SAND2010-6224P

Solubility of $FeC_2O_4 \cdot 2H_2O$ and PbC_2O_4 in $MgCl_2$ and NaCl Solution[1]

Presentation at the
German-U.S. DOE Technical Exchange on the Chemistry of Salt Repositories
September 15 and 16, 2010

J.-H. Jang, Y.-L. Xiong, and M.B. Nemer
Carlsbad Programs Group
Sandia National Laboratories[2]
Carlsbad, NM 88220

1. This research is funded by WIPP programs administered by the U.S. Department of Energy (DOE).
2. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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Introduction

- Oxalate
  - Present in the waste
  - Capable of solubilizing actinides via aqueous complexation
- Fe and Pb
  - Present in the waste and (shielded) containers
  - Forms insoluble minerals with oxalate, such as, $FeC_2O_4 \cdot 2H_2O$ and PbC_2O_4

Objectives

- To determine the solubility of $FeC_2O_4 \cdot 2H_2O$ and PbC_2O_4 and Pitzer ion-interaction parameters for following aqueous species
  - FeOx(aq)~Na^+; PbOx(aq)~Na^+
  - FeOx(aq)~Mg^{2+}; PbOx(aq)~Mg^{2+}
  - FeOx(aq)~Cl^-; PbOx(aq)~Cl^-

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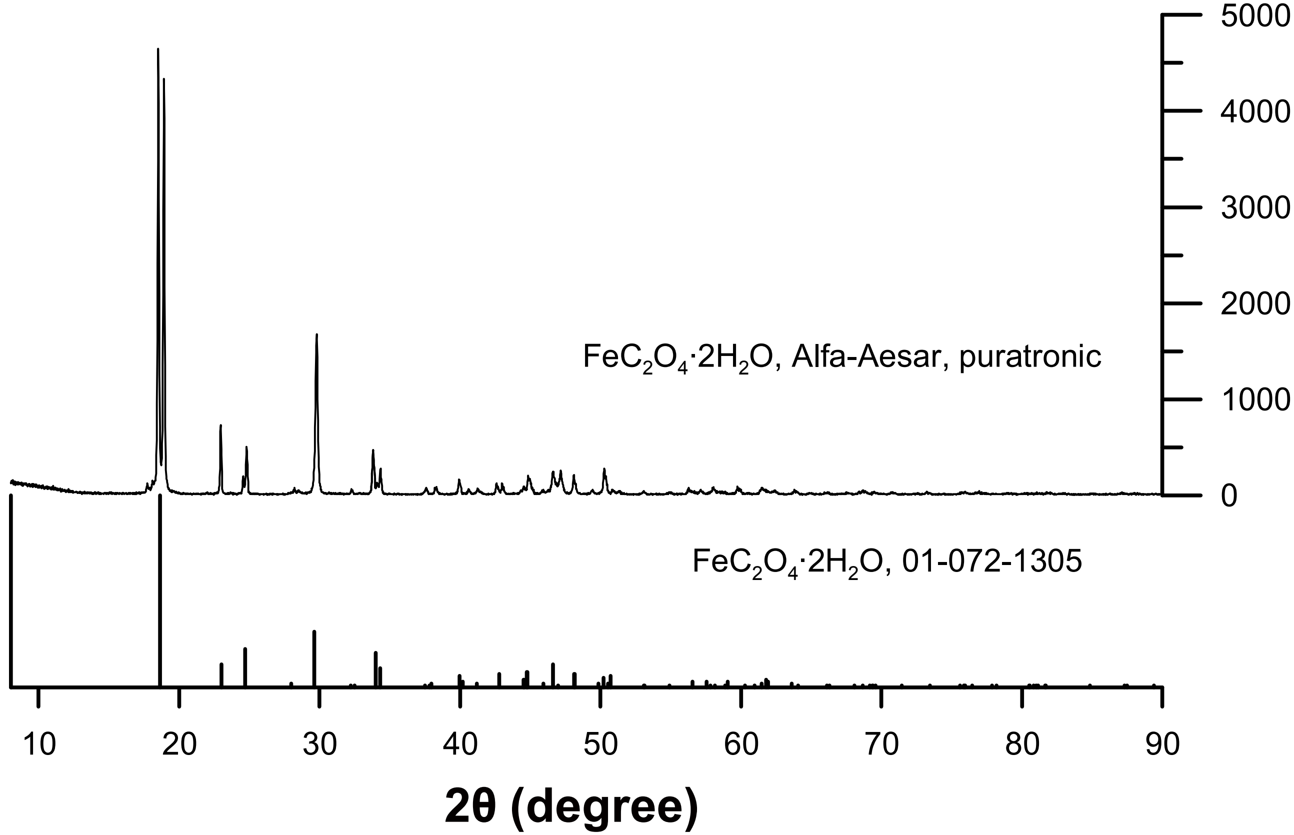
Material and Methods

- Iron(II) oxalate dihydrate ($FeC_2O_4{\cdot}2H_2O$, 99.999 % metal basis, Alfa Aesar)
- Lead oxalate (PbC_2O_4, 99.999 %, Alfa Aesar)
- Reactors (glass serum bottles, 50 or 120 mL) were prepared in the glovebox (P_{O_2} less than 10 ppm, 26 ± 1.5 °C)
  - $FeC_2O_4{\cdot}2H_2O$ in $MgCl_2$ and NaCl solutions of various concentrations
  - Known volume of deoxygenated, deionized water was mixed with preweighed salts in the glovebox
  - For most conditions, more than two replicates prepared

Material and Methods

- Fe(II) and Fe_T: ferrozine method coupled with UV-VIS spectrophotometer
- ICP-AES for Pb, Mg, and Na
- IC for oxalate and Cl
- pH: glass combination electrode calibrated using commercial pH buffers
- XRD: characterization of solid

XRD of $FeC_2O_4 \cdot 2H_2O$



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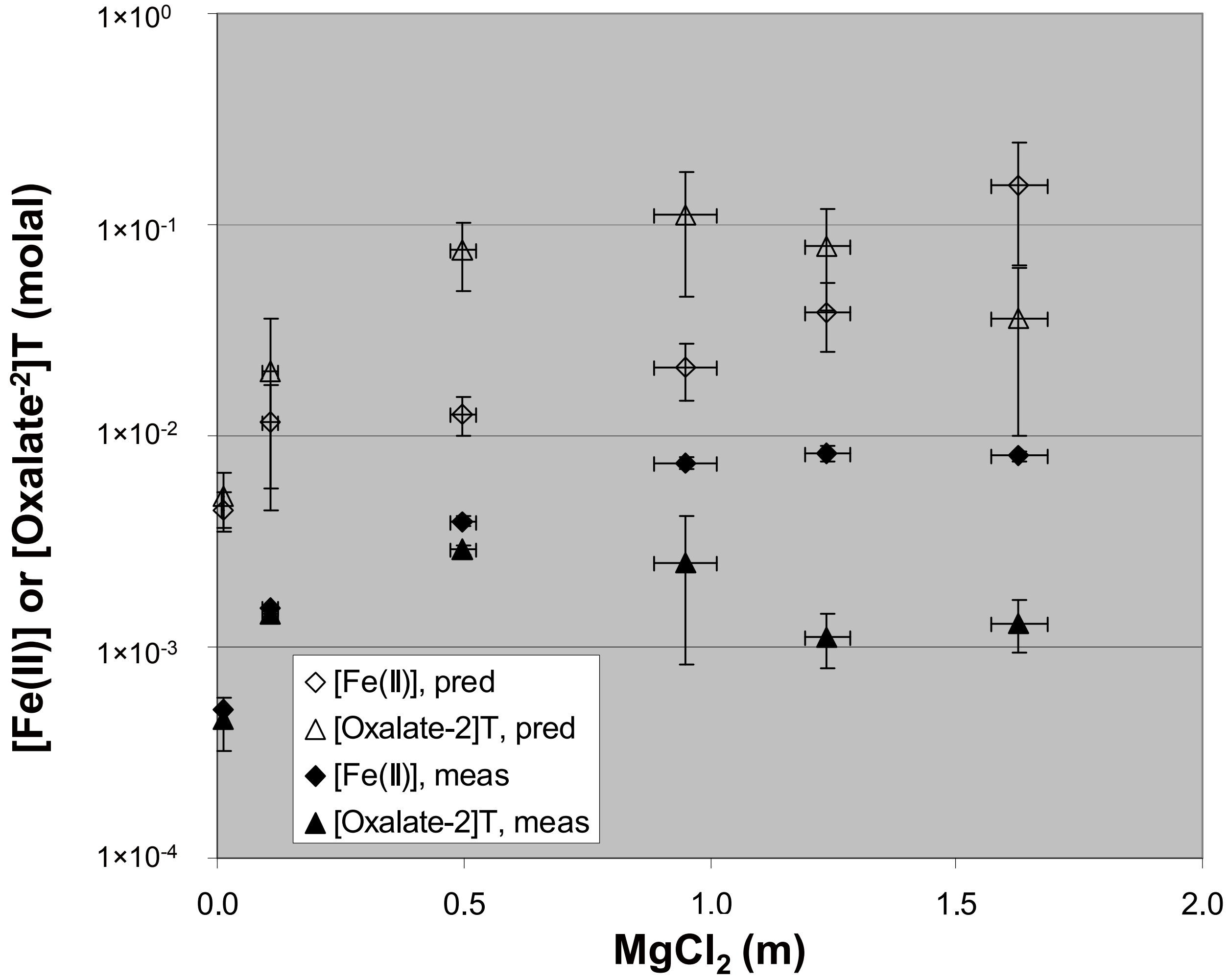
Speciation model for Fe^{+2}

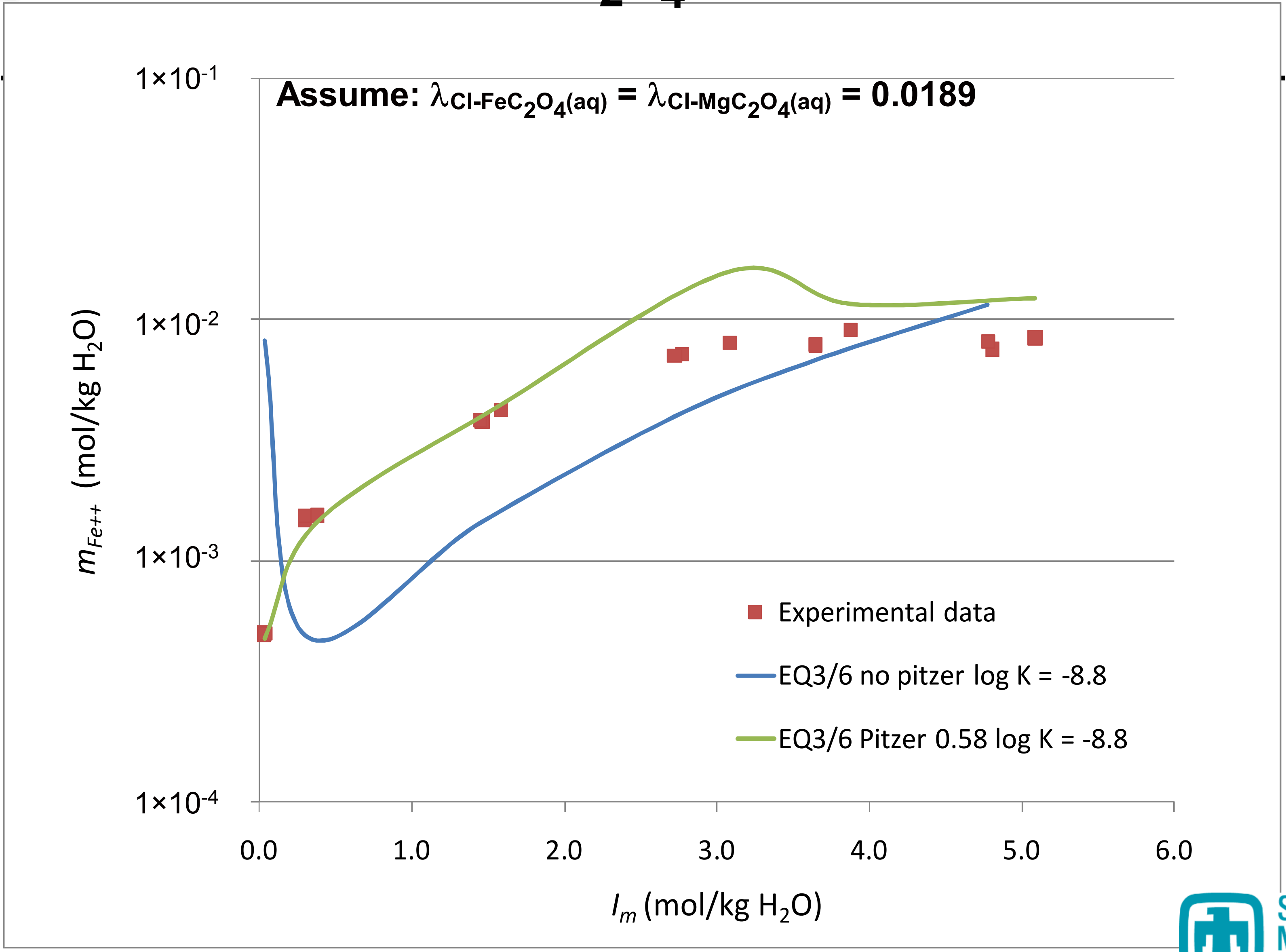
	logK
$FeOH^{+} + H^{+} \Leftrightarrow Fe^{2+} + H_2O$:	9.31
$FeC_2O_4(aq) \Leftrightarrow Fe^{2+} + C_2O_4^{-2}$:	-3.79
$Fe(C_2O_4)_2^{-2} \Leftrightarrow Fe^{2+} + 2C_2O_4^{-2}$:	-5.90
$FeC_2O_4 \cdot 2H_2O(s) \Leftrightarrow Fe^{2+} + C_2O_4^{-2} + 2H_2O$:	-6.68

- Activity correction based on the Pitzer parameters in slide 9 and 12

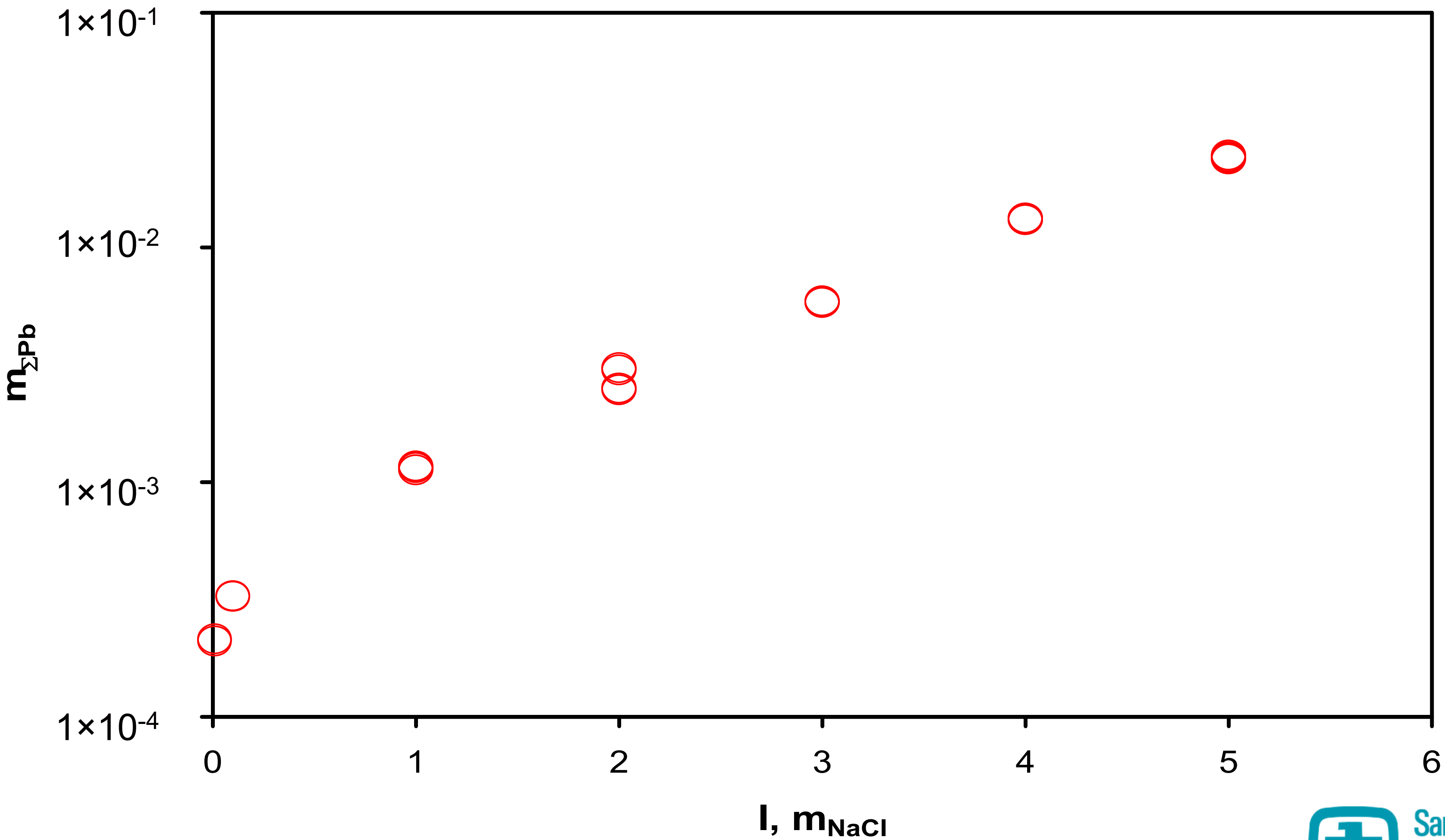
Experimental and Calculated Results



Fit with log K = -8.78 and $\lambda_{Mg\text{-}FeC_2O_4(aq)}$ = 0.58



Experimental Results for PbC_2O_4 in NaCl Solutions



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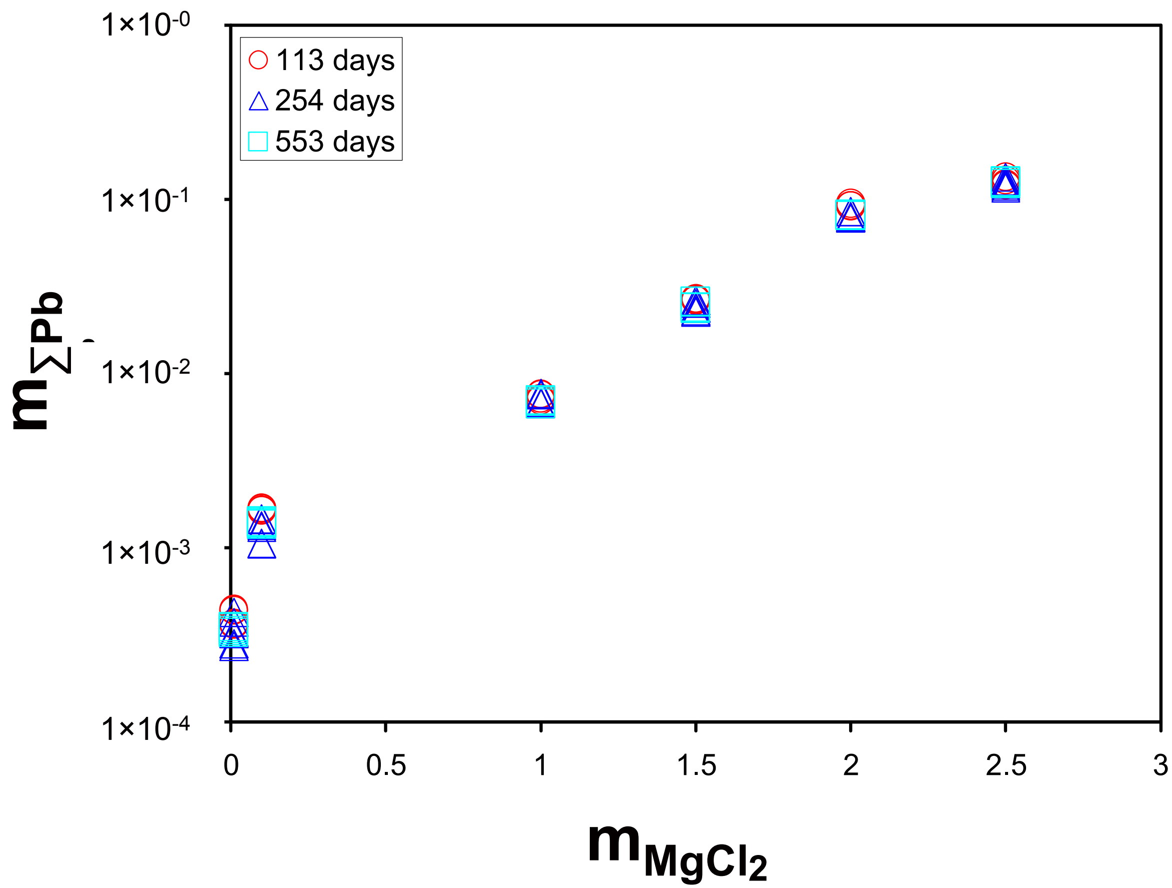
Experimental Results for PbC_2O_4 in $MgCl_2$ Solutions



Pitzer Parameters for $PbC_2O_4(aq)$

The following parameters have been obtained:

$$\lambda_{Cl\text{-}PbC_2O_4(aq)} = -0.560$$

$$\lambda_{Mg\text{-}PbC_2O_4(aq)} = -0.675$$

$$\zeta_{Mg\text{-}Cl\text{-}PbC_2O_4(aq)} = -0.0856$$

Conclusions

- Model prediction and experimental data showed significant differences.
- Solubility constant for $FeC_2O_4 \cdot 2H_2O$ and Pitzer ion-interaction parameters for important aqueous complexes should be improved.
- Preliminary modeling results indicated that use of lower solubility constant and selection of different ion pairs would improve the fitting.
- Pitzer parameters for $PbC_2O_4(aq)$ in $MgCl_2$ have been obtained.