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URANYL OXALATE SPECIES IN NATURAL ENVIRONMENTS: STABILITY CONSTANTS FOR AQUEOUS AND SOLID URANYL OXALATE COMPLEXES

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OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- Evaluation of Stability Constants of Uranyl-Oxalate Aqueous Complexes as a Function of Ionic Strength
- Results
- Summary and Future Work

INTRODUCTION

- Actinide oxalates are important to nuclear industry and other fields:
  - Precipitation of actinide(III), actinide(IV) and actinide(VI) 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 or form aqueous actinide complexes (such as uranyl oxalate complexes) to facilitate the transport of actinide.

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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 (Cont.)

- Uranyl Oxalate Aqueous Complexes and Solid Phases:
  - In oxidizing environments, uranium is expected to be present as U(VI).
  - Uranyl ion, UO_2^{2+}, is complexed with inorganic and organic ligands including oxalate to form aqueous complexes.
  - In groundwaters and soil solutions, concentrations of oxalate are likely to be limited by precipitation of whewellite, $CaC_2O_4 \bullet H_2O$[4], which would be ~10^{-3} $mol \bullet kg^{-1}$.
    - At this level of oxalate concentrations, the contributions of uranyl oxalate complexes, $UO_2C_2O_4(aq)$ and $UO_2(C_2O_4)_2^{2-}$, are expected to be important.

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[4] Purvis, O.W., Bailey, E.H., McLean, J., Kasama, T. and Williamson, B.J., 2004. Uranium biosorption by the lichen Trapelia involuta at a uranium mine. *Geomicrobiology Journal*, *21*(3), pp.159-167.

INTRODUCTION (Cont.)

- Uranyl Oxalate Aqueous Complexes and Solid Phases:
  - In the NEA review, the U(VI)-Oxalate system was reviewed using the SIT model [5].
    - The validity of the NEA review is limited to the ionic strength of ~3.5 mol•kg^{-1}.
    - The application of the NEA review to higher ionic strength environments, such as disposal concepts in sedimentary basins and salt formations, is beyond its validity.
    - Therefore, there is a need for a model valid to higher ionic strengths.

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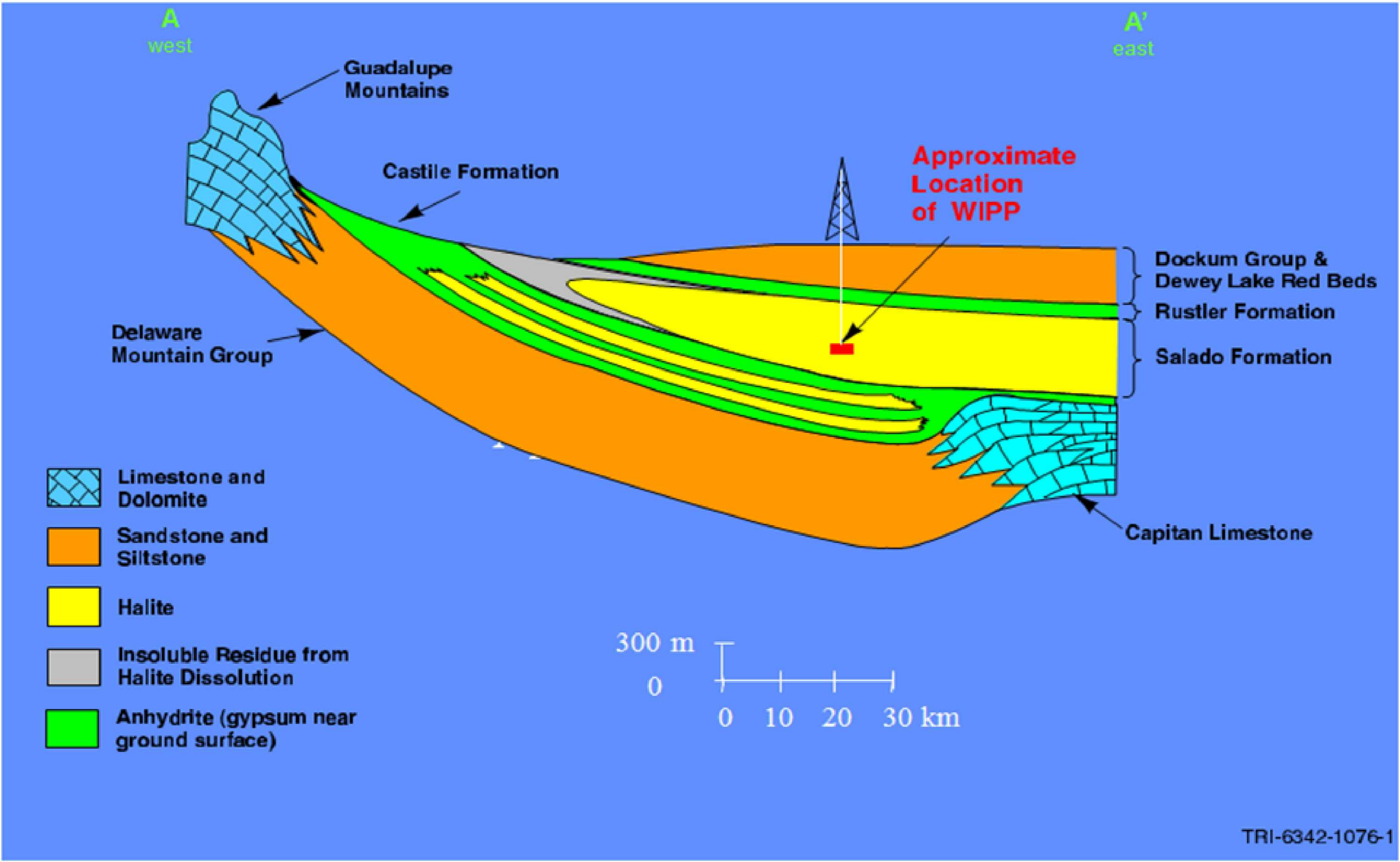
[5] Hummel, W., Puigdomènech, I., Rao, L. and Tochiyama, O., 2007. Thermodynamic data of compounds and complexes of U, Np, Pu and Am with selected organic ligands. *Comptes Rendus Chimie*, *10*(10-11), pp.948-958.

INTRODUCTION (Cont.), WIPP



INTRODUCTION (Cont.), WIPP Brines

Appendix B

Concentration Scales in Molarity (Moles/L Solution) and Molality (Moles/kg H_2O) for Synthetic Salado (GWB) and Castile (ERDA-6) Brines

Chemical Species	GWB	GWB	ERDA-6	ERDA-6
	Moles/L sol'n	Moles/kg H_2O	Moles/L sol'n	Moles/kg H_2O
Na^+	3.53	3.98	4.85	5.44
K^+	0.467	0.526	9.70×10^{-2}	0.109
Li^+	4.48×10^{-3}	5.05×10^{-3}	None	None
Ca^{2+}	1.38×10^{-2}	1.56×10^{-2}	1.20×10^{-2}	1.34×10^{-2}
Mg^{2+}	1.02	1.15	1.90×10^{-2}	2.13×10^{-2}
Cl^-	5.61	6.32	4.64	5.20
Br^-	2.66×10^{-2}	3.00×10^{-2}	1.10×10^{-2}	1.23×10^{-2}
SO_4^{2-}	0.178	0.200	0.167	0.187
$B_4O_7^{2-}$	3.95×10^{-2}	4.45×10^{-2}	1.57×10^{-2}	1.76×10^{-2}

OBJECTIVE OF THIS STUDY

- Using the Pitzer model, we evaluate the stability constants for $UO_2C_2O_4(aq)$ and $UO_2(C_2O_4)_2^{2-}$.
- Modeling platform: EQ3/6 Version 8.0a [5, 6] with the DATA0.FM2 database [7].
- The basis for the oxalate system in our modeling is that of Thakur et al. [8].

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[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., Domski, P.S.: (2016) Updating the WIPP Thermodynamic Database, Revision 1, Supersedes ERMS 565730. Carlsbad, NM: Sandia National Laboratories. ERMS 566047

[8] P. THAKUR, Y.-L. XIONG AND BORKOWSKI, M., "An improved thermodynamic model for the complexation of trivalent actinides and lanthanide with oxalic acid valid to high ionic strength," *Chemical Geology*, ***413***, 7-17 (2015).

Results

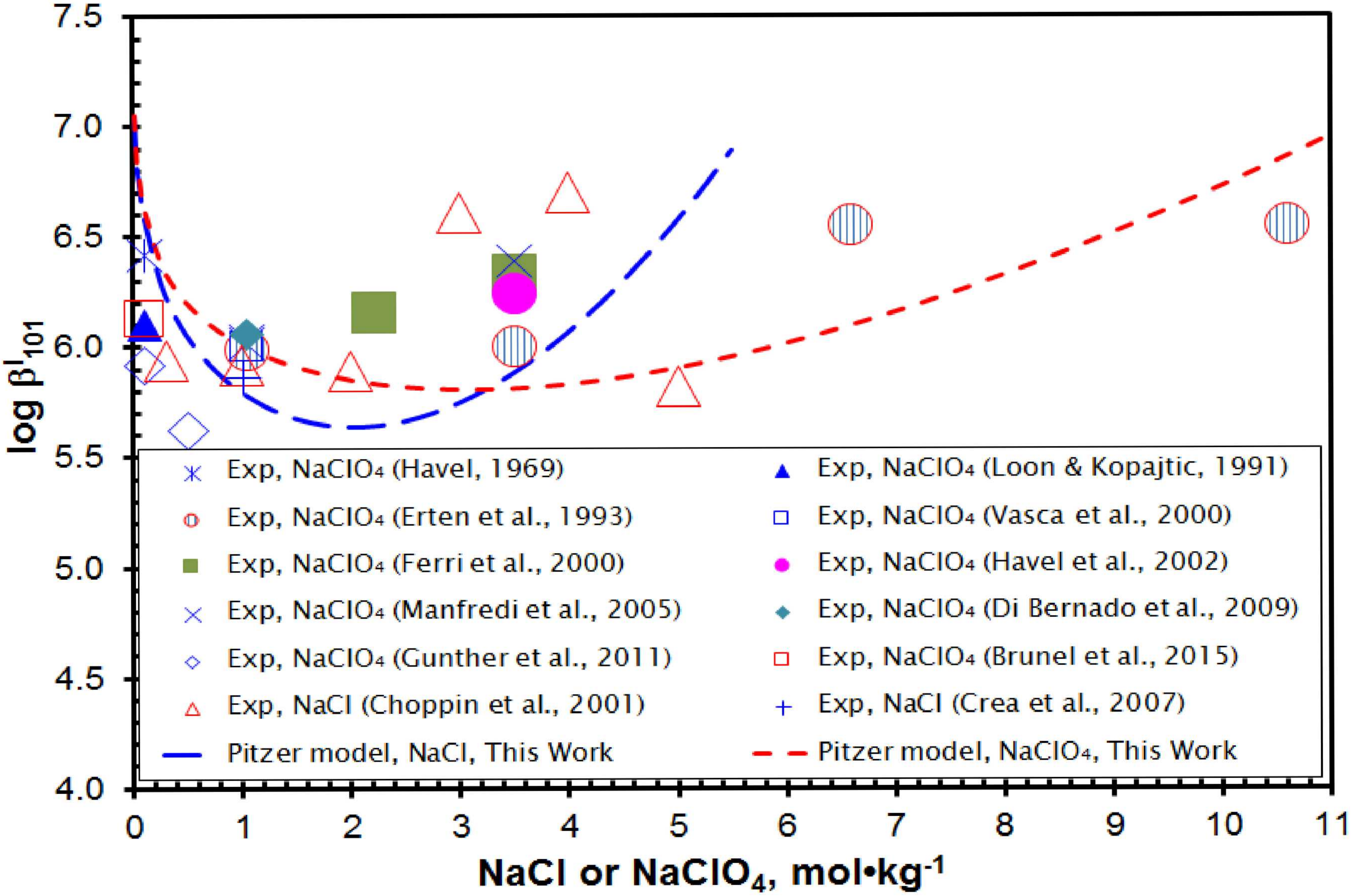
Table 1. A thermodynamic model with the Pitzer formalism for the system Na^+— UO_2^{2+}— Cl^-— ClO_4^-— $C_2O_4^{2-}$ at 25°C.

Pitzer binary interaction parameters				
Pair	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	Ref
UO_2^{2+}—Cl^-	0.4274	1.644	–0.0184	[9]
UO_2^{2+}—ClO_4^-	0.61133	2.14425	0.02164	[9]
Na^+—$HC_2O_4^-$	–0.2886	0.29	0.068	[8]
Na^+—$C_2O_4^{2-}$	–0.2770	1.74	0.122	[8]
Na^+—$UO_2(C_2O_4)_2^{2-}$	-1.0368	1.74	0.3646	PW
Pitzer ternary interaction parameters for neutral species				
Pair			ζ	Ref
Na^+—Cl^-—$UO_2C_2O_4(aq)$			–0.08479	PW
Na^+—ClO_4^-—$UO_2C_2O_4(aq)$			0.09149	PW
Pitzer mixing parameters				
ClO_4^-—$UO_2(C_2O_4)_2^{2-}$			0.1148	PW
Equilibrium Constants				
Reaction			log K	Ref
$H_2C_2O_4(aq) \rightleftharpoons 2H^+ + C_2O_4^{2-}$			–6.07	[8]
$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{2-}$			–4.36	[8]
$UO_2^{2+} + C_2O_4^{2-} \rightleftharpoons UO_2C_2O_4(aq)$			7.54±0.20	PW
$UO_2^{2+} + 2C_2O_4^{2-} \rightleftharpoons UO_2(C_2O_4)_2^{2-}$			11.57±0.20	PW

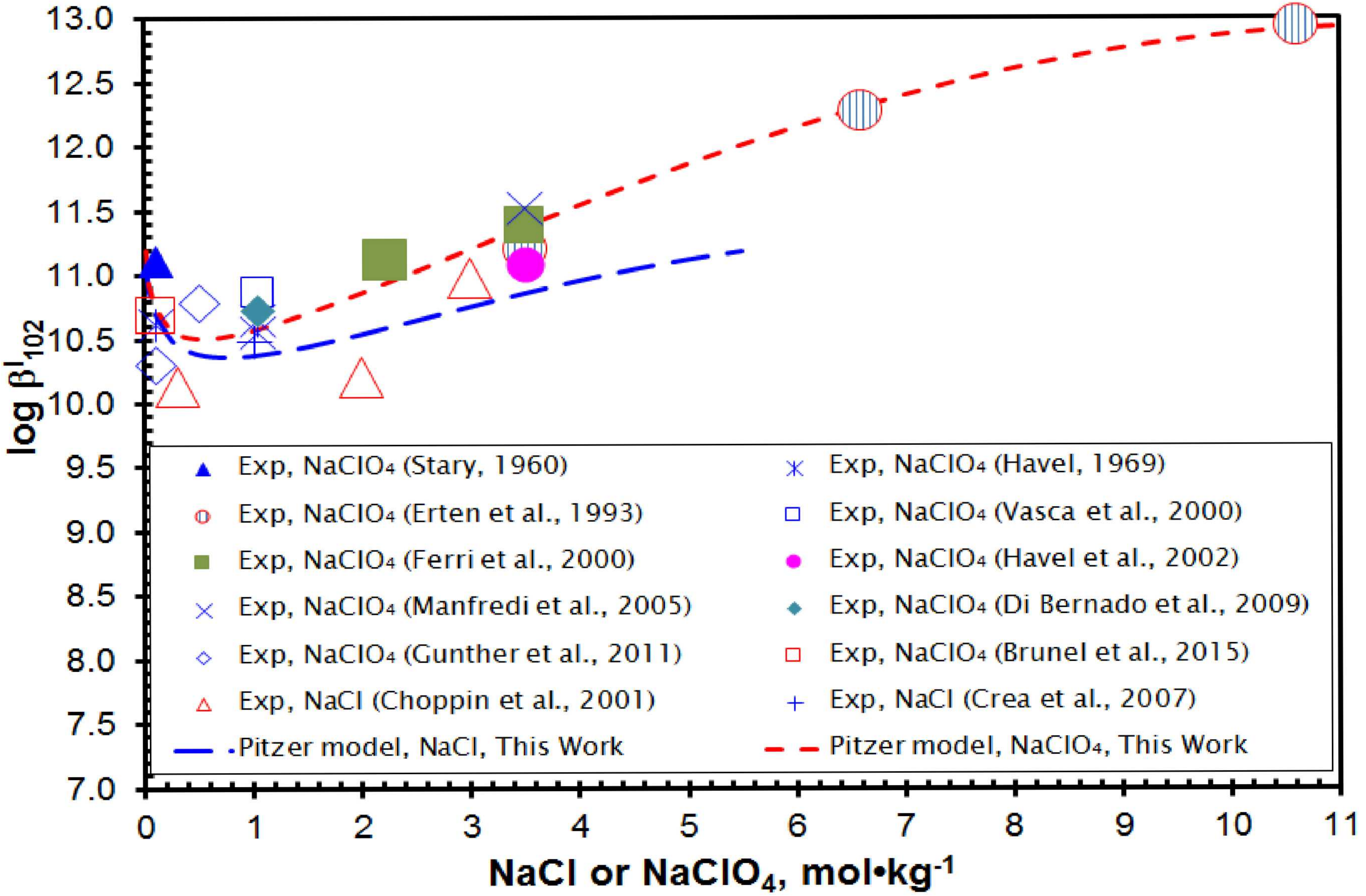
PW: Present Work.

[9] K. S. PITZER, Ion interaction approach: theory and data correlation. *Activity coefficients in electrolyte solutions*, *2*, pp.75-153 (1991).

Model Verification



Model Verification



Comparison with Previous Results

Equilibrium Constants			
Reaction	log β	log β	log β
$UO_2^{2+} + C_2O_4^{2-} \rightleftharpoons UO_2C_2O_4(aq)$	7.54±0.20	7.13±0.16	7.38±0.07
$UO_2^{2+} + 2C_2O_4^{2-} \rightleftharpoons UO_2(C_2O_4)_2^{2-}$	11.57±0.20	11.65±0.15	11.72±0.10
References	PW [A]	NEA [B]	Ferri et al. [2] [C]

[A] Pitzer model

[B] SIT model

[C] SIT model

Summary and Future Work

- In this work, we evaluated the stability constants for $UO_2C_2O_4(aq)$ and $UO_2(C_2O_4)_2^{2-}$, based on the Pitzer model.
- The model developed in this work is valid to high ionic strength, up to ~11 mol•kg^{-1}.
- In the future, we are to evaluate the solubility product constants of uranyl oxalates based on the model established in this work.