Experimental Determination of Solubilities of Di-calcium
Ethylenediaminetetraacetic Acid Hydrate
[Ca₂C₁₀H₁₂N₂O₈•7H₂O(s)] in NaCl and MgCl₂ 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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ABSTRACT

In this study, solubility measurements on di-calcium ethylenediaminetetraacetic acid hydrate [$\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8 \cdot 7\text{H}_2\text{O}(\text{s})$, abbreviated as $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$] as a function of ionic strength are conducted in NaCl solutions up to $I = 4.4 \text{ mol} \cdot \text{kg}^{-1}$ and in MgCl_2 solutions up to $I = 7.5 \text{ mol} \cdot \text{kg}^{-1}$, at room temperature ($22.5 \pm 0.5^\circ\text{C}$). The solubility constant ($\log K_{sp}^0$) for $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ and formation constant ($\log \beta_1^0$) for CaEDTA^{2-} ,

are determined as -15.57 ± 0.10 and 11.50 ± 0.05 , respectively, based on the Pitzer model with a set of Pitzer parameters describing the specific interactions in NaCl and MgCl_2 media.

The solubility measurements and thermodynamic modeling indicate that $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ could become a solubility-controlling phase for EDTA in geological repositories for nuclear waste when the inventories of EDTA reach the saturation concentrations for $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$. The model developed in this work would also enable researchers to calculate the optimal EDTA concentrations to be used for remediation of soils contaminated with heavy metals, and to calculate the maximum

EDTA concentrations that could be present in soils after an EDTA washing technology has been applied.

1. INTRODUCTION

Ethylenediaminetetraacetate acid ($C_{10}H_{16}N_2O_8$, and its dissociated forms, abbreviated as EDTA hereafter) is present in nuclear waste streams (Brush and Xiong, 2009), as EDTA is used in decontamination processes in the nuclear field (Hummel et al., 2005). Therefore, 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 the +III oxidation state, increasing solubilities of actinides. As an example, the 2009 EDTA inventory in the form of NaH_3EDTA for the Waste Isolation Pilot Plant (WIPP), a U.S. DOE geological repository for defense-related transuranic (TRU) waste, was 3.54×10^2 kg for the 2009 Compliance Recertification Application Performance Assessment Baseline Calculations (CRA-2009 PABC) (Brush and Xiong, 2009), and the calculated EDTA concentration in brines for CRA-2009 was 7.42×10^{-5} mol•kg⁻¹ (Brush and Xiong, 2009). The predicted total solubility of $Am(OH)_3(s)$ in equilibrium with the assemblage of halite($NaCl$)-anhydrite($CaSO_4$)-brucite($Mg(OH)_3$)-hydromagnesite($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$)-phase 5 ($Mg_5Cl(OH)_5 \cdot 4H_2O$) in the WIPP Generic Weep Brine (GWB) was 2.26×10^{-6} mol•kg⁻¹ in which $AmEDTA^-$ accounted for 90.5% (i.e., 2.05×10^{-6} mol•kg⁻¹) (Brush et al., 2009). Similarly, the predicted total solubility of $Am(OH)_3(s)$ in equilibrium with the assemblage of halite($NaCl$)-anhydrite($CaSO_4$)-brucite($Mg(OH)_3$)-hydromagnesite($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) in the WIPP Energy Research and Development Administration Well 6 (EDRA-6) brine was 1.70×10^{-6} mol•kg⁻¹, in which $AmEDTA^-$ accounted for 93.9% (i.e., 1.59×10^{-6} mol•kg⁻¹) (Brush et al., 2009). Interestingly, the estimated EDTA inventory present in

the CANDECON resin for the Canadian reference low and intermediate level waste destined for deep geologic disposal is also high, on the order of 4.8×10^4 kg (Ontario Power Generation, 2010).

In addition, EDTA is present in other low temperature environments. EDTA is widely used in industry including pharmaceutical, photographic, and textile and paper industries, in household detergents, and in industrial cleaning. The annual usage of EDTA in Europe alone is on the order of 30,000 metric tons (Kari and Giger, 1996). Therefore, EDTA is present in waste waters, even municipal wastewaters, and since it is not biodegradable and it persists in the environment (e.g., Kari and Giger, 1996; Barber et al., 2013). Hence, it is an environmental concern. For instance, in UK sewage effluents, the concentrations of EDTA are up to 1.6 mg/L ($\sim 5.5 \times 10^{-6}$ mol•kg⁻¹) (Garland et al., 1985). A concern is that the presence of EDTA in such wastewaters could remobilize toxic heavy metals from sediments and sewage sludges. On the other hand, this known affiliation of EDTA with heavy metals makes it useful in decontamination of soils polluted by heavy metals such as Pb and Zn (e.g., Theodoratos et al., 2000; Zeng et al., 2005), because it forms strong aqueous complexes with targeted heavy metals, and therefore is an important complexing agent for extraction of targeted metal ions presented as contaminants.

The solid phases for EDTA include solid EDTA acid (Karhu et al., 1999), i.e., H₄EDTA(s), acidic forms of EDTA salts with alkali and alkaline earth metal ions such as M₂^(+I)H₂EDTA and M^(+II)H₂EDTA (Fiorucci et al., 2002), where M(+I) and M(+II) denote alkali and alkali earth metal ions, respectively. There are also EDTA basic salts with alkali and alkali earth metals such as M^(+II)M^(+I)₂EDTA and M^(+II)₂EDTA

(Vorob'ev et al., 1970), and EDTA salts with transition metal ions such as Ag_2EDTA (e.g., Saran et al., 1995). Among these solids, $\text{H}_4\text{EDTA(s)}$, $\text{M}_2^{(+I)}\text{H}_2\text{EDTA}$ and $\text{M}^{(+II)}\text{H}_2\text{EDTA}$ salts are stable only in very low pH range, and have high solubilities on the order of $\sim 1 \text{ mol}\cdot\text{dm}^{-3}$ beyond their respective stability pH ranges. Therefore, these phases cannot be solubility-controlling phases for EDTA in natural systems. For instance, the solubility of $\text{H}_4\text{EDTA(s)}$ is $\sim 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ at pH 1, whereas it increases to $\sim 1 \text{ mol}\cdot\text{dm}^{-3}$ at pH 4 (Karhu et al., 1999).

There are solubility studies on EDTA salts in their acidic forms (e.g., Fiorucci et al., 2002), such as $\text{M}_2^{(+I)}\text{H}_2\text{EDTA}$ and $\text{M}^{(+II)}\text{H}_2\text{EDTA}$. The solubilities of $\text{Na}_2\text{H}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{H}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ are also $\sim 0.3 \text{ mol}\cdot\text{dm}^{-3}$ and $\sim 2 \text{ mol}\cdot\text{dm}^{-3}$ at pH 4.4 and 4.7, respectively (Fiorucci et al., 2002). Similarly, $\text{M}^{(+II)}\text{M}^{(+I)}_2\text{EDTA}$ salts such as $\text{CaNa}_2\text{EDTA}\cdot 6\text{H}_2\text{O}$ have high solubilities on the order of $\sim 2 \text{ mol}\cdot\text{kg}^{-1}$ (Vorob'ev et al., 1970), and consequently they cannot be solubility-controlling phases in natural environments.

In contrast, $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O(s)}$ has relatively low solubilities in comparison with other EDTA-containing solids, and could be a solubility-controlling phase for EDTA. Since calcium is a major component in natural systems, $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O(s)}$ could be a solubility-controlling phase for EDTA in these systems. However, the solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O(s)}$ as a function of ionic strength is unknown, whereas this knowledge is required for geochemical modeling of natural waters which may vary from dilute surface and groundwater to highly concentrated brines saturated. Therefore, the objective of this work is to determine solubilities of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O(s)}$ as a function of ionic strength to $4.4 \text{ mol}\cdot\text{kg}^{-1}$ in a NaCl medium, and to $7.5 \text{ mol}\cdot\text{kg}^{-1}$ in MgCl_2 medium, as NaCl and

MgCl₂ are the most common and important components in natural aqueous systems, and they are dominant components in the WIPP Generic Weep Brine (GWB) and Energy Research and Development Administration Well 6 (ERDA-6) (Xiong and Lord, 2008). Based on the measured solubilities, a Pitzer model was developed here for solubilities of Ca₂EDTA•7H₂O(s), and the interactions of EDTA with NaCl and MgCl₂ media. The model would enable researchers to estimate with a degree of high precision solubilities of Ca₂EDTA•7H₂O(s) in various environments over a wide range of ionic strengths.

2. EXPERIMENTAL SECTION

In these solubility experiments, about 2-10 grams of the starting material—ACS reagent grade di-calcium ethylenediaminetetraacetic acid (Ca₂EDTA(s), Ca₂C₁₀H₁₂N₂O₈(s), CAS 19709-85-4) from ACROS ORGANICS was weighed out and placed into 150 mL plastic bottles. Then, 100 mL of supporting electrolyte solution were added to those bottles. Once filled, the lids of the bottles were sealed with parafilm. After hydration in supporting solutions, Ca₂EDTA(s) transforms to Ca₂EDTA•7H₂O(s). Therefore, the solubility-controlling phase is Ca₂EDTA•7H₂O(s) (see the following for details).

The supporting electrolytes are a series of NaCl solutions ranging from 0.010 mol•kg⁻¹ to 4.4 mol•kg⁻¹, and MgCl₂ solutions ranging from 0.01 mol•kg⁻¹ to 2.5 mol•kg⁻¹. The supporting electrolyte solutions were prepared from degassed deionized (DI) water. The degassed DI water was prepared by following a procedure similar to that

used by Wood et al. (2002) to remove dissolved CO₂. The Undersaturation experiments are conducted at laboratory room temperature ($22.5 \pm 0.5^{\circ}\text{C}$).

The pH readings were measured with an Orion-Ross combination pH glass electrode, coupled with an Orion Research EA 940 pH meter that was calibrated with three pH buffers (pH 4, pH 7, and pH 10). In solutions with an ionic strength higher than $0.10 \text{ mol}\cdot\text{kg}^{-1}$, hydrogen-ion concentrations on molar scale (pcH) were determined from pH readings by using correction factors for NaCl and MgCl₂ solutions determined by Rai et al. (1995) and Hansen (2001), respectively. Based on the equation in Xiong et al. (2010), pcHs are converted to hydrogen-ion concentrations on the molal scale (pmH).

Solution samples were periodically withdrawn from experimental runs. Before solution samples were taken, pH readings of experimental runs were measured. The sample size was usually 3 mL. After a solution sample was withdrawn from an experiment and filtered with a $0.2 \text{ }\mu\text{m}$ syringe filter, the filtered solution was then weighed, acidified with 0.5 mL of concentrated TraceMetal® grade HNO₃ from Fisher Scientific, and finally diluted to a volume of 10 mL with DI water. If subsequent dilutions were needed, aliquots were taken from the first dilution samples for the second dilution, and aliquots of the second dilution were then taken for further dilution.

Calcium concentrations of solutions were analyzed with a Perkin Elmer dual-view inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer DV 3300). Calibration blanks and standards were precisely matched with experimental matrices. The linear correlation coefficients of calibration curves in all measurements were better than 0.9995. The analytical precision for ICP-AES is better than 1.00% in terms of the relative standard deviation (RSD) based on replicate analyses.

Stoichiometric dissolution of di-calcium ethylenediaminetetraacetic acid hydrate was confirmed by analyzing for EDTA concentrations with a DIONEX ion chromatograph (IC) (DIONEX IC 3000) for selected samples.

Solid phases were analyzed using a Bruker D8 Advance X-ray diffractometer with a Sol-X detector, before and after experiments. The initial, anhydrous phase, $\text{Ca}_2\text{EDTA(s)}$ (the top XRD pattern in Figure 1), became the hydrous phase, $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}$, after experiments (see the XRD patterns in lower portions in Figure 1). Notice that the peak for halite appeared in the XRD pattern in the sample from the experimental run $\text{Ca}_2\text{EDTA-4.0-1}$ in $4.4 \text{ mol}\cdot\text{kg}^{-1}$ NaCl, because halite crystallized from the residual NaCl solution when the sample was dried.

3. EXPERIMENTAL RESULTS, THERMODYNAMIC MODELING AND DISCUSSION

3.1 Experimental Results

The XRD patterns from the representative samples in experiments indicate that the solubility-controlling phase is $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ (Figure 1).

Experimental results for solubilities in NaCl and MgCl_2 solutions are tabulated in Tables 1 and 2, respectively. In Figure 2, solubilities of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ as a function of experimental time in NaCl solutions are displayed. From Figure 2, it is clear that steady-state concentrations in NaCl solutions are achieved in the second sampling, which was taken at 965 days (Table 1). Solubilities of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ as a function of experimental time in MgCl_2 solutions are displayed in Figure 3. It is clear from Figure 3 that steady-state concentrations in MgCl_2 solutions are achieved in the first sampling, which was taken at 767 days (Table 2). It is assumed that steady-state concentrations represent equilibrium concentrations, as the duration of experiments in this work, up to 1,435 days, is significantly longer than previous studies under similar conditions. For instance, in the experiments of Vorob'ev et al. (1970), they mentioned that equilibrium was established in several hours in their study.

In Figure 4, concentrations of calcium as a function of molalities of NaCl are displayed. Figure 4 indicates that concentrations of calcium in equilibrium with $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ have a dependence on concentrations of NaCl. The calcium concentrations first increase with NaCl molality in the range of $0.01 \text{ mol}\cdot\text{kg}^{-1}$ to $1.0 \text{ mol}\cdot\text{kg}^{-1}$. Above $1.0 \text{ mol}\cdot\text{kg}^{-1}$, the calcium concentrations decrease with increasing concentrations of NaCl. For instance, the calcium concentrations are $\sim 0.07 \text{ mol}\cdot\text{kg}^{-1}$ in a

0.01 mol•kg⁻¹ NaCl solution, increasing to ~0.12 mol•kg⁻¹ in a 1.0 mol•kg⁻¹ NaCl solution, and decreasing to ~0.09 mol•kg⁻¹ in a 4.4 mol•kg⁻¹ NaCl solution. An explanation for this observation is given later in the following thermodynamic modeling section regarding the solubility of Ca₂EDTA•7H₂O in NaCl solutions.

Similarly, concentrations of calcium as a function of ionic strength in MgCl₂ solutions are displayed in Figure 5. Figure 5 suggests that concentrations of calcium in equilibrium with Ca₂EDTA•7H₂O(s) have a dependence on concentrations of MgCl₂ with rising solubilities with increasing MgCl₂ concentrations. For instance, the calcium concentrations are ~0.08 mol•kg⁻¹ in a 0.01 mol•kg⁻¹ MgCl₂ solution (Figure 5, and Table 2), increasing to ~0.3 mol•kg⁻¹ in a 2.5 mol•kg⁻¹ MgCl₂ solution. Of note, the calcium concentrations in a 0.01 mol•kg⁻¹ MgCl₂ solution are similar to those in a 0.01 mol•kg⁻¹ NaCl solution, which are ~0.07 mol•kg⁻¹. However, the calcium concentrations in concentrated MgCl₂ solutions are much higher than those in concentrated NaCl solutions. The reason for this difference is that Mg²⁺ forms a complex with EDTA⁴⁻, i.e., MgEDTA²⁻, which enhances the solubility of Ca₂EDTA•7H₂O(s). An explanation for this observation is provided later in the following thermodynamic modeling section regarding the solubility of Ca₂EDTA•7H₂O in MgCl₂ solutions.

3.2 Thermodynamic Modeling

In the following, the experimental data described above are used to derive the thermodynamic parameters. The dissolution of Ca₂EDTA•7H₂O(s) can be expressed as,

At the same time, the formation of CaEDTA^{2-} complex can be expressed as,

Using experimental data produced in this study, the solubility constant of $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ related to Reaction (1) and formation constant related to Reaction (2) along with a set of Pitzer parameters are obtained (Table 3), based on thermodynamic modeling with the Pitzer equations. The auxiliary parameters are listed in Table 3. The computer code, EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011), is used as the modeling platform, which was also used in previous modeling work for obtaining thermodynamic properties including the Pitzer parameters (e.g., Nemer et al., 2011; Xiong et al., 2013; Xiong, 2013, 2015). The database containing all parameters necessary including thermodynamic properties for the modeling, is data0.fm1 (Xiong, 2011). In the database, data0.fm1, the interaction parameters for major ions are from Harvie et al. (1984), and the interaction parameters for organic ligands are from Choppin et al. (2001).

In the model fitting, the experimental data were first used to generate EQ3/6 input files. Then, a script such as a Python script was generated to call the targeted parameters, and call EQ3/6. The minimization subroutine in the script automatically compares differences between experimental values [i.e., total calcium concentrations, $\Sigma\text{Ca}(\text{II})/\text{mol} \cdot \text{kg}^{-1}$] and model-predicted values produced by a set of inputted parameters in each iteration. The iteration is completed when the difference is finally minimized.

In Table 3, the dissolution constant for $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O(s)}$, the formation constant for CaEDTA^{2-} , and a set of Pitzer parameters describing the specific interactions of EDTA species in NaCl and MgCl_2 media are listed. These Pitzer parameters are similar to those found in the literature for the similar interactions in terms of magnitude. For instance, the $\beta^{(0)}$ for $\text{Mg}^{2+}\text{---CaEDTA}^{2-}$ interaction, a 2:2 interaction, is 0.51 (Table 3), which is similar to the $\beta^{(0)}$ of 0.221 for $\text{Mg}^{2+}\text{---SO}_4^{2-}$ interaction (Harvie et al., 1984), also a 2:2 interaction. The $\beta^{(0)}$ for $\text{Na}^{2+}\text{---CaEDTA}^{2-}$ interaction, a 1:2 interaction, is 0.1535 (Table 3), which is similar to the $\beta^{(0)}$ of 0.32 for $\text{Na}^{2+}\text{---H}_2\text{SiO}_4^{2-}$ interaction (Hershey and Millero, 1986), also a 1:2 interaction. It is worth noting that the formation constant for CaEDTA^{2-} obtained in this study is in excellent agreement with the literature values. In this work, the derived $\log \beta_1^0$ is 11.50. The $\log \beta_1^0$ experimentally determined by Carini and Martell (1954) at 25°C is 10.98. In an evaluation performed by Anderegg (1977), the $\log \beta_1^*$ at 20°C and $I = 0.1 \text{ mol}\cdot\text{kg}^{-1}$ is 10.7. This agreement between the value determined in this study and those in the literature provide the additional support for the model presented here.

In the NEA review, $\log \beta_1^0$ for CaEDTA^{2-} has a value of 12.69 ± 0.06 (Hummel et al., 2005), evaluated with the SIT model. It is worth noting that the value evaluated in the NEA review is based on experimental data in low ionic strength range, i.e., the majority of them is at $0.1 \text{ mol}\cdot\text{kg}^{-3}$. The NEA review series also mentioned that when the Pitzer and SIT models apply to the same data set for a reaction involving highly charged species such as $\text{NpO}_2(\text{CO}_3)_3^{5-}$, to calculate activity coefficients, the $\log K'$ can differ by ~ 0.5 logarithmic units (Guillaumont et al., 2003). Therefore, it is expected that

the $\log \beta_1^0$ evaluated in this work using the Pitzer model based on a data set over a wide range of ionic strengths would differ from the value in the NEA review with the SIT model based on a data set in low ionic strength range predominantly at $0.1 \text{ mol}\cdot\text{kg}^{-3}$.

It should be noted that the $\beta^{(1)}$'s in Table 3 were not calculated. Instead, they are pre-set to the average values for the respective interactions, following the paradigm of Choppin et al. (2001). In Choppin et al. (2001), they calculated and recommended a set of average values of $\beta^{(1)}$'s for various interactions (e.g., 1:1, 1:2/2:1, 1:3/3:1, etc., interactions), based on the $\beta^{(1)}$ values for respective interactions from literature.

In the following, solubilities of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in a wide range of ionic strengths predicted by the model are compared with experimental data. The solubilities of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ as a function of ionic strength in a NaCl medium predicted by the model developed in this study are represented by the solid curve in Figure 4. From Figure 4, it is clear that the model developed in this study can accurately describe solubilities of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ over a wide range of ionic strengths. There are few experimental studies on solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$. Vorob'ev et al. (1970) conducted an experimental measurement of solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in water at 25°C . The solubility of that phase obtained by them is 0.117 M with the total calcium concentration of 0.234 M, which is much higher than those determined in this work at $0.01 \text{ mol}\cdot\text{kg}^{-1}$ NaCl (Figure 4). The pH for their measurement of the solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ was not mentioned.

Notice that the model-predicted values are in excellent agreement with the model-independent solubility data of $\text{Ca}_2\text{EDTA}\cdot 2\text{H}_2\text{O}(\text{s})$ in water from Bersin et al. (1957) and of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ also in water from Myachina et al. (1974) (Figure 4).

The solubility dependence of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ as a function of ionic strength in NaCl solutions depicted in Figure 4 is parallel to the ionic strength dependence of the fourth acid dissociation constant of EDTA acid in NaCl and NaClO_4 media (i.e., $\log Q_{a4}$, see Choppin et al., 2001; Thakur et al., 2014). The fourth acid dissociation constant of EDTA can be described by the following reaction.

The solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ as a function of ionic strength indicates that the solubility increases with ionic strength for ionic strengths below $2.1 \text{ mol}\cdot\text{kg}^{-1}$. The solubility reaches its maximum at an ionic strength of $2.1 \text{ mol}\cdot\text{kg}^{-1}$ (Figure 4). Above an ionic strength of $2.1 \text{ mol}\cdot\text{kg}^{-1}$, the solubility decreases with ionic strength (Figure 4). In the work of Choppin et al. (2001) and Thakur et al. (2014) measuring the fourth conditional dissociation constants of EDTA acid, i.e., $\log Q_{a4}$, in NaCl and NaClO_4 solutions, respectively, $\log Q_{a4}$ also increases with ionic strength in the ionic strength range below $2.0 \text{ mol}\cdot\text{kg}^{-1}$ (also see Figure 4 in Thakur et al., 2014). $\log Q_{a4}$ reaches its maximum at an ionic strength of $2.0 \text{ mol}\cdot\text{kg}^{-1}$. Above an ionic strength of $2.0 \text{ mol}\cdot\text{kg}^{-1}$, $\log Q_{a4}$ decreases with ionic strength. The similarity in the dependency of solubilities of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ and the fourth dissociation constant of EDTA acid on ionic strength is due to the variations of activity coefficients. In the case of the solubility of the fourth dissociation constant of EDTA acid, the term $[\log \gamma_{\text{H}^+} + \log \gamma_{\text{EDTA}^{4-}} - \log \gamma_{\text{HEDTA}^{3-}}]$ first decreases with ionic strength, and then increases with ionic strength above an ionic strength of $2.0 \text{ mol}\cdot\text{kg}^{-1}$. In the case of the solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$, the term

$[\log \gamma_{Ca^{2+}} + \log \gamma_{EDTA^{4-}} - \log \gamma_{CaEDTA^{2-}}]$ first decreases with ionic strength with a minimum at the ionic strength of $2.1 \text{ mol} \cdot \text{kg}^{-1}$, and then increases with ionic strength above an ionic strength of $2.1 \text{ mol} \cdot \text{kg}^{-1}$.

Similarly, the solubilities of $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ as a function of ionic strength in a MgCl_2 medium predicted by the model developed in this study are represented by the solid curve in Figure 5. It is clear from Figure 5 that the model developed in this study can satisfactorily reproduce solubilities of $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ in MgCl_2 solutions over a wide range of ionic strengths. In contrast with the trend in a NaCl medium, there is no minimum for the term $[\log \gamma_{Ca^{2+}} + \log \gamma_{EDTA^{4-}} - \log \gamma_{CaEDTA^{2-}}]$ in an MgCl_2 medium. Instead, this term monotonically decreases over the entire ionic strength range investigated in this study.

3.3 Discussions and Applications

$\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ in Low Temperature Environments: As mentioned before, $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ may be a solubility-limiting phase for EDTA aqueous concentrations in geological repositories when inventories of EDTA increase to a level reaching the solubility limit of $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$. As an example of application of the model developed herein, the total EDTA concentrations limited by $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ in the Okkiluoto site, Finland, a potential geological repository in granite, are calculated based on the model developed in this study (Table 4 and Figure 6). Figure 6 shows the predicted EDTA concentrations in equilibrium with $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ as a function of pH. Figure 6 indicates that the EDTA concentration is slightly higher at pH 4.5, and then it remains constant at $2.5 \times 10^{-2} \text{ mol} \cdot \text{kg}^{-1}$ from pH 5 to pH 9.5. In the calculation,

the EQ3/6 database, data0.fmt (Wolery et al., 2010; Xiong, 2011), supported by the Pitzer equations for activity coefficients, was used. The database with the Pitzer equations was used as the ionic strength of the groundwater is above $1.0 \text{ mol}\cdot\text{kg}^{-1}$ (Table 4).

EDTA has been used to decontaminate soils polluted by heavy metals such as Pb, Cd and Zn in normal soil washing techniques (e.g., Li and Shuman, 1996; Papassiopi et al., 1999; Lo and Zhang, 2005; Qui et al., 2010). During this process, $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ could be precipitated as a solubility-limiting phase. The model developed in this work, especially the $\log K_{sp}^0$ obtained by this study, would enable environmental engineers to use the optimal EDTA concentrations for remediation of the soils contaminated with heavy metals, and to calculate the maximum EDTA concentrations that could be present in the soils after the EDTA washing technology has been applied. To demonstrate these applications, solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in a model soil solution is calculated as an example. In the calculation, the model soil solution originated from Wood (2000), which has been slightly modified (Xiong, 2009) (Table 5). The concentrations of calcium and sulfate are assumed to be in equilibrium with gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), as gypsum is widespread in gypsiferous soils (Boyadgiev and Verheye, 1996). The soil solutions in gypsiferous soils are slightly alkaline, with pH ranging from 7.4 to 8.4 (Boyadgiev and Verheye, 1996). Therefore, in the model calculation, the pH is taken as a range from 4.5 to 9.5 in order to take account for the full range of pH that would be present (Table 5). In the calculation, the EQ3/6 database, data0.sup (Wolery, 1992), supported by both the Davies and B-dot equations for activity coefficients, was used. The Davies equation was selected for the calculation, as the model soil solution is dilute (Table 5).

Shown in Figure 7 are the predicted EDTA concentrations in equilibrium with $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in the model soil solution as a function of pH. From Figure 7, we can see that the EDTA concentration is $7.5 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ at pH 4.5. It remains constant at $\sim 2 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ from pH 5.5 to pH ~ 9 . Above pH 9.0, the EDTA concentration drops to $1.5 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$. Of note is the fact that the above total EDTA concentrations limited by $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in the model soil solution (Figure 7, Table 5) are above the EDTA concentrations (0.025 to 0.25 M) proposed for usage in the soil washing process for decontamination of heavy metals (e.g., Papassiopi et al., 1999; Qiu et al., 2010). This implies that when the above EDTA concentrations are applied, $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ could become a solubility controlling phase for EDTA in soil. Under these circumstances, the excess EDTA would be combined with calcium in soil to form $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$, resulting in the loss of EDTA. Consequently, the optimal EDTA concentrations for decontamination of heavy metals in soils should be around $1 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ in alkaline soils. At this level of EDTA concentrations, it would be below the saturation limit of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ without the loss of EDTA because of forming $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$, while the EDTA concentrations are still high enough to form strong complexes with heavy metals. For soils with mildly acidic pH, the optimal EDTA concentrations for decontamination of heavy metals would be around $1 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$.

4. CONCLUSIONS

Long-term solubility measurements up to 1,435 days and to high ionic strengths for $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in NaCl and MgCl_2 solutions produced at Sandia National Laboratories Carlsbad Facility are presented in this work. A Pitzer model is developed

based on these solubility measurements. This model would provide accurate descriptions about the interaction of EDTA with NaCl and MgCl₂ matrixes under various conditions with applications to many fields such as nuclear waste management and environmental remediation of heavy metal contamination.

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Table1. Experimental results concerning solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O(s)}$ in NaCl solutions produced in this work at 22.5 ± 0.5 °C.

Experimental Number	Supporting Medium, NaCl, Experimental $\text{mol}\cdot\text{kg}^{-1}$	time, days	pmH*	Solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O(s)}$ as total calcium concentrations, $\text{mol}\cdot\text{kg}^{-1}$, $m_{\Sigma\text{Ca}}$
$\text{Ca}_2\text{EDTA-0.01-1}$	0.010	365	8.23	7.09E-02
$\text{Ca}_2\text{EDTA-0.01-2}$	0.010	365	8.20	7.15E-02
$\text{Ca}_2\text{EDTA-0.1-1}$	0.10	365	8.37	8.61E-02
$\text{Ca}_2\text{EDTA-0.1-2}$	0.10	365	7.90	8.69E-02
$\text{Ca}_2\text{EDTA-1.0-1}$	1.0	365	8.39	1.35E-01
$\text{Ca}_2\text{EDTA-1.0-2}$	1.0	365	7.92	1.35E-01
$\text{Ca}_2\text{EDTA-2.0-1}$	2.1	365	8.54	1.40E-01
$\text{Ca}_2\text{EDTA-2.0-2}$	2.1	365	8.49	1.42E-01
$\text{Ca}_2\text{EDTA-3.0-1}$	3.2	365	8.71	1.35E-01
$\text{Ca}_2\text{EDTA-3.0-2}$	3.2	365	8.47	1.31E-01
$\text{Ca}_2\text{EDTA-4.0-1}$	4.4	365	8.69	1.19E-01
$\text{Ca}_2\text{EDTA-4.0-2}$	4.4	365	8.63	1.19E-01
$\text{Ca}_2\text{EDTA-0.01-1}$	0.010	940	7.79	7.27E-02
$\text{Ca}_2\text{EDTA-0.01-2}$	0.010	940	7.85	7.28E-02
$\text{Ca}_2\text{EDTA-0.1-1}$	0.10	940	7.88	8.36E-02
$\text{Ca}_2\text{EDTA-0.1-2}$	0.10	940	7.81	7.99E-02
$\text{Ca}_2\text{EDTA-1.0-1}$	1.0	940	8.09	1.22E-01
$\text{Ca}_2\text{EDTA-1.0-2}$	1.0	940	7.77	1.23E-01
$\text{Ca}_2\text{EDTA-2.0-1}$	2.1	940	8.18	1.21E-01
$\text{Ca}_2\text{EDTA-2.0-2}$	2.1	940	8.20	1.20E-01
$\text{Ca}_2\text{EDTA-3.0-1}$	3.2	940	8.43	1.09E-01
$\text{Ca}_2\text{EDTA-3.0-2}$	3.2	940	8.30	1.10E-01
$\text{Ca}_2\text{EDTA-4.0-1}$	4.4	940	8.41	9.45E-02
$\text{Ca}_2\text{EDTA-4.0-2}$	4.4	940	8.40	9.29E-02
$\text{Ca}_2\text{EDTA-0.01-1}$	0.010	1025	7.84	7.30E-02
$\text{Ca}_2\text{EDTA-0.01-2}$	0.010	1025	7.83	7.27E-02
$\text{Ca}_2\text{EDTA-0.1-1}$	0.10	1025	7.81	8.49E-02
$\text{Ca}_2\text{EDTA-0.1-2}$	0.10	1025	7.81	8.52E-02
$\text{Ca}_2\text{EDTA-1.0-1}$	1.0	1025	8.00	1.22E-01

Ca ₂ EDTA-1.0-2	1.0	1025	7.68	1.22E-01
Ca ₂ EDTA-2.0-1	2.1	1025	8.13	1.21E-01
Ca ₂ EDTA-2.0-2	2.1	1025	8.11	1.24E-01
Ca ₂ EDTA-3.0-1	3.2	1025	8.23	1.10E-01
Ca ₂ EDTA-3.0-2	3.2	1025	8.20	1.09E-01
Ca ₂ EDTA-4.0-1	4.4	1025	8.37	9.28E-02
Ca ₂ EDTA-4.0-2	4.4	1025	8.33	9.54E-02
Ca ₂ EDTA-0.01-1	0.010	1074	7.88	7.33E-02
Ca ₂ EDTA-0.01-2	0.010	1074	7.86	7.25E-02
Ca ₂ EDTA-0.1-1	0.10	1074	7.90	8.42E-02
Ca ₂ EDTA-0.1-2	0.10	1074	7.85	8.17E-02
Ca ₂ EDTA-1.0-1	1.0	1074	8.03	1.23E-01
Ca ₂ EDTA-1.0-2	1.0	1074	7.72	1.24E-01
Ca ₂ EDTA-2.0-1	2.1	1074	8.13	1.22E-01
Ca ₂ EDTA-2.0-2	2.1	1074	8.11	1.21E-01
Ca ₂ EDTA-3.0-1	3.2	1074	8.25	1.08E-01
Ca ₂ EDTA-3.0-2	3.2	1074	8.19	1.06E-01
Ca ₂ EDTA-4.0-1	4.4	1074	8.33	9.24E-02
Ca ₂ EDTA-4.0-2	4.4	1074	8.31	9.49E-02
Ca ₂ EDTA-0.01-1	0.010	1124	7.94	7.24E-02
Ca ₂ EDTA-0.01-2	0.010	1124	7.92	6.64E-02
Ca ₂ EDTA-0.1-1	0.10	1124	7.96	8.39E-02
Ca ₂ EDTA-0.1-2	0.10	1124	7.90	8.40E-02
Ca ₂ EDTA-1.0-1	1.0	1124	8.02	1.21E-01
Ca ₂ EDTA-1.0-2	1.0	1124	7.73	1.18E-01
Ca ₂ EDTA-2.0-1	2.1	1124	8.09	1.21E-01
Ca ₂ EDTA-2.0-2	2.1	1124	8.14	1.25E-01
Ca ₂ EDTA-3.0-1	3.2	1124	8.35	1.10E-01
Ca ₂ EDTA-3.0-2	3.2	1124	8.22	1.12E-01
Ca ₂ EDTA-4.0-1	4.4	1124	8.34	9.76E-02
Ca ₂ EDTA-4.0-2	4.4	1124	8.35	9.42E-02
Ca ₂ EDTA-0.01-1	0.010	1172	7.86	7.10E-02
Ca ₂ EDTA-0.01-2	0.010	1172	7.87	7.13E-02
Ca ₂ EDTA-0.1-1	0.10	1172	7.90	8.46E-02
Ca ₂ EDTA-0.1-2	0.10	1172	7.91	8.49E-02
Ca ₂ EDTA-1.0-1	1.0	1172	8.00	1.22E-01

Ca ₂ EDTA-1.0-2	1.0	1172	7.72	1.21E-01
Ca ₂ EDTA-2.0-1	2.1	1172	8.10	1.19E-01
Ca ₂ EDTA-2.0-2	2.1	1172	8.07	1.21E-01
Ca ₂ EDTA-3.0-1	3.2	1172	8.23	1.06E-01
Ca ₂ EDTA-3.0-2	3.2	1172	8.19	1.08E-01
Ca ₂ EDTA-4.0-1	4.4	1172	8.31	9.39E-02
Ca ₂ EDTA-4.0-2	4.4	1172	8.30	9.25E-02
Ca ₂ EDTA-0.01-1	0.010	1323	7.85	7.31E-02
Ca ₂ EDTA-0.01-2	0.010	1323	7.86	7.26E-02
Ca ₂ EDTA-0.1-1	0.10	1323	7.88	8.55E-02
Ca ₂ EDTA-0.1-2	0.10	1323	7.88	8.60E-02
Ca ₂ EDTA-1.0-1	1.0	1323	7.99	1.24E-01
Ca ₂ EDTA-1.0-2	1.0	1323	7.72	1.24E-01
Ca ₂ EDTA-2.0-1	2.1	1323	8.11	1.22E-01
Ca ₂ EDTA-2.0-2	2.1	1323	8.10	1.22E-01
Ca ₂ EDTA-3.0-1	3.2	1323	8.23	1.12E-01
Ca ₂ EDTA-3.0-2	3.2	1323	8.19	1.10E-01
Ca ₂ EDTA-4.0-1	4.4	1323	8.33	9.55E-02
Ca ₂ EDTA-4.0-2	4.4	1323	8.32	9.52E-02
Ca ₂ EDTA-0.01-1	0.010	1431	7.88	7.32E-02
Ca ₂ EDTA-0.01-2	0.010	1431	7.88	7.30E-02
Ca ₂ EDTA-0.1-1	0.10	1431	7.85	8.54E-02
Ca ₂ EDTA-0.1-2	0.10	1431	7.90	8.63E-02
Ca ₂ EDTA-1.0-1	1.0	1431	7.98	1.22E-01
Ca ₂ EDTA-1.0-2	1.0	1431	7.71	1.24E-01
Ca ₂ EDTA-2.0-1	2.1	1431	8.07	1.22E-01
Ca ₂ EDTA-2.0-2	2.1	1431	8.05	1.23E-01
Ca ₂ EDTA-3.0-1	3.2	1431	8.17	1.11E-01
Ca ₂ EDTA-3.0-2	3.2	1431	8.14	1.11E-01
Ca ₂ EDTA-4.0-1	4.4	1431	8.24	9.55E-02
Ca ₂ EDTA-4.0-2	4.4	1431	8.24	9.51E-02

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* Values of pmH reported are calculated by using the correction factors (A_M) from Rai et al. (1995) for pH readings, and conversion factors (Θ) from molarity to molality, $\text{pmH} = \text{pH}_{\text{ob}} + A_M - \log \Theta$ (Xiong et al., 2010). The conversion factors are calculated from densities for NaCl solutions, which are from Söhnel and Novotný (1985).

Table 2. Experimental results concerning solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}$ (s) in MgCl_2 solutions produced in this work at 22.5 ± 0.5 °C

Experimental Number	Supporting Medium, MgCl_2 , $\text{mol}\cdot\text{kg}^{-1}$	Experimental time, days	pmH*	Solubility expressed as total calcium on molal scale, $m_{\Sigma\text{Ca}}$
Ca2EDTA-0.01MgCl2-1	0.010	767	7.88	7.27E-02
Ca2EDTA-0.01MgCl2-2	0.010	767	7.80	7.24E-02
Ca2EDTA-0.1MgCl2-1	0.10	767	7.78	1.10E-01
Ca2EDTA-0.1MgCl2-2	0.10	767	7.32	1.11E-01
Ca2EDTA-1.0MgCl2-1	1.0	767	7.49	1.74E-01
Ca2EDTA-1.0MgCl2-2	1.0	767	7.53	1.59E-01
Ca2EDTA-1.5MgCl2-1	1.5	767	7.38	2.10E-01
Ca2EDTA-1.5MgCl2-2	1.5	767	7.33	2.07E-01
Ca2EDTA-2.0MgCl2-1	2.0	767	7.34	2.24E-01
Ca2EDTA-2.0MgCl2-2	2.0	767	7.52	2.05E-01
Ca2EDTA-2.5MgCl2-1	2.5	767	7.45	2.96E-01
Ca2EDTA-2.5MgCl2-2	2.5	767	7.60	2.88E-01
Ca2EDTA-0.01MgCl2-1	0.010	941	7.72	8.06E-02
Ca2EDTA-0.01MgCl2-2	0.010	941	7.73	7.72E-02
Ca2EDTA-0.1MgCl2-1	0.10	941	7.77	1.18E-01
Ca2EDTA-0.1MgCl2-2	0.10	941	7.48	1.16E-01
Ca2EDTA-1.0MgCl2-1	1.0	941	7.57	1.84E-01
Ca2EDTA-1.0MgCl2-2	1.0	941	7.55	1.71E-01
Ca2EDTA-1.5MgCl2-1	1.5	941	7.60	2.28E-01
Ca2EDTA-1.5MgCl2-2	1.5	941	7.54	2.19E-01
Ca2EDTA-2.0MgCl2-1	2.0	941	7.62	2.29E-01
Ca2EDTA-2.0MgCl2-2	2.0	941	7.62	2.20E-01
Ca2EDTA-2.5MgCl2-1	2.5	941	7.68	3.04E-01
Ca2EDTA-2.5MgCl2-2	2.5	941	7.63	2.93E-01
Ca2EDTA-0.01MgCl2-1	0.010	1025	7.77	7.65E-02
Ca2EDTA-0.01MgCl2-2	0.010	1025	7.69	7.37E-02
Ca2EDTA-0.1MgCl2-1	0.10	1025	7.74	1.12E-01
Ca2EDTA-0.1MgCl2-2	0.10	1025	7.46	1.11E-01
Ca2EDTA-1.0MgCl2-1	1.0	1025	7.50	1.79E-01
Ca2EDTA-1.0MgCl2-2	1.0	1025	7.50	1.64E-01
Ca2EDTA-1.5MgCl2-1	1.5	1025	7.58	2.21E-01
Ca2EDTA-1.5MgCl2-2	1.5	1025	7.55	2.08E-01

Ca2EDTA-2.0MgCl2-1	2.0	1025	7.60	2.26E-01
Ca2EDTA-2.0MgCl2-2	2.0	1025	7.59	2.25E-01
Ca2EDTA-2.5MgCl2-1	2.5	1025	7.62	2.90E-01
Ca2EDTA-2.5MgCl2-2	2.5	1025	7.60	2.52E-01
Ca2EDTA-0.01MgCl2-1	0.010	1075	7.84	7.78E-02
Ca2EDTA-0.01MgCl2-2	0.010	1075	7.73	7.66E-02
Ca2EDTA-0.1MgCl2-1	0.10	1075	7.78	1.14E-01
Ca2EDTA-0.1MgCl2-2	0.10	1075	7.52	1.13E-01
Ca2EDTA-1.0MgCl2-1	1.0	1075	7.57	1.83E-01
Ca2EDTA-1.0MgCl2-2	1.0	1075	7.56	1.75E-01
Ca2EDTA-1.5MgCl2-1	1.5	1075	7.64	2.26E-01
Ca2EDTA-1.5MgCl2-2	1.5	1075	7.61	2.23E-01
Ca2EDTA-2.0MgCl2-1	2.0	1075	7.66	2.38E-01
Ca2EDTA-2.0MgCl2-2	2.0	1075	7.62	2.29E-01
Ca2EDTA-2.5MgCl2-1	2.5	1075	7.68	3.07E-01
Ca2EDTA-2.5MgCl2-2	2.5	1075	7.64	3.04E-01
Ca2EDTA-0.01MgCl2-1	0.010	1124	7.90	8.24E-02
Ca2EDTA-0.01MgCl2-2	0.010	1124	7.69	7.82E-02
Ca2EDTA-0.1MgCl2-1	0.10	1124	7.80	1.20E-01
Ca2EDTA-0.1MgCl2-2	0.10	1124	7.56	1.18E-01
Ca2EDTA-1.0MgCl2-1	1.0	1124	7.59	1.57E-01
Ca2EDTA-1.0MgCl2-2	1.0	1124	7.61	1.75E-01
Ca2EDTA-1.5MgCl2-1	1.5	1124	7.50	2.26E-01
Ca2EDTA-1.5MgCl2-2	1.5	1124	7.58	2.10E-01
Ca2EDTA-2.0MgCl2-1	2.0	1124	7.63	2.42E-01
Ca2EDTA-2.0MgCl2-2	2.0	1124	7.69	2.42E-01
Ca2EDTA-2.5MgCl2-1	2.5	1124	7.73	3.05E-01
Ca2EDTA-2.5MgCl2-2	2.5	1124	7.72	3.17E-01
Ca2EDTA-0.01MgCl2-1	0.010	1176	7.79	7.63E-02
Ca2EDTA-0.01MgCl2-2	0.010	1176	7.65	7.53E-02
Ca2EDTA-0.1MgCl2-1	0.10	1176	7.75	1.14E-01
Ca2EDTA-0.1MgCl2-2	0.10	1176	7.46	1.10E-01
Ca2EDTA-1.0MgCl2-1	1.0	1176	7.60	1.78E-01
Ca2EDTA-1.0MgCl2-2	1.0	1176	7.59	1.71E-01
Ca2EDTA-1.5MgCl2-1	1.5	1176	7.63	2.22E-01
Ca2EDTA-1.5MgCl2-2	1.5	1176	7.60	2.11E-01
Ca2EDTA-2.0MgCl2-1	2.0	1176	7.67	2.36E-01

Ca2EDTA-2.0MgCl2-2	2.0	1176	7.70	2.25E-01
Ca2EDTA-2.5MgCl2-1	2.5	1176	7.73	2.98E-01
Ca2EDTA-2.5MgCl2-2	2.5	1176	7.71	2.97E-01
Ca2EDTA-0.01MgCl2-1	0.010	1324	7.79	7.74E-02
Ca2EDTA-0.01MgCl2-2	0.010	1324	7.67	7.73E-02
Ca2EDTA-0.1MgCl2-1	0.10	1324	7.77	1.16E-01
Ca2EDTA-0.1MgCl2-2	0.10	1324	7.51	1.16E-01
Ca2EDTA-1.0MgCl2-1	1.0	1324	7.62	1.80E-01
Ca2EDTA-1.0MgCl2-2	1.0	1324	7.59	1.75E-01
Ca2EDTA-1.5MgCl2-1	1.5	1324	7.65	2.25E-01
Ca2EDTA-1.5MgCl2-2	1.5	1324	7.63	2.25E-01
Ca2EDTA-2.0MgCl2-1	2.0	1324	7.69	2.34E-01
Ca2EDTA-2.0MgCl2-2	2.0	1324	7.72	2.27E-01
Ca2EDTA-2.5MgCl2-1	2.5	1324	7.75	2.96E-01
Ca2EDTA-2.5MgCl2-2	2.5	1324	7.74	2.98E-01
Ca2EDTA-0.01MgCl2-1	0.010	1435	7.77	7.78E-02
Ca2EDTA-0.01MgCl2-2	0.010	1435	7.67	7.73E-02
Ca2EDTA-0.1MgCl2-1	0.10	1435	7.77	1.16E-01
Ca2EDTA-0.1MgCl2-2	0.10	1435	7.53	1.17E-01
Ca2EDTA-1.0MgCl2-1	1.0	1435	7.61	1.78E-01
Ca2EDTA-1.0MgCl2-2	1.0	1435	7.60	1.73E-01
Ca2EDTA-1.5MgCl2-1	1.5	1435	7.65	2.24E-01
Ca2EDTA-1.5MgCl2-2	1.5	1435	7.62	2.22E-01
Ca2EDTA-2.0MgCl2-1	2.0	1435	7.68	2.29E-01
Ca2EDTA-2.0MgCl2-2	2.0	1435	7.68	2.28E-01
Ca2EDTA-2.5MgCl2-1	2.5	1435	7.71	2.97E-01
Ca2EDTA-2.5MgCl2-2	2.5	1435	7.70	2.95E-01

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* Values of pmH reported are calculated by using the correction factors (A_M) from Hansen (2001) for pH readings, and conversion factors (Θ) from molarity to molality, $\text{pmH} = \text{pH}_{\text{ob}} + A_M - \log \Theta$ (Xiong et al., 2010). The conversion factors are from the EQ3 output files with the respective MgCl_2 concentrations.

Table 3. The Pitzer model for the $\text{Na}^+ - \text{Mg}^{2+} - \text{Ca}^{2+} - \text{Cl}^- - \text{EDTA}^{4-} - \text{H}_2\text{O}$ system at 25°C

Pitzer Parameters*				
Species, i	Species, j	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
Na^+	CaEDTA^{2-}	0.1535^{A}	1.74^{C}	0.025^{A}
Na^+	EDTA^{4-}	1.016^{B}	11.6^{C}	0.001^{B}
Na^+	HEDTA^{3-}	0.5458^{B}	5.22^{C}	-0.048^{B}
Mg^{2+}	CaEDTA^{2-}	0.51^{A}	3.27^{C}	0
Ca^{2+}	MgEDTA^{2-}	0.08604^{A}	3.27^{C}	0
Mg^{2+}	EDTA^{4-}	-0.0102^{A}	11.6^{C}	0.306^{A}
Equilibrium Constants at infinite dilution for Dissolution Reaction of $\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s})$ and Formation Reaction of CaEDTA^{2-}				
Reactions			$\log K_{sp}^0$ or $\log \beta_1^0$	
$\text{Ca}_2\text{EDTA} \cdot 7\text{H}_2\text{O}(\text{s}) = 2\text{Ca}^{2+} + \text{EDTA}^{4-} + 7\text{H}_2\text{O}(\text{l})$			$-15.57 \pm 0.10^{\text{A}}$	
$\text{Ca}^{2+} + \text{EDTA}^{4-} = \text{CaEDTA}^{2-}$			$11.50 \pm 0.05^{\text{A}}$	

^A Evaluated in this study.

^B From the data0.fmt (Wolery et al., 2010; Xiong, 2011).

^C These parameters are not evaluated. Instead, they are set to the pre-fixed, average values for the respective interactions, following the methodology of Choppin et al. (2001).

* α_1 for all interactions except for $\text{Mg}^{2+} - \text{EDTA}^{4-}$ is 2.0. For $\text{Mg}^{2+} - \text{EDTA}^{4-}$ interaction, α_1 is set to 1.4 in modeling, in analog to α_1 for the $\text{Th}^{4+} - \text{SO}_4^{2-}$ interaction (Felmy and Rai, 1992).

Table 4. The chemical compositions of the groundwater and predicted total EDTA concentration in equilibrium with $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ at 25°C for the geological repository in granite at Olkiluoto, Finland*

Total Dissolved Salts (TDS), mg/L	Ionic Strength, $\text{mol}\cdot\text{kg}^{-1}$	pH**	Na^+ $\text{mol}\cdot\text{kg}^{-1}$	K^+ $\text{mol}\cdot\text{kg}^{-1}$	Mg^{2+} $\text{mol}\cdot\text{kg}^{-1}$	Ca^{2+} $\text{mol}\cdot\text{kg}^{-1}$
49,483	1.36	4.5 to 9.5	0.3672	5.0×10^{-4}	0.0015	0.2590
$\text{Sr}^{2+ \text{ A}}$ $\text{mol}\cdot\text{kg}^{-1}$	$\text{Mn}^{2+ \text{ A}}$ $\text{mol}\cdot\text{kg}^{-1}$	Cl^- $\text{mol}\cdot\text{kg}^{-1}$	SO_4^{2-} $\text{mol}\cdot\text{kg}^{-1}$	$\Sigma\text{H}_4\text{SiO}_4^{\text{ A}}$ $\text{mol}\cdot\text{kg}^{-1}$	ΣCO_3^{2-} $\text{mol}\cdot\text{kg}^{-1}$	$\Sigma\text{EDTA}^{4- \text{ B}}$ $\text{mol}\cdot\text{kg}^{-1}$
0.00116	9.5×10^{-5}	0.8783	5×10^{-5}	2.1×10^{-4}	4×10^{-5}	2.7×10^{-4} to 2.5×10^{-4}

* 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 ($\text{mol}\cdot\text{L}^{-1}$) are converted to those on molal scale ($\text{mol}\cdot\text{kg}^{-1}$) 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 inputted for the calculation of EDTA concentration, as they are not supported by the database and do not affect the solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$.

^B Calculated based on equilibrium with $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$.

Table 4. The initial compositions of the modified model soil solution* at 25°C used in calculation of solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in gypsiferous soils

Species ^A and parameters	Concentration (M, $\text{mol}\cdot\text{dm}^{-3}$)
Na	1.85354×10^{-5}
K	10^{-4}
Mg	10^{-5}
Ca ^B	10^{-4}
Cu	10^{-8}
Zn	10^{-8}
Pb	10^{-8}
Al	10^{-8}
Fe	10^{-7}
F ⁻	5×10^{-6}
Cl ⁻	10^{-5}
SO ₄ ^{2-B}	10^{-4}
HCO ₃ ^{-C}	10^{-4}
HPO ₄ ²⁻	10^{-7}
NO ₃ ⁻	10^{-5}
H ₂ AsO ₄ ⁻	10^{-8}
Acetate, Ac	2×10^{-6}
Citrate, Cit	2×10^{-6}
Ethylenediaminetetraacetic acid, EDTA ^D	7.4×10^{-3} to 1.5×10^{-3}
Oxalate	2×10^{-6}
Succinate, Suc	2×10^{-6}
pH ^E	4.5 to 9.5
Eh ^F	0

* From the recipe in Xiong (2009), which was modified from Wood (2000).

^A Elemental concentrations represent the total concentrations of respective elements including several species.

^B In the calculation of solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in gypsiferous soils, both calcium and sulfate concentrations are assumed to be controlled by the equilibrium with gypsum.

^C In the calculation of solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$ in gypsiferous soils, total dissolved inorganic carbon is assumed to be controlled by the equilibrium with the atmospheric CO₂ ($10^{-3.5}$ bars)

^D In the recipe in Xiong (2009), EDTA is not included. The listed values are the calculated total EDTA concentrations in equilibrium with $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$.

^E In Wood (2000), pH has a single value of 6.5, and in Xiong (2009), pH ranges from 5.5 to 8.5. In this work, pH is modeled from 4.5 to 9.5 for gypsiferous soils. Please see text for the justifications.

^F In Wood (2000), Eh has a single value of 0.1 V, and in Xiong (2009), Eh ranges from 0 to 0.55 V. In this work, Eh is assigned to 0 for gypsiferous soils, as it does not affect solubility of $\text{Ca}_2\text{EDTA}\cdot 7\text{H}_2\text{O}(\text{s})$.

Figure Captions

Figure 1. XRD patterns of the solubility-controlling phase from the representative samples from experiments, in comparison with the initial starting material. The reference standard of $\text{Ca}_2\text{EDDA}\cdot 7\text{H}_2\text{O}(\text{cr})$ is from PDF-4+ 2016 (Software Version 4.16.04, Database Version 4.1605) of the International Center for Diffraction Data (ICDD). Notice that the peak for halite appeared in the XRD pattern in the sample from the experimental run $\text{Ca}_2\text{EDTA-4.0-1}$ in $4.4 \text{ mol}\cdot\text{kg}^{-1}$ NaCl, because halite crystallized from the residual NaCl solution when the sample was dried.

Figure 2. A plot showing experimental total calcium concentrations in equilibrium with $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ in NaCl solutions as a function of experimental time produced in this study.

Figure 3. A plot showing experimental total calcium concentrations in equilibrium with $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ in MgCl_2 solutions as a function of experimental time produced in this study.

Figure 4. A plot showing experimental total calcium concentrations in equilibrium with $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ produced in this study as a function of molalities of NaCl. The experimental data from Bersin et al. (1957) refers to the solubility of $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 2\text{H}_2\text{O}(\text{s})$ in water at 25°C . The experimental data from Vorob'ev et al. (1970) refers to the solubility of $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ in water at 25°C . The experimental data from Myachina et al. (1974) refers to the solubility of $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ in water at 25°C . All of the experimental data from literature are model-independent.

Figure 5. A plot showing experimental total calcium concentrations in equilibrium with $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ produced in this study as a function of ionic strengths in MgCl_2 solutions. The experimental data from Bersin et al. (1957) refers to the solubility of $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 2\text{H}_2\text{O}(\text{s})$ in water at 25°C . The experimental data from Vorob'ev et al. (1970) refers to the solubility of $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ in water at 25°C . The experimental data from Myachina et al. (1974) refers to the solubility of $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ in water at 25°C . All of the experimental data from literature are model-independent.

Figure 6 A plot showing experimental total EDTA concentrations in equilibrium with $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\cdot 7\text{H}_2\text{O}(\text{s})$ as a function of pH in the granite brine from Okkiluoto, Finland.

Figure 7. A plot showing experimental total EDTA concentrations in equilibrium with $\text{Ca}_2\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8 \cdot 7\text{H}_2\text{O}(\text{s})$ as a function of pH in the model soil solution.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.