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

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Need for This Study

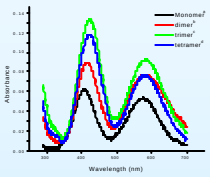
- Cr is an important component of tank wastes
- Chromium affects
  - Volume and quality of glass
  - Operation of vitrification process
- Identified in technology and science needs
  - Enhanced sludge washing process data
  - Sludge treatment
  - Process models for sludge treatment
- Fundamental data on solubility and oxidation reactions applicable to highly alkaline and concentrated electrolytes not available

Objectives

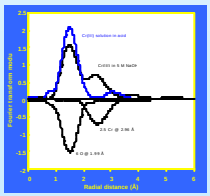
- Develop fundamental data on solubility and oxidation reactions of Cr applicable to highly alkaline and concentrated electrolytes

Aqueous Speciation

- Important in
  - Developing reliable thermodynamic models
  - Understanding kinetics of oxidation
- Data developed from
  - Ion exchange separation (Thompson and Connick 1964)
  - Ion exchange combined with UV-Vis-NIR or XAS
  - XAS
  - Thermodynamic analyses of data
- Results
  - Under acidic conditions different species can be isolated by ion exchange methods (Thompson and Connick 1964) and were characterized by absorption spectroscopy and XAS
  - Under highly alkaline conditions the XAS, ion exchange, and thermodynamic analyses of Cr(III) solubility data show that the nature of species is complex and consist of polymeric species

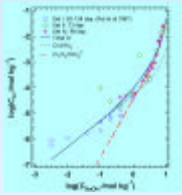


Absorption Spectra of Cr(III) Species Under Acidic Conditions

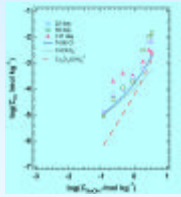


$Cr(OH)_3$ (am) Solubility Studies

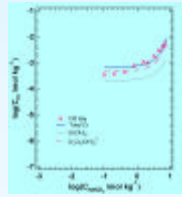
Solubility was determined in NaOH and in mixtures of NaOH and $NaNO_3$ ranging in concentrations to as high as 11 m. Thermodynamic model was developed from NaOH system and was used to predict concentrations in mixtures of NaOH and $NaNO_3$. The proposed aqueous species are consistent with literature data and XAS studies. The close agreement between the observed and predicted concentra tions shows the reliability of the model.



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



Solubility of $Cr(OH)_3$(am) in 4.6 M $NaNO_3$ and as a Function of NaOH



Solubility of $Cr(OH)_3$(am) in 3M NaOH and as a Function of $NaNO_3$

Thermodynamic Model

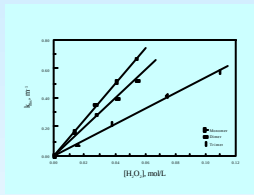
Species	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Reference
Binary Parameters				
Na^+-OH^-	0.0864	0.253	0.0044	Pitzer (1991)
Na^+-ClO_4^-	0.0554	0.2755	-0.00118	Pitzer (1991)
Na^+-NO_3^-	0.0068	0.1783	-0.00072	Pitzer (1991)
Na^+-$Cr(OH)^-$	0.045	0.310	-0.003	This study[a]
Na+-C42	0.41	0.70	-0.038	This study[b]
Ternary Parameters				
OH^--$Cr(OH)_4^-$		0.014		This study[a]
OH^--Na^+-$Cr(OH)_4^-$		-0.0048		This study[a]
Dissolution Reactions				
$Cr(OH)_3(am) + OH^- \rightleftharpoons Cr(OH)_4^-$			Log K^o = -4.30	Rai et al. (1987)
$2Cr(OH)_3(am) + 2OH^- \rightleftharpoons Cr_2O_2(OH)_4^{2-} + 2H_2O$			Log K^o = -5.29	This study

[a] Based on analogous Na^+-$Al(OH)_4^-$, Wesolowski (1992)

[b] Based on $\beta^{(0)}$ and $\beta^{(1)}$ values from Na^+-$Cd(OH)_4^-$, Rai et al. (1991)

Oxidation of Cr(III) to Cr(VI)

- The effects of H_2O_2 and persulfate to oxidize Cr(III) were evaluated.
- Rates of oxidation were found to be dependent on the types of species, oxidant, NaOH concentration, and temperature.



Oxidation of Separated Cr(III) Species in 1 M NaOH by H_2O_2

Redox Reactions

Species	Oxidant (m)	K_{obs} (min^{-1})	$t_{1/2}$ (min)
H_2O_2 (1.0 M NaOH, 25°C)			
Monomer	0.017	6	0.12
Dimer	0.017	0.2	0.06
Trimer	0.017	3.5	12
Unseparated	0.017	-	>900
Persulfate (1.0 M NaOH, 22°C)			
0.005 M $Cr(III)_T$	0.05	0.05	19.9
	0.98	0.357	2.8
Persulfate (5.0 M NaOH, 22°C)			
0.005 M $Cr(II)_T$	0.05	0.155	6.5
	0.99	1.20	0.8

Summary

- We have made considerable progress on developing fundamental data on solubility and redox kinetics
- Rate constants developed for oxidation of Cr(III) species by H_2O_2 and persulfate
- Solubility of $Cr(OH)_3$(am) determined in concentrated electrolytes
  - NaOH
  - NaOH + $NaNO_3$
- Pitzer ion-interaction model developed for Cr(II) in high base
- Model required $Cr(OH)_4^-$ and $Cr_2O_2(OH)_4^{2-}$
- The data and model would be useful in developing and optimizing Cr removal technologies from tank wastes

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