Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes

Dhanpat Rai (PNNL)
Linfeng Rao (LBNL)
Sue B. Clark (WSU)

Battelle

U.S. Department of Energy
Pacific Northwest National Laboratory

Objectives

Develop fundamental data on chromium solubility and oxidation reactions for removing Cr from HLW tanks

Discussion format

- Need for these studies
- Role of aqueous speciation in redox reactions
- Thermodynamic model applicable to concentrated hydroxide and nitrate systems
- Relevance/application of data
- Fundamental data for additional oxidants and chemical systems
- Summary

Need for these studies

- Chromium is an important component of tank wastes
- Chromium affects

  Volume and quality of glass

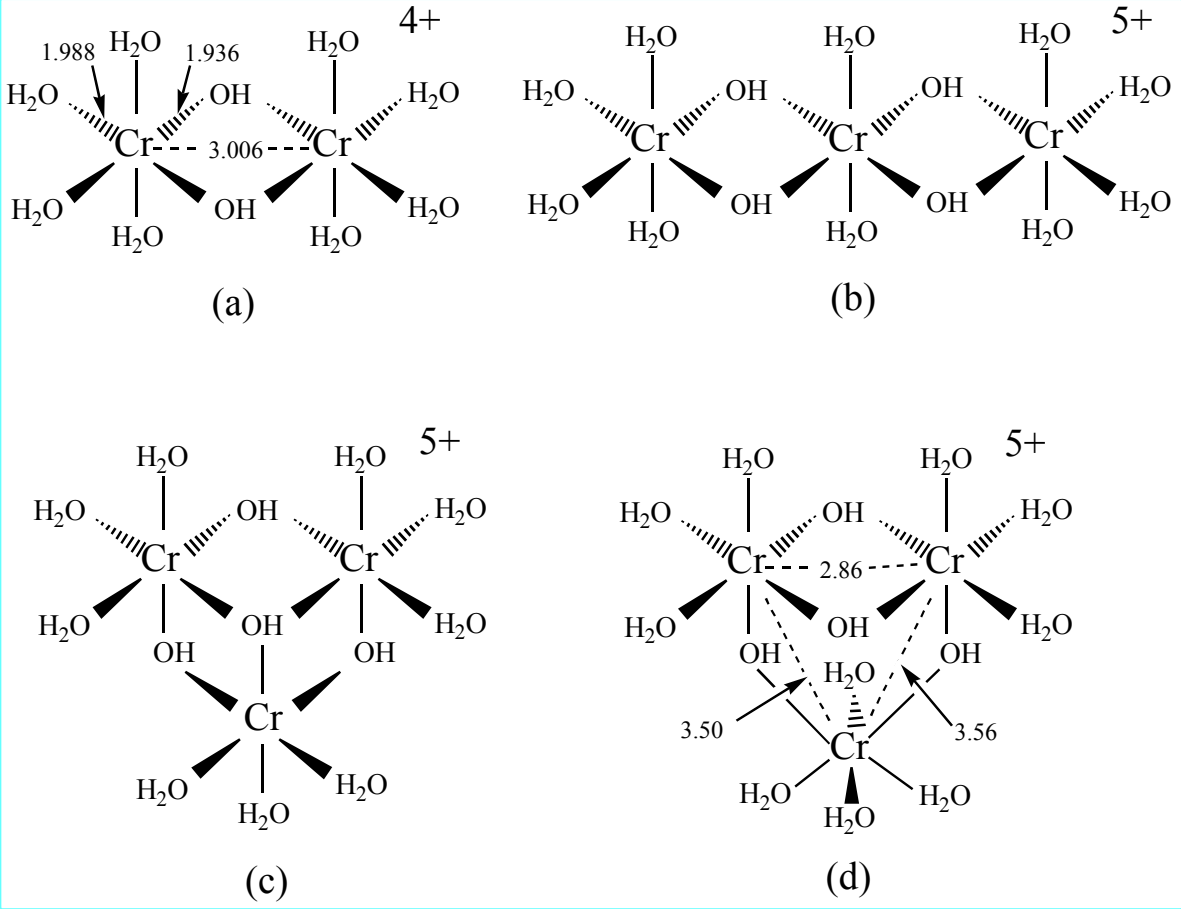
  Operation of vitrification process
- Identified to be important in technology and science needs
- Fundamental data needed for developing/verifying technologies to remove Cr from tank sludges

Importance of Aqueous Speciation

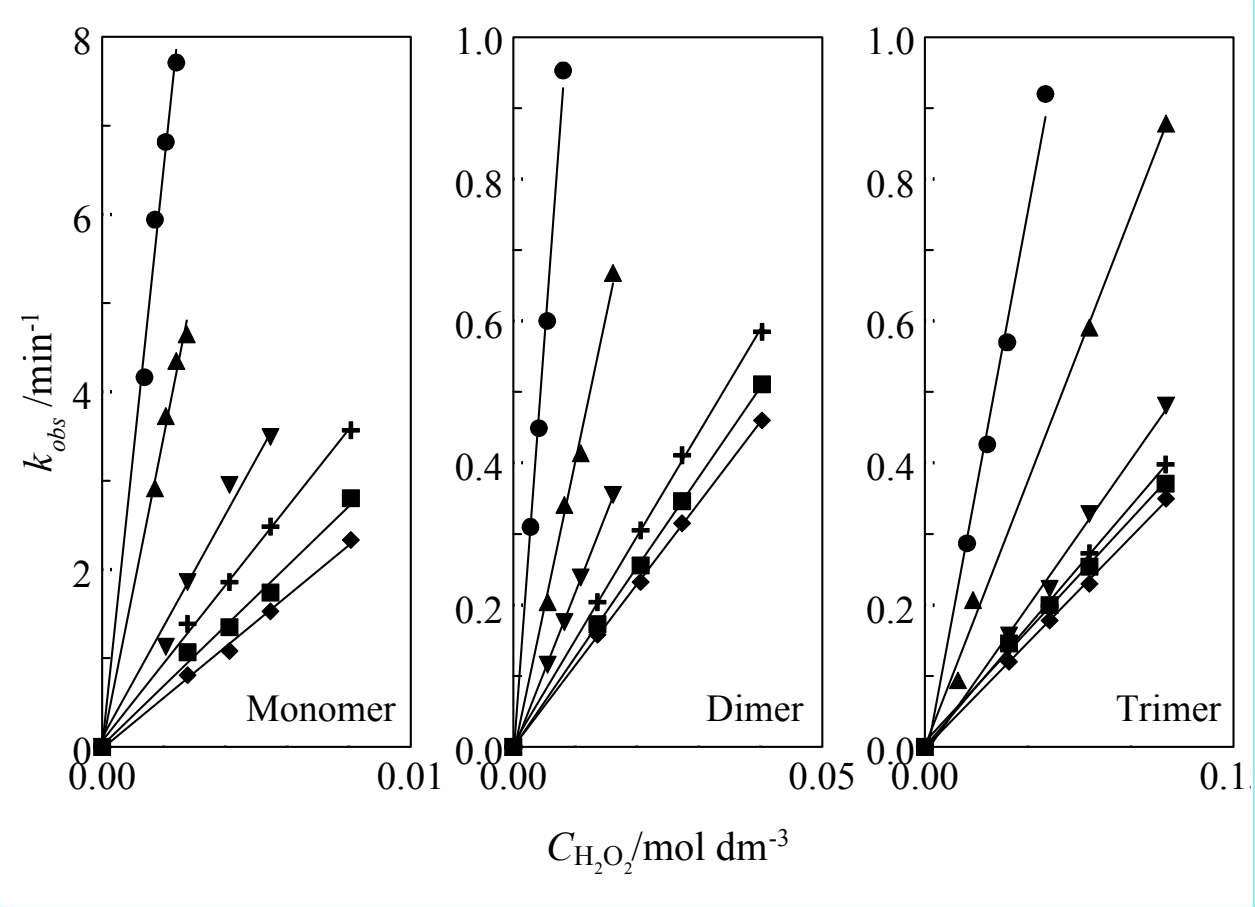
- Understanding kinetics of oxidation
- Developing reliable thermodynamic models

Data developed from ion exchange separation and its combination with UV-Vis-NIR or XAS, XAS, and thermodynamic analyses of data

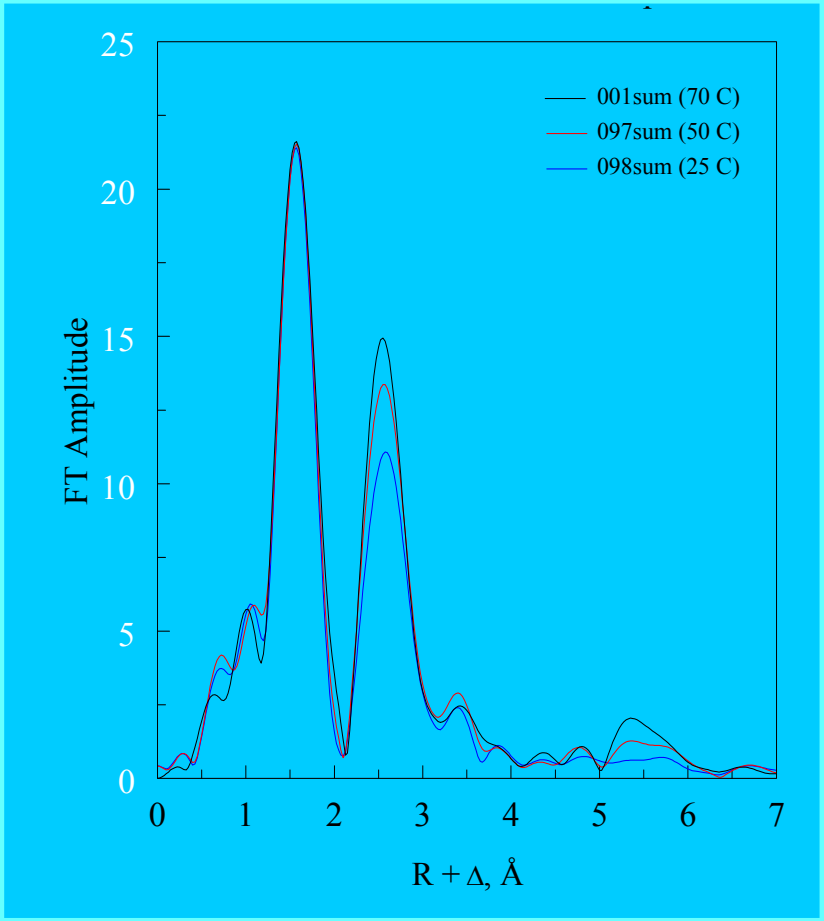
Cr(III) dimer and trimer



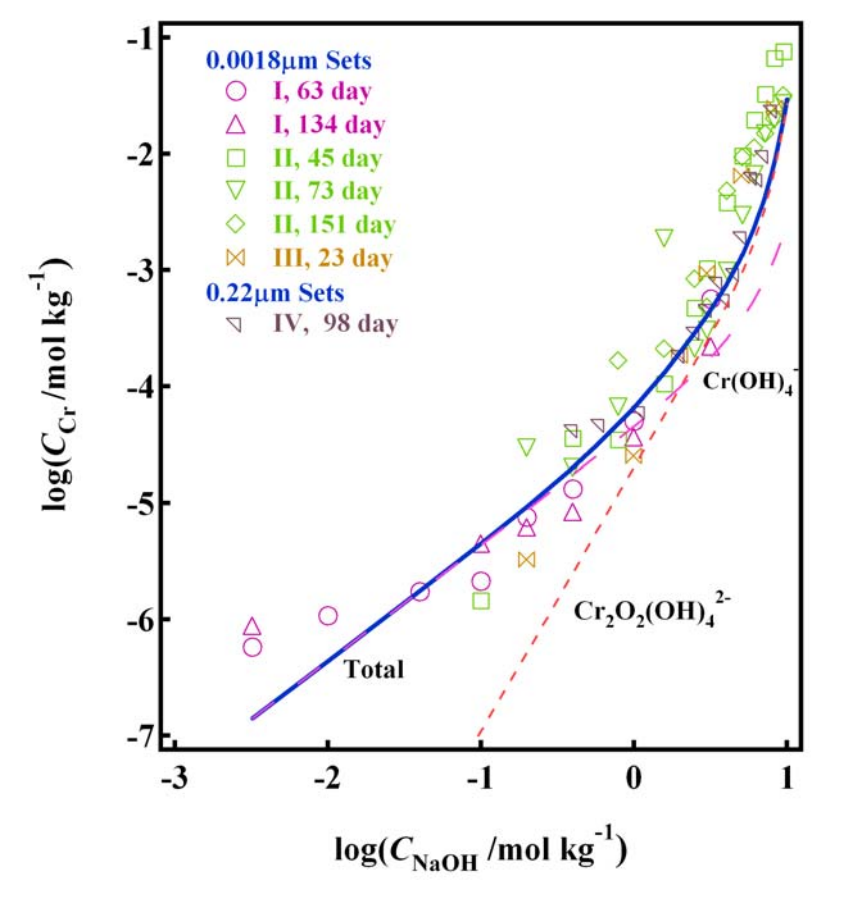
Oxidation of Cr(III) by H_2O_2 in 0.1-1.2 M NaOH



Cr(III) hydroxide in equilibrium with 5.5 M NaOH at different temperatures



Solubility of $Cr(OH)_3(am)$ in NaOH solutions



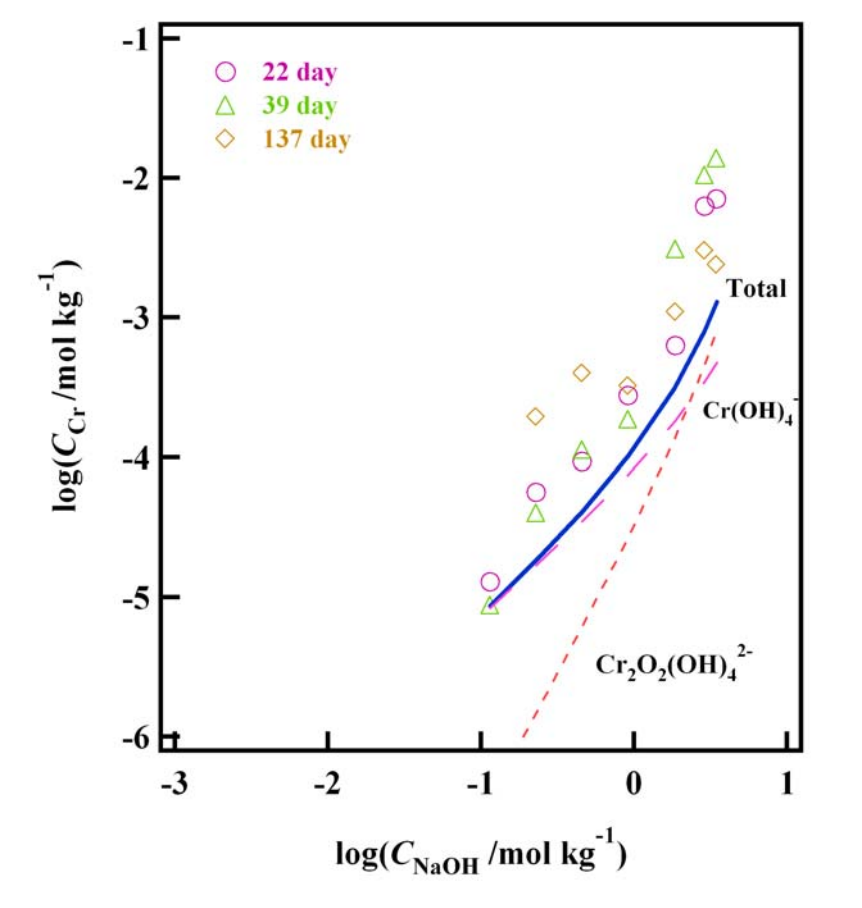
Thermodynamic data developed under this project

Species	Binary Parameters $\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{\varnothing}$	Reference
H^+-ClO_4^-	0.1747	0.2931	0.00	0.00819	91PIT
Na^+-OH^-	0.0864	0.253	0.00	0.0044	91PIT
Na^+-ClO_4^-	0.0554	0.2755	0.00	-0.00118	91PIT
Na^+-$Cr(OH)_4^-$	0.045	0.31	0.00	-0.003	This study[a]
Na^+-NO_3^-	0.0068	0.1783	0.00	-0.00072	91PIT
Na^+-$Al(OH)_4^-$	0.045	0.31	0.00	-0.003	92WES
Na^+-$Cr_2O_2(OH)_4^{2-}$	0.41	0.7	0.00	-0.03768	This study[b]

	Common-Ion Ternary Parameters Value	
OH^--$Cr(OH)_4^-$	0.014	This study[a]
OH^--$Cr(OH)_4^-$-Na^+	-0.0048	This study[a]
OH^--$Al(OH)_4^-$	0.014	92WES
OH^--$Al(OH^-)_4^-$-Na^+	-0.0048	92WES
H^+-Na^+	0.036	91PIT

Reaction	Equilibrium Constants $\log K^0$	
$Cr(OH)_3(am) \equiv Cr(OH)_3$	<-6.84	87RAI/SAS
$Cr(OH)_3(am) + OH^- \equiv Cr(OH)_4^-$	-4.36 $\forall$ 0.24	This study[c]
$2Cr(OH)_3(am) + 2OH^- \equiv Cr_2O_2(OH)_4^{2-} + 2H_2O$	-5.24 $\forall$ 0.24	This study

$Cr(OH)_3$(am) solubility in 4.6 m $NaNO_3$ and as a function of NaOH



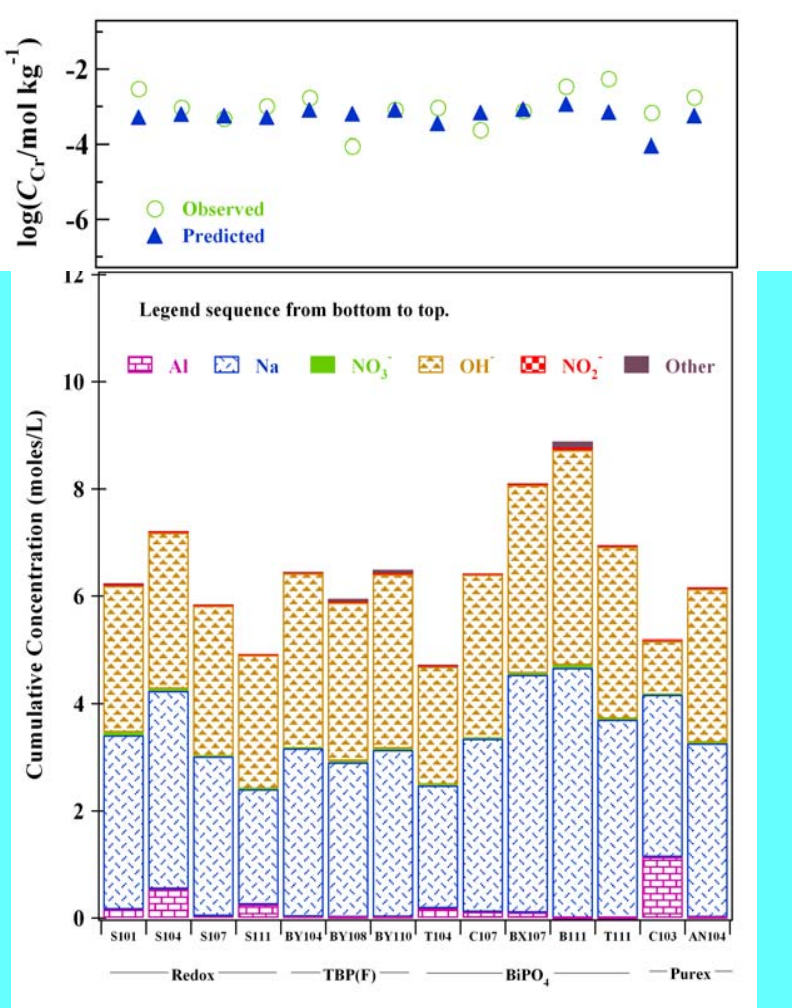
Relevance/application of data

- Included thermodynamic data in the *Environmental Simulations Program*
- Disseminated data in open literature publications
- Used data in predicting Cr leachability from HLW tank sludges

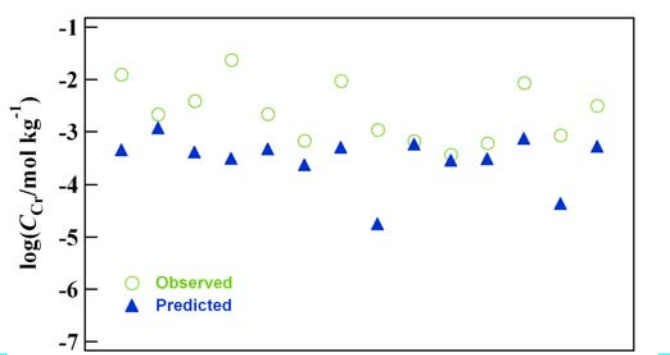
Journal Articles

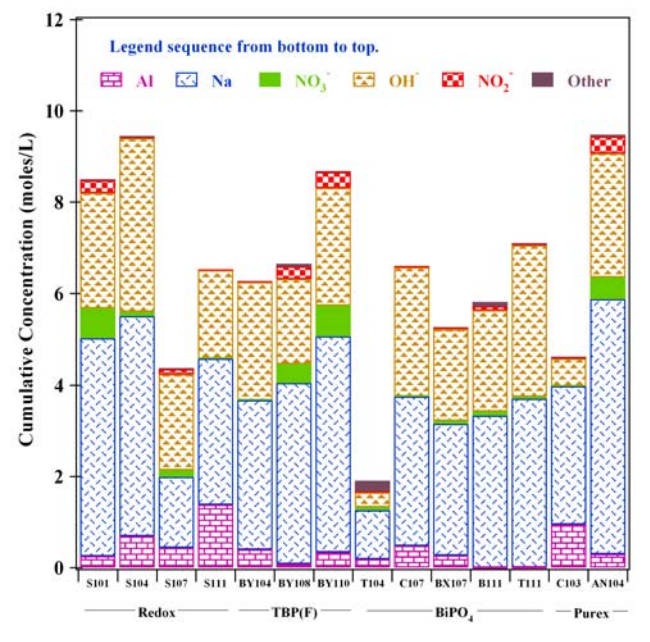
- Chromatographic separations and characterization of Cr(III) species. *Analytical Chemistry* 74:2977-2984 (2002).
- Thermodynamic model for Cr(III) in concentrated NaOH. *Journal of Solution Chemistry* 31:343-367 (2002).
- Oxidation of Cr(III) by H_2O_2. *Journal Chemical Society, DaltonTransactions*: 2:267-274 (2002)
- Oxidation of Cr(III) by peroxydisulfate. *Inorganic Chemistry* (submitted).
- Thermodynamic model for Cr(III)-phosphate system. *Journal of Solution Chemistry* (to be submitted)

Predicted and observed Cr concentrations in the second caustic wash of tank solids



Predicted and observed Cr concentrations in the first caustic wash of tank solids



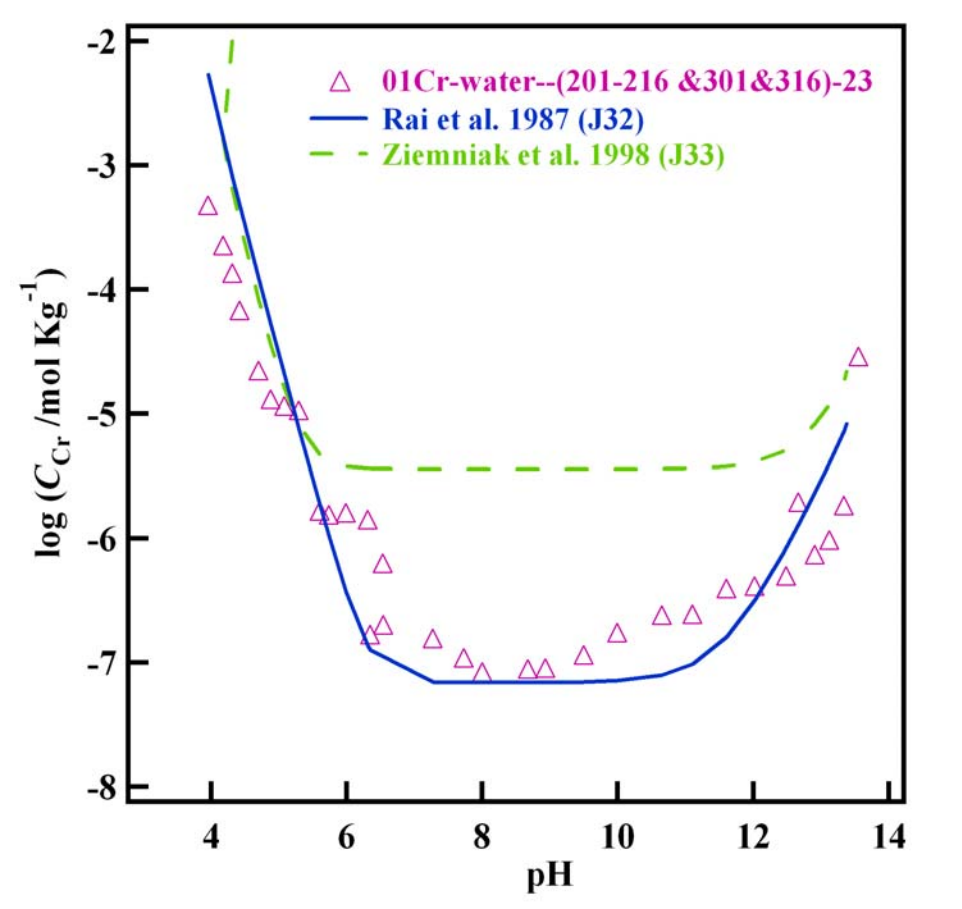


Aqueous chromium(III) species in the hydroxide and phosphate systems

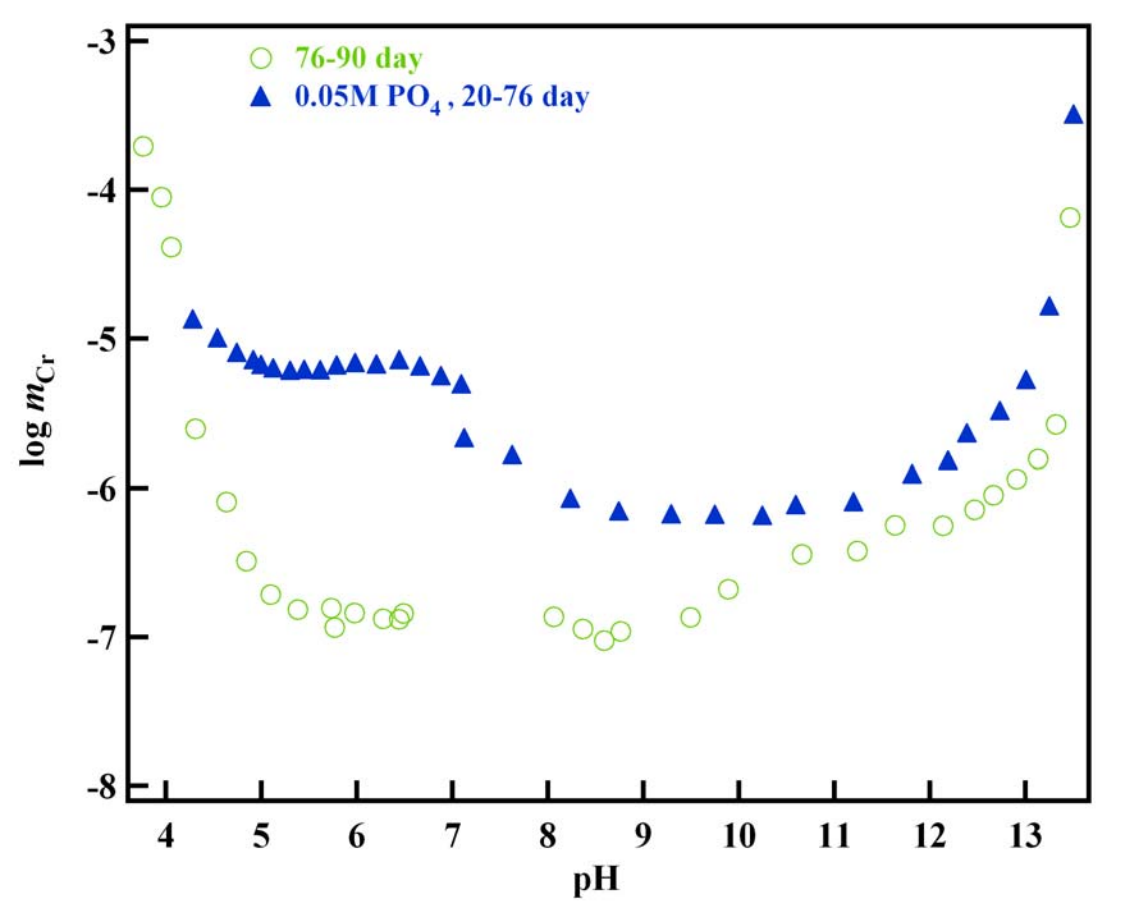
87RAI/SAS & 02RAI/HES	98ZIE/JON	
$CrOH^{2+}$	Cr^{3+}	$Cr(HPO_4)^{+}$
$Cr(OH)_2^{+}$	$CrOH^{2+}$	$Cr(H_2PO_4)^{2+}$
$Cr(OH)_3(aq)$	$Cr(OH)_2^{+}$	$Cr(OH)_3(H_2PO_4)^{-}$
$Cr(OH)_4^{-}$	$Cr(OH)_3(aq)$	$Cr(OH)_3(HPO_4)^{2-}$
$Cr_2O_2(OH)_4^{2-}$	$Cr(OH)_4^{-}$	$Cr(OH)_3(PO_4)^{3-}$
		$Cr(OH)_4(HPO_4)(H_2PO_4)^{4-}$

- Hydroxide system models at odds with each other
- A large number of mixed hydroxy-phosphato species proposed
- Validation required

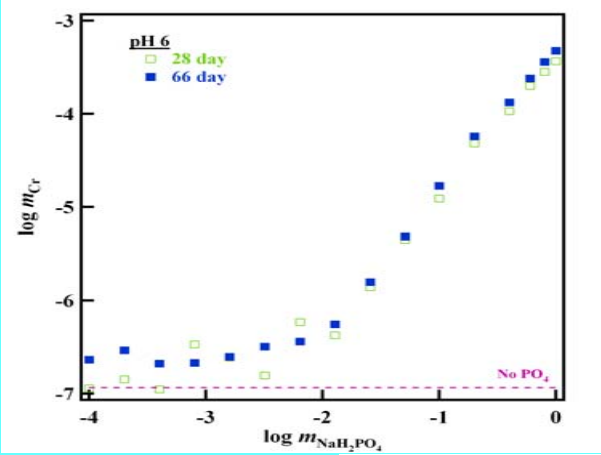
Solubility of $Cr(OH)_3(am)$ as a function of pH: Predictions using different aqueous phase models

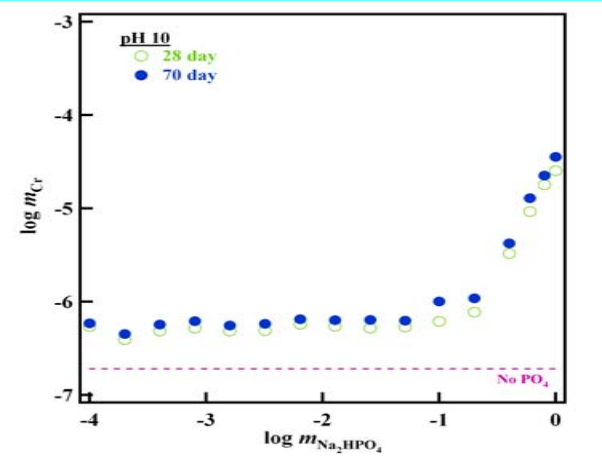


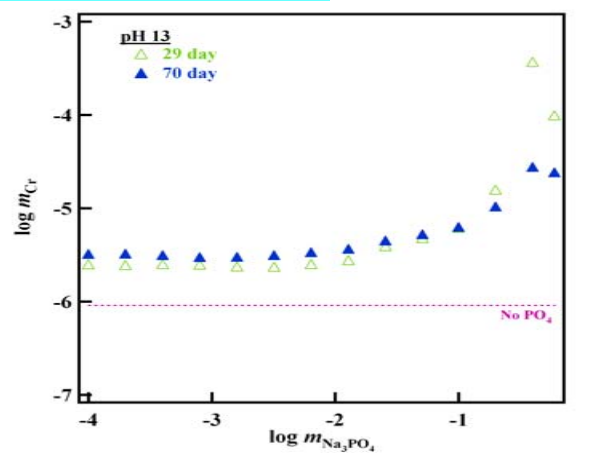
$Cr(OH)_3(am)$ solubility as a function of pH and with and without 0.05 M phosphate



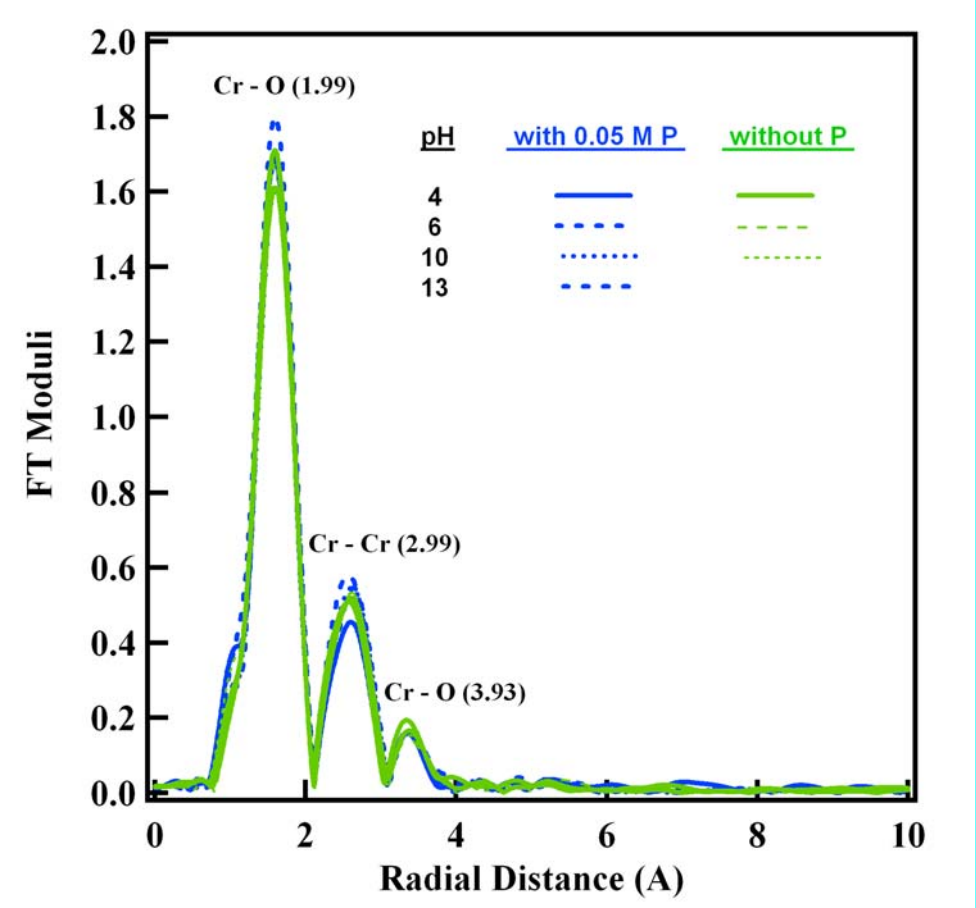
$Cr(OH)_3(am)$ solubility as a function of phosphate at different pH values



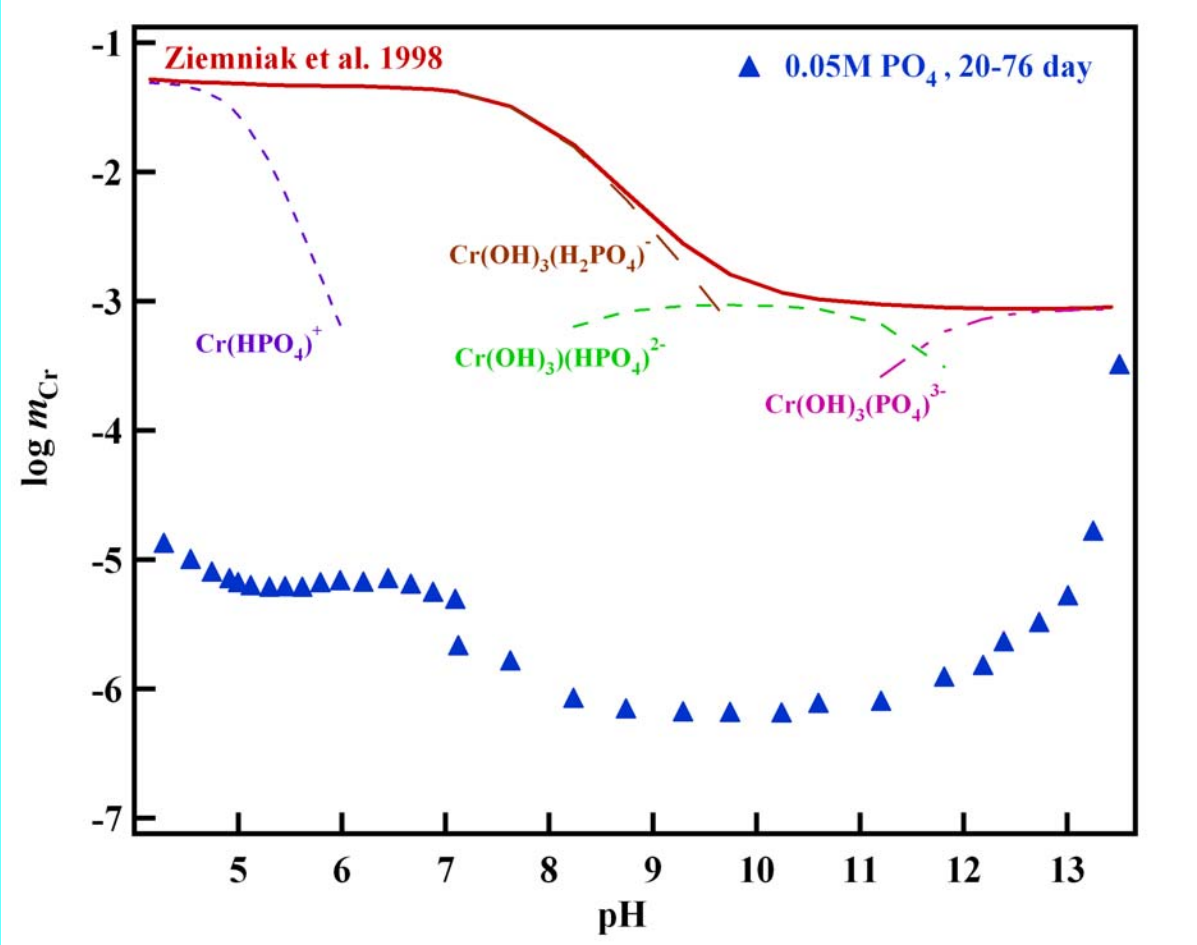




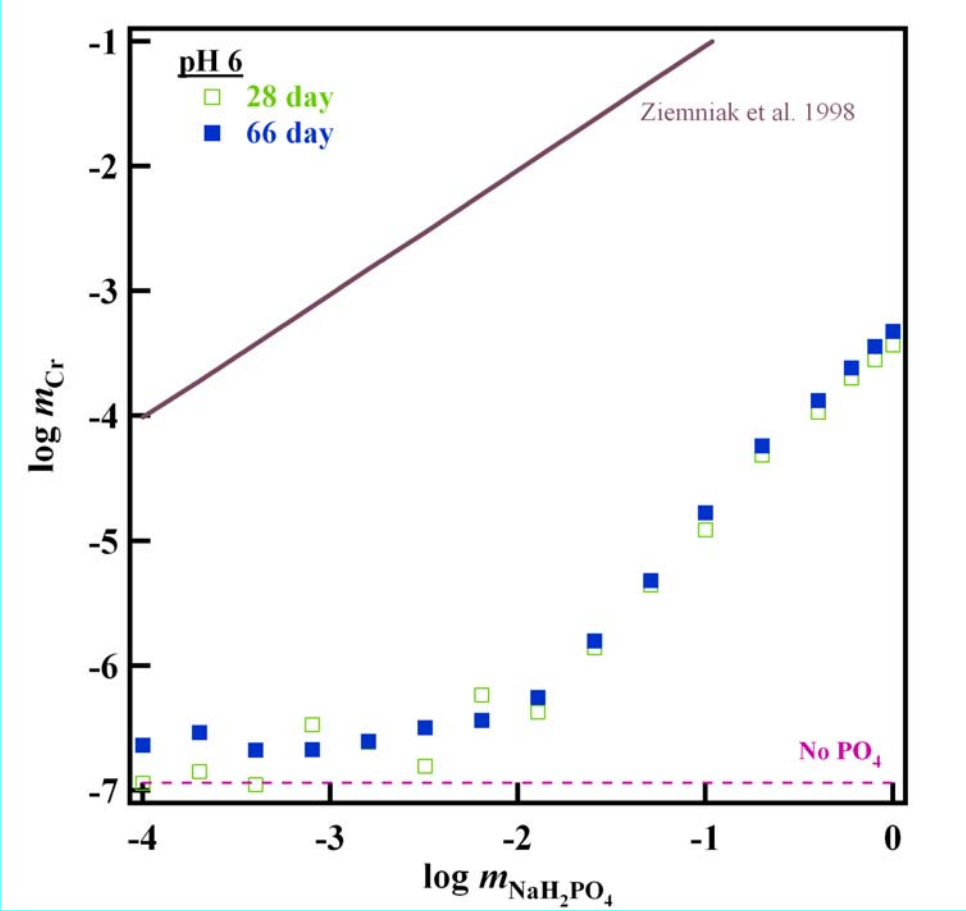
EXAFS of Cr(III) solids equilibrated with and without phosphate



Predicted and observed Cr concentrations in equilibrium with $Cr(OH)_3(am)$ in 0.05 M P



Predicted and observed Cr concentrations in equilibrium with $Cr(OH)_3(am)$ as a function of P



Future emphasis

- Effect of alkalinity, time, and temperature on speciation and solubility of Cr hydroxide.
- Kinetics of Cr(III)/Cr(VI) transformation.
- Phosphato and sulfato complexes of Cr(III)
- Solubility/speciation in the Cr(III)-Fe(III)-Al(III) systems
- Open literature publications

Summary

- Developed methodologies for isolation/characterization of aqueous species
- Developed fundamental data on redox reactions involving H_2O_2 and $S_2O_8^{2-}$
- Developed thermodynamic model applicable to concentrated hydroxide and nitrate systems
- Extending studies to other oxidants and chemical systems
- Applying fundamental data to HLW tanks