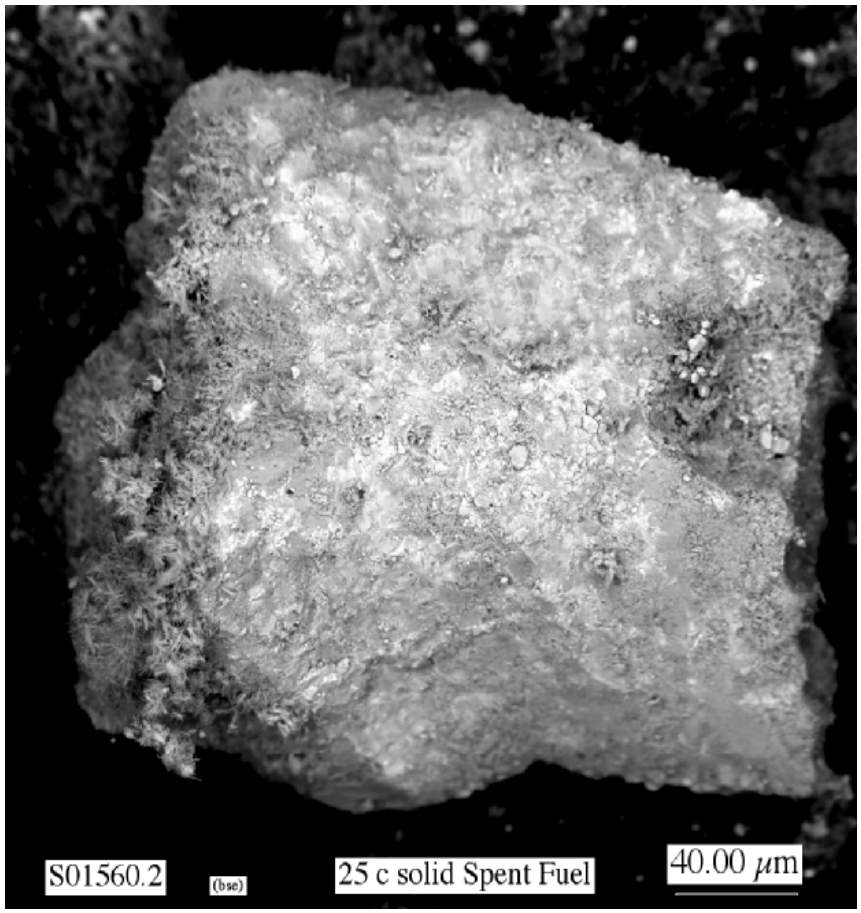
Studtite: $UO_2O_2(H_2O)_4$

Metastudtite: $UO_2O_2(H_2O)_2$



Burns & Hughes (2003): Am. Mineral.

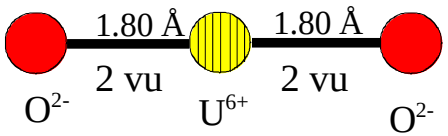
SNF in water, 25ºC, 1.5 years



McNamara et al. 2002

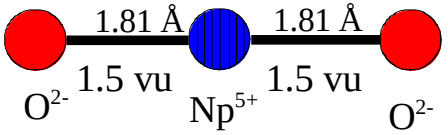
Np^{5+} Crystal Chemistry

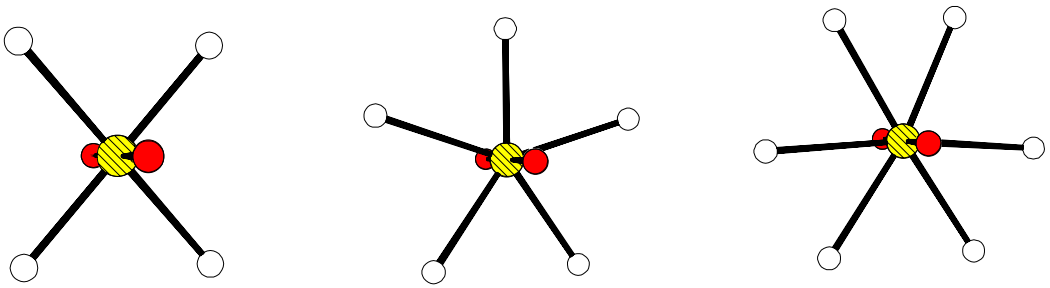
$(U^{6+}O_2)^{2+}$ Uranyl Ion



Np-237
$t^{1/2}$ = 2,140,000

$(Np^{5+}O_2)^{+}$ Neptunyl Ion



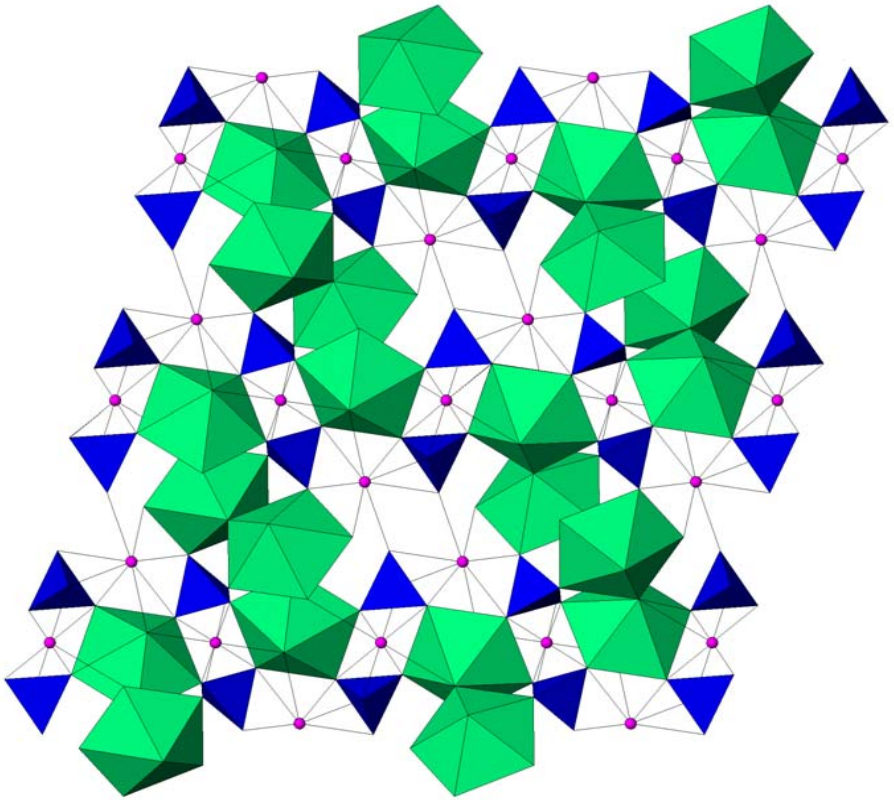


Uranyl	2.26	2.34	2.46 Å
Neptunyl	2.39	2.45	2.56 Å

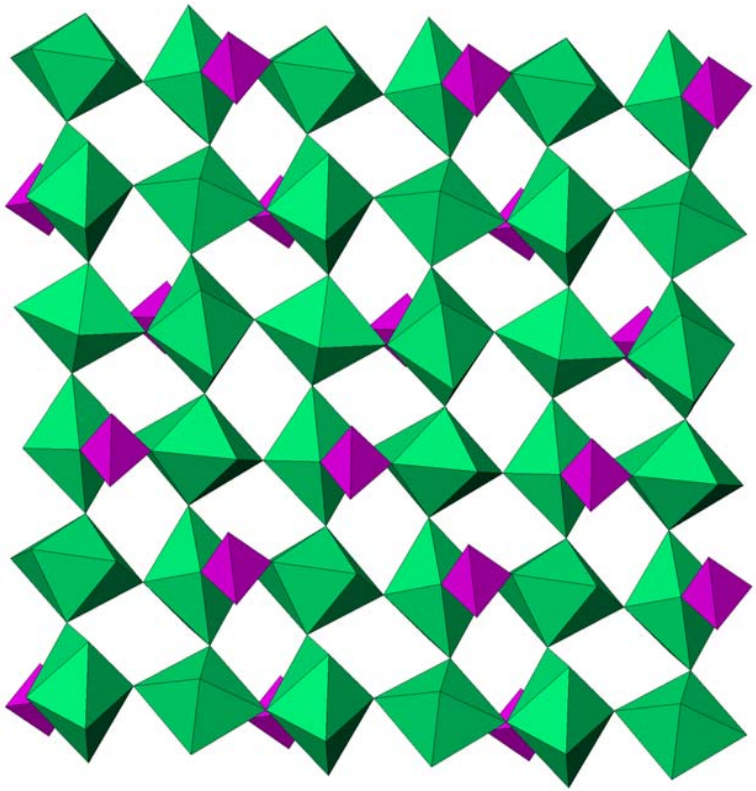
Burns et al. (1997): Journal of Nuclear Materials

Np^{5+} Crystal Chemistry

$K_2(NpO_2)_2(SO_4)_2(H_2O)$



$[(NpO_2)_8(SO_4)_4(H_2O)_{16}]$



Unpublished

Studies of Incorporation of Np^{5+}

Some Phases Important for Repository Performance

Na-compreignacite: $Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$

Uranophane: $Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$

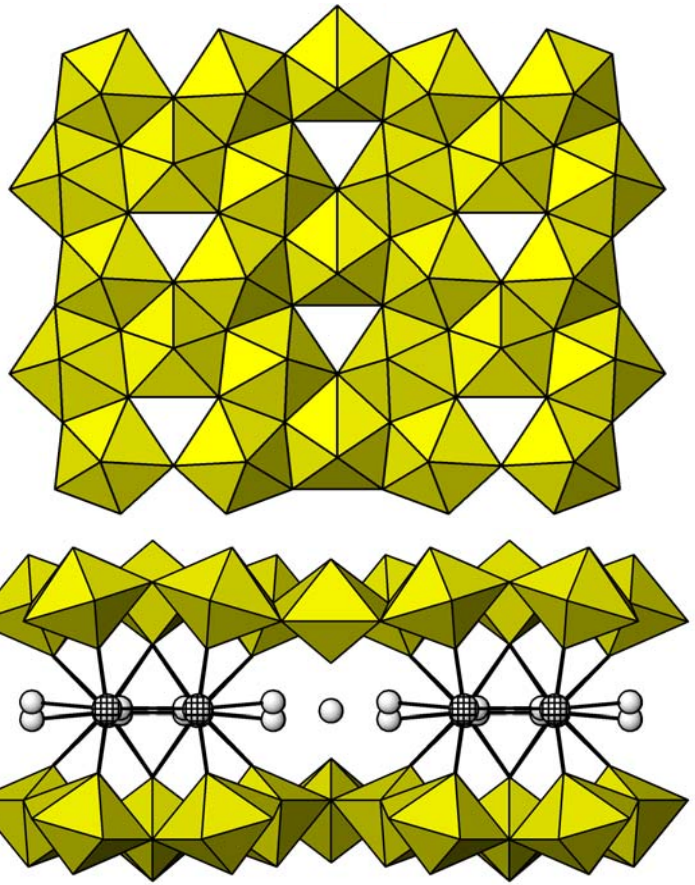
Meta-schoepite: $UO_3(H_2O)_2$

β-$UO_2(OH)_2$

Soddyite: $(UO_2)_2(SiO_4)(H_2O)_2$

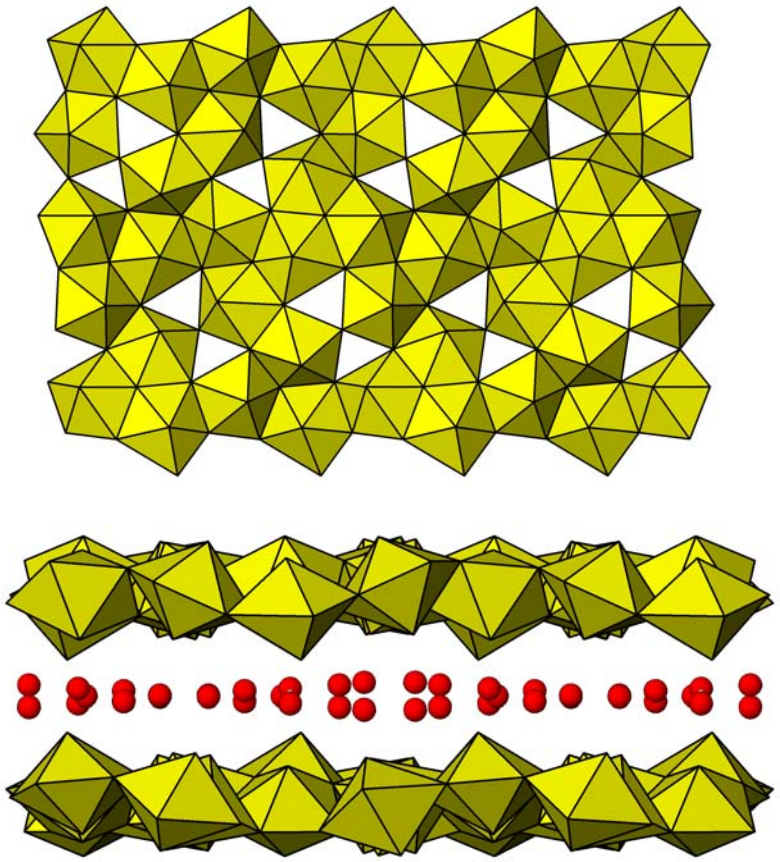
Studies of Incorporation of Np^{5+}

Na-compreignacite



$Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$

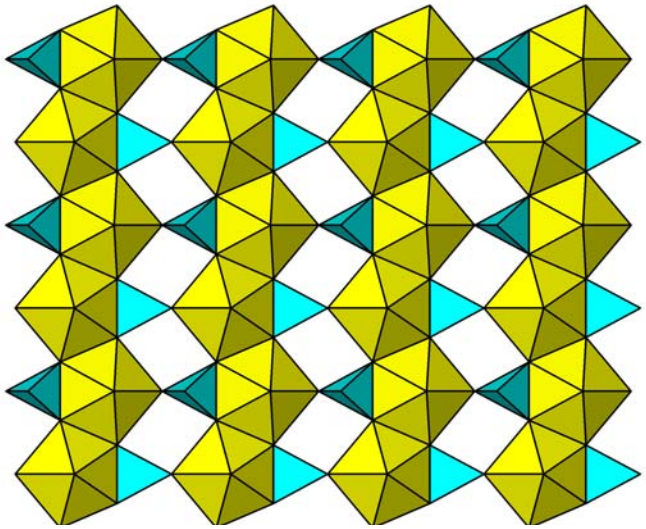
Meta-schoepite

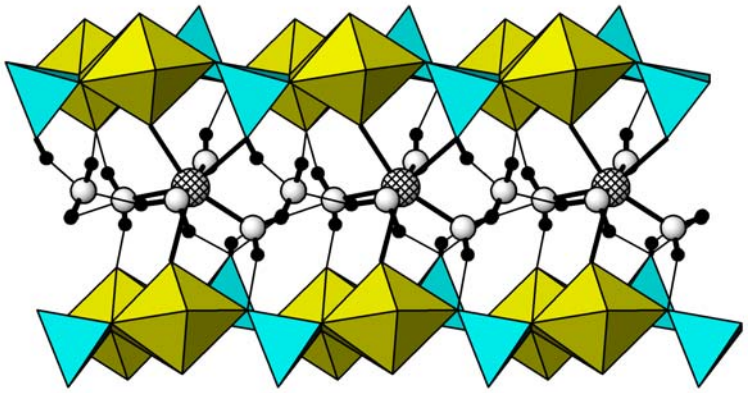


$UO_3(H_2O)_2$

Studies of Incorporation of Np^{5+}

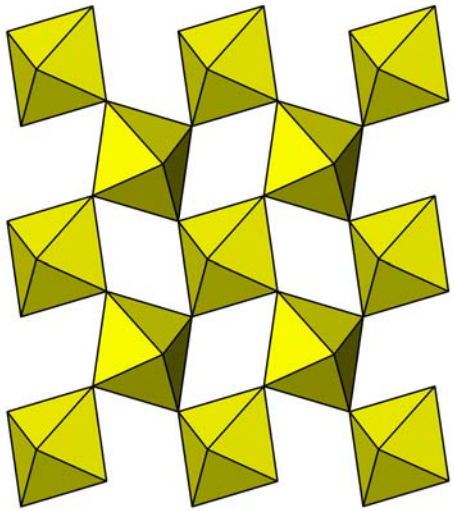
Uranophane

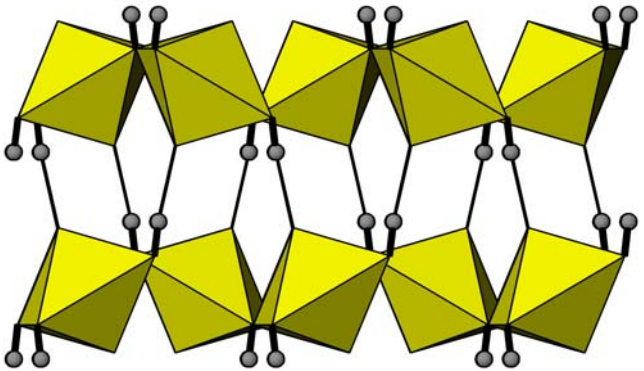




$Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$

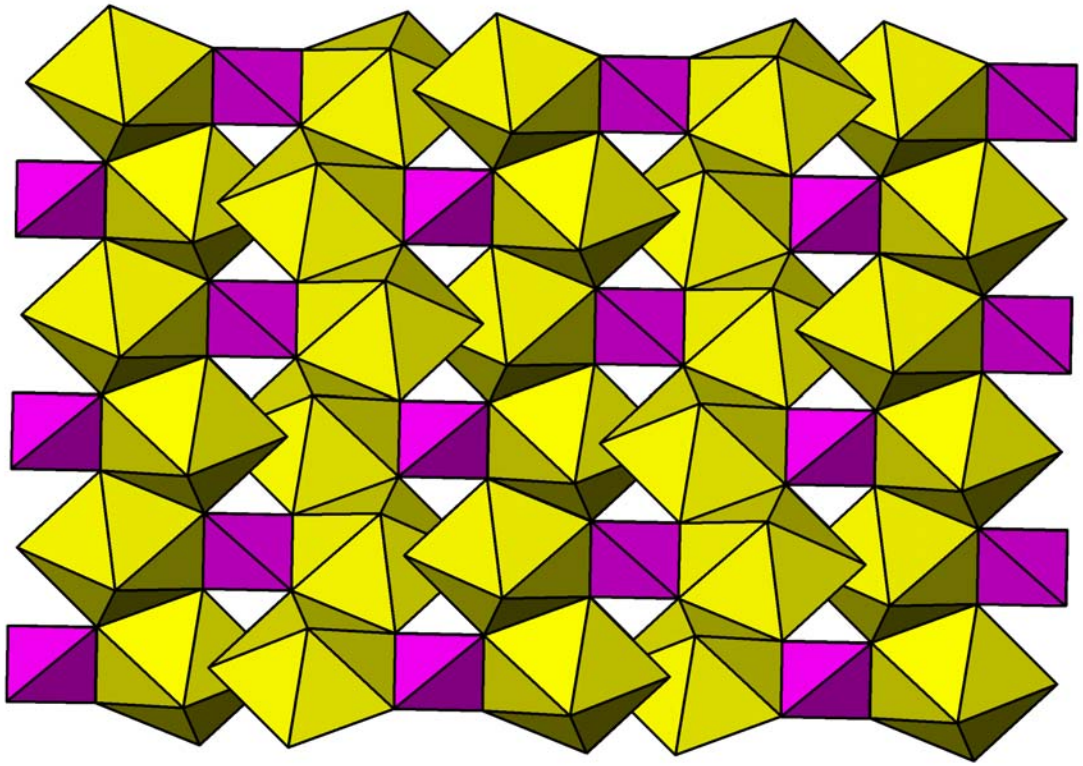
β-$UO_2(OH)_2$





Studies of Incorporation of Np^{5+}

Soddyite



$(UO_2)_2(SiO_4)(H_2O)_2$

Studies of Incorporation of Np^{5+}

- *Synthesis in presence of ppm-levels of Np^{5+}*
- *Washed in boiling water and 0.5 M acetic acid*
- *Characterization by powder XRD*
- *Analyses using ICP-AES and ICP-MS*

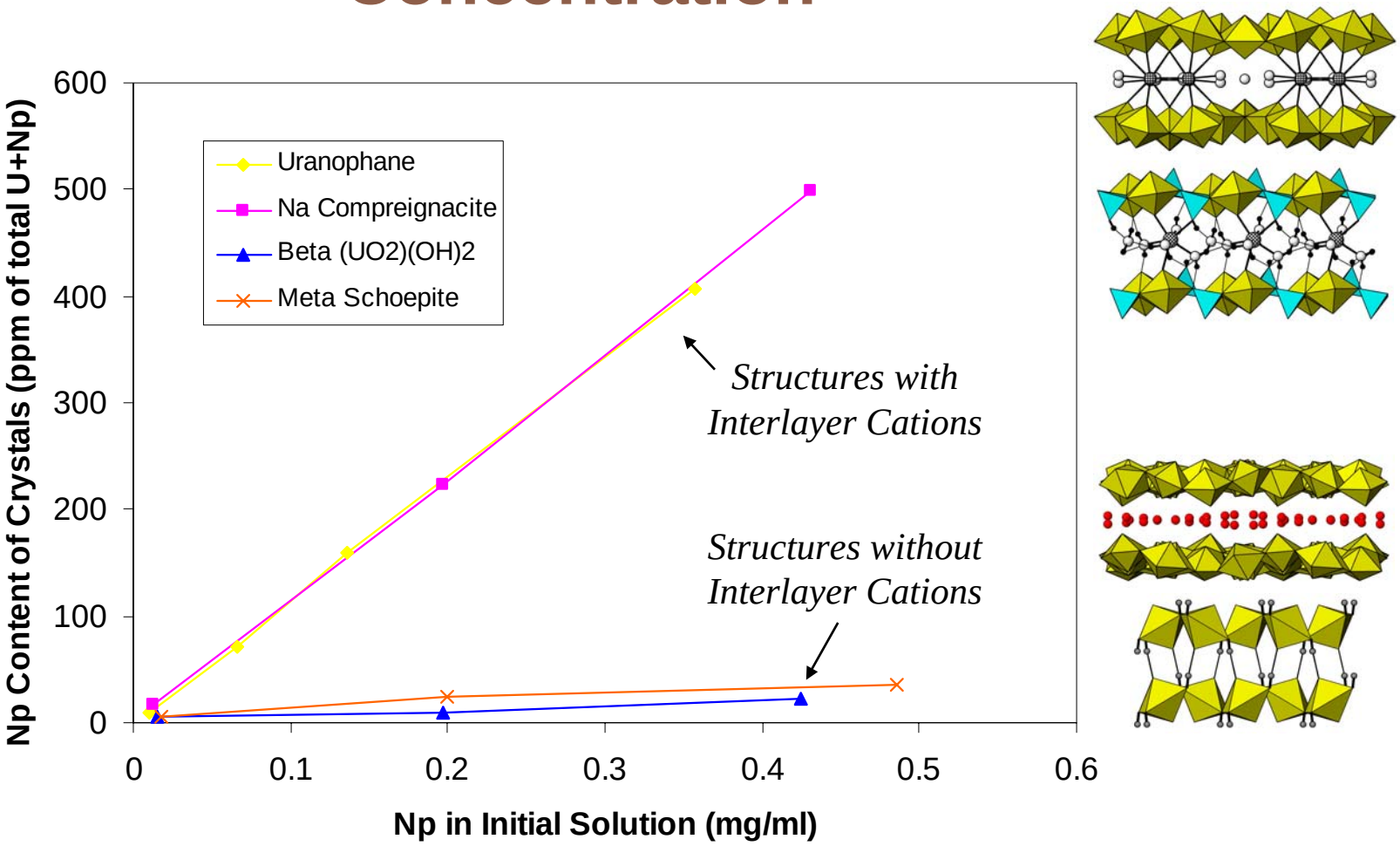
Na-compreignacite: pH = 5.2-5.7, T = 100ºC, 24h

Uranophane: pH = 5.4, T = 100ºC, 24h

β-$(UO_2(OH)_2$: pH = 4.2-4.4, T = 100ºC, 24h

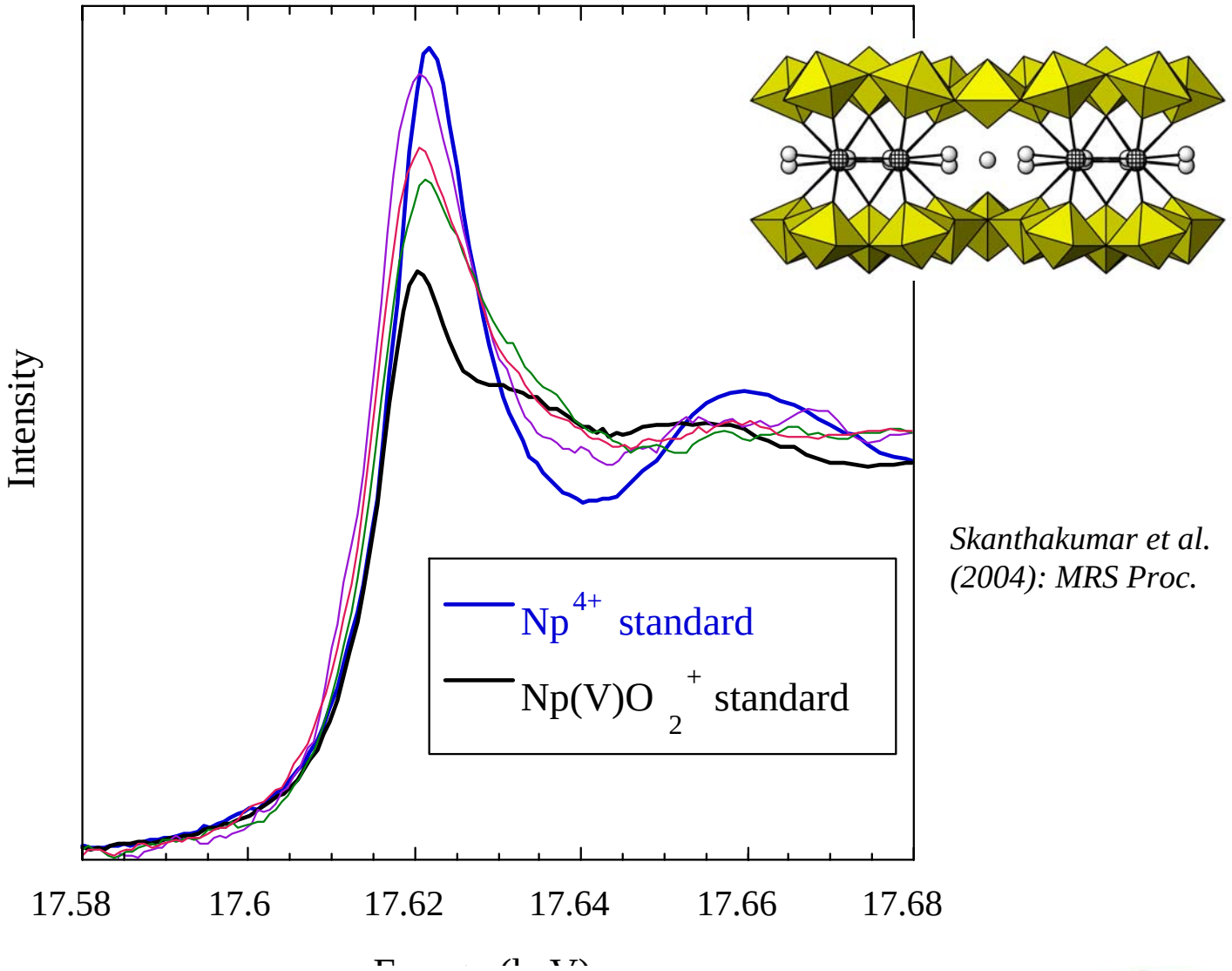
Metaschoepite: pH = 4.0-4.2, T = 75ºC, 24h

Incorporation of Np^{5+}: Function of Concentration



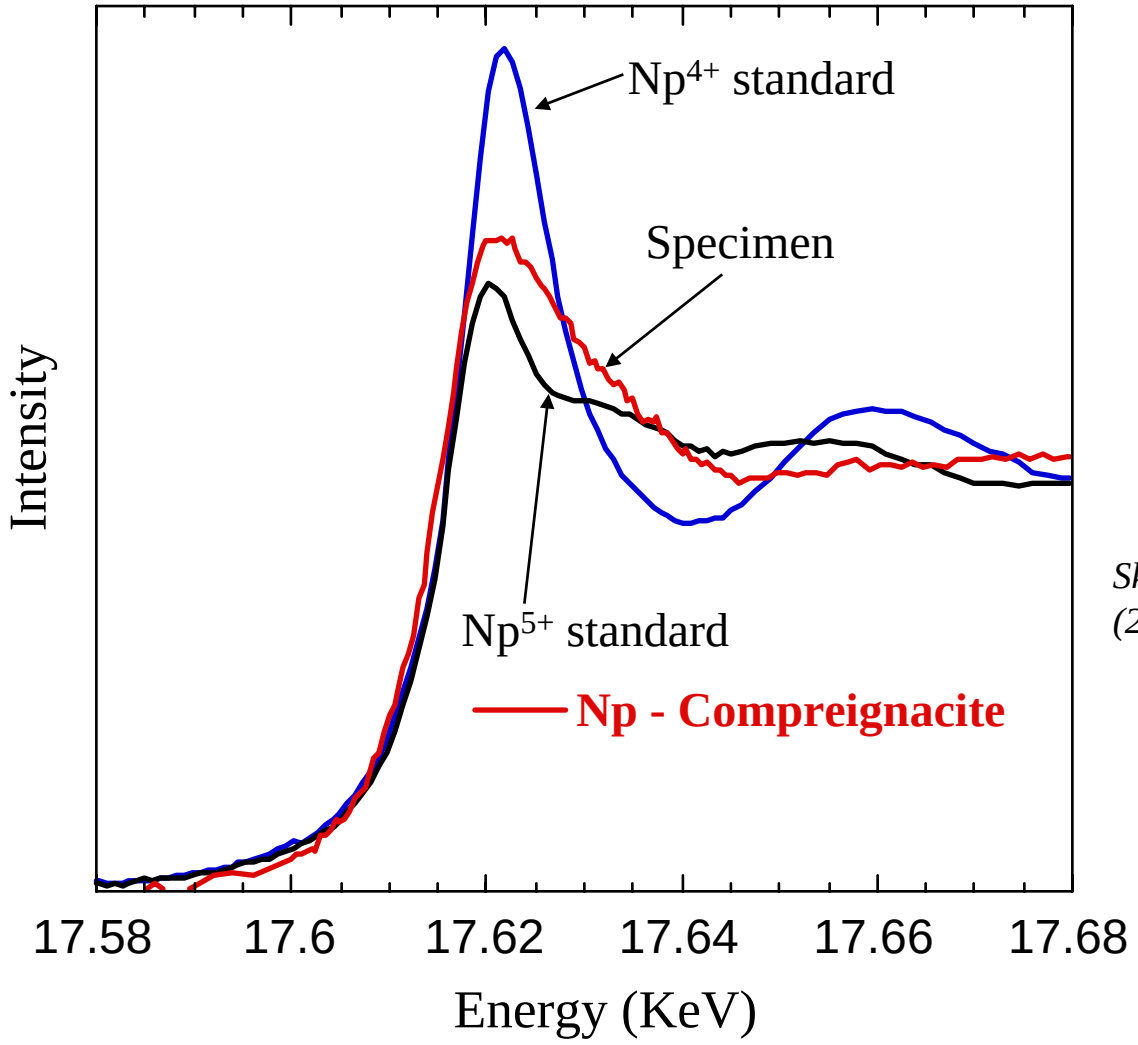
Burns et al. (2004): Radiochimica Acta

Np XANES: Na-compreignacite (400 ppm)



Skanthakumar et al. (2004): MRS Proc.

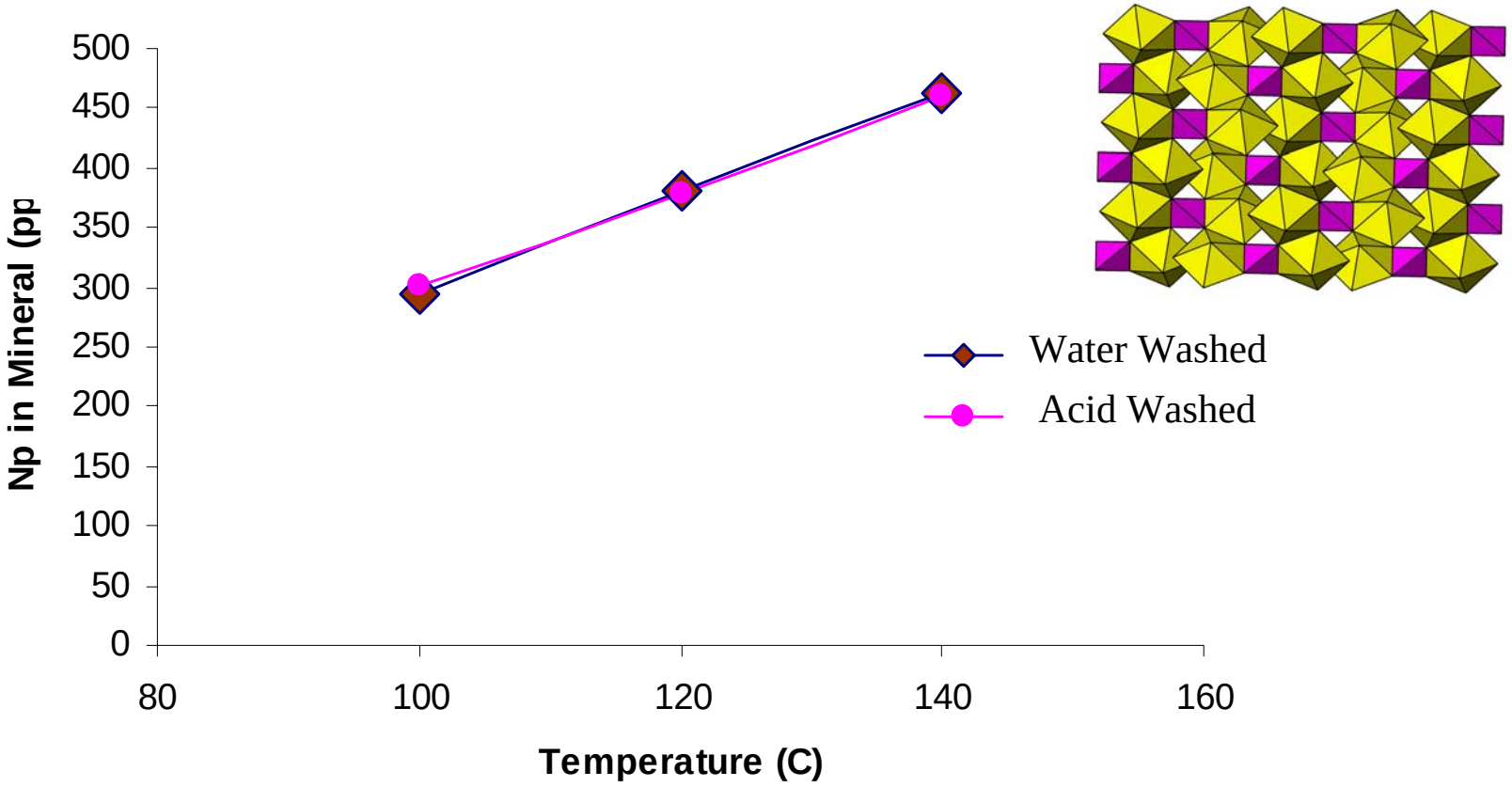
Np XANES: Na-compreignacite (400 ppm)



Skanthakumar et al. (2004): MRS Proc.

Np^{5+} Incorporation in Soddyite: Temperature Variation

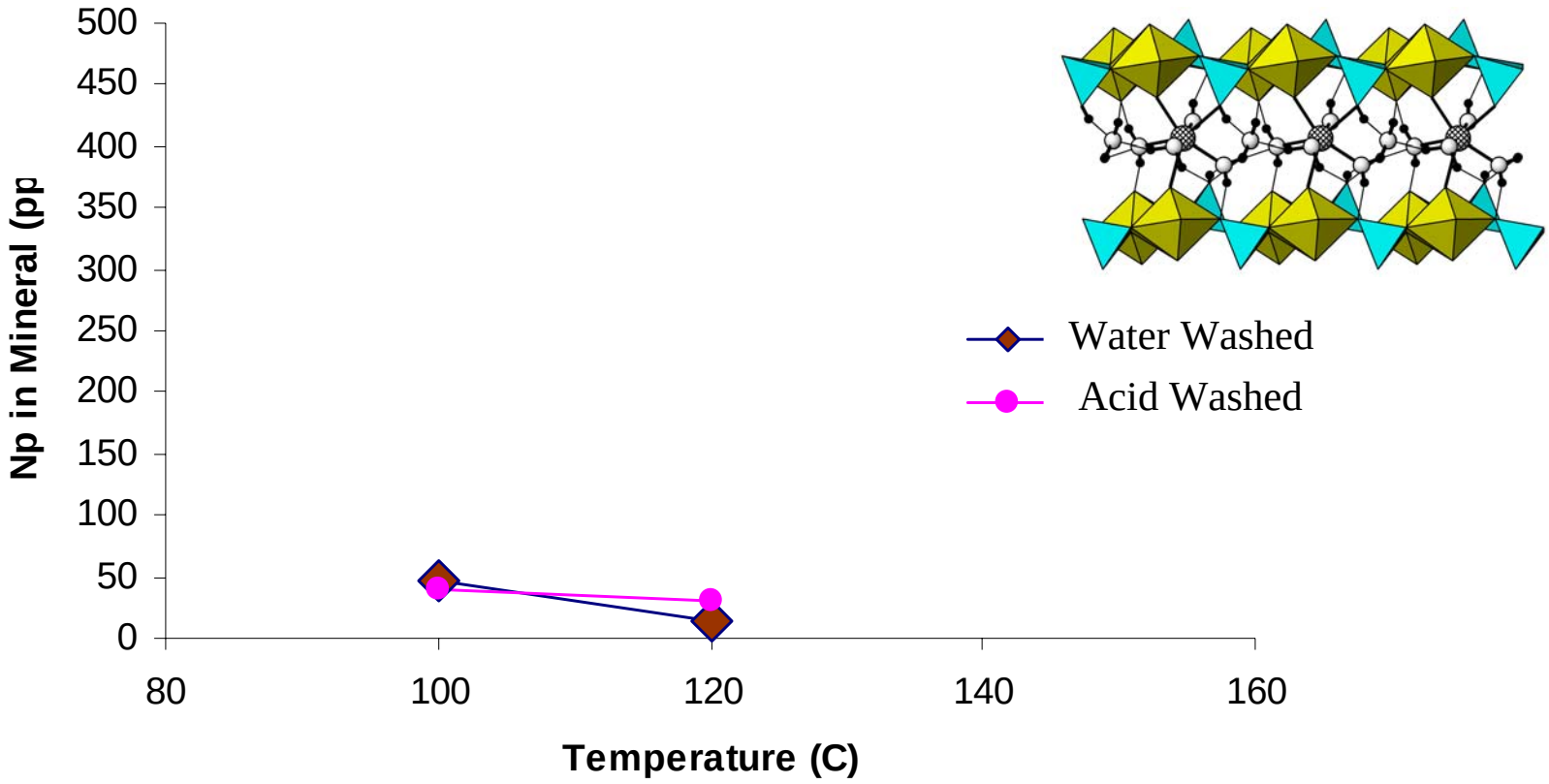
Soddyite: pH = 4, t = 24h, 160-180 ppm Np^{5+} in mother solution



Unpublished

Np^{5+} Incorporation in Uranophane: Temperature Variation

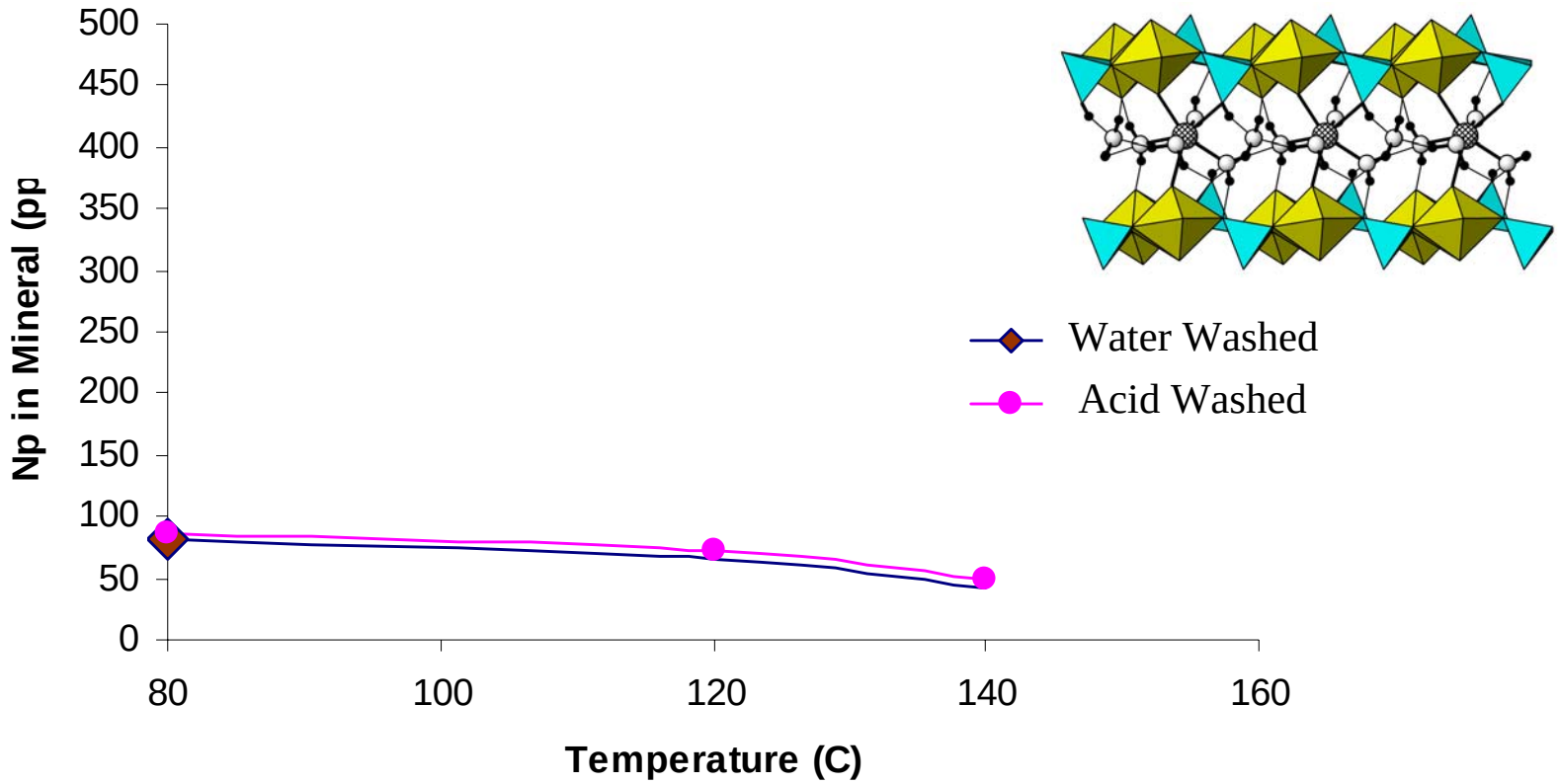
Uranophane: pH = 4, t = 24h, 160-180 ppm Np^{5+} in mother solution



Unpublished

Np^{5+} Incorporation in Uranophane: Temperature Variation

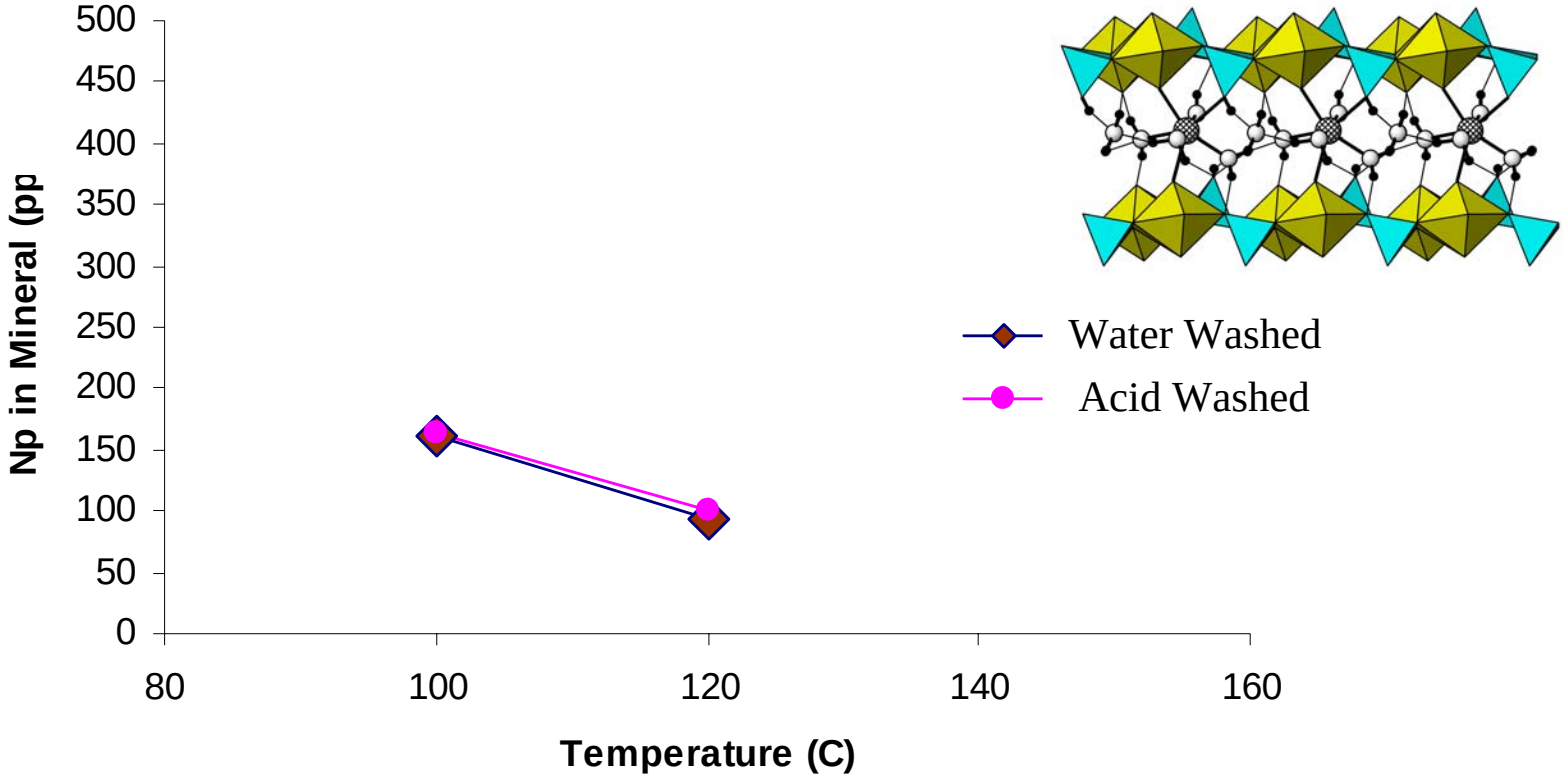
Uranophane: pH = 5, t = 24h, 160-180 ppm Np^{5+} in mother solution



Unpublished

Np^{5+} Incorporation in Uranophane: Temperature Variation

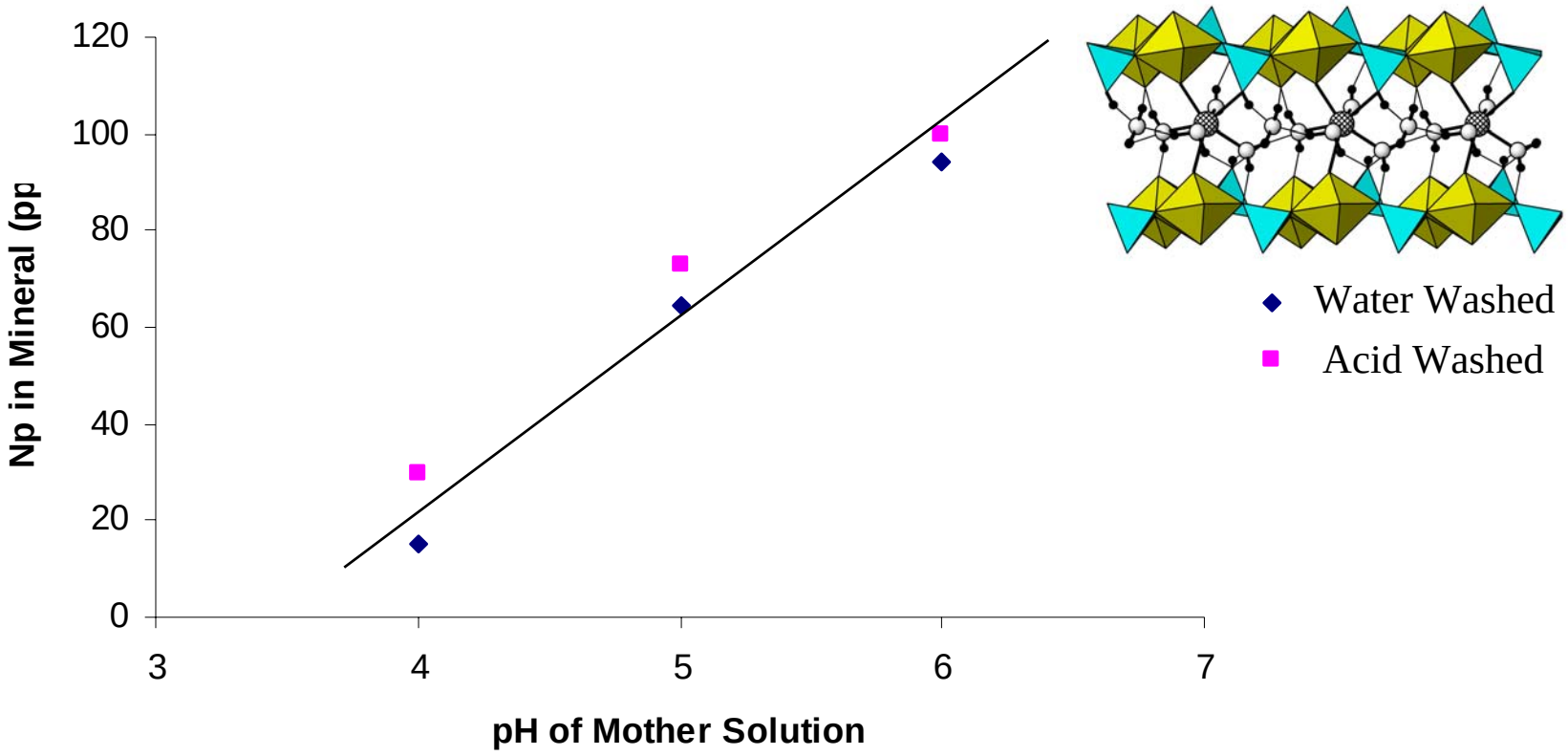
Uranophane: pH = 6, t = 24h, 160-180 ppm Np^{5+} in mother solution



Unpublished

Np^{5+} Incorporation in Uranophane: Temperature Variation

Uranophane: T = 120C, t = 24h, 160-180 ppm Np^{5+} in solution



Unpublished

Summary

- **Uranyl minerals are likely to form as products of alteration of SNF in Yucca Mountain**
- **Uranyl minerals are likely to impact the future mobility of key radionuclides in Yucca Mountain**
  - **Np^{5+} has been incorporated into powders of synthetic uranophane, Na-compreignacite and soddyite**
  - **There is a significant temperature and pH dependence of incorporation of Np^{5+} in powders of synthetic uranophane and soddyite**
    - **Soddyite: increases with temperature**
    - **Uranophane: decreases with temperature**
    - **Uranophane: increases with pH**