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SOLUTION CHEMISTRY FOR ACTINIDE OXALATES TO HIGH IONIC STRENGTHS: SOLUBILITY CONSTANTS FOR ACTINIDE OXALATE SOLID PHASES

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OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- Evaluation of Solubility Constants of Pu(III), Am(III) and Cm(III) Oxalates
- Comparison of Solubility Constants of Pu(III), Am(III) and Cm(III) Oxalates with Those for Lanthanide Oxalates from the literature
- Summary

INTRODUCTION

- Actinide oxalates are important to nuclear industry and other fields:
  - Precipitation of actinide(III) and actinide(IV) is widely used as technological method for isolation and purification of actinides [1].
  - Such oxalates are the precursors of oxide fuels.
  - Actinide oxalates, easily obtained as single crystals, offer the opportunity of numerous unique topologies.
  - Uranyl oxalate can be used as chemical actinometers: counting the number of photons in a beam absorbed into a defined space of a chemical reactor.

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[1] Abraham, F., Arab-Chapelet, B., Rivenet, M., Tamain, C. and Grandjean, S., 2014. Actinide oxalates, solid state structures and applications. *Coordination Chemistry Reviews*, *266*, pp.28-68.

INTRODUCTION (Cont.)

- Actinide Oxalate to Nuclear Waste Management:
  - Oxalate is one of the most important degradation products of humic and fulvic acids [2]. Such natural oxalate can impact the mobility of radionuclides.
  - Oxalate is present in waste stream for geological repositories.
    - For instance, at the Waste Isolation Pilot Plant (WIPP), the oxalate concentration for the Performance Assessment for Compliance Recertification Application in 2014 (CRA-2014) was 1.18×10^{-2} M [3].
  - Oxalate in natural environments and oxalate in waste stream for geological repositories could form actinide oxalates.

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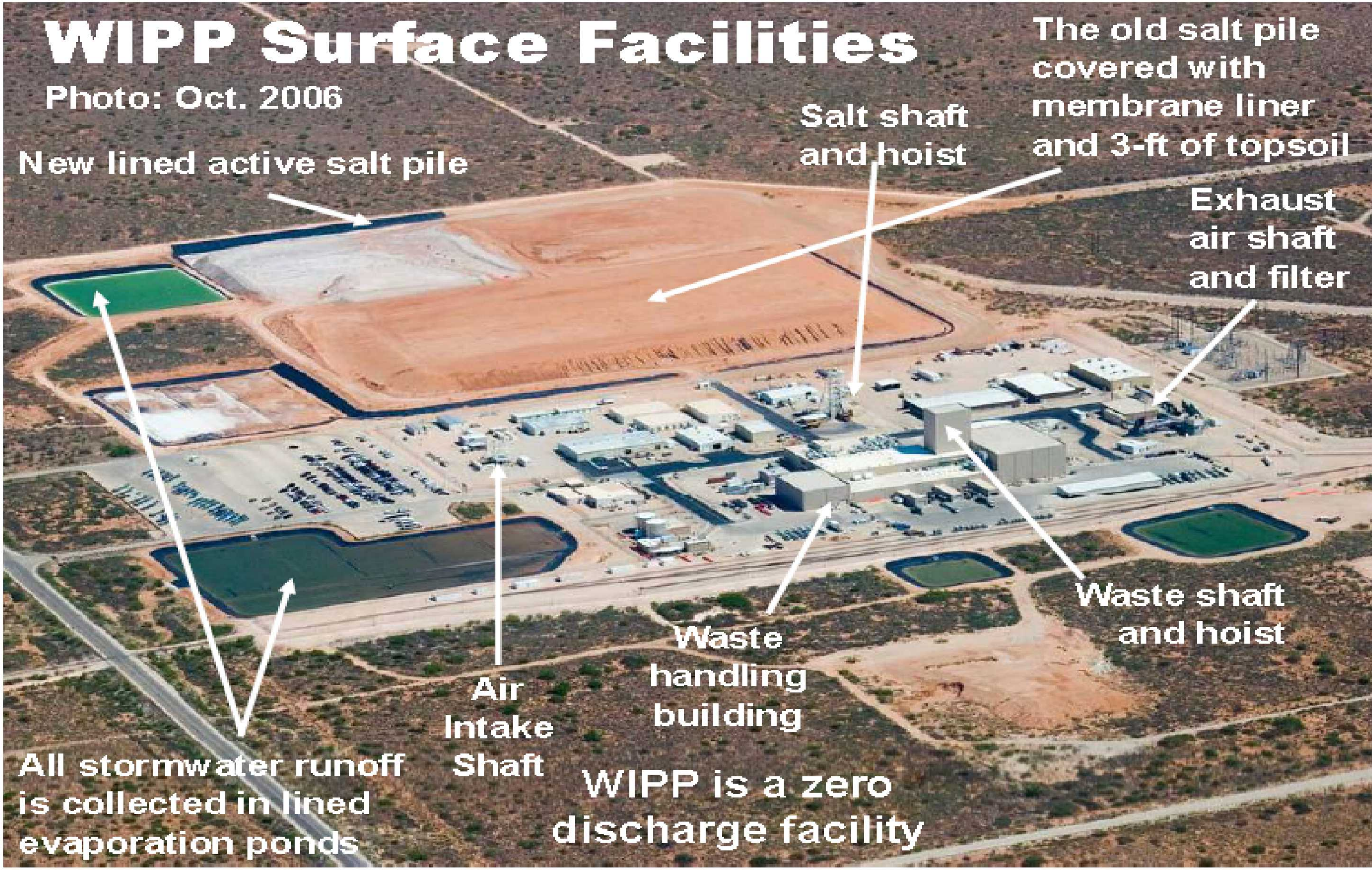
[2] Ferri, D., Iuliano, M., Manfredi, C., Vasca, E., Caruso, T., Clemente, M. and Fontanella, C., 2000. Dioxouranium (VI) oxalate complexes. *Journal of the Chemical Society, Dalton Transactions*, (19), pp.3460-3466.

[3] Brush, L.H. and Domski, P.S., 2013. Calculation of Organic Ligand Concentrations for the WIPP CRA-2014 PA. *Analysis report, January*, *14*, p.2013.

INTRODUCTION (Continued), WIPP

INTRODUCTION (Continued), WIPP



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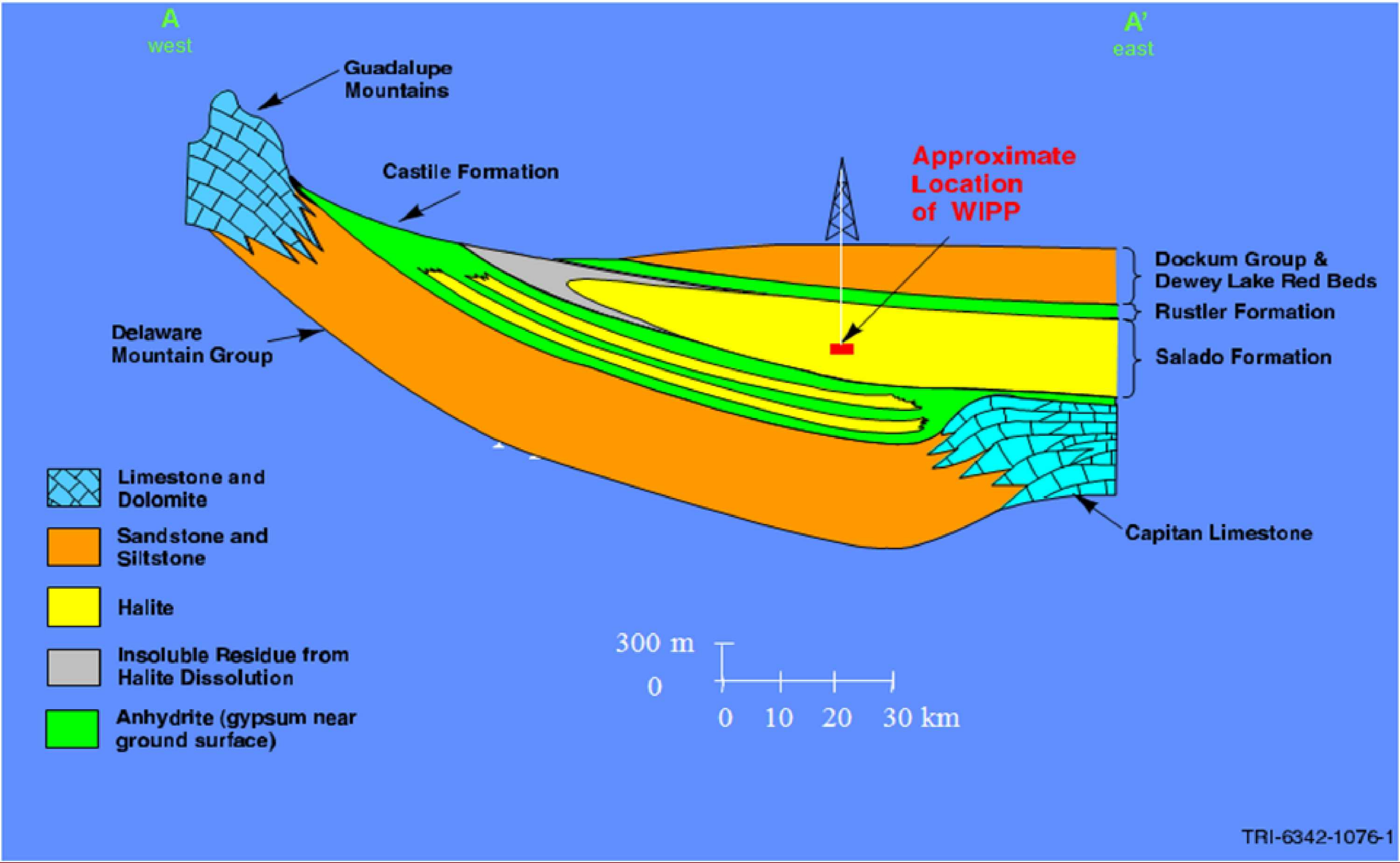

OBJECTIVE OF THIS STUDY

- To evaluate the solubility constants for $Pu_2(C_2O_4)_3 \bullet 10H_2O$, $Am_2(C_2O_4)_3 \bullet 10H_2O$, and $Cm_2(C_2O_4)_3 \bullet 10H_2O$, based on the raw solubility data in HNO_3+$H_2C_2O_4$ from [4].
- Modeling platform: EQ3/6 Version 8.0a [5, 6] with the DATA0.FM1 database [7].
- To compare the solubility constants of actinide oxalates evaluated in this work with those for lanthanide oxalates from the literature.

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[4] Burney, G.A. and Porter, J.A. (1967) Solubilities of Pu (III), Am (III), and Cm (III) Oxalates. *Inorganic and Nuclear Chemistry Letters*, *3*(3), pp.79-85.

[5] Wolery, T.J., Xiong, Y.-L., and Long, J. (2010) Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10. Carlsbad, NM: Sandia National laboratories. ERMS 550239.

[6] Xiong, Y.-L. (2011) WIPP Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Revision 1, Document Version 8.20. Supersedes ERMS 550239. Carlsbad, NM. Sandia National Laboratories. ERMS 555358

[7] Xiong, Y.-L. (2011) Release of EQ3/6 Database DATA0.FM1. Carlsbad, NM. Sandia National Laboratories. ERMS 555152, and the associated document, ERMS 555154.

Results

Table 1. Equilibrium constants at infinite dilution, 25°C and 1 bar, Pitzer interaction parameters in the Am^{3+}—NO_3^-—$C_2O_4^{2-}$ system (Preliminary)

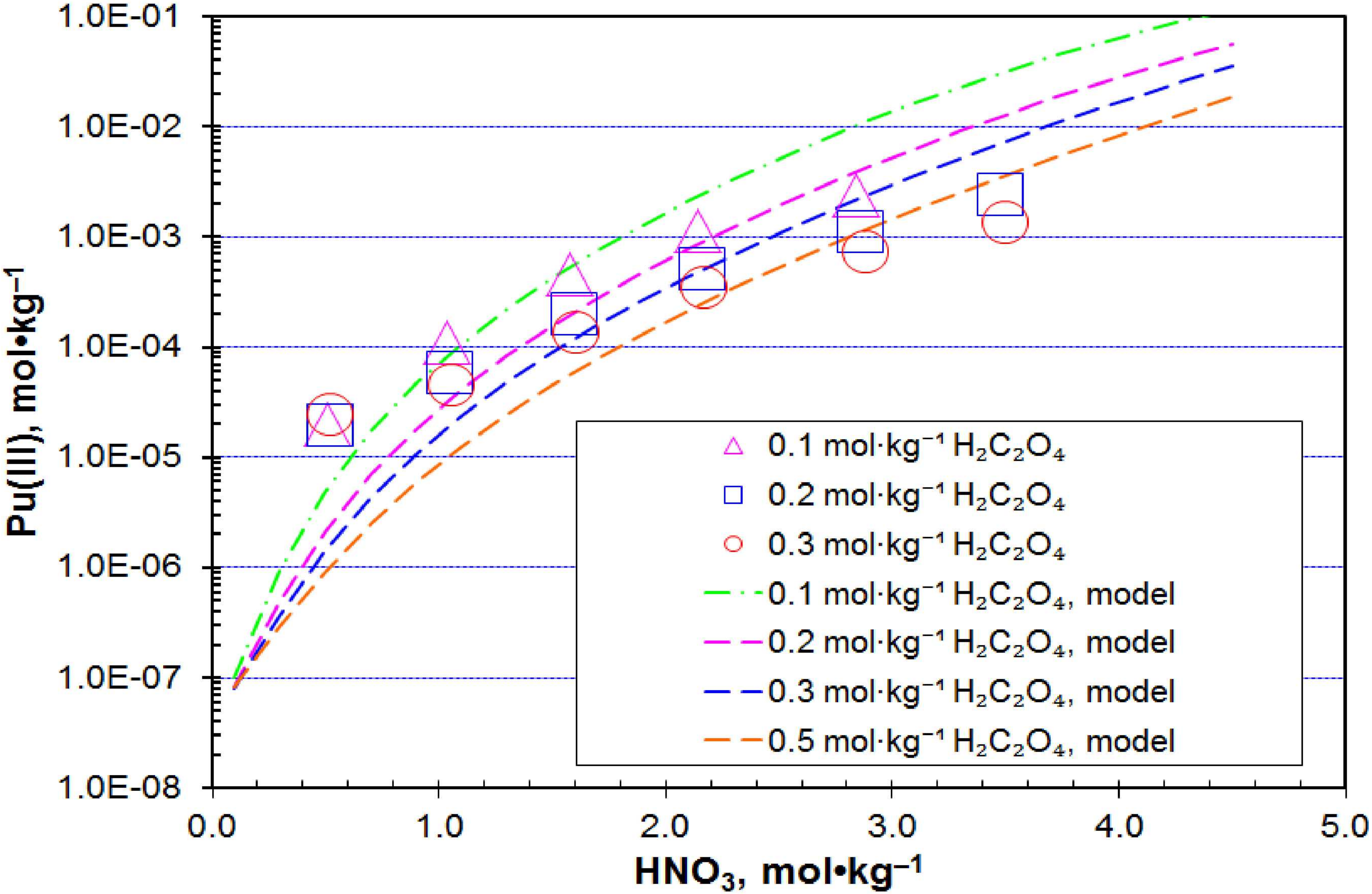
Reactions	log K_{sp}	Remarks
$Pu_2(C_2O_4)_3{\bullet}10H_2O \rightleftharpoons 2Pu^{3+} + 3C_2O_4^{2-} + 10H_2O(l)$	–31.97	This study, based on solubility data in HNO_3 + $H_2C_2O_4$
$Am_2(C_2O_4)_3{\bullet}10H_2O \rightleftharpoons 2Am^{3+} + 3C_2O_4^{2-} + 10H_2O(l)$	–30.22	This study, based on solubility data in HNO_3 + $H_2C_2O_4$
$Cm_2(C_2O_4)_3{\bullet}10H_2O \rightleftharpoons 2Cm^{3+} + 3C_2O_4^{2-} + 10H_2O(l)$	–30.80	This study, based on solubility data in HNO_3 + $H_2C_2O_4$

Pitzer Binary Interaction Parameters (Preliminary)

Species *i*	Species *j*	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}
Am^{3+}	NO_3^-	0.36175	2.97348 [A]	4.00020 [A]	0.20138

[A] These parameters are not evaluated in this work. These parameters are set to the values for Nd^{3+}—NO_3^- interaction from the database DATA0.PIT from the EQ3/6 package.

Model Verification



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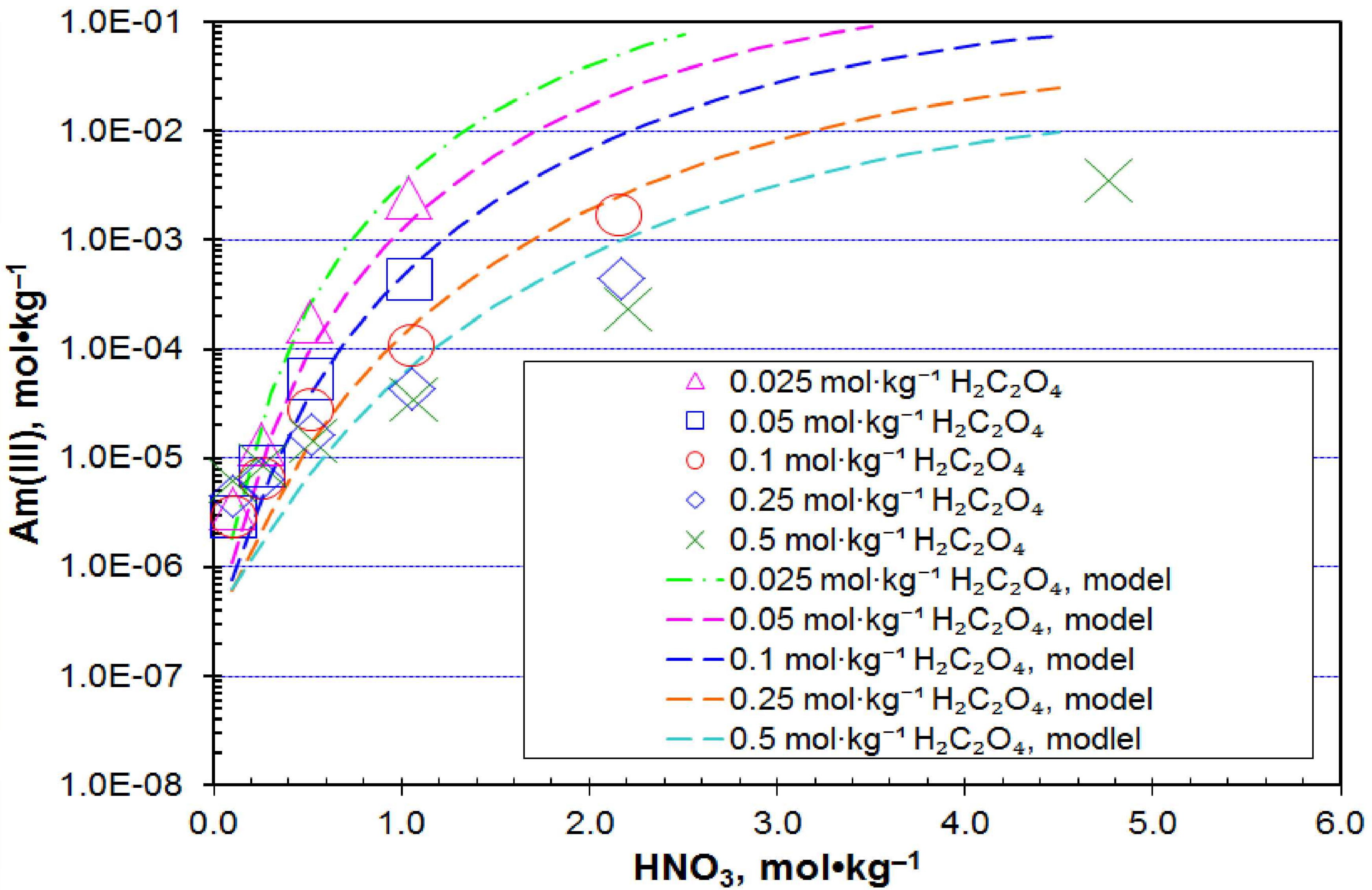
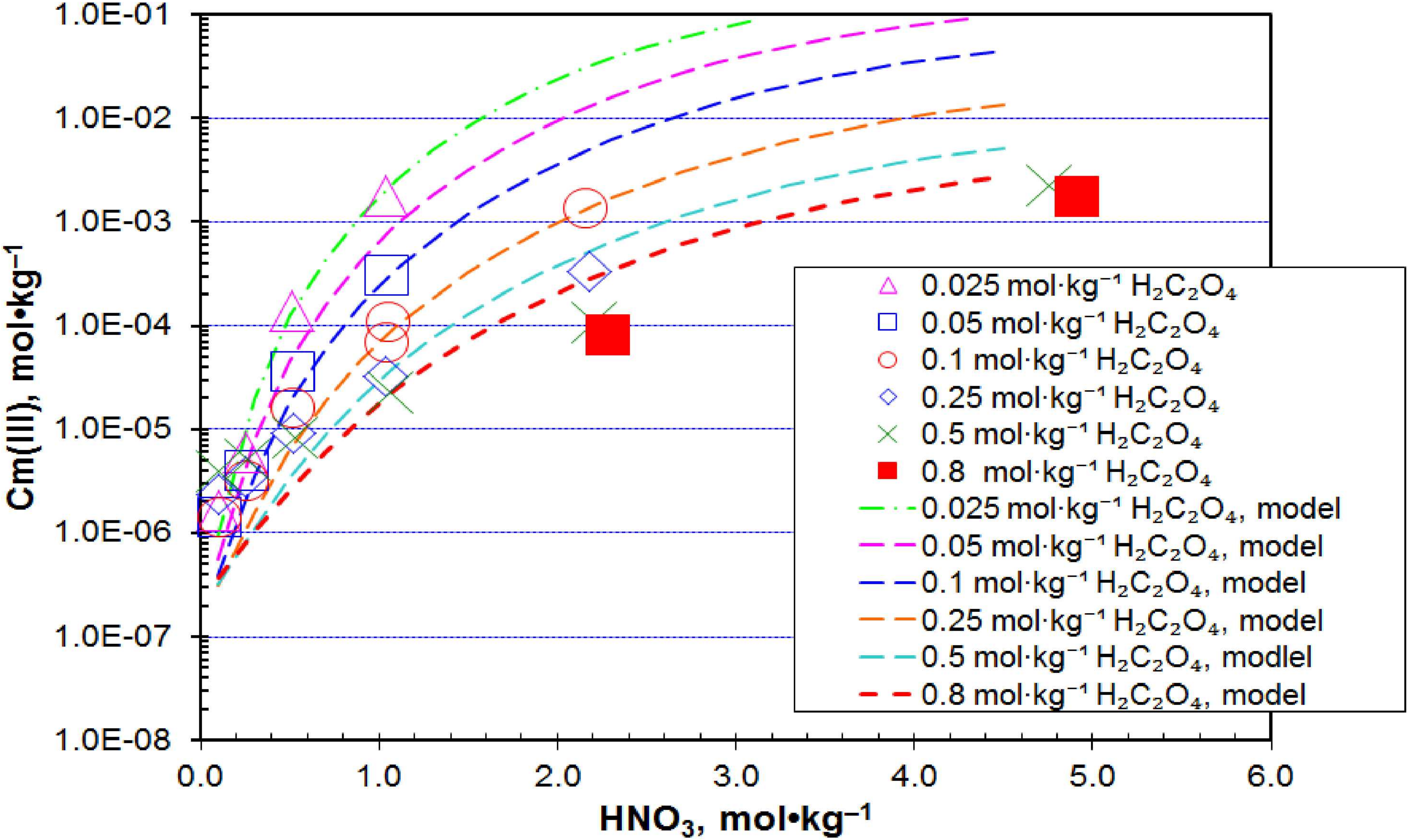


Model Verification



Comparison with Lanthanide Oxalates

Table 2. Comparison of Solubility Product Constants of Actinide Oxalates at infinite dilution, 25°C and 1 bar, with Those for Lanthanide Oxalates from Xiong (2011)

Reactions	log K_{sp}	Remarks
$Pu_2(C_2O_4)_3{\bullet}10H_2O \rightleftharpoons 2Pu^{3+} + 3C_2O_4^{2-} + 10H_2O(l)$	–31.97	This study, based on solubility data in HNO_3 + $H_2C_2O_4$, Pitzer model
$Am_2(C_2O_4)_3{\bullet}10H_2O \rightleftharpoons 2Am^{3+} + 3C_2O_4^{2-} + 10H_2O(l)$	–30.22	This study, based on solubility data in HNO_3 + $H_2C_2O_4$, Pitzer model
$Cm_2(C_2O_4)_3{\bullet}10H_2O \rightleftharpoons 2Cm^{3+} + 3C_2O_4^{2-} + 10H_2O(l)$	–30.80	This study, based on solubility data in HNO_3 + $H_2C_2O_4$, Pitzer model
$La_2(C_2O_4)_3 \rightleftharpoons 2La^{3+} + 3C_2O_4^{2-}$	–29.15 ± 0.35 (2σ)	Xiong (2011), SIT model
$Ce_2(C_2O_4)_3 \rightleftharpoons 2Ce^{3+} + 3C_2O_4^{2-}$	–30.18 ± 0.36 (2σ)	Xiong (2011), SIT model
$Pr_2(C_2O_4)_3 \rightleftharpoons 2Pr^{3+} + 3C_2O_4^{2-}$	–30.91 ± 0.42 (2σ)	Xiong (2011), SIT model
$Nd_2(C_2O_4)_3 \rightleftharpoons 2Nd^{3+} + 3C_2O_4^{2-}$	–31.57 ± 0.62 (2σ)	Xiong (2011), SIT model
$Sm_2(C_2O_4)_3 \rightleftharpoons 2Sm^{3+} + 3C_2O_4^{2-}$	–31.59 ± 0.70 (2σ)	Xiong (2011), SIT model
$Gd_2(C_2O_4)_3 \rightleftharpoons 2Gd^{3+} + 3C_2O_4^{2-}$	–32.31 ± 0.50 (2σ)	Xiong (2011), SIT model

Xiong, Y., 2011. Organic species of lanthanum in natural environments: Implications to mobility of rare earth elements in low temperature environments. *Applied geochemistry*, *26*(7), pp.1130-1137.

Summary and Future Work

- In this work, we evaluated the solubility product constants for actinide oxalates in +III oxidation state from the solubility data from the literature, based on the Pitzer model.
- The solubility product constants for actinide oxalates obtained in this work are highly consistent with those for lanthanide oxalates from the literature.
- In the future, we are to evaluate the solubility product constants for actinide oxalates in +IV, +V, and +VI oxidation states.