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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

Analysis Plan for Derivation of Pitzer Parameters in Support of Experimental Work at LANL-CO

Task 1.4.2.2

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1 Introduction and Objectives

1.1 Introduction

Los Alamos National Laboratory-Carlsbad Operation (LANL-CO) and Carlsbad Environmental Monitoring and Research Center (CEMRC) of New Mexico State University at Carlsbad have been conducting experimental work concerning the chemistry of actinides and their analogs. In their experiments at high ionic strengths, the Pitzer interaction parameters could be derived. When those Pitzer interaction parameters are derived, they could be employed to refine or enlarge the current database used for predicting the actinide solubility for the WIPP performance assessment. This analysis is a Programmatic Decision analysis per NP 9-1.

1.2 Objectives

The objective of this Analysis Plan (AP) is to derive the Pitzer interaction parameters in support of the experimental work at LANL-CO and at CEMRC. The Pitzer interaction parameters between Co^{2+}-, Ni^{2+}- and Gd^{3+}-EDTA, and Nd-borate complexes, and the bulk background electrolytes (i.e., NaCl, Na_2SO_4), will be derived. Revision 2 of this AP added that experimental data provided by Punam Thakur at CEMRC would be modeled to derive the Pitzer interaction parameters between citric acid, EDTA and background electrolyte, $NaClO_4$, and between EDTA complexes (i.e., $AmEDTA^-$, $CmEDTA^-$ and $EuEDTA^-$) and $NaClO_4$, and between citrate complexes (i.e., $AmCit^o$, $CmCit^o$ and $EuCit^o$) and $NaClO_4$. In this revision, additional experimental data provided by Punam Thakur will be modeled to derive the Pitzer interaction parameters between oxalic acid and background electrolyte, $NaClO_4$, and between oxalate complexes (i.e., $AmOx^+$, $CmOx^+$ and $EuOx^+$) and $NaClO_4$. The data from Punam Thakur were originally produced by her at Florida State University.

2 Approach

2.1 Project Resources

Sandia National Laboratories has a computer program called NONLIN (Babb, 1996; Ismail, 2008). NONLIN fits parameters for the Pitzer's aqueous electrolyte model based on experimental data on stability constants of aqueous complexes, mineral solubility, osmotic coefficients, electromotive force (emf) and solvent extraction. Therefore, this computer program is suitable to achieving the objectives of this AP.

2.2 Project Tasks and Milestones

The project tasks are detailed in Section 4.

3 Software List

The software to be used is NONLIN Version 2.01 (system configuration: OpenVMS 8.2 hp AlphaServer ES47; HP ProLiant Intel Xeon Red Hat Linux 5.1).

4 Tasks

The tasks for Revision 3 of this AP include:

(1) Derivation of Pitzer parameters for the interaction between $CoHEDTA^{-}$ and the bulk electrolyte, NaCl.
(2) Derivation of Pitzer parameters for the interaction between $CoEDTA^{2-}$ and the bulk electrolyte, NaCl.
(3) Derivation of Pitzer parameters for the interaction between $NiEDTA^{2-}$ and the bulk electrolyte, NaCl.
(4) Derivation of Pitzer parameters for the interaction between $GdEDTA^{-}$ and the bulk electrolyte, NaCl.
(5) Derivation of Pitzer parameters for the interaction between $NdHB_4O_7^{2+}$ and the bulk electrolytes, NaCl and Na_2SO_4.
(6) Derivation of Pitzer parameters for the interaction between H_2Cit^{-} and the bulk electrolyte, $NaClO_4$.
(7) Derivation of Pitzer parameters for the interaction between $HCit^{2-}$ and the bulk electrolyte, $NaClO_4$.
(8) Derivation of Pitzer parameters for the interaction between Cit^{3-} and the bulk electrolyte, $NaClO_4$.
(9) Derivation of Pitzer parameters for the interaction between H_3EDTA^{-} and the bulk electrolyte, $NaClO_4$.
(10) Derivation of Pitzer parameters for the interaction between H_2EDTA^{2-} and the bulk electrolyte, $NaClO_4$.
(11) Derivation of Pitzer parameters for the interaction between $HEDTA^{3-}$ and the bulk electrolyte, $NaClO_4$.
(12) Derivation of Pitzer parameters for the interaction between $EDTA^{4-}$ and the bulk electrolyte, $NaClO_4$.
(13) Derivation of Pitzer parameters for the interaction between $AmCit^{o}$ and the bulk electrolyte, $NaClO_4$.
(14) Derivation of Pitzer parameters for the interaction between $CmCit^{o}$ and the bulk electrolyte, $NaClO_4$.
(15) Derivation of Pitzer parameters for the interaction between $EuCit^{o}$ and the bulk electrolyte, $NaClO_4$.
(16) Derivation of Pitzer parameters for the interaction between $AmEDTA^{-}$ and the bulk electrolyte, $NaClO_4$.
(17) Derivation of Pitzer parameters for the interaction between $CmEDTA^{-}$ and the bulk electrolyte, $NaClO_4$.
(18) Derivation of Pitzer parameters for the interaction between $EuEDTA^{-}$ and the bulk electrolyte, $NaClO_4$.
(19) Derivation of Pitzer parameters for the interaction between HOx^{-} and the bulk electrolyte, $NaClO_4$.
(20) Derivation of Pitzer parameters for the interaction between Ox^{2-} and the bulk electrolyte, $NaClO_4$.
(21) Derivation of Pitzer parameters for the interaction between $AmOx^{+}$ and the bulk electrolyte, $NaClO_4$.

(22) Derivation of Pitzer parameters for the interaction between $CmOx^+$ and the bulk electrolyte, $NaClO_4$.
(23) Derivation of Pitzer parameters for the interaction between $EuOx^+$ and the bulk electrolyte, $NaClO_4$.
(24) Derivation of Pitzer parameters for the interaction between $Am(Ox)_2^-$ and the bulk electrolyte, $NaClO_4$.
(25) Derivation of Pitzer parameters for the interaction between $Cm(Ox)_2^-$ and the bulk electrolyte, $NaClO_4$.
(26) Derivation of Pitzer parameters for the interaction between $Eu(Ox)_2^-$ and the bulk electrolyte, $NaClO_4$.

Task 5 has been completed (Xiong, 2010).

Yongliang Xiong will conduct those remaining tasks, and the completion date is estimated to be by the end of FY12.

5 Special Considerations

Pitzer interaction parameters will be derived from the conditional equilibrium constants generated at LANL-CO (Borkowski, 2007). The Pitzer interaction parameters derived in this AP will be summarized in a memo that will be submitted to the WIPP Record Center.

6 Applicable Procedures

All applicable WIPP QA procedures will be followed when conducting this AP.

- Training of personnel will be conducted in accordance with the requirements of NP 2-1, *Qualification and Training*.
- Analyses will be conducted and documented in accordance with the requirements of NP 9-1, *Analyses*.
- All software used will meet the requirements laid out in NP 19-1, *Software Requirements* and NP 9-1, as applicable.
- The analyses will be reviewed following NP 6-1, *Document Review Process*.
- All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records*.

7 References

Babb, S.C. 1996. "NONLIN, Ver. 2.00, User's Manual." Unpublished report, January 31, 1996. Albuquerque, NM: Sandia National Laboratories. WPO 30740.

Borkowski, M., 2007. "Table 1. The conditional stability constants and protonation constants for CoEDTA complex and log β_{101} values for Co^{2+}, Ni^{2+} and Gd^{3+} as a function of NaCl ionic strength." Sent to Yongliang Xiong on February 7, 2007 via e-mail. ERMS #546107.

Ismail, A.E., 2008. “WIPP PA User’s Manual for NONLIN, Version 2.01.” Carlsbad, NM: Sandia National Laboratories, ERMS #54617.

Xiong, Y.-L., 2010. Calculations of Thermodynamic Parameters for Experimental Data Generated at Los Alamos National Laboratory Carlsbad Operation (LANL-CO). Memo to Record Center, ERMS # 552873.

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