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Experimental Determination of Solubilities of Di-calcium Ethylenediaminetetraacetic Acid [$Ca_2C_{10}H_{12}N_2O_8(s)$] in NaCl and $MgCl_2$ Solutions to High Ionic Strengths and Its Pitzer Model: Applications to Geological Disposal of Nuclear Waste and Other Low Temperature Environments

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INTRODUCTION

- Ethylenediaminetetraacetate acid ($C_{10}H_{16}N_2O_8$, and its dissociated forms, abbreviated as EDTA hereafter) is present in nuclear waste streams in the Waste Isolation Pilot Plant (WIPP), a U.S. Department of Energy (DOE) repository in southeast New Mexico for defense-related transuranic (TRU) waste.
- It has a significant effect on the Performance Assessment (PA) for the geological repositories for nuclear waste because of its ability to form strong aqueous complexes with actinides, especially actinides in +III oxidation state, increasing solubilities of actinides.
- The EDTA inventory for the WIPP was 3.54×10^2 kg for the 2009 Compliance Recertification Application Performance Assessment Baseline Calculations (CRA-2009 PABC) (Brush and Xiong, 2009).
- The estimated EDTA inventory present in the CANDECON resin for the Canadian reference low and intermediate level waste inventory for the deep geologic repository is much higher, and in the order of 4.8×10^4 kg (Ontario Power Generation, 2010).
- In the current PA in the WIPP, EDTA concentrations are inventory-limited.
- Should the inventory of EDTA increase, the concentrations of EDTA would be limited by solubility of $Ca_2EDTA(s)$, as $Ca_2EDTA(s)$ has relatively low solubilities in comparison with other EDTA-containing solids.

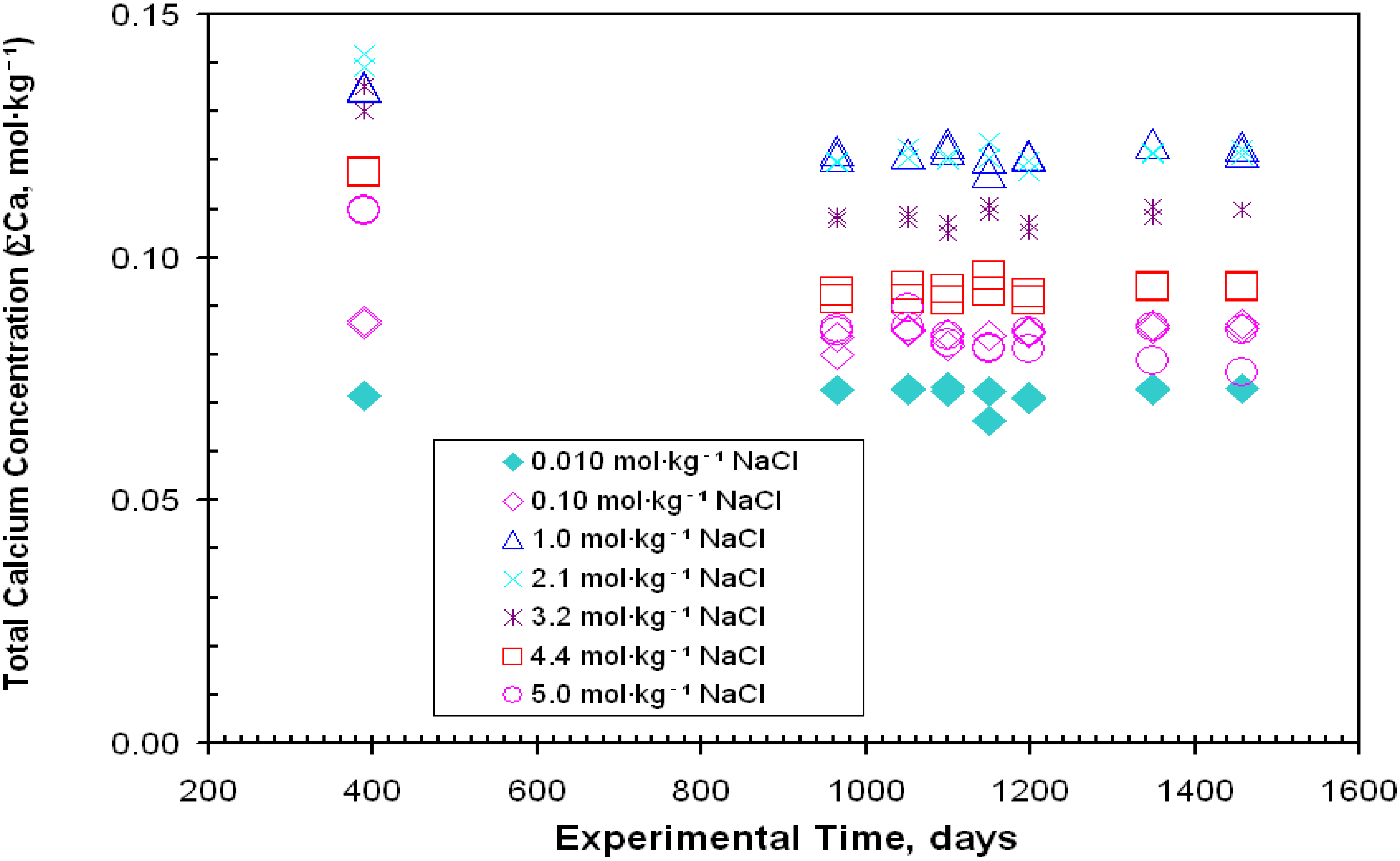
PURPOSE OF THIS STUDY

- To determine solubilities of $Ca_2EDTA(s)$ in a wide range of ionic strengths.
- Based on solubility data obtained, to develop a Pitzer model to describe accurately the Na^{+}—Ca^{2+}—Mg^{2+}—Cl^{-}—$EDTA^{4-}$ system.
- Modeling platform: EQ3/6 Version 8.0a (Wolery, Xiong, Long, 2010; Xiong, 2011)

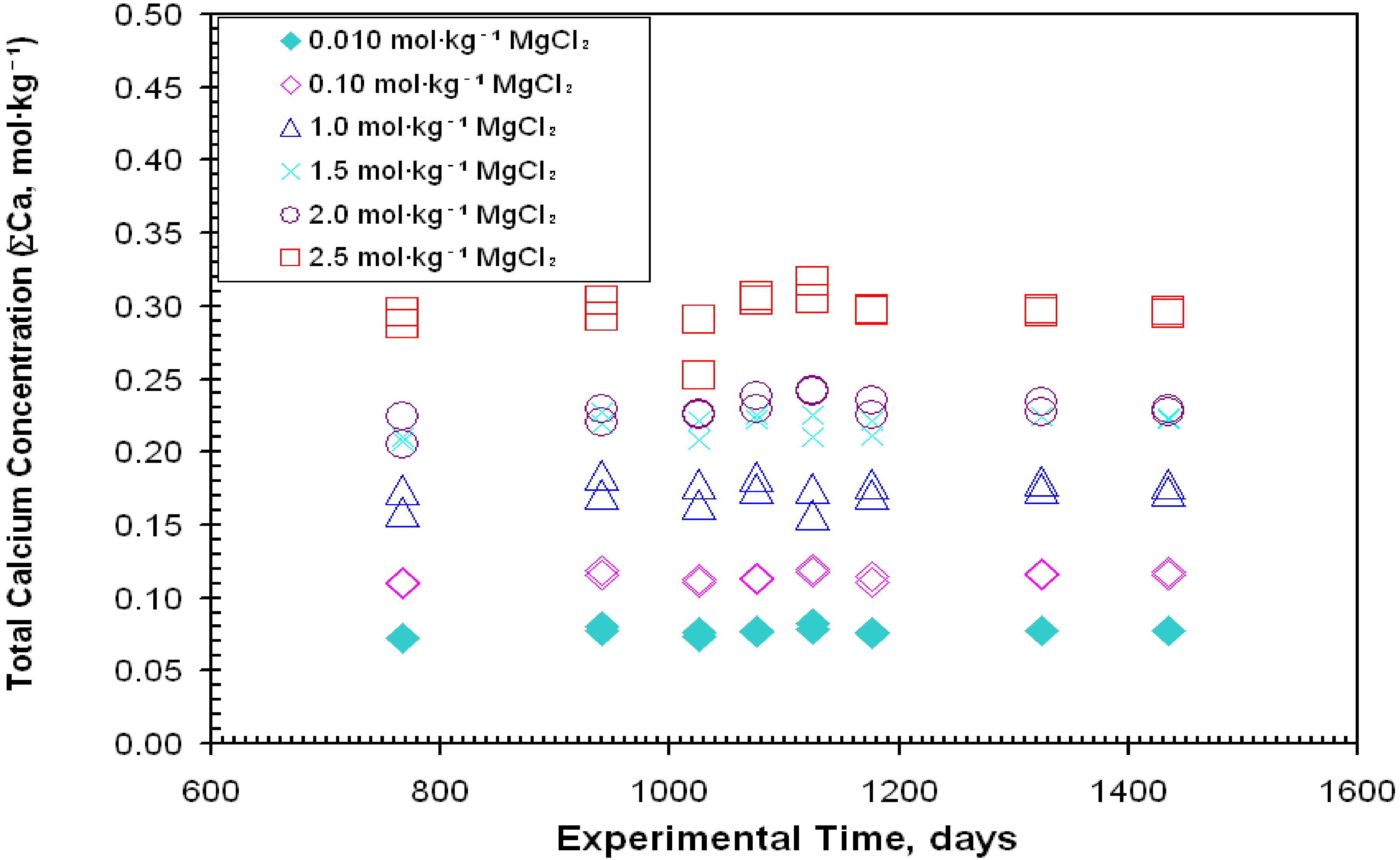
EXPERIMENTAL METHOD

- Experimental conditions: T = 22.5 ± 0.5 ^{o}C
- Starting material: high purity $Ca_2EDTA(s)$ from ACROS ORGANICS
- Long-term undersaturation experiments
- Supporting solutions:
  - 0.010-5.0 mol•kg^{-1} NaCl
  - 0.010-2.5 mol•kg^{-1} $MgCl_2$ with ionic strengths up to 7.5 mol•kg^{-1}
- Ca concentrations determined by using inductively coupled plasma atomic emission spectrometer (ICP-AES). EDTA by using ion chromatograph (IC)
- pcH measured using pH electrode with correction factors

Experimental Results



Experimental Results



Pitzer Model

Table 1. The Pitzer model for the Na^{+}—Mg^{2+}—Ca^{2+}—Cl^{-}—$EDTA^{4-}$—H_2O system at 25°C

Pitzer Parameters				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Na^{+}	$CaEDTA^{2-}$	–0.1935 [A]	1.74 [A]	0.1458 [A]
Na^{+}	$EDTA^{4-}$	1.016 [B]	11.6 [B]	0.001 [B]
Na^{+}	$HEDTA^{3-}$	0.5458 [B]	5.22 [B]	–0.048 [B]
Mg^{2+}	$CaEDTA^{2-}$	0.525 [A]	3.27 [A]	0 [A]
Ca^{2+}	$MgEDTA^{2-}$	0.08436 [A]	3.27 [A]	0 [A]
Mg^{2+}	$EDTA^{4-}$	–0.01 [A]	11.6 [A]	0.3 [A]
Equilibrium Constants at infinite dilution for Dissolution Reaction of $Ca_2EDTA(s)$ and Formation Reaction of $CaEDTA^{2-}$				
Reactions			$\log K_{sp}^{0}$ or $\log \beta_1^{0}$	
$Ca_2EDTA(s) = 2Ca^{2+} + EDTA^{4-}$			–15.39 ± 0.10 [A]	
$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-}$			11.02 ± 0.05 [A]	

[A] Evaluated in this study.
[B] From the data0.fmt (Wolery et al., 2010; Xiong, 2011).

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Model Verification

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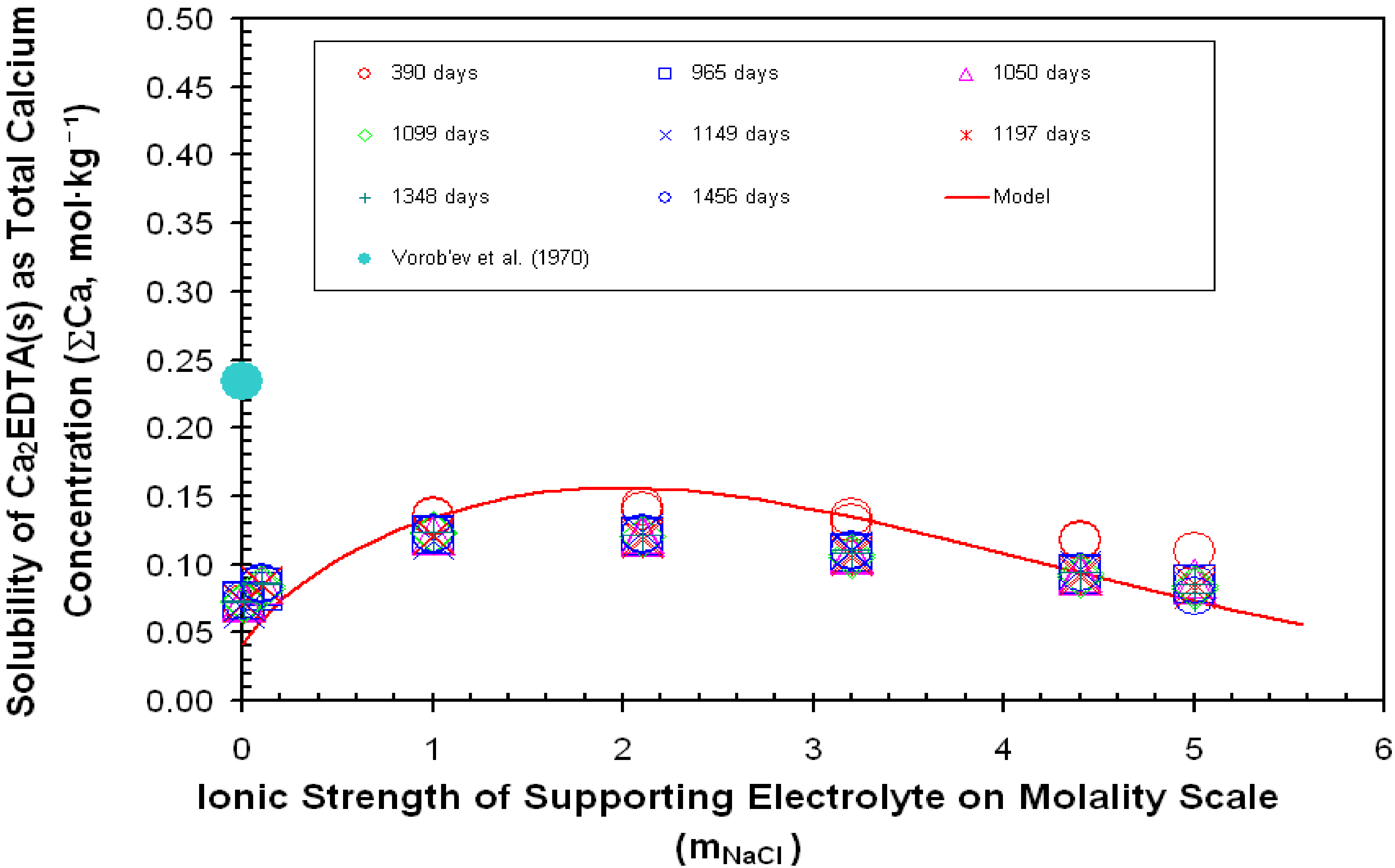
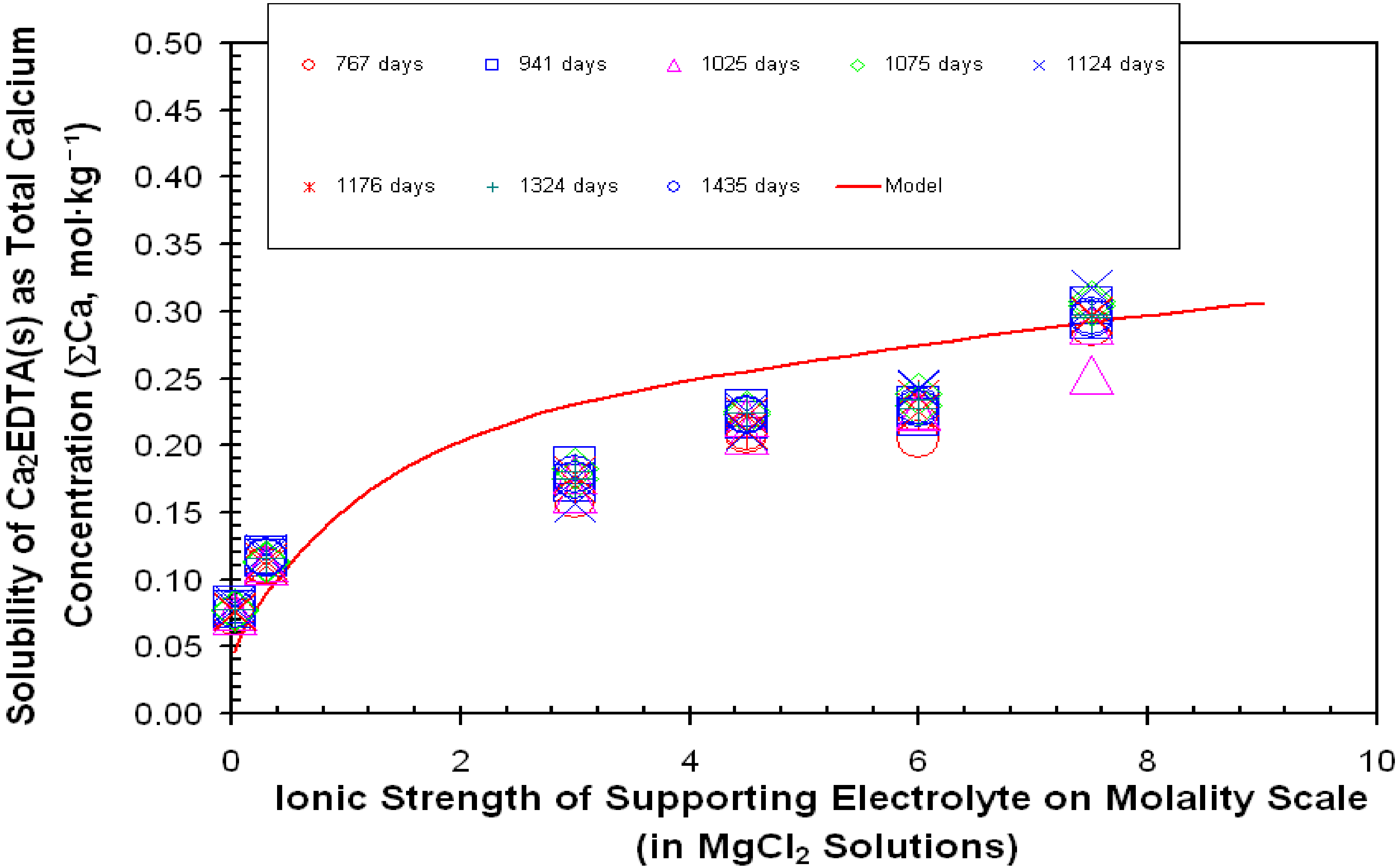


Model Verification (continued)



Applications: Geological Repository in Granite

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Table 2. The chemical compositions of the groundwater and predicted total EDTA concentration in equibrium with $Ca_2EDTA(s)$ at 25°C for the geological repository in granite at Olkiluoto, Finland*

Total Dissoved Salts (TDS), mg/L	Ionic Strength, $mol \bullet kg^{-1}$	pH**	Na^+ $mol \bullet kg^{-1}$	K^+ $mol \bullet kg^{-1}$	Mg^{2+} $mol \bullet kg^{-1}$	Ca^{2+} $mol \bullet kg^{-1}$
49,483	1.36	4.5 to 9.5	0.3672	5.0×10^{-4}	0.0015	0.2590
Sr^{2+} A $mol \bullet kg^{-1}$	Mn^{2+} A $mol \bullet kg^{-1}$	Cl^- $mol \bullet kg^{-1}$	SO_4^{2-} $mol \bullet kg^{-1}$	ΣH_4SiO_4 A $mol \bullet kg^{-1}$	ΣCO_3^{2-} $mol \bullet kg^{-1}$	$\Sigma EDTA^{4-}$, B $mol \bullet kg^{-1}$
0.00116	9.5×10^{-5}	0.8783	5×10^{-5}	2.1×10^{-4}	4×10^{-5}	2.7×10^{-2} to 2.5×10^{-2}

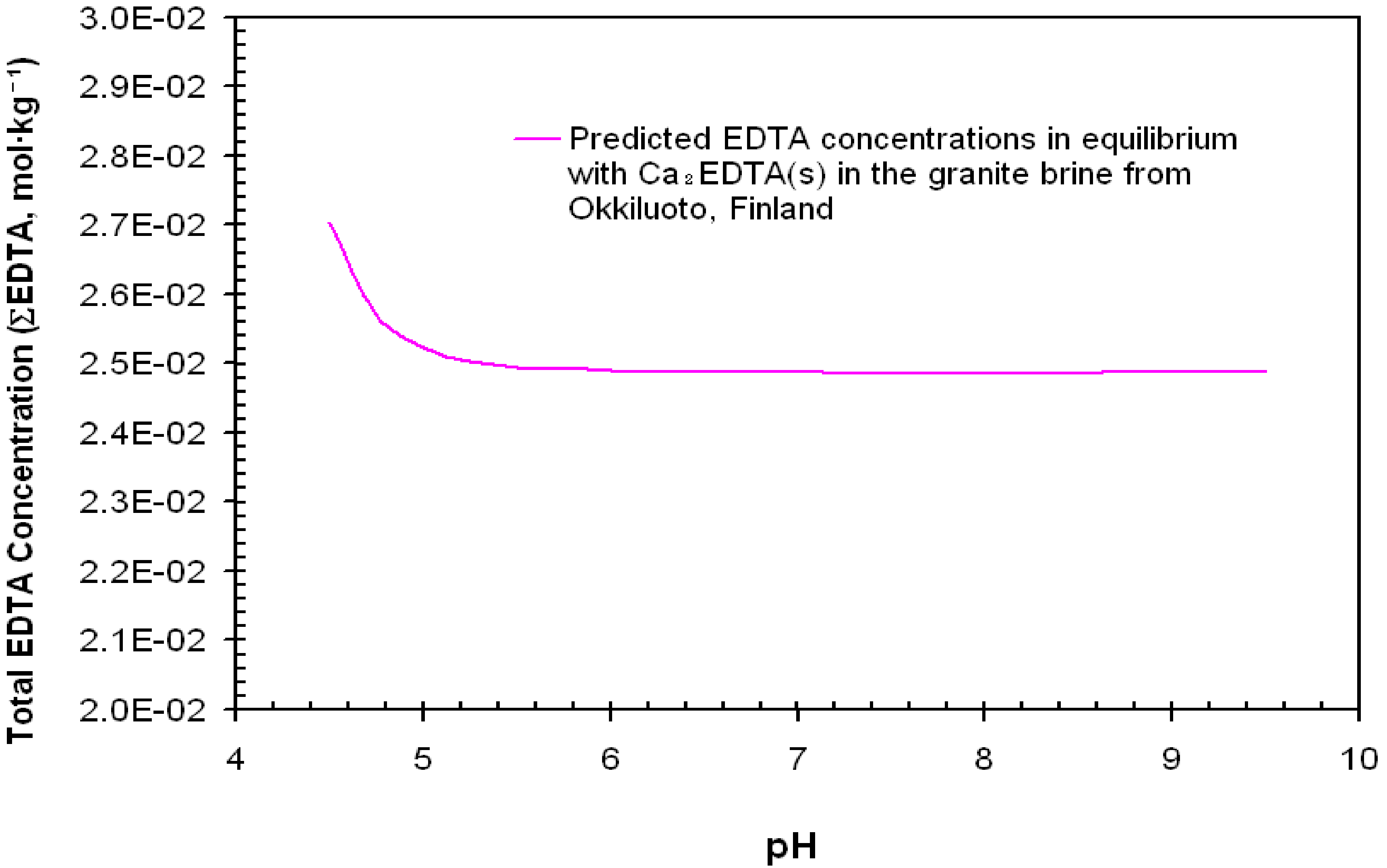
* The chemical compositions refer to the groundwater from the OL-KR12 borehole at the depth of 708 m taken from Pitkanen et al. (2007) and POSIVA (2010). The original concentrations on molar scale ($mol \bullet L^{-1}$) are converted to those on molal scale ($mol \bullet kg^{-1}$) based on the solution density (1.0323 g/mL) calculated from TDS, according to the density model of NaCl solutions.

** In POSIVA (2010), the pH is 8.2. In the model calculations, the pH is modelled from 4.5 to 9.5.

[A] Those components are not inputed for the calculation of EDTA concentration, as they are not supported by the database and do not affect the solubility of $Ca_2EDTA(s)$.

[B] Calculated based on equilibrium with $Ca_2EDTA(s)$.

Applications: Geological Repository in Granite



Applications: Model Soil Solution

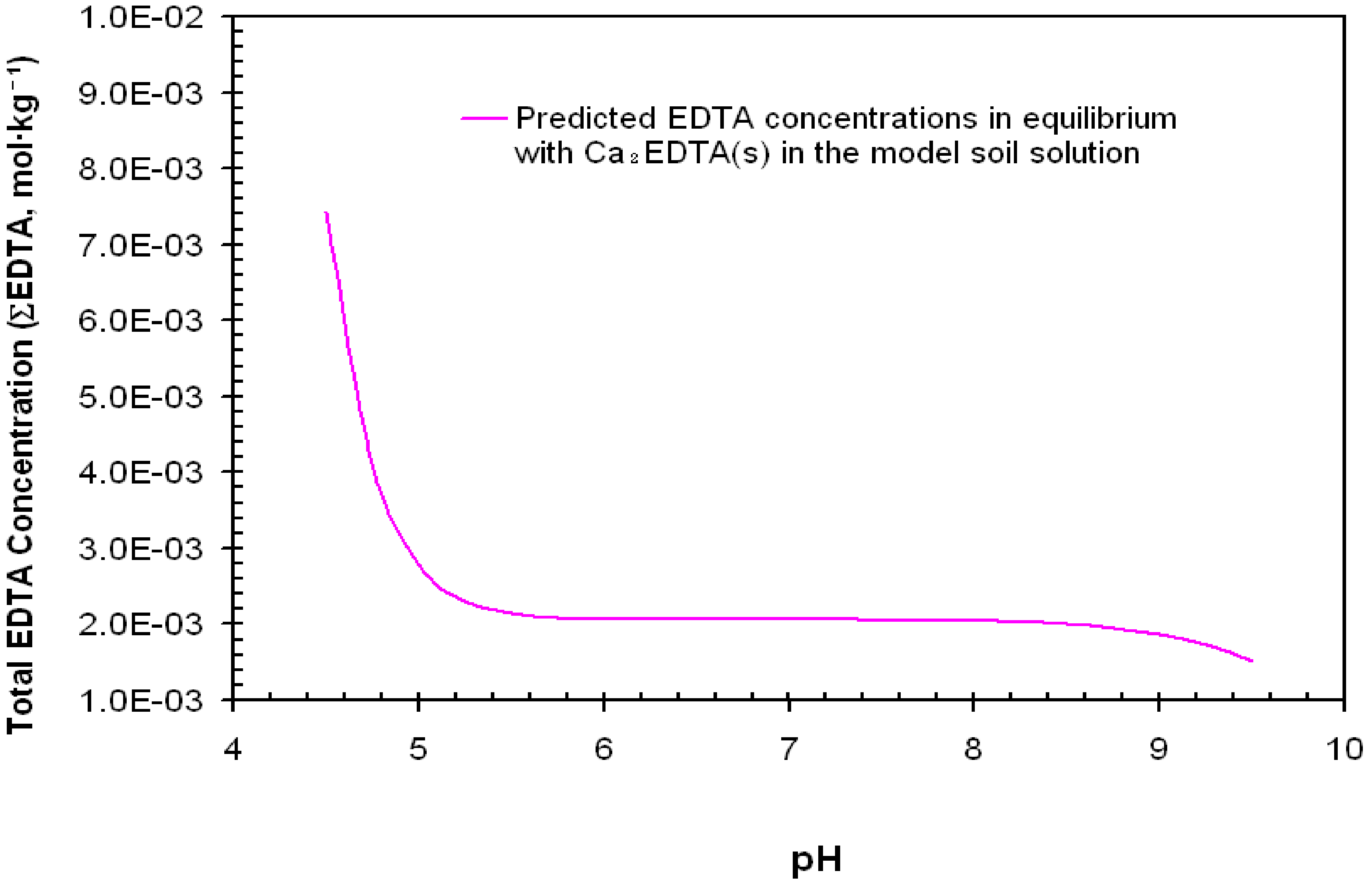
Model soil solution is from the recipe in Xiong (2009), which was modified from Wood (2000).

- In the calculation of solubility of $Ca_2EDTA(s)$ in gypsiferous soils, both calcium and sulfate concentrations are assumed to be controlled by the equilibrium with gypsum.
- Total dissolved inorganic carbon is assumed to be controlled by the equilibrium with the atmospheric CO_2 ($10^{-3.5}$ bars).

Wood, S.A., 2000. Organic matter: Supergene Enrichment and Dispersion, in *Ore Genesis and Exploration: The Roles of organic matter. Reviews in Economic Geology, Vol. 9* (Eds T. H. Giordano, R. M. Kettler, S. A. Wood), pp. 157–192 (Society of Economic Geologist, Littleton, CO).

Xiong, Y.-L., 2009. The aqueous geochemistry of thallium: speciation and solubility of thallium in low temperature system. Environmental Chemistry, 6(5): 441–451.

Applications: Model Soil Solution



Conclusions

In this study, an accurate thermodynamic model has been developed for the Na^{+}—Ca^{2+}—Mg^{2+}—Cl^{-}—$EDTA^{4-}$ system to high ionic strengths

- For the first time, the solubility constant for $Ca_2EDTA(s)$ is determined. The log K at 25°C and infinite dilution is –15.39 ± 0.10.
- In addition to the interactions between Na^{+} and EDTA-containing species, the model also contains the interactions between Mg^{2+} and $CaEDTA^{2-}$, between Ca^{2+} and $MgEDTA^{2-}$, etc.
- $Ca_2EDTA(s)$ could become a solubility-controlling phase for EDTA in the geological repositories for nuclear waste when the inventories of EDTA reach certain levels.

References

Brush, L.H., and Xiong, Y.-L. (2009). Calculation of Organic-Ligand Concentrations for the WIPP CRA-2009 PABC. Analysis Report, June 16, 2009. Carlsbad, NM: Sandia National Laboratories. ERMS 551481.

Ontario Power Generation, Inc. (2010). Reference Low and Intermediate Level Waste Inventory for the Deep Geologic Repository. 00216-REP-03902-00003-R003.

Pitkänen, P., Ahokas, H., Ylä-Mella, M., Partamies, S., Snellman, M. and Hellä, P. (2007). Quality review of hydrochemical baseline data from the Olkiluoto site. Olkiluoto, Finland: Posiva Oy. Report POSIVA 2007-05.

POSIVA (2010). Models and Data Report 2010. POSIVA 2010-01. Posiva Oy, Olkiluoto, Finland.

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.

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.