Thermodynamic approach to evaluating complexants for environmental performance assessment and decontamination

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Objectives

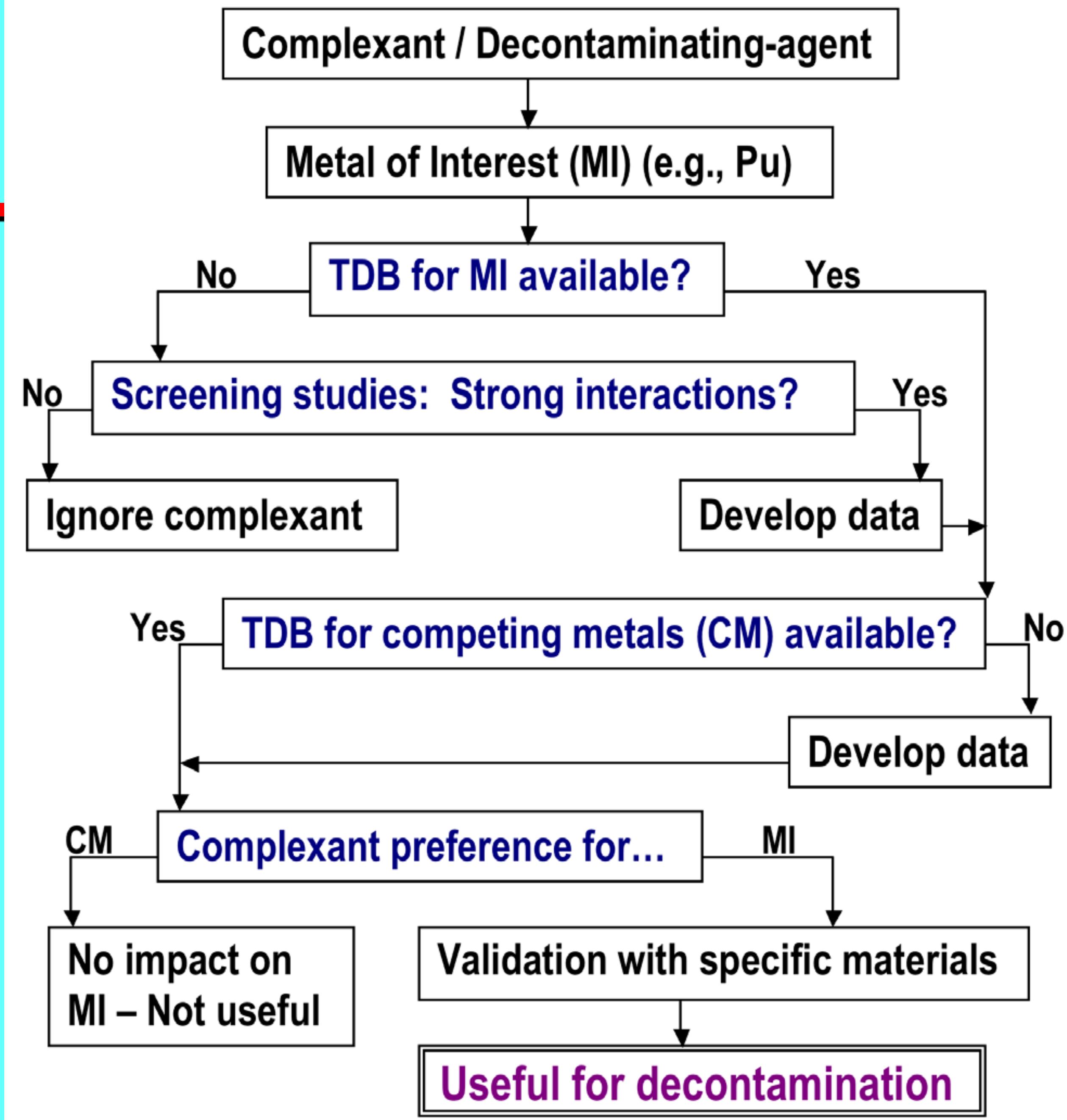
Discuss methodology to:

- Evaluate different complexants for their usefulness in decontamination
- Determine the influence of a given complexant on solubilization

Discussion Format

- General approach
- Using EDTA as an example discuss:
  - EDTA data needs for simple systems (e.g., Pu(IV), Fe(III), Ca)
  - Data validation in complex systems
  - Application of data to decontamination and PA
- Using ISA as an example discuss:
  - ISA data needs for simple systems (e.g., Th, Fe(III), Np(IV), Ca)
  - Application of data to decontamination and PA
- Brief summary

Fundamental approach for selecting decontaminating agents



Important aspects of general approach

- Develop thermodynamic data in simple systems consistent with all of the available reliable data
- Validate data in complex systems (e.g., brines, in the presence of MI and CM)
- Evaluate whether a given ligand will increase solubility or be useful for decontamination, which will depend on relative:
  - Values of complexation constants
  - Metal ion activities

Example: Pu(IV)-EDTA

Using fundamental data determine whether EDTA can:

- Make Pu(IV) mobile in geologic environments
- Be used for Pu(IV) decontamination activities

Factors governing EDTA-mediated Pu mobility or decontaminating ability

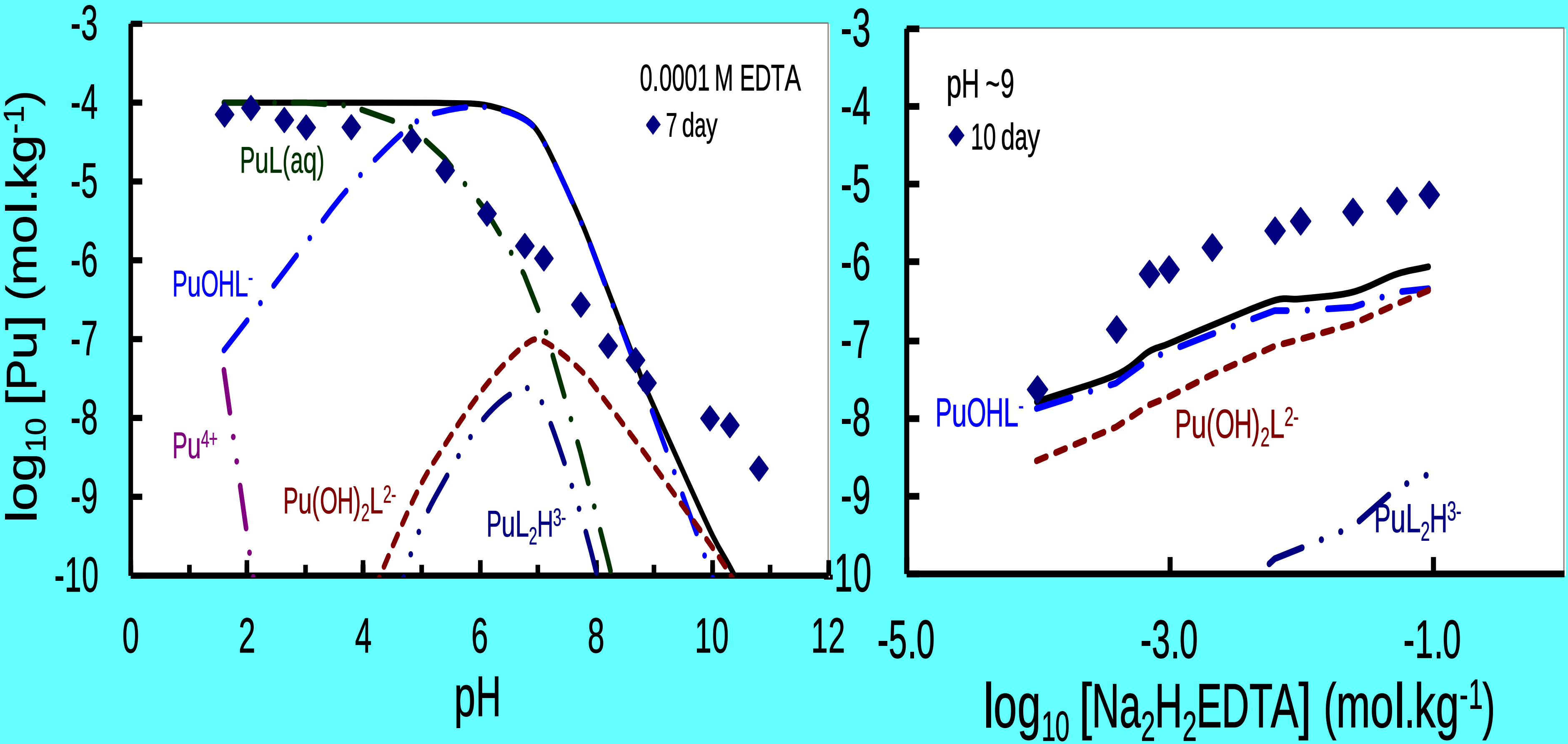
- Oxidation state of Pu
- pH
- EDTA concentration in solution, which depends on
  - Total amount disposed or used
  - Microbial degradation
  - Adsorption
- Competing metal ions (e.g., Ca^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+})
  - Complexation constants
  - Activities of bare ions

Thermodynamic data for EDTA complexes

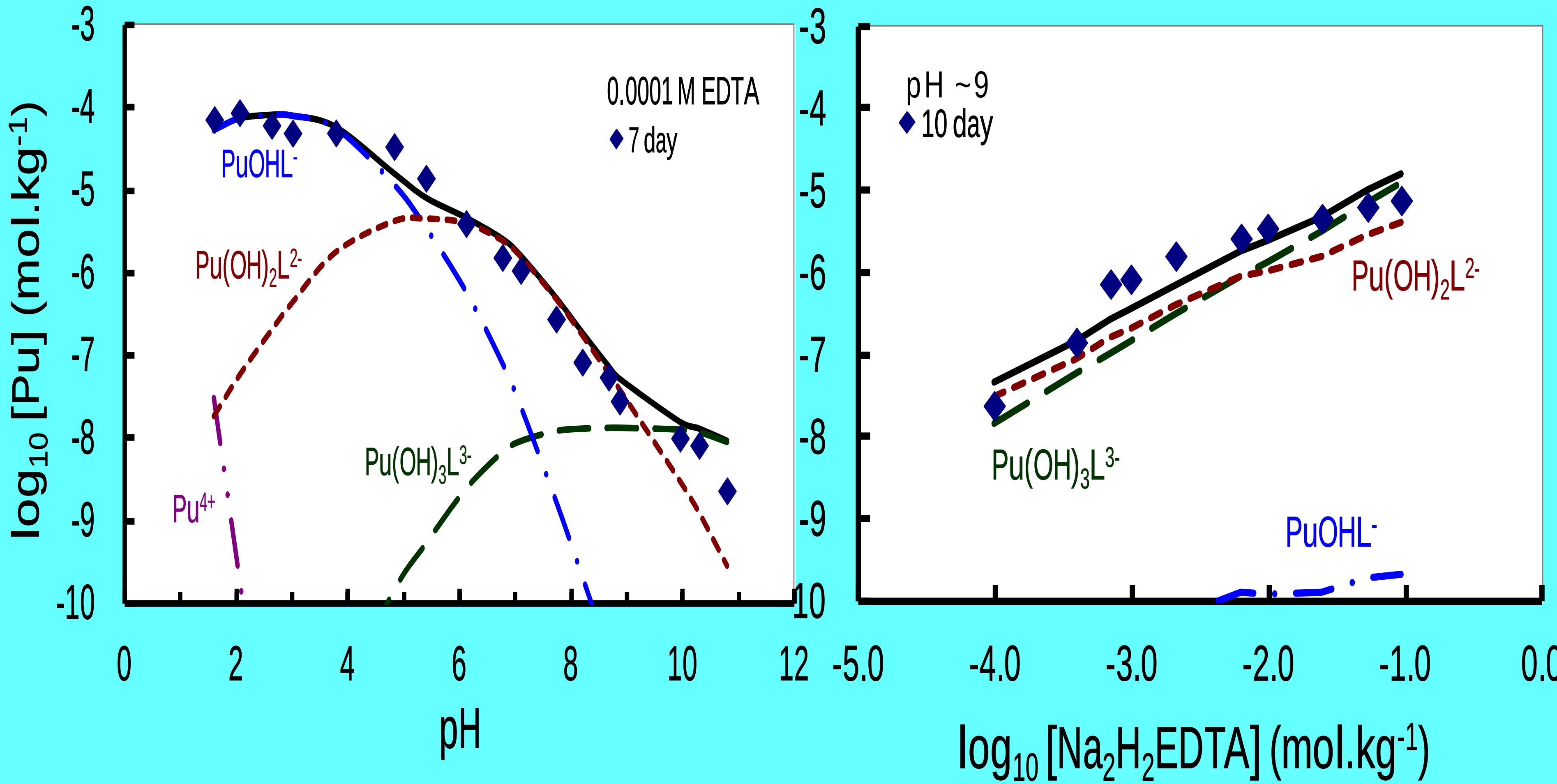
Prior to our study [Rai et al. 2008], reliable data were not available for:

- Pu(IV)-EDTA
  - Large number of species proposed [$Pu(OH)EDTA^{-}$, $Pu(OH)_2EDTA^{2-}$, $Pu(OH)_3EDTA^{3-}$, PuEDTA(aq), $PuHEDTA^{+}$, $Pu(EDTA)_2^{4-}$, $PuH(EDTA)_2^{3-}$, $PuH_3(EDTA)_2^{-}$]
  - Poor quality data with large variability
- Fe(III)) with OH and EDTA
  - Large number of hydroxide species proposed [$FeOH^{2+}$, $Fe(OH)_2^{+}$, $Fe(OH)_4^{-}$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$]
  - Large number of EDTA species proposed [FeEDTA-, Fe(OH)EDTA2-, $Fe_2(OH)_2(EDTA)_2^{4-}$, FeHEDTA(aq)
  - Poor quality data with large variability

Comparison of experimental PuO_2(am) solubility (Rai et al. 2001) to the literature model (Rai et al. 2008)



Thermodynamic interpretations of PuO_2(am) solubility data (Rai et al. 2008)



Important Pu(IV)-EDTA species

Literature	Rai et al. 2008
$Pu(OH)EDTA^{-}$	$Pu(OH)EDTA^{-}$
$Pu(OH)_2EDTA^{2-}$	$Pu(OH)_2EDTA^{2-}$
$Pu(OH)_3EDTA^{3-}$	$Pu(OH)_3EDTA^{3-}$
PuEDTA(aq)	NR
$PuHEDTA^{+}$	NR
$Pu(EDTA)_2^{4-}$	NR
$PuH(EDTA)_2^{3-}$	HR
$PuH_3(EDTA)_2^{-}$	NR
NR = Not required	

Thermodynamic data for EDTA complexes

Prior to our study [Rai et al. 2008], reliable data were not available for:

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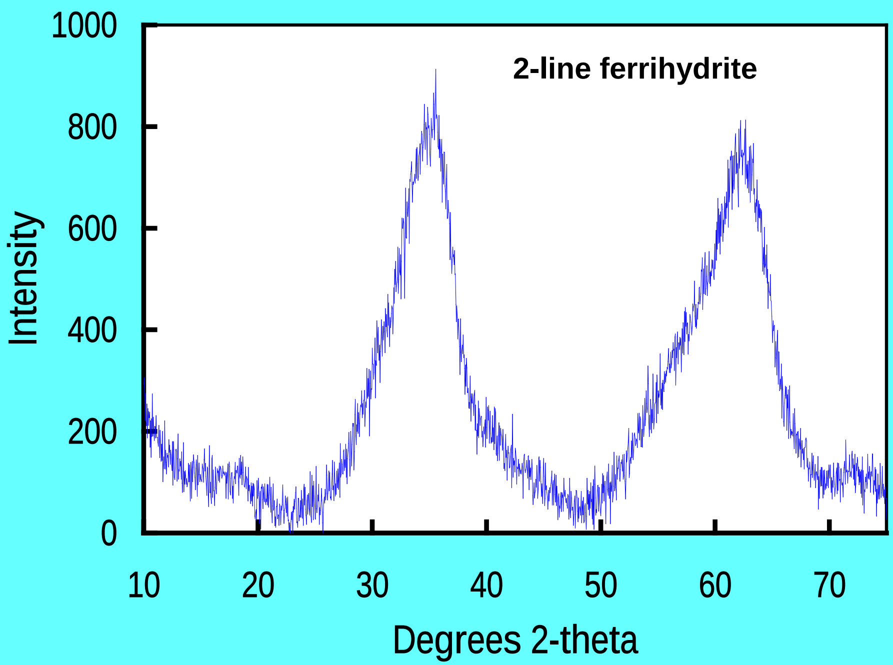
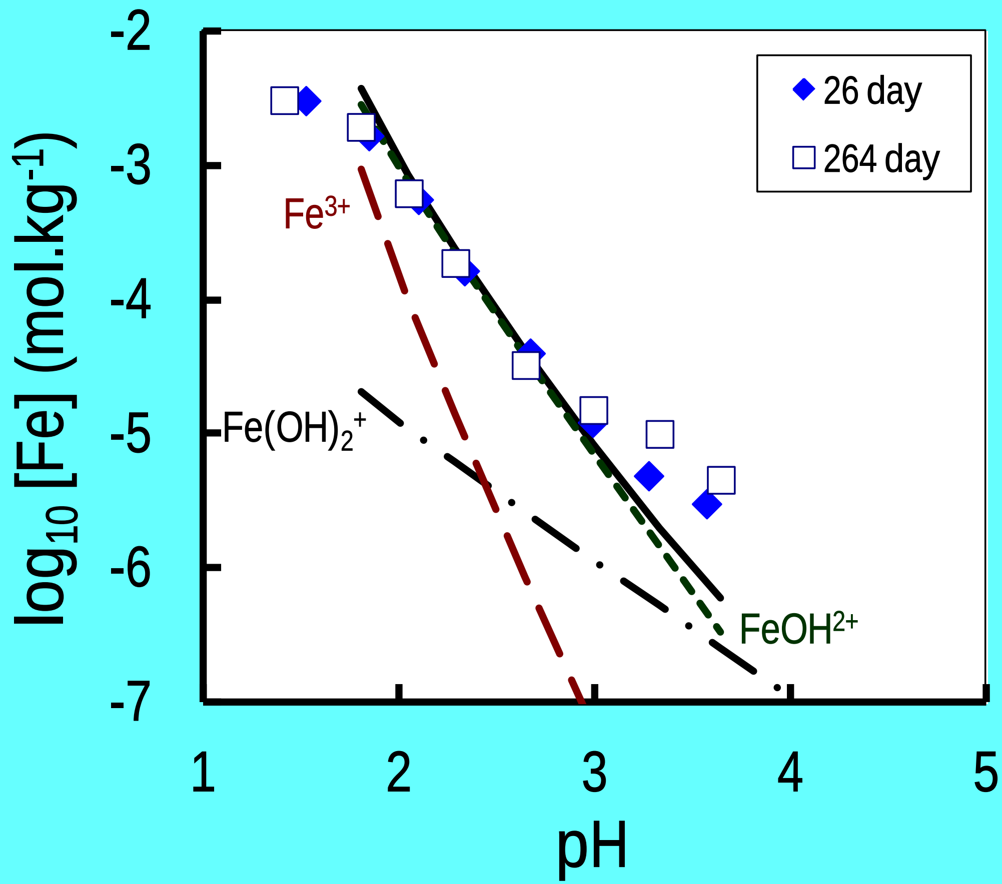
  - Large number of species proposed [$Pu(OH)EDTA^-$, $Pu(OH)_2EDTA^{2-}$, $Pu(OH)_3EDTA^{3-}$, PuEDTA(aq), $PuHEDTA^+$, $Pu(EDTA)_2^{4-}$, $PuH(EDTA)_2^{3-}$, $PuH_3(EDTA)_2^-$]
  - Poor quality data with large variability
- Fe(III)) with OH and EDTA
  - Large number of hydroxide species proposed [$FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_4^-$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$]
  - Large number of EDTA species proposed [FeEDTA-, Fe(OH)EDTA2-, $Fe_2(OH)_2(EDTA)_2^{4-}$, FeHEDTA(aq)
  - Poor quality data with large variability

$Fe(OH)_3$(s) solubility as a function of pH (Rai et al. 2008)

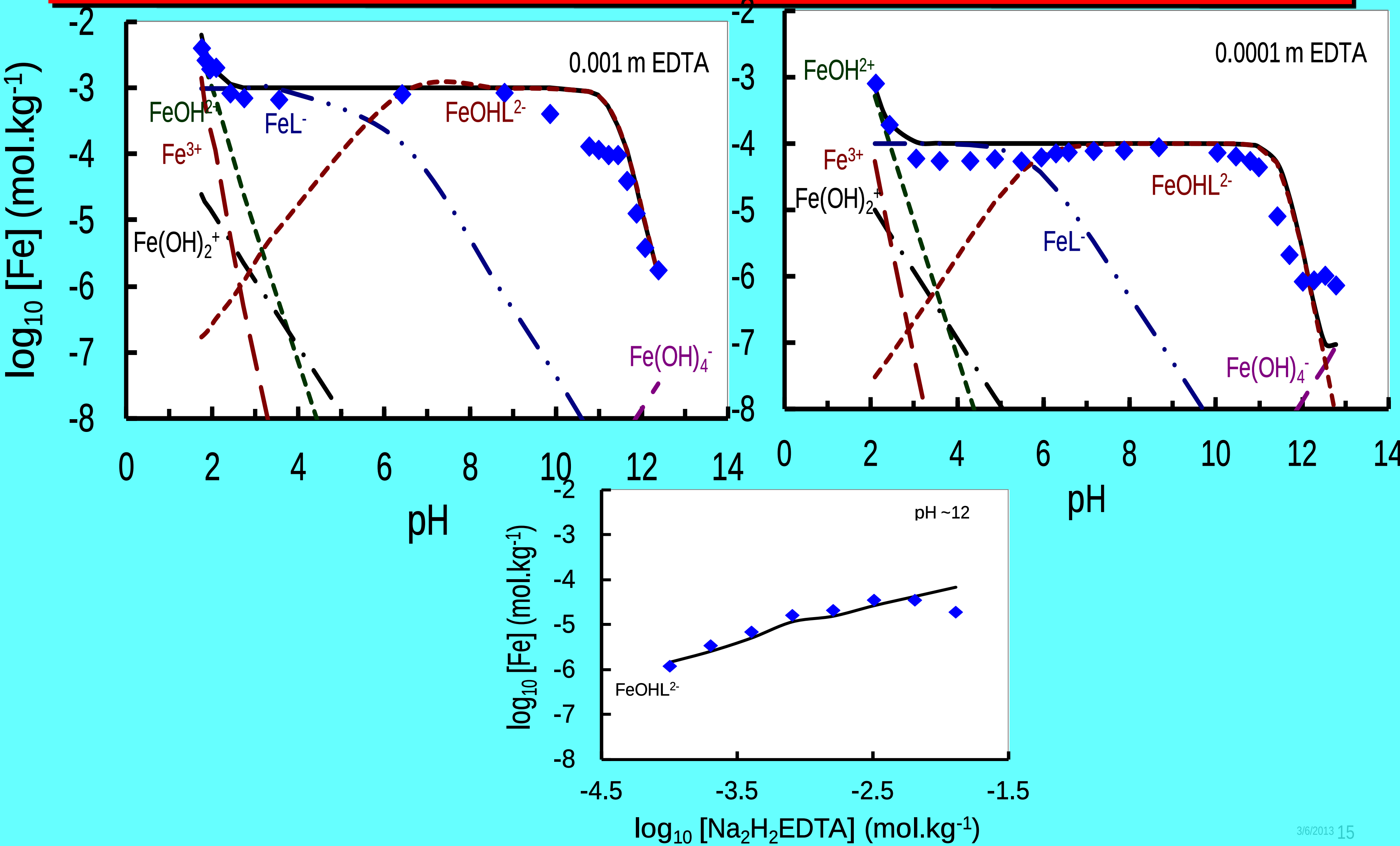




Important Fe-EDTA species

Literature	Rai et al. 2008
$Fe(OH)^{2+}$	$Fe(OH)^{2+}$
$Fe(OH)_2^{2+}$	$Fe(OH)_2^{2+}$
$Fe(OH)_4^{-}$	$Fe(OH)_4^{-}$
$Fe_2(OH)_2^{4+}$	NR
$Fe_3(OH)_4^{5+}$	NR
NR = Not required	

$Fe(OH)_3$(am) solubility as a function of pH and EDTA (Rai et al. 2008)



Important Fe-EDTA species

Literature	Rai et al. 2008
$Fe(EDTA)^-$	$Fe(EDTA)^-$
$FeOH(EDTA)^{2-}$	$FeOH(EDTA)^{2-}$
$Fe_2(OH)_2(EDTA)_2^{4-}$	NR
FeH(EDTA)(aq)	NR
NR = Not required	

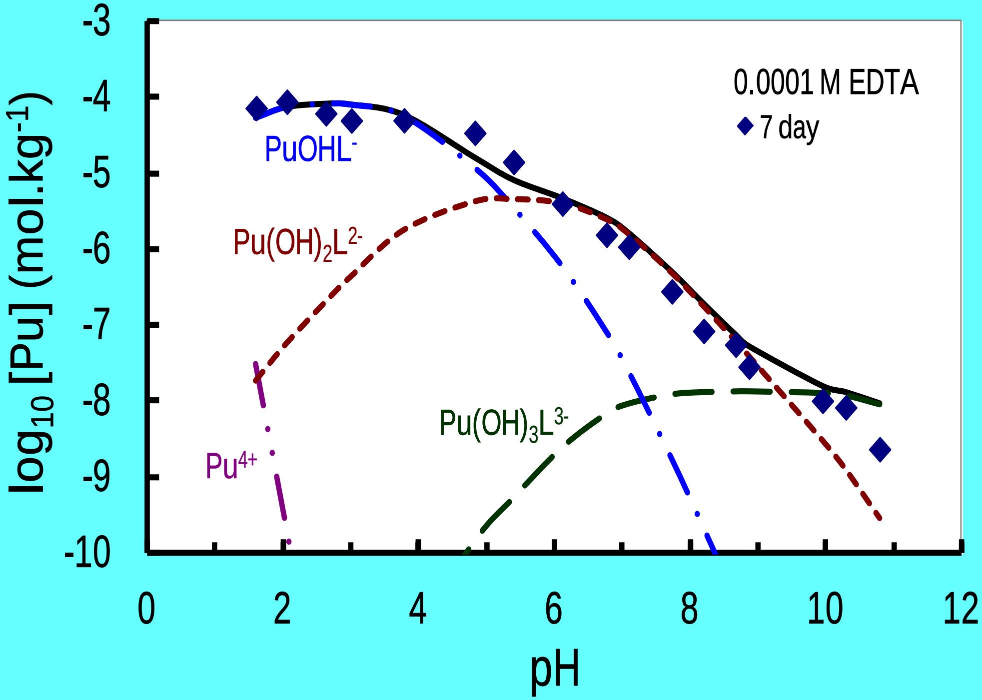
Recommended values for EDTA complexes
(Rai et al. 2008)

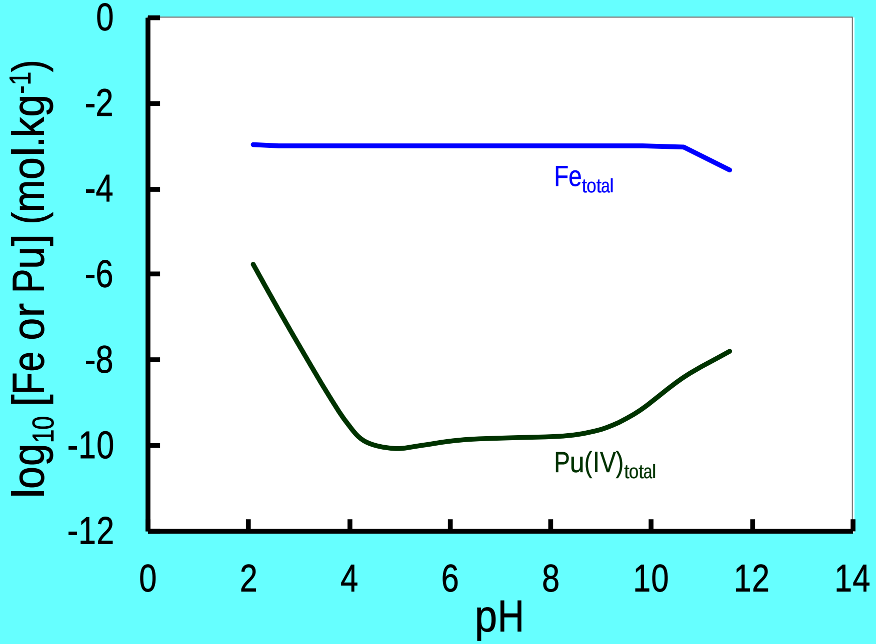
Reaction	$\log_{10} K^o$
$Fe(OH)_3(s) = Fe^{3+} + 3OH^-$	-40.35 ± 0.5
$Fe^{3+} + OH^- = FeOH^{2+}$	11.81 ± 0.5
$Fe^{3+} + EDTA^{4-} = Fe(EDTA)^-$	27.66 ± 0.209
$Fe^{3+} + EDTA^{4-} + H_2O = FeOH(EDTA)^{2-} + H^+$	21.935± 0.226
$Pu^{4+} + EDTA^{4-} + OH^- = Pu(OH)EDTA$	38.422 ± 0.258
$Pu^{4+} + EDTA^{4-} + 2OH^- = Pu(OH)_2EDTA^{2-}$	47.093 ± 0.258
$Pu^{4+} + EDTA^{4-} + 3OH^- = Pu(OH)_3EDTA^{3-}$	51.769 ± 0.258
$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-}$	12.36[a]
[a] Value from Felmy and Mason (2003)	

Impact of Fe(III) and Ca on Pu(IV) behavior in the presence of EDTA

- Iron and Ca are very common in geologic environments
- Thermodynamic data for Pu(IV), Fe(III), and Ca are now available
- Use thermodynamic data to predict potential Pu(IV):
  - Mobility in the presence of EDTA and Fe(III) and Ca
  - Decontamination with EDTA in the presence of Fe(III) and Ca

PuO_2 solubility in the presence of $Fe(OH)_3(s)$ and 0.001 M EDTA (Rai et al. 2008)



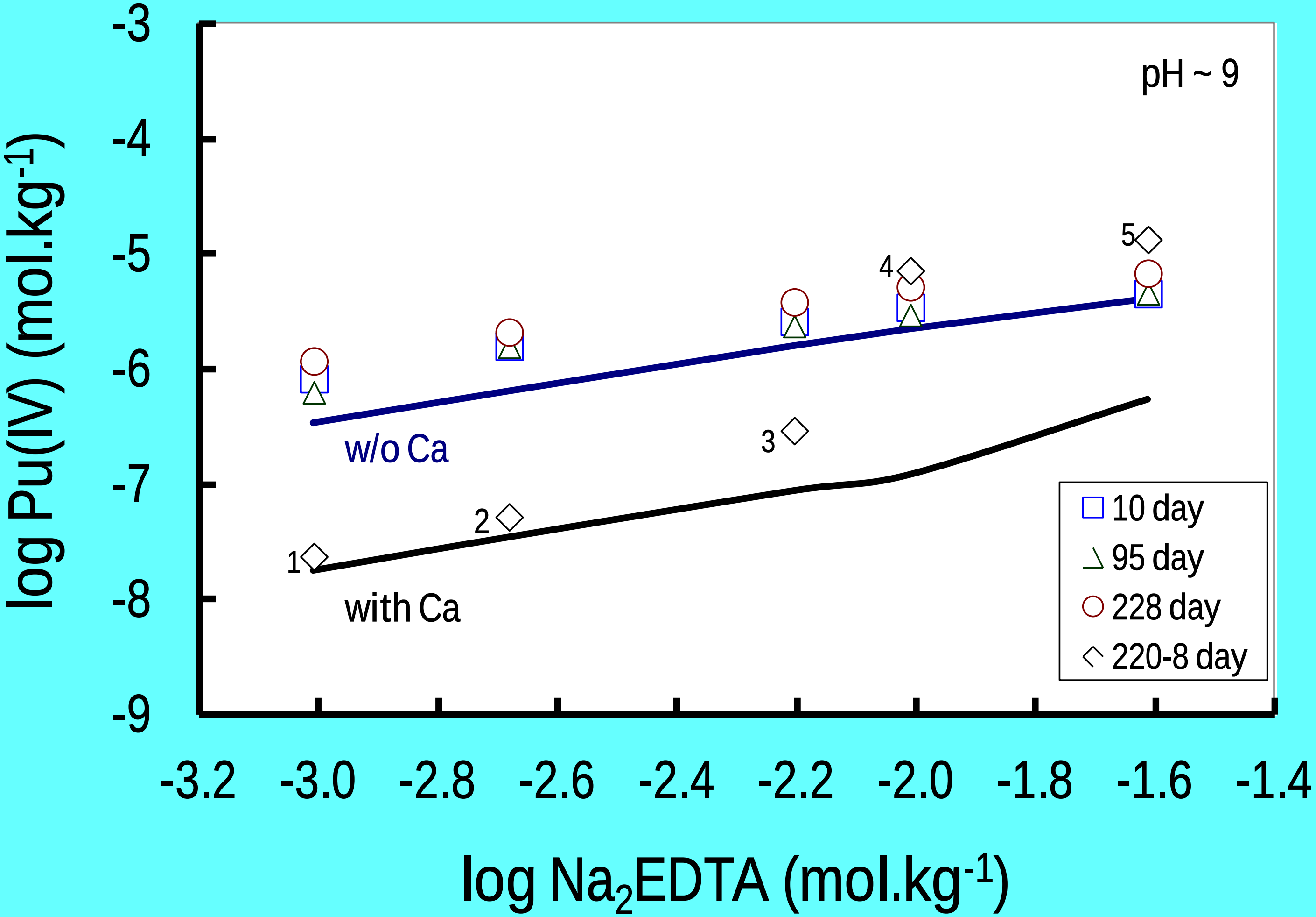


Why does Fe(III) out competes Pu(IV) for EDTA binding?

It is because of both

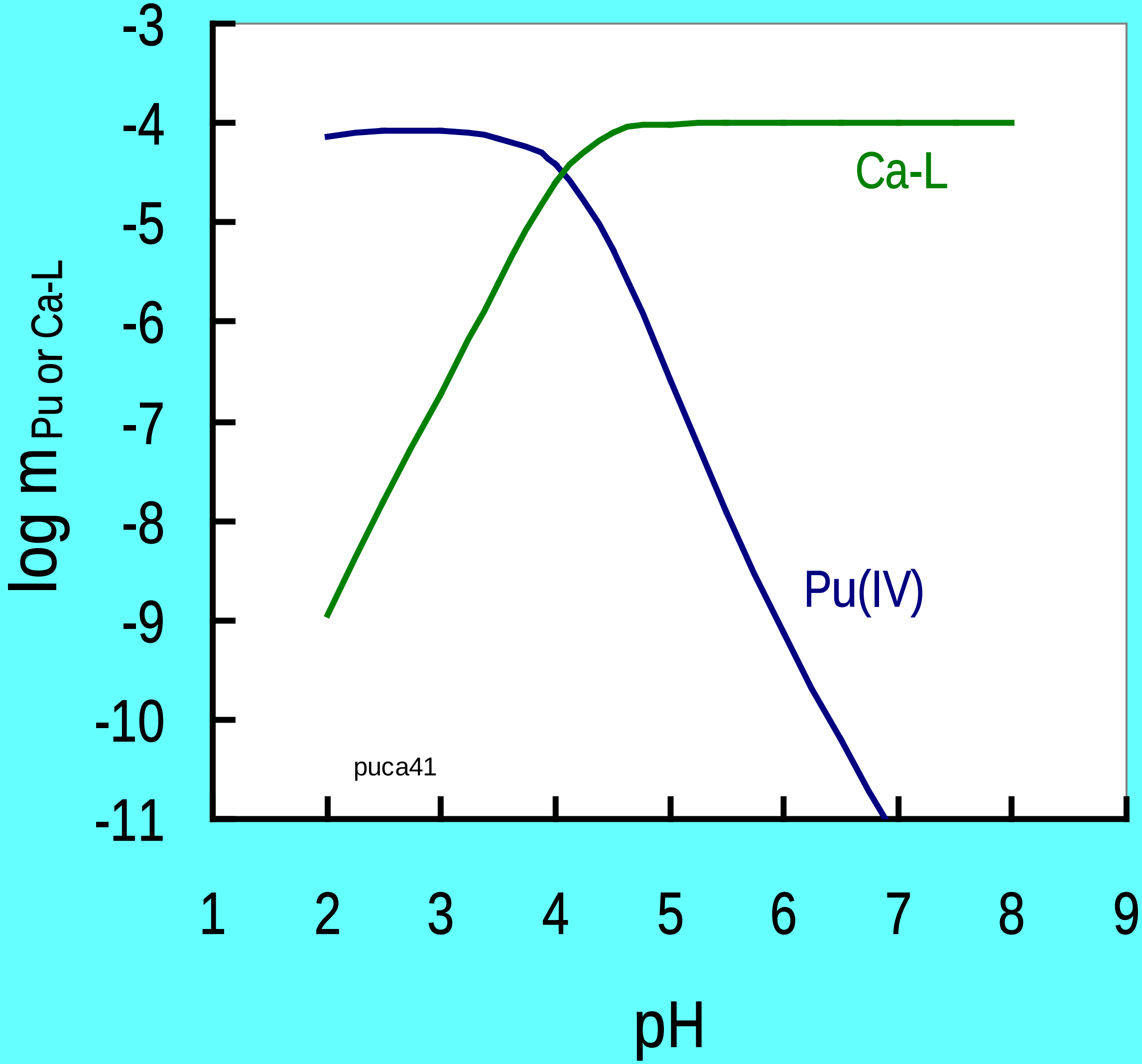
- Relativley stronger complexation constant
  - log $K_{FeEDTA^-} = 27.66$
  - log $K_{PuEDTA^0} \sim 26$
- Higher bare ion activity
  - log $K_{Fe^{3+}} = 1.65 - 3pH$
  - log $K_{Pu^{4+}} = -2.3 - 4pH$

Experimental evaluation of the effect of Ca on PuO_2(am) solubility as a function of EDTA



1: log Ca = -3.0
2: log Ca = -2.7

PuO_2(am) solubility in the presence of 0.001 M Ca and 0.0001 M EDTA



Why does Ca out competes Pu(IV) for EDTA binding?

- It is due to higher bare ion activity
  - $\log K_{Ca}^{2+} \approx -3$
  - $\log K_{Pu}^{4+} = -2.3 - 4pH$

Because of relatively higher bare ion activity Ca out competes Pu^{4+} for binding with EDTA even though the complexation constant for $PuEDTA^{0}$ is over 13 orders of magnitude stronger than the $CaEDTA^{2-}$

Conclusions for Pu(IV)-EDTA

EDTA is not expected to make Pu(IV) mobile and it is not desirable decontaminating agent for Pu(IV) in complex geologic systems which is contrary to previously long-held opinions.

Past opinions based on:

- Pu(IV) co-disposed with EDTA
- Pu(IV)-EDTA complexes implicated for Pu mobility in field studies [81CLE/REE; 82REE/CLE]
- EDTA complexes of Pu(V, VI) convert to Pu(IV) [57FOR/SMI; 73Cau/Gui; 96ALM/ ;98 REE/WYG]
- Pu(III) spontaneously converts to Pu(IV) [94RUS/QUI]
- EDTA forms strong complexes with Pu(IV) [57FOR/SMI; 73Cau/Gui]

Discussion Format

- General approach
- Using EDTA as an example discuss:
  - EDTA TDB needs for simple systems (e.g., Pu(IV), Fe(III), Ca)
  - TDB validation in complex systems
  - Application of TDB to decontamination and PA
- Using ISA as an example discuss:
  - ISA TDB needs for simple systems (e.g., Th, Fe(III), Np(IV), Ca)
  - Application of TDB to decontamination and PA
- Brief summary

Literature Th-ISA model [2006ALL/EKB] based on solvent extraction data

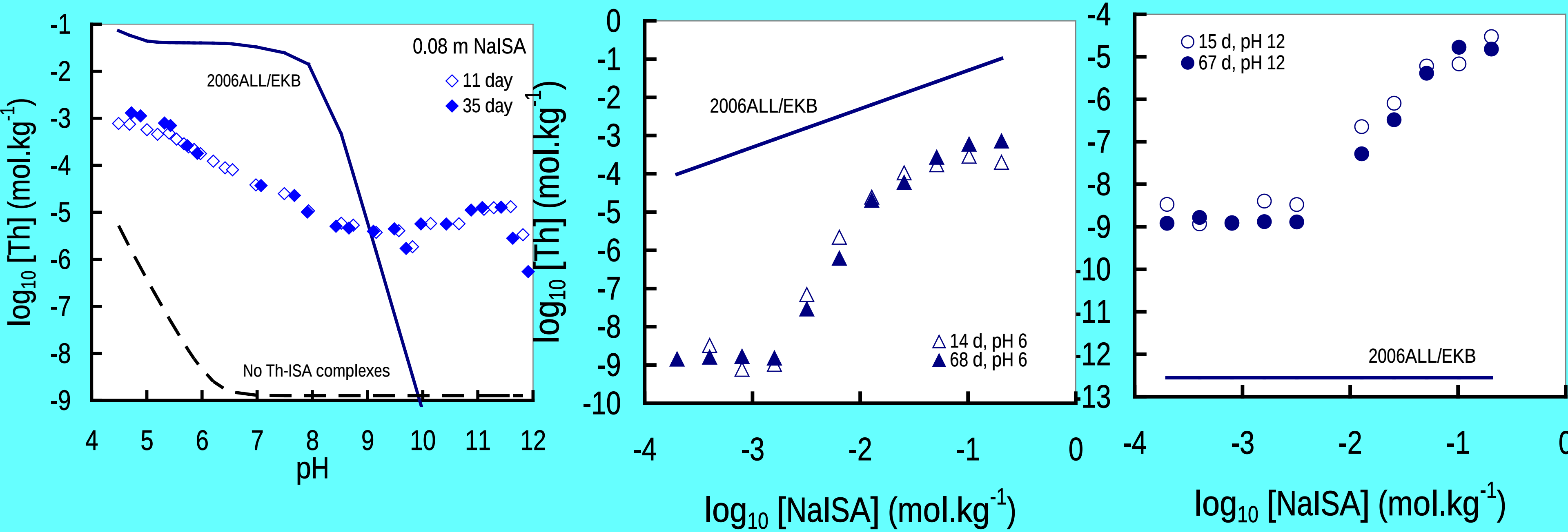
Modeling species

- $ThISA^{3+}$
- $Th(ISA)_2^{2+}$
- $Th\ (ISA)_3^{+}$

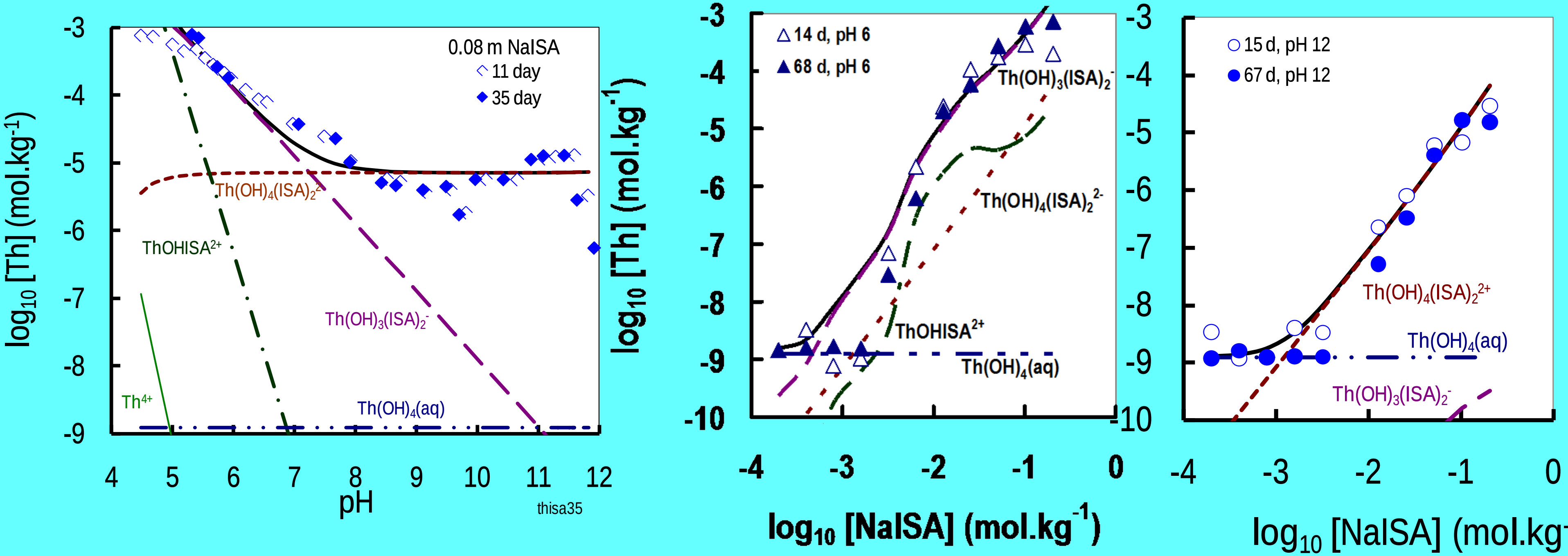
Limitations of the 2006ALL/EKB study

- Conducted at only one ionic strength (1.0 M)
  - SIT ion-interaction parameters cannot be determined to convert equilibrium constants to zero ionic strength
- Conducted at only one pH (8.3)
  - Structure and type of species may be different at pH values other than 8.3
  - Impossible to differentiate between species they report that have the same ISA dependence but differ in H or OH (e.g., between $Th(ISA)_2^{2+}$, and $Th(OH)_3(ISA)_2^{-}$ or $Th(OH)_4(ISA)_2^{2-}$)
- Extremely unreliable value (log $\boldsymbol{\beta}_1 = 12.56 \pm 5.01$) for the formation of $Th(ISA)^{3+}$

ThO_2(am) solubility in 0.08 m NaISA [2009RAI/YUI]: Predictions using 2006ALL/EKB model



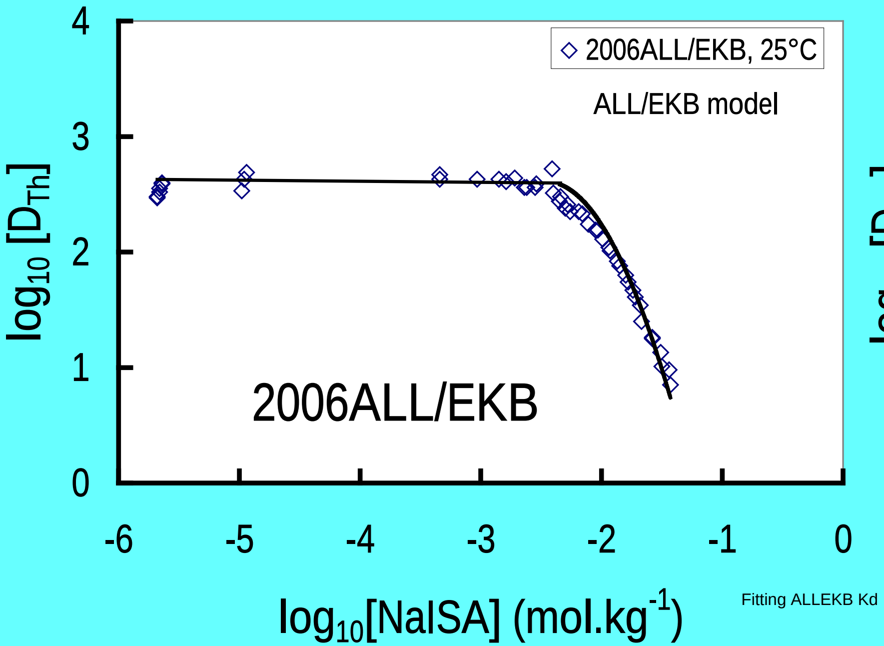
ThO_2(am) solubility [2009RAI/YUI]

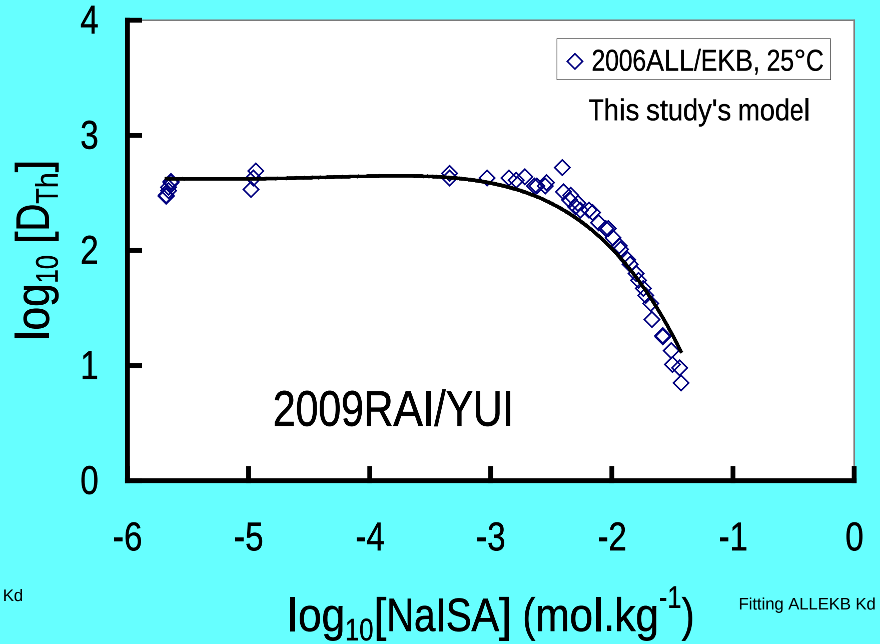


Important Th-ISA species

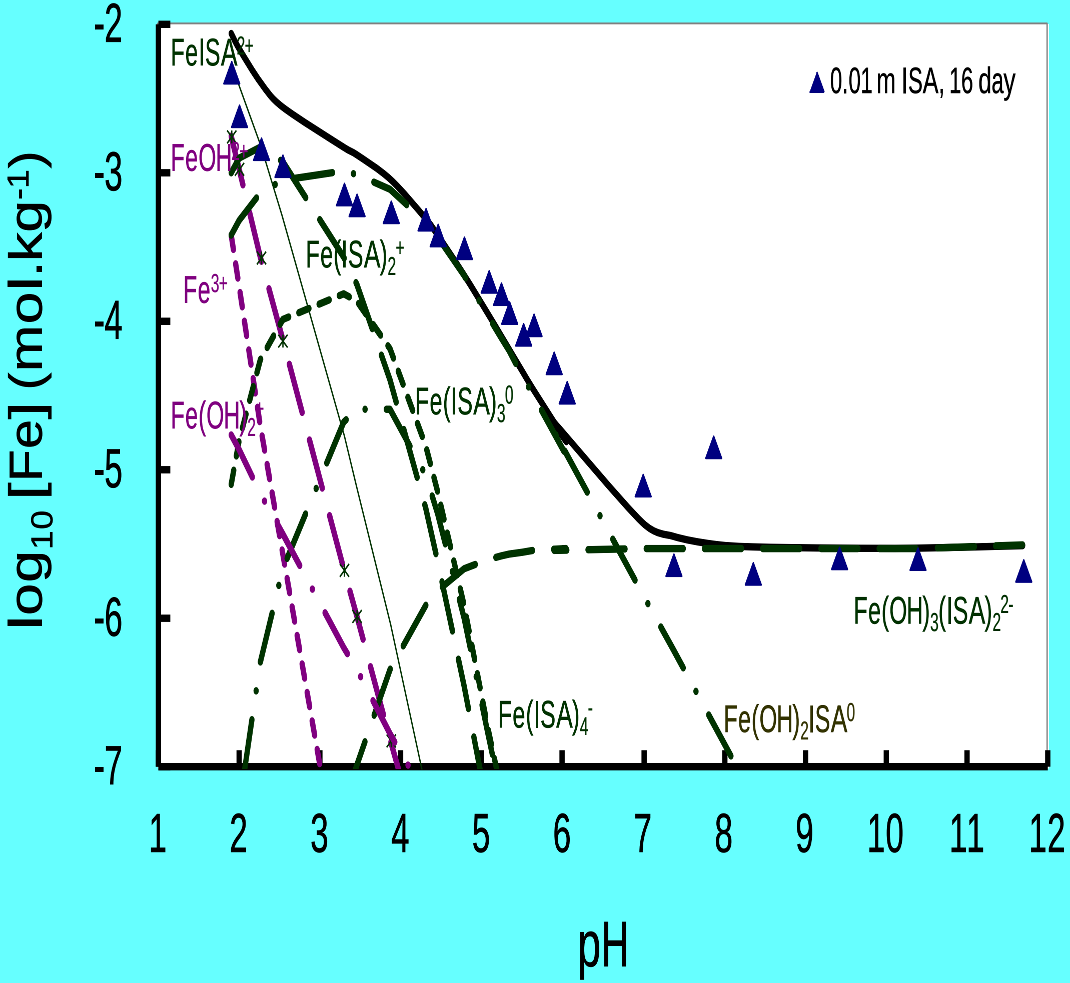
2006ALL/EKB	2009RAI/YUI
$ThISA^{3+}$	NR
$Th(ISA)_2^{2+}$	NR
$Th(ISA)_3^{+}$	NR
	$Th(OH)ISA^{2+}$
	$Th(OH)_3(ISA)_2^{-}$
	$Th(OH)_4(ISA)_2^{2-}$
NR = Not required	

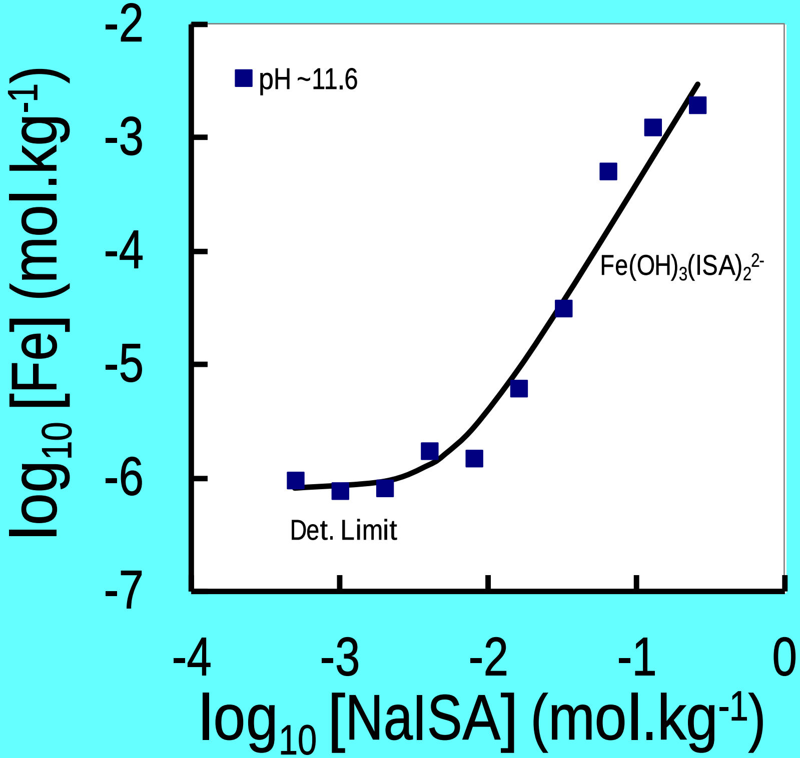
Observed and predicted Th distribution coefficients: 1.05 m $NaClO_4$, pH 8.3, 25ºC





$Fe(OH)_3$(s) solubility in NaISA [2012RAI/YUI]





Fe(III)-ISA species based on our studies [2004RAO/GAR and 2012RAI/YUI]

Important in wide range of pH values

- $Fe(OH)_2ISA(aq)$
- $Fe(OH)_3(ISA)_2^{2-}$

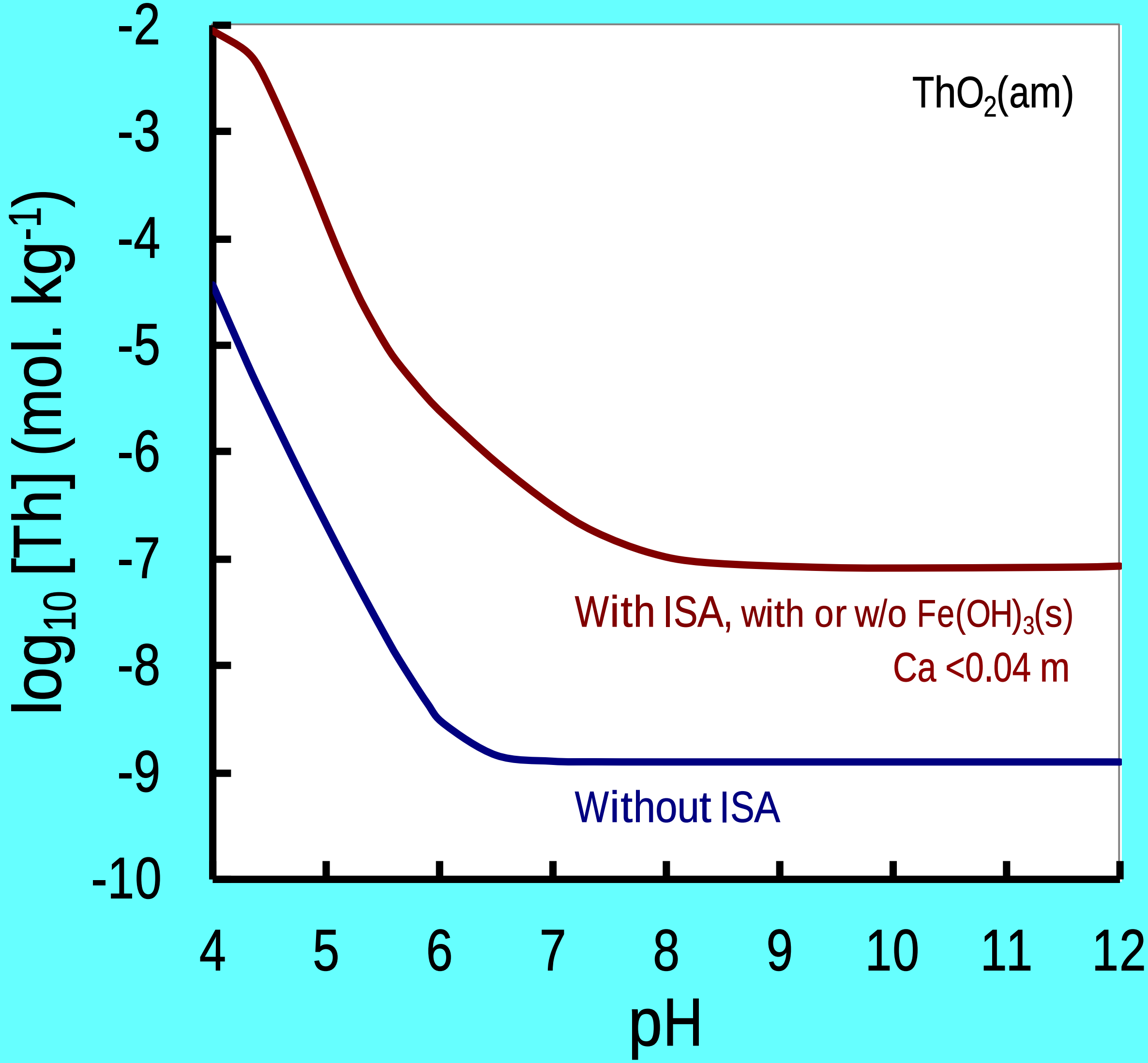
Important only in acidic conditions

- $FeISA^{2+}$
- $Fe(ISA)_2^{+}$
- $Fe(ISA)_3^{0}$
- $Fe(ISA)_4^{-}$

Thermodynamic data for the Th-Fe-OH-ISA system

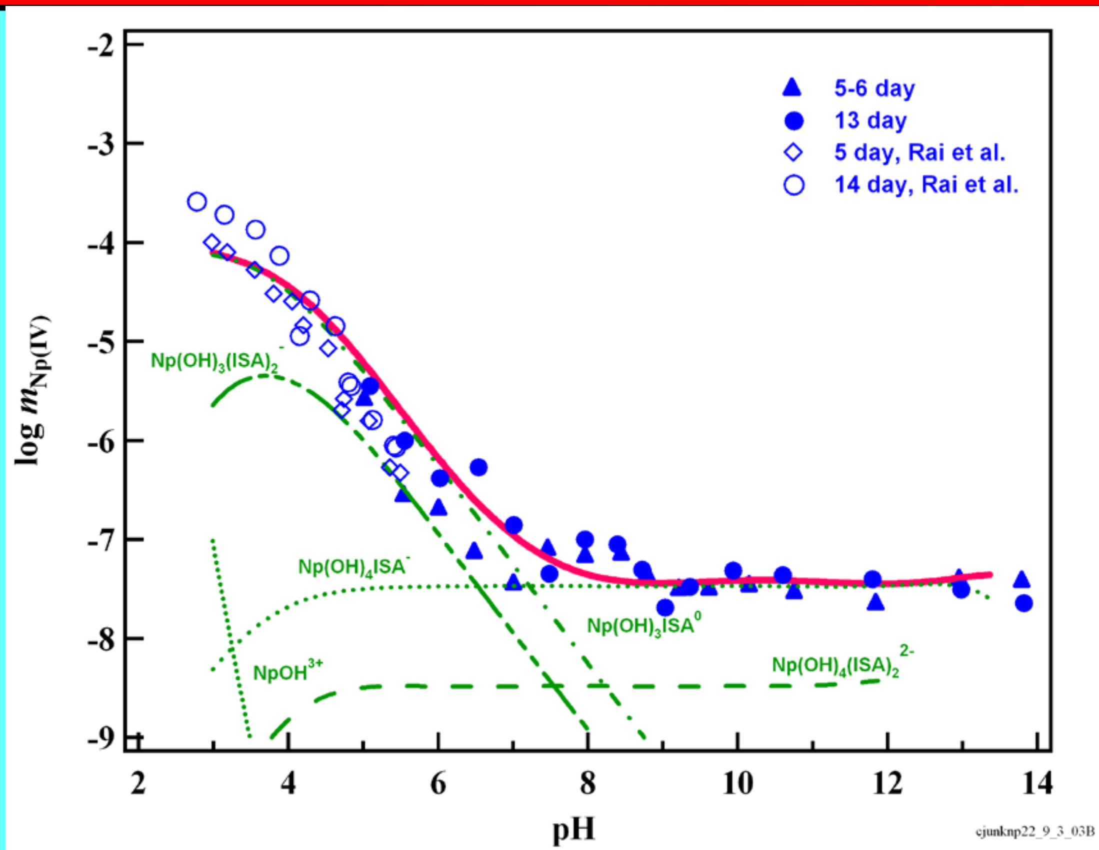
Reaction	**$\log_{10} K^0$**	**Reference**
$Fe(OH)_3$**(s)** $\leftrightarrow$ **Fe^{3+}** + $3OH^-$	-40.35 ± 0.5	2008RAI/MOO
Fe^{3+} **+** $\leftrightarrow$ **$FeOH^{2+}$**	11.81 ± 0.5	2008RAI/MOO
Fe^{3+} + $2OH^-$ $\leftrightarrow$ **$Fe(OH)_2^+$**	23.4 ± 1.0	2001SMI/MAR
ISA^- + H^+ $\leftrightarrow$ **HISA(aq)**	4.0 ± 0.5	2005HUM/AND
Fe^{3+} + ISA^- + $2H_2O$ $\leftrightarrow$ **$Fe(OH)_2$**ISA(aq) + $2H^+$	1.55 ± 0.38	2012RAI/YUI
Fe^{3+} + $2ISA^-$ + $3H_2O$ $\leftrightarrow$ **$Fe(OH)_3$**$(ISA)_2^{2-}$ + $3H^+$	-3.27 ± 0.32	2012RAI/YUI
Fe^{3+} + ISA^- = $FeISA^{2+}$	6.20	2004RAO/GAR
Fe^{3+} + $2ISA^-$ = $Fe(ISA)_2^+$	10.41	2004RAO/GAR
Fe^{3+} + $3ISA^-$ = $Fe(ISA)_3^0$	13.10	2004RAO/GAR
Fe^{3+} + $4ISA^-$ = $Fe(ISA)_4^-$	15.09	2004RAO/GAR
ThO_2(am) + $3H^+$ + ISA^- = $ThOH(ISA)^-$ + H_2O	12.5 ± 0.47	2009RAI/YUI
ThO_2(am) + H^+ + $2ISA^-$ + H_2O = $Th(OH)_3(ISA)_2^-$	4.41 ± 0.47	2009RAI/YUI

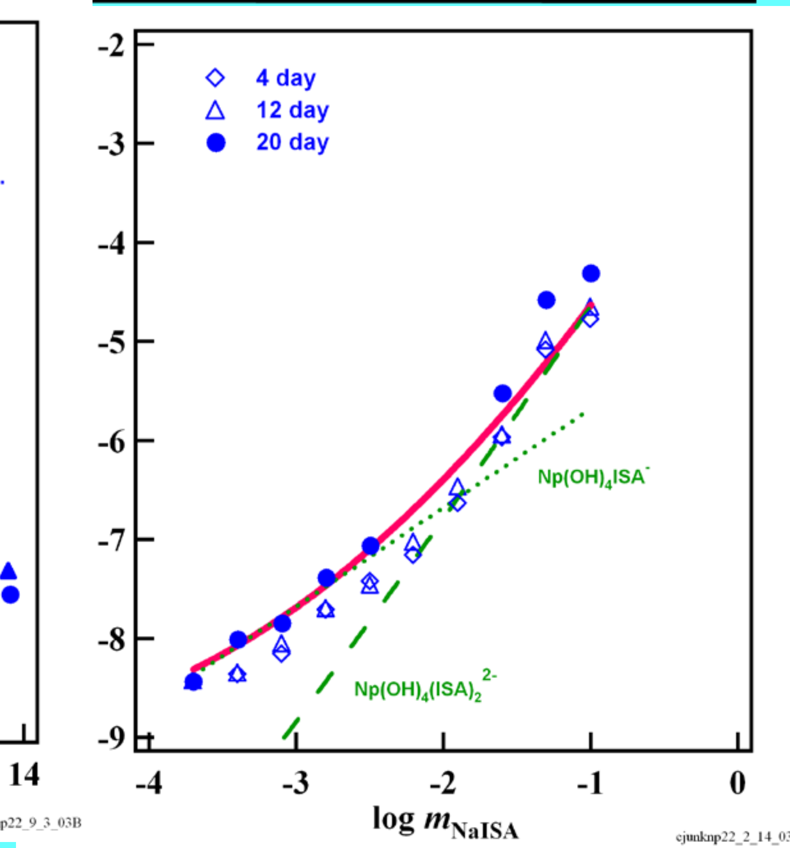
ThO_2(am) solubility in 0.01 m NaCl and the presence and the absence of 0.01 m ISA [2009RAI/YUI]



Because of relatively stronger Th complexes, Fe(III) and Ca have no impact

NpO_2 solubility in 0.0016 M ISA as a function of pH and at pH 12 and function of ISA [2003RAI/HES]





No changes in Np(IV) concentrations in the presence of $Fe(OH)_3$(s) and normal Ca levels

Summary

- Outlined general methodology for evaluating complexants for their effect on solubility or use in decontamination
- Using EDTA and ISA as examples I showed:
  - The need for development of reliable data consistent with all of the available data in simple and complex systems
  - The role of both the complexation constants and bare ion activities in PA calculations and selecting decontaminating agents
- The effect of competing metal ions must be considered, which is generally ignored in these kinds of evaluations

Major references used in presentation

- Rai, Dhanpat, M. Yui, D. A. Moore. 2012. Isosaccharinate Complexes of Fe(III). *Journal of Solution Chemistry* 41: 1906-1921
- Rai, Dhanpat, Mikazu Yui, D. A. Moore, L. Rao 2009. Thermodynamic Model for ThO_2(am) Solubility in Isosaccharinate Solutions. *Journal of Solution Chemistry* 38: 1573 - 1587
- Rai, Dhanpat, D. A. Moore, K. M. Rosso, A. R. Felmy, H. Bolton, Jr.. 2008. Environmental Mobility of Pu(IV) in the Presence of Ethtylenediaminetetraacetic acid: Myth or Reality. *Journal of Solution Chemistry* 37: 957 – 986.
- Rao, L., A. Yu. Garnov, Dhanpat Rai, Y. Xia, R. C. Moore. 2004. Protonation and Complexation of Isosaccharinic Acid With U(VI) and Fe(III) in Acidic Solution: Potentiometric and Calorimetric Studies. *Radiochimica Acta* 92: 575-581
- Rai, Dhanpat, N. J. Hess, Y. Xia, L. Rao, H. M. Cho, R. C. Moore, Luc R. Van Loon 2003. Comprehensive Thermodynamic Model Applicable to Highly Acidic to Basic Conditions for Isosaccharinate Reactions with Ca(II) and Np(IV). *Journal of Solution Chemistry* 32: 665-689.
- Cho, H. M., Dhanpat Rai, N. J. Hess, Y. Xia, and L. Rao. 2003. Acidity and Structure of Isosaccharinate in Aqueous Solution: A Nuclear Magnetic Resonance Study. *Journal of Solution Chemistry* 32: 691-702.
- Rai, Dhanpat, H. Bolton, D. A. Moore, N. J. Hess, G. R. Choppin. 2001. Thermodynamic Model for the Solubility of PuO_2(am) in the Aqueous Na^+-H^+-OH^--Cl^--H_2O-Ethylenediaminetetraacetate System *Radiochimica Acta* 89: 67-74

Pitzer ion-interaction parameters (Rai et al. 2008)

Species	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Na^+ -$Pu(OH)EDTA^-$	-0.2345	0.29	0.059
Na^+-$Pu(OH)_2EDTA^{2-}$	-0.1262	1.74	0.054
Na^+-$Pu(OH)_3EDTA^{3-}$	0.59	5.39	0.00
Na^+-$FeEDTA^-$	-0.2345	0.29	0.059
Na^+-$Fe(OH)EDTA^{2-}$	-0.1262	1.74	0.054

SIT Ion-interaction parameters determined by [2012RAI/YUI]

Species	ε(kg·mol^{-1})
Na^+, $Fe(OH)_3(ISA)_2^{2-}$	-0.125
Na^+, $Th(OH)_3(ISA)_2^-$	-0.07
Na^+, $Th(OH)_4(ISA)_2^{2-}$	-0.125
$FeISA^{2+}$, ClO_4^-	0.4
$Fe(ISA)_2^+$, ClO_4^-	0.27
$Fe(ISA)_3^0$, ClO_4^-	0.00
$Fe(ISA)_4^-$, ClO_4^-	-0.07

Thermodynamic interpretations of PuO_2(am) solubility data (Rai et al. 2008)