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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

Yongliang Xiong[1],

Sandia National Laboratories (SNL)*
Carlsbad Programs Group
4100 National Parks Highway, Carlsbad, NM 88220, USA

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[1] Corresponding author, e-mail: yxiong@sandia.gov.

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ABSTRACT

In this study, solubility measurements on di-calcium ethylenediaminetetraacetic acid [$Ca_2C_{10}H_{12}N_2O_8$(s), abbreviated as Ca_2EDTA(s)] as a function of ionic strength are conducted in NaCl solutions up to $I = 5.0$ mol•kg^{-1} and in $MgCl_2$ solutions up to $I = 7.5$ mol•kg^{-1}, at room temperature (22.5 ± 0.5°C). The solubility constant (log K_{sp}) for Ca_2EDTA(s) and formation constant for CaEDTA^{2-},

$$Ca_2EDTA(s) = 2Ca^{2+} + EDTA^{4-} \quad (1)$$

$$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-} \quad (2)$$

are determined as –15.39 ± 0.10 and 11.16 ± 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 Ca_2EDTA(s) could become a solubility-controlling phase for EDTA in geological repositories for nuclear waste when the inventories of EDTA reach certain levels. 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 ETDA washing technology has been applied.

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 6.47×10^{-5} M (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($Mg_5(CO_3)_4(OH)_2$•$4H_2O$)-phase 5 ($Mg_5Cl(OH)_5$•$4H_2O$) in the WIPP Generic Weep Brine (GWB) was 1.97×10^{-6} M in which $AmEDTA^-$ accounted for 90.5% (i.e., 1.79×10^{-6} M) (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($Mg_5(CO_3)_4(OH)_2$•$4H_2O$) in the WIPP Energy Research and Development Administration Well 6 (EDRA-6) brine was 1.51×10^{-6} M, in which $AmEDTA^-$ accounted for 93.9% (i.e., 1.42×10^{-6} M) (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 is therefore persistent 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 (5.5×10^{-6} M) (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., $H_4EDTA(s)$, acidic forms of EDTA salts with alkali and alkaline earth metal ions such as $M_2^{(+I)}H_2EDTA$ and $M^{(+II)}H_2EDTA$ (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, $H_4EDTA(s)$, $M_2^{(+I)}H_2EDTA$ and $M^{(+II)}H_2EDTA$ salts are stable only in very low pH range, and have high solubilities on the order of ~1 M beyond their respective stability pH ranges. Therefore, these phases cannot be solubility-controlling phases for EDTA the natural systems. For instance, the solubility of $H_4EDTA(s)$ is $\sim 10^{-2}$ M at pH 1, whereas it increases to ~1 M 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 $M_2^{(+I)}H_2EDTA$ and $M^{(+II)}H_2EDTA$. The solubilities of $Na_2H_2EDTA \bullet 2H_2O$ and $K_2H_2EDTA \bullet 2H_2O$ are also ~0.3 M and ~2 M at pH 4.4 and 4.7, respectively (Fiorucci et al., 2002). Similarly, $M^{(+II)}M^{(+I)}{}_2EDTA$ salts such as $CaNa_2EDTA \bullet 6H_2O$ have high solubilities on the order of $\sim 2\ mol \bullet kg^{-1}$ (Vorob'ev et al., 1970), and consequently they cannot be solubility-controlling phases in natural environments.

In contrast, $Ca_2EDTA(s)$ 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, $Ca_2EDTA(s)$ could be a solubility-controlling phase for EDTA in these systems. However, the solubility of $Ca_2EDTA(s)$ 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 $Ca_2EDTA(s)$ as a function of ionic strength to 5.0 $mol \bullet kg^{-1}$ in a NaCl medium, and to 7.5 $mol \bullet kg^{-1}$ in $MgCl_2$ medium, as NaCl and $MgCl_2$ 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 $Ca_2EDTA(s)$, and the interactions of EDTA with NaCl and $MgCl_2$ media. The model would enable researchers to estimate with a degree of high precision solubilities of $Ca_2EDTA(s)$ in various environments over a wide range of ionic strengths.

EXPERIMENTAL SECTION

In these solubility experiments, about 2-10 grams of the solubility controlling material—ACS reagent grade di-calcium ethylenediaminetetraacetic acid ($Ca_2EDTA(s)$, $Ca_2C_{10}H_{12}N_2O_8(s)$, 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. The supporting electrolytes are a series of NaCl solutions ranging from 0.010 $mol{\bullet}kg^{-1}$ to 5.0 $mol{\bullet}kg^{-1}$, and $MgCl_2$ solutions ranging from 0.01 $mol{\bullet}kg^{-1}$ to 2.5 $mol{\bullet}kg^{-1}$. 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). The Undersaturation experiments are conducted at laboratory room temperature ($22.5 \pm 0.5^{o}C$).

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 $mol{\bullet}kg^{-1}$, hydrogen-ion concentrations on molar scale (pcH) were determined from pH readings by using correction factors for NaCl and $MgCl_2$ 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 μm syringe filter, the filtered solution was then weighed, acidified with 0.5 mL of concentrated TraceMetal® grade HNO_3 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 $Ca_2EDTA(s)$ was confirmed by analyzing for EDTA concentrations with a DIONEX ion chromatograph (IC) (DIONEX IC 3000).

Solid phases were analyzed using a Bruker D8 Advance X-ray diffractometer with a Sol-X detector. There was no phase change during the experiments.

EXPERIMENTAL RESULTS, THERMODYNAMIC MODELING AND DISCUSSION

Experimental results for solubilities in NaCl and $MgCl_2$ solutions are tabulated in Tables 1 and 2, respectively. In Figure 1, solubilities of $Ca_2EDTA(s)$ as a function of experimental time in NaCl solutions are displayed. From Figure 1, 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 $Ca_2EDTA(s)$ as a function of experimental time in $MgCl_2$ solutions are displayed in Figure 2. It is clear from Figure 2 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 3, concentrations of calcium as a function of molalities of NaCl are displayed. Figure 3 indicates that concentrations of calcium in equilibrium with $Ca_2EDTA(s)$ have a strong dependence on concentrations of NaCl. The calcium concentrations first increase with NaCl molality in the range of 0.01 $mol{\bullet}kg^{-1}$ to 1.0 $mol{\bullet}kg^{-1}$. Above 1.0 $mol{\bullet}kg^{-1}$, the calcium concentrations decrease with increasing concentrations of NaCl. For instance, the calcium concentrations are ~0.07 $mol{\bullet}kg^{-1}$ in a 0.01 $mol{\bullet}kg^{-1}$ NaCl solution, increasing to ~0.1 $mol{\bullet}kg^{-1}$ in a 1.0 $mol{\bullet}kg^{-1}$ NaCl solution, and decreasing to ~0.08 $mol{\bullet}kg^{-1}$ in a 5.0 $mol{\bullet}kg^{-1}$ NaCl solution.

Similarly, concentrations of calcium as a function of ionic strength in $MgCl_2$ solutions are displayed in Figure 4. Figure 4 suggests that concentrations of calcium in equilibrium with $Ca_2EDTA(s)$ have a strong dependence on concentrations of $MgCl_2$ with rising solubilities with increasing $MgCl_2$ concentrations. For instance, the calcium concentrations are ~0.08 mol•kg^{-1} in a 0.01 mol•kg^{-1} $MgCl_2$ solution (Figure 4, and Table 2), increasing to ~0.3 mol•kg^{-1} in a 2.5 mol•kg^{-1} $MgCl_2$ solution. Of note, the calcium concentrations in a 0.01 mol•kg^{-1} $MgCl_2$ 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 $MgCl_2$ solutions are much higher than those in concentrated NaCl solutions. The reason for this difference is that Mg^{2+} forms a complex with $EDTA^{4-}$, i.e., $MgEDTA^{2-}$, which enhances the solubility of $Ca_2EDTA(s)$.

In the following, the experimental data described above are used to derive the thermodynamic parameters. The dissolution of $Ca_2EDTA(s)$ can be expressed as,

$$Ca_2EDTA(s) = 2Ca^{2+} + EDTA^{4-} \tag{1}$$

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

$$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-} \tag{2}$$

Using experimental data produced in this study, the solubility constant of $Ca_2EDTA(s)$ 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, 2015a).

In Table 3, the dissolution constant for $Ca_2EDTA(s)$, 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. 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 11.16. 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 $I = 0.1$ mol•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 following, solubilities of $Ca_2EDTA(s)$ in a wide range of ionic strengths predicted by the model are compared with experimental data. The solubilities of $Ca_2EDTA(s)$ 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 3. From Figure 3, it is clear that the model developed in this study can accurately describe solubilities of $Ca_2EDTA(s)$ over a wide range of ionic strengths. There are few experimental studies on solubility of $Ca_2EDTA(s)$. Vorob'ev et al. (1970) conducted an experimental measurement of solubility of $Ca_2EDTA \bullet 7H_2O(s)$ 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 mol•kg^{-1} NaCl (Figure 3). The pH for their measurement of the solubility of $Ca_2EDTA \bullet 7H_2O(s)$ was not mentioned.

It is worth noting that the solubility dependence of $Ca_2EDTA(s)$ as a function of ionic strength in NaCl solutions is similar to variations in the fourth acid dissociation constant of EDTA acid (i.e., log Q_{a4}, see Choppin et al., 2001; Thakur et al., 2014) as a function of ionic strength. The fourth acid dissociation constant of EDTA can be described by the following reaction.

$$HEDTA^{3-} = H^+ + EDTA^{4-} \tag{3}$$

The solubility of $Ca_2EDTA(s)$ as a function of ionic strength indicates that the solubility increases with ionic strength for ionic strengths below 2.1 mol•kg^{-1}. The solubility reaches its maximum at an ionic strength of 2.1 mol•kg^{-1}. Above an ionic strength of 2.1 mol•kg^{-1}, the solubility deceases with ionic strength. 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 mol•kg^{-1} (also see Figure 3 in Thakur et al., 2014). Log Q_{a4} reaches its maximum at an ionic strength of 2.0 mol•kg^{-1}. Above an ionic strength of 2.0 mol•kg^{-1}, log Q_{a4} deceases with ionic strength. The similarity in the dependency of solubilities of

$Ca_2EDTA(s)$ 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 $[\log\gamma_{H^+} + \log\gamma_{EDTA^{4-}} - \log\gamma_{HEDTA^{3-}}]$ first decreases with ionic strength, and then increases with ionic strength above an ionic strength of 2.0 mol•kg^{-1}. In the case of the solubility of $Ca_2EDTA(s)$, 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 mol•kg^{-1}, and then increases with ionic strength above an ionic strength of 2.1 mol•kg^{-1}.

Similarly, the solubilities of $Ca_2EDTA(s)$ 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 4. It is clear from Figure 4 that the model developed in this study can satisfactorily reproduce solubilities of $Ca_2EDTA(s)$ 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.

$Ca_2EDTA(s)$ in Low Temperature Environments: As mentioned before, $Ca_2EDTA(s)$ 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 $Ca_2EDTA(s)$. As an example of application of the model developed herein, the total EDTA concentrations limited by $Ca_2EDTA(s)$ 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 5). Figure 5 shows the predicted EDTA concentrations in equilibrium with $Ca_2EDTA(s)$ as a function of pH. Figure 5 indicates that the EDTA concentration is slightly higher at pH 4.5, and then it remains constant at 2.5×10^{-2} mol•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 mol•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, $Ca_2EDTA(s)$ 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 ETDA washing technology has been applied. To demonstrate these applications, solubility of $Ca_2EDTA(s)$ 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 ($CaSO_4$•$2H_2O$), 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 6 are the predicted EDTA concentrations in equilibrium with $Ca_2EDTA(s)$ in the model soil solution as a function of pH. From Figure 6, we can see that the EDTA concentration is 7.5×10^{-3} mol•kg^{-1} at pH 4.5. It remains constant at ~2×10^{-3} mol•kg^{-1} from pH 5.5 to pH ~9. Above pH 9.0, the EDTA concentration drops to 1.5×10^{-3} mol•kg^{-1}. Of note is the fact that the above total EDTA concentrations limited by $Ca_2EDTA(s)$ in the model soil solution (Figure 6, 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, $Ca_2EDTA(s)$ 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 $Ca_2EDTA(s)$, resulting in the loss of EDTA. Consequently, the optimal EDTA concentrations for decontamination of heavy metals in soils should be around 1×10^{-3} mol•kg^{-1} in alkaline soils. At this level of EDTA concentrations, it would be below the saturation limit of $Ca_2EDTA(s)$ without the loss of EDTA because of forming $Ca_2EDTA(s)$, 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 1×10^{-2} mol•kg^{-1}.

CONCLUSIONS

Long-term solubility measurements up to 1,435 days and to high ionic strengths for $Ca_2EDTA(s)$ 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 $MgCl_2$ 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 $Ca_2EDTA(s)$ in NaCl solutions produced in this work at 22.5 ± 0.5 °C*.

Experimental Number	Supporting Medium, NaCl, mol•kg^{-1}	Experimental time, days	pmH*	Solubility of $Ca_2EDTA(s)$ as total calcium concentrations, mol•kg^{-1}, $m_{\Sigma Ca}$
Ca_2EDTA-0.01-1	0.010	365	8.23	7.09E-02
Ca_2EDTA-0.01-2	0.010	365	8.20	7.15E-02
Ca_2EDTA-0.1-1	0.10	365	8.37	8.61E-02
Ca_2EDTA-0.1-2	0.10	365	7.90	8.69E-02
Ca_2EDTA-1.0-1	1.0	365	8.39	1.35E-01
Ca_2EDTA-1.0-2	1.0	365	7.92	1.35E-01
Ca_2EDTA-2.0-1	2.1	365	8.54	1.40E-01
Ca_2EDTA-2.0-2	2.1	365	8.49	1.42E-01
Ca_2EDTA-3.0-1	3.2	365	8.71	1.35E-01
Ca_2EDTA-3.0-2	3.2	365	8.47	1.31E-01
Ca_2EDTA-4.0-1	4.4	365	8.69	1.19E-01
Ca_2EDTA-4.0-2	4.4	365	8.63	1.19E-01
Ca_2EDTA-5.0-1	5.0	365	8.19	1.10E-01
Ca_2EDTA-5.0-2	5.0	365	8.19	1.10E-01
Ca_2EDTA-0.01-1	0.010	940	7.79	7.27E-02
Ca_2EDTA-0.01-2	0.010	940	7.85	7.28E-02
Ca_2EDTA-0.1-1	0.10	940	7.88	8.36E-02
Ca_2EDTA-0.1-2	0.10	940	7.81	7.99E-02
Ca_2EDTA-1.0-1	1.0	940	8.09	1.22E-01
Ca_2EDTA-1.0-2	1.0	940	7.77	1.23E-01
Ca_2EDTA-2.0-1	2.1	940	8.18	1.21E-01
Ca_2EDTA-2.0-2	2.1	940	8.20	1.20E-01
Ca_2EDTA-3.0-1	3.2	940	8.43	1.09E-01
Ca_2EDTA-3.0-2	3.2	940	8.30	1.10E-01
Ca_2EDTA-4.0-1	4.4	940	8.41	9.45E-02
Ca_2EDTA-4.0-2	4.4	940	8.40	9.29E-02
Ca_2EDTA-5.0-1	5.0	940	8.11	8.60E-02
Ca_2EDTA-5.0-2	5.0	940	8.10	8.54E-02
Ca_2EDTA-0.01-1	0.010	1025	7.84	7.30E-02

Ca$_2$EDTA-0.01-2	0.010	1025	7.83	7.27E-02
Ca$_2$EDTA-0.1-1	0.10	1025	7.81	8.49E-02
Ca$_2$EDTA-0.1-2	0.10	1025	7.81	8.52E-02
Ca$_2$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-5.0-1	5.0	1025	8.14	9.02E-02
Ca$_2$EDTA-5.0-2	5.0	1025	8.10	8.62E-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-5.0-1	5.0	1074	8.14	8.43E-02
Ca$_2$EDTA-5.0-2	5.0	1074	8.14	8.27E-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_2EDTA-4.0-2	4.4	1124	8.35	9.42E-02
Ca_2EDTA-5.0-1	5.0	1124	8.23	8.16E-02
Ca_2EDTA-5.0-2	5.0	1124	8.18	8.18E-02

Ca_2EDTA-0.01-1	0.010	1172	7.86	7.10E-02
Ca_2EDTA-0.01-2	0.010	1172	7.87	7.13E-02
Ca_2EDTA-0.1-1	0.10	1172	7.90	8.46E-02
Ca_2EDTA-0.1-2	0.10	1172	7.91	8.49E-02
Ca_2EDTA-1.0-1	1.0	1172	8.00	1.22E-01
Ca_2EDTA-1.0-2	1.0	1172	7.72	1.21E-01
Ca_2EDTA-2.0-1	2.1	1172	8.10	1.19E-01
Ca_2EDTA-2.0-2	2.1	1172	8.07	1.21E-01
Ca_2EDTA-3.0-1	3.2	1172	8.23	1.06E-01
Ca_2EDTA-3.0-2	3.2	1172	8.19	1.08E-01
Ca_2EDTA-4.0-1	4.4	1172	8.31	9.39E-02
Ca_2EDTA-4.0-2	4.4	1172	8.30	9.25E-02
Ca_2EDTA-5.0-1	5.0	1172	8.19	8.54E-02
Ca_2EDTA-5.0-2	5.0	1172	8.15	8.17E-02

Ca_2EDTA-0.01-1	0.010	1323	7.85	7.31E-02
Ca_2EDTA-0.01-2	0.010	1323	7.86	7.26E-02
Ca_2EDTA-0.1-1	0.10	1323	7.88	8.55E-02
Ca_2EDTA-0.1-2	0.10	1323	7.88	8.60E-02
Ca_2EDTA-1.0-1	1.0	1323	7.99	1.24E-01
Ca_2EDTA-1.0-2	1.0	1323	7.72	1.24E-01
Ca_2EDTA-2.0-1	2.1	1323	8.11	1.22E-01
Ca_2EDTA-2.0-2	2.1	1323	8.10	1.22E-01
Ca_2EDTA-3.0-1	3.2	1323	8.23	1.12E-01
Ca_2EDTA-3.0-2	3.2	1323	8.19	1.10E-01
Ca_2EDTA-4.0-1	4.4	1323	8.33	9.55E-02
Ca_2EDTA-4.0-2	4.4	1323	8.32	9.52E-02
Ca_2EDTA-5.0-1	5.0	1323	8.20	7.94E-02
Ca_2EDTA-5.0-2	5.0	1323	8.19	8.63E-02

Ca_2EDTA-0.01-1	0.010	1431	7.88	7.32E-02
Ca_2EDTA-0.01-2	0.010	1431	7.88	7.30E-02
Ca_2EDTA-0.1-1	0.10	1431	7.85	8.54E-02
Ca_2EDTA-0.1-2	0.10	1431	7.90	8.63E-02
Ca_2EDTA-1.0-1	1.0	1431	7.98	1.22E-01

Ca_2EDTA-1.0-2	1.0	1431	7.71	1.24E-01
Ca_2EDTA-2.0-1	2.1	1431	8.07	1.22E-01
Ca_2EDTA-2.0-2	2.1	1431	8.05	1.23E-01
Ca_2EDTA-3.0-1	3.2	1431	8.17	1.11E-01
Ca_2EDTA-3.0-2	3.2	1431	8.14	1.11E-01
Ca_2EDTA-4.0-1	4.4	1431	8.24	9.55E-02
Ca_2EDTA-4.0-2	4.4	1431	8.24	9.51E-02
Ca_2EDTA-5.0-1	5.0	1431	8.12	7.69E-02
Ca_2EDTA-5.0-2	5.0	1431	8.12	8.58E-02

* From Xiong (2015). 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 Sőhnel and Novotný (1985).

Table 2. Experimental results concerning solubility of $Ca_2EDTA(s)$ in $MgCl_2$ solutions produced in this work at 22.5 ± 0.5 °C

Experimental Number	Supporting Medium, $MgCl_2$, mol•kg^{-1}	Experimental time, days	pmH**	Solubility expressed as total calcium on molal scale, $m_{\Sigma Ca}$
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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* From Xiong (2015). 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 Na^+—Mg^{2+}—Ca^{2+}—Cl^-—$EDTA^{4-}$—H_2O system at 25°C

<table>
<tr><td colspan="5">Pitzer Parameters*</td></tr>
<tr><td>Species, i</td><td>Species, j</td><td>$\beta^{(0)}$</td><td>$\beta^{(1)}$</td><td>C^{ϕ}</td></tr>
<tr><td>Na^+</td><td>$CaEDTA^{2-}$</td><td>–0.0956 [A]</td><td>1.74 [A]</td><td>0.0131 [A]</td></tr>
<tr><td>Na^+</td><td>$EDTA^{4-}$</td><td>1.016 [B]</td><td>11.6 [B]</td><td>0.001 [B]</td></tr>
<tr><td>Na^+</td><td>$HEDTA^{3-}$</td><td>0.5458 [B]</td><td>5.22 [B]</td><td>–0.048 [B]</td></tr>
<tr><td>Mg^{2+}</td><td>$CaEDTA^{2-}$</td><td>0.525 [A]</td><td>3.27 [A]</td><td>0 [A]</td></tr>
<tr><td>Ca^{2+}</td><td>$MgEDTA^{2-}$</td><td>0.08436 [A]</td><td>3.27 [A]</td><td>0 [A]</td></tr>
<tr><td>Mg^{2+}</td><td>$EDTA^{4-}$</td><td>–0.01 [A]</td><td>11.6 [A]</td><td>0.3 [A]</td></tr>
<tr><td colspan="5">Equilibrium Constants at infinite dilution for Dissolution Reaction of $Ca_2EDTA(s)$ and Formation Reaction of $CaEDTA^{2-}$</td></tr>
<tr><td colspan="3">Reactions</td><td colspan="2">$\log K_{sp}^{0}$ or $\log \beta_1^{0}$</td></tr>
<tr><td colspan="3">$Ca_2EDTA(s) = 2Ca^{2+} + EDTA^{4-}$</td><td colspan="2">$-15.39 \pm 0.10$ [A]</td></tr>
<tr><td colspan="3">$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-}$</td><td colspan="2">$11.16 \pm 0.05$ [A]</td></tr>
</table>

[A] Evaluated in this study.

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

* α_1 for all interactions except for Mg^{2+}—$EDTA^{4-}$ is 2.0. For Mg^{2+}—$EDTA^{4-}$ interaction, α_1 is set to 1.4 in modeling, in analog to α_1 for the Th^{4+}—SO_4^{2-} interaction (Felmy and Rai, 1992).

Table 4. The chemical compositions of the groundwater and predicted total EDTA concentration in equibrium with $Ca_2EDTA(s)$ at 25^{o}C for the geological repository in granite at Olkiluoto, Finland*

Total Dissoved Salts (TDS), mg/L	Ionic Strength, mol•kg^{-1}	pH**	Na^+ mol•kg^{-1}	K^+ mol•kg^{-1}	Mg^{2+} mol•kg^{-1}	Ca^{2+} mol•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•kg^{-1}	$Mn^{2+\ A}$ mol•kg^{-1}	Cl^- mol•kg^{-1}	SO_4^{2-} mol•kg^{-1}	$\Sigma H_4SiO_4{}^{A}$ mol•kg^{-1}	ΣCO_3^{2-} mol•kg^{-1}	$\Sigma EDTA^{4-}$,^{B} mol•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 (mol•L^{-1}) are converted to those on molal scale (mol•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 $Ca_2EDTA(s)$.

Table 4. The initial compositions of the modified model soil solution* at 25°C used in calculation of solubility of $Ca_2EDTA(s)$ in gypsiferous soils

Species [A] and parameters	Concentration (M, mol•L^{-1})
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}
$HPO4^{2-}$	10^{-7}
NO_3^-	10^{-5}
$H_2AsO_4^-$	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 $Ca_2EDTA(s)$ 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 $Ca_2EDTA(s)$ in gypsiferous soils, total dissolved inorganic carbon is assumed to be controled by the equilibrium with the atmosphereic CO_2 ($10^{-3.5}$ bars)

[D] In the recipe in Xiong (2009), EDTA is not included. The listed values are the calculated total EDTA concentrations in equilibrium with $Ca_2EDTA(s)$.

[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 $Ca_2EDTA(s)$.

Figure Captions

Figure 1. A plot showing experimental total calcium concentrations in equilibrium with $Ca_2C_{10}H_{12}N_2O_8(s)$ in NaCl solutions as a function of experimental time produced in this study.

Figure 2. A plot showing experimental total calcium concentrations in equilibrium with $Ca_2C_{10}H_{12}N_2O_8(s)$ in $MgCl_2$ solutions as a function of experimental time produced in this study.

Figure 3. A plot showing experimental total calcium concentrations in equilibrium with $Ca_2C_{10}H_{12}N_2O_8(s)$ produced in this study as a function of molalities of NaCl. The experimental data from Vorob'ev et al. (1970) refers to the solubility of $Ca_2EDTA{\bullet}7H_2O(s)$ in water at 25°C.

Figure 4. A plot showing experimental total calcium concentrations in equilibrium with $Ca_2C_{10}H_{12}N_2O_8(s)$ produced in this study as a function of ionic strengths in $MgCl_2$ solutions.

Figure 5. A plot showing experimental total EDTA concentrations in equilibrium with $Ca_2C_{10}H_{12}N_2O_8(s)$ as a function of pH in the granite brine from Okkiluoto, Finland.

Figure 6. A plot showing experimental total EDTA concentrations in equilibrium with $Ca_2C_{10}H_{12}N_2O_8(s)$ as a function of pH in the model soil solution.

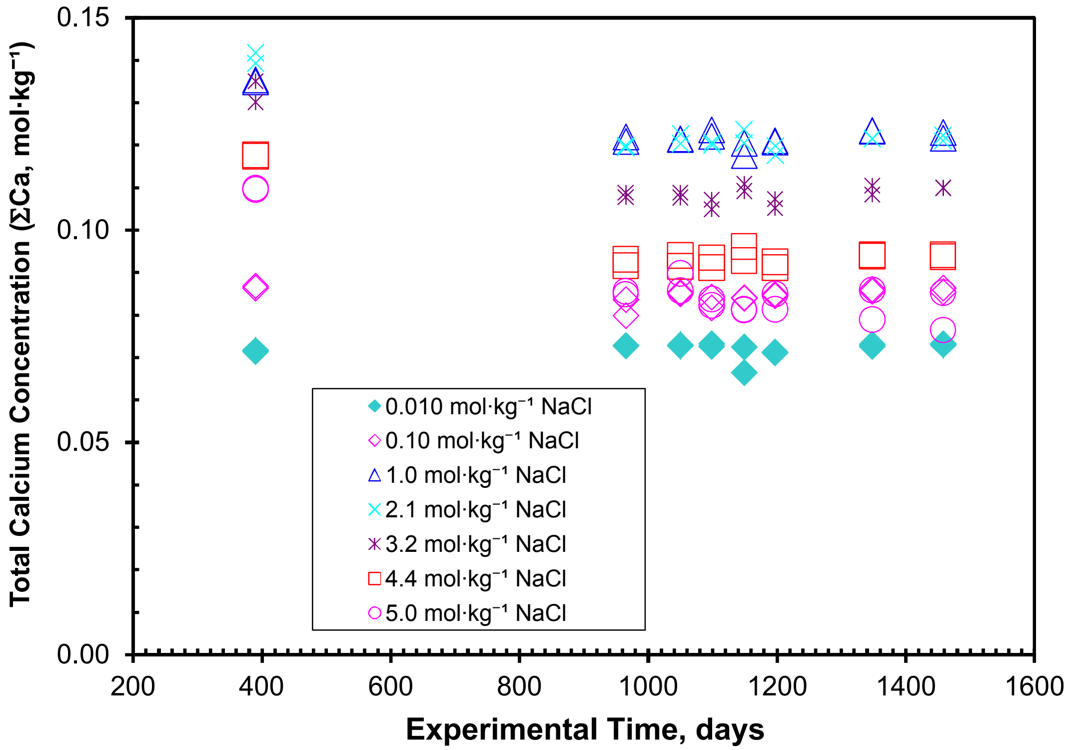
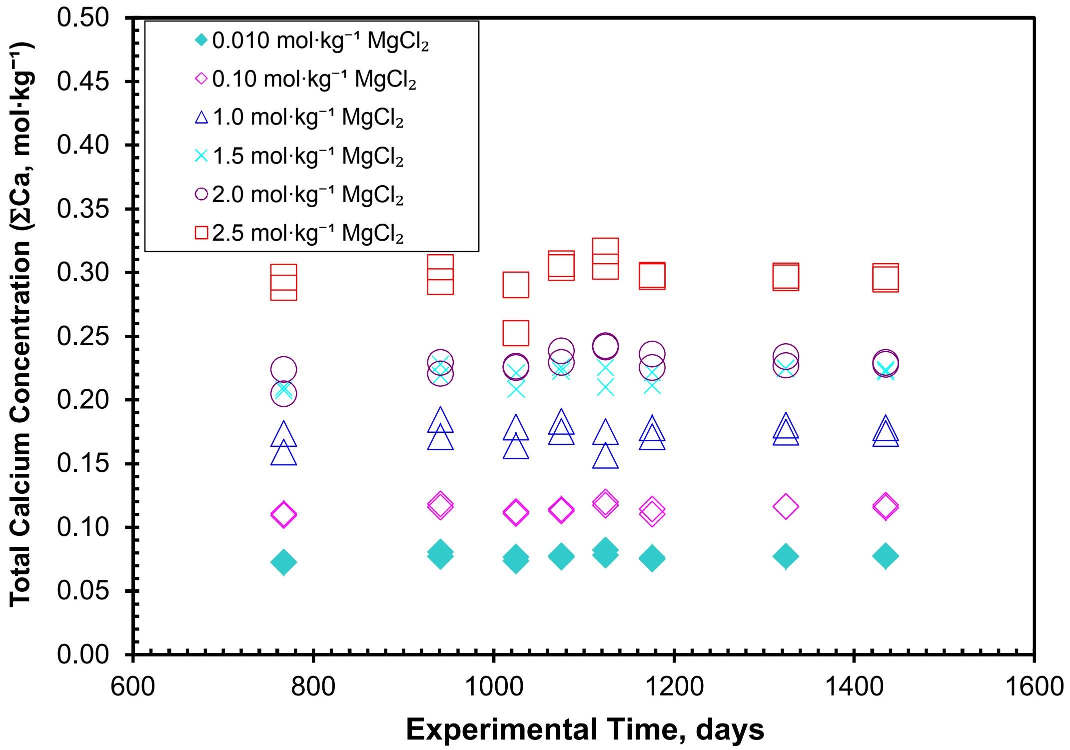
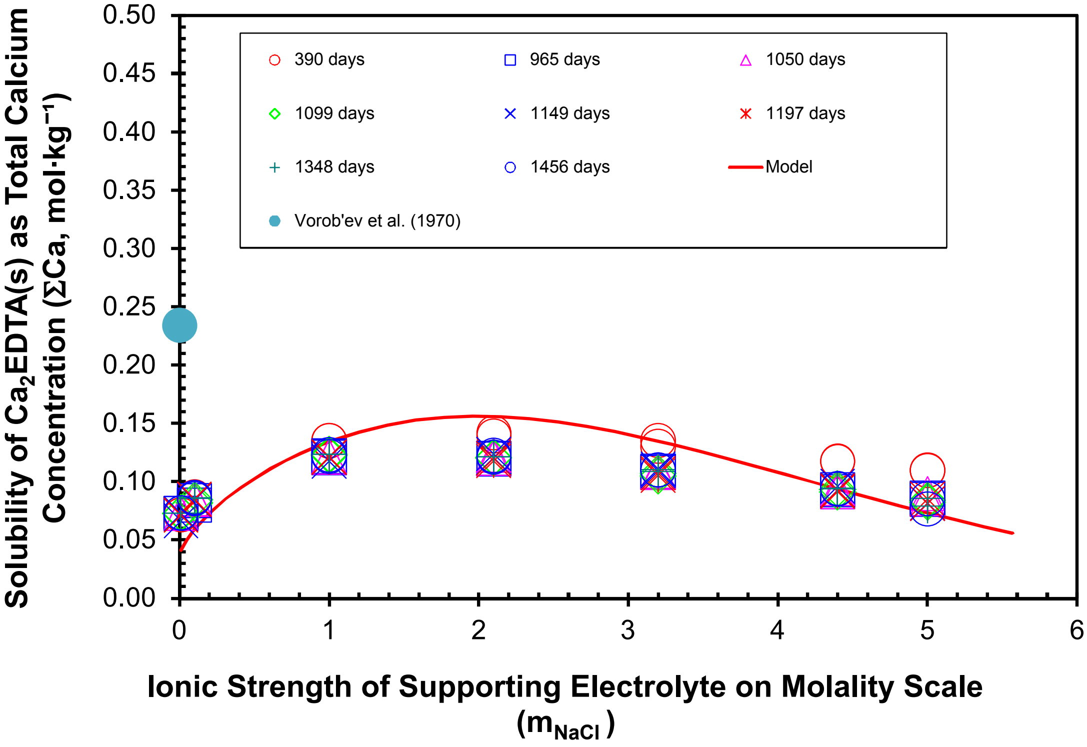

Total Calcium Concentration (ΣCa, mol·kg⁻¹)
0.15
0.10
0.05
0.00
200
400
600
800
1000
1200
1400
1600
Experimental Time, days
◆ 0.010 mol·kg⁻¹ NaCl
◇ 0.10 mol·kg⁻¹ NaCl
△ 1.0 mol·kg⁻¹ NaCl
× 2.1 mol·kg⁻¹ NaCl
⁎ 3.2 mol·kg⁻¹ NaCl
□ 4.4 mol·kg⁻¹ NaCl
○ 5.0 mol·kg⁻¹ NaCl

Figure 1.



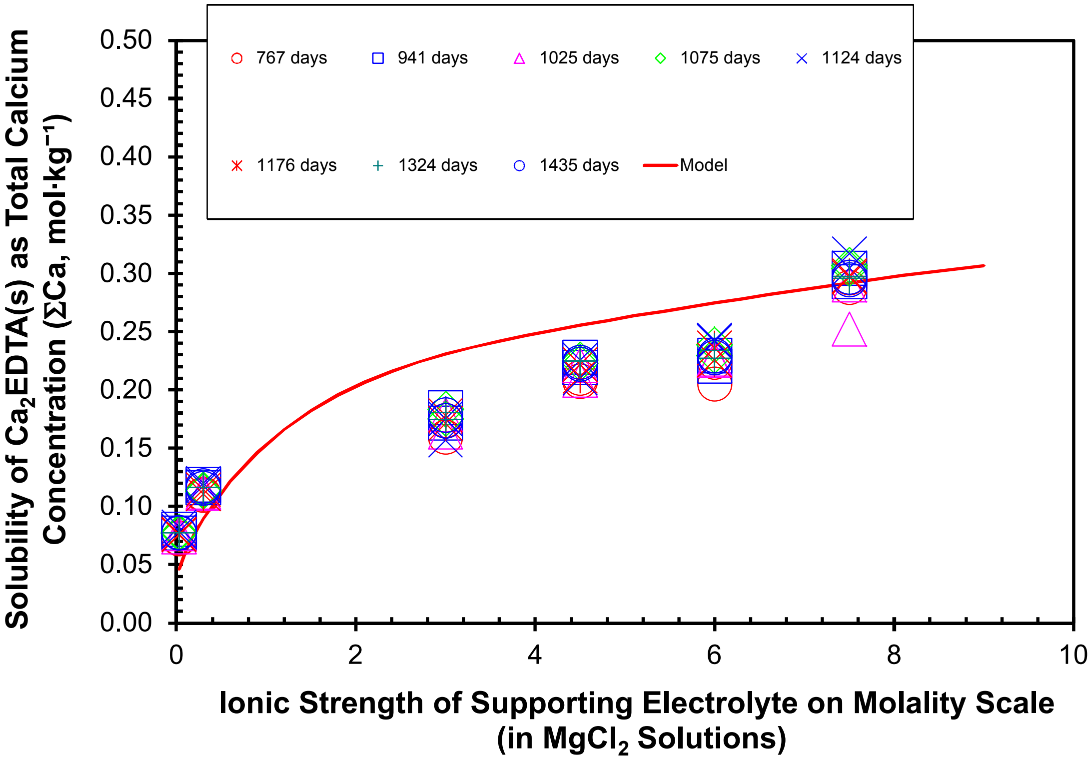
0.010 mol·kg⁻¹ MgCl₂
0.10 mol·kg⁻¹ MgCl₂
1.0 mol·kg⁻¹ MgCl₂
1.5 mol·kg⁻¹ MgCl₂
2.0 mol·kg⁻¹ MgCl₂
2.5 mol·kg⁻¹ MgCl₂
Total Calcium Concentration (ΣCa, mol·kg⁻¹)
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
600
800
1000
1200
1400
1600
Experimental Time, days

Figure 2.



Solubility of $Ca_2EDTA(s)$ as Total Calcium Concentration (ΣCa, $mol \cdot kg^{-1}$)
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
Ionic Strength of Supporting Electrolyte on Molality Scale (m_{NaCl})
390 days
965 days
1050 days
1099 days
1149 days
1197 days
1348 days
1456 days
Model
Vorob'ev et al. (1970)

Figure 3.



○ 767 days
□ 941 days
△ 1025 days
◇ 1075 days
× 1124 days
✕ 1176 days
+ 1324 days
○ 1435 days
Model
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
2
4
6
8
10
Solubility of Ca2EDTA(s) as Total Calcium Concentration (ΣCa, mol·kg⁻¹)
Ionic Strength of Supporting Electrolyte on Molality Scale (in MgCl2 Solutions)

Figure 4.

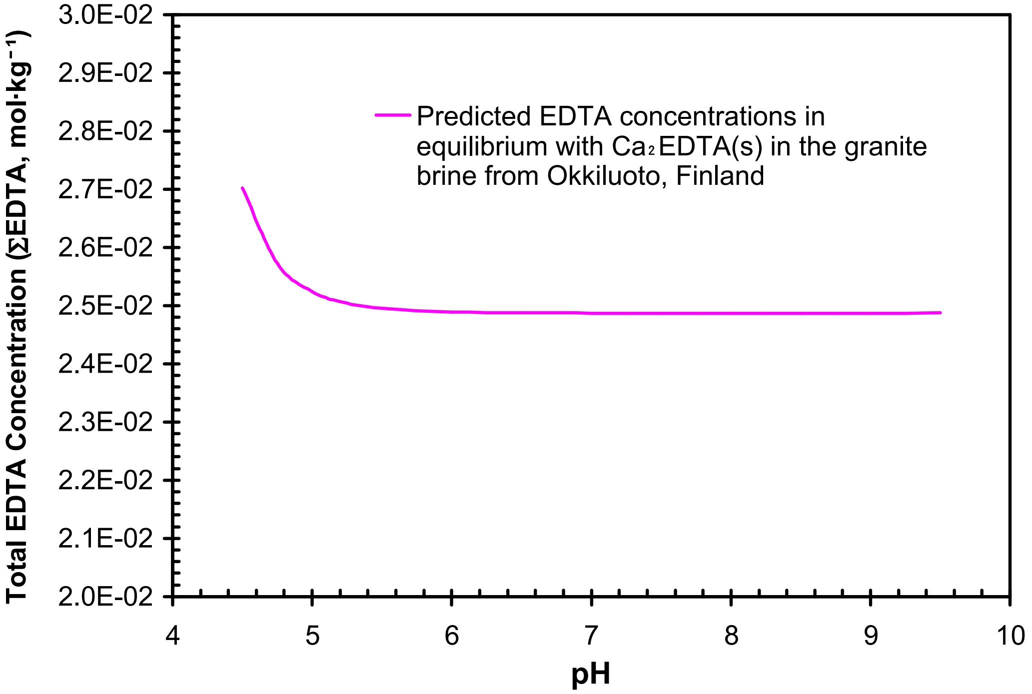

Total EDTA Concentration (ΣEDTA, mol·kg⁻¹)
3.0E-02
2.9E-02
2.8E-02
2.7E-02
2.6E-02
2.5E-02
2.4E-02
2.3E-02
2.2E-02
2.1E-02
2.0E-02
4
5
6
7
8
9
10
pH
Predicted EDTA concentrations in equilibrium with Ca₂EDTA(s) in the granite brine from Okkiluoto, Finland

Figure 5.

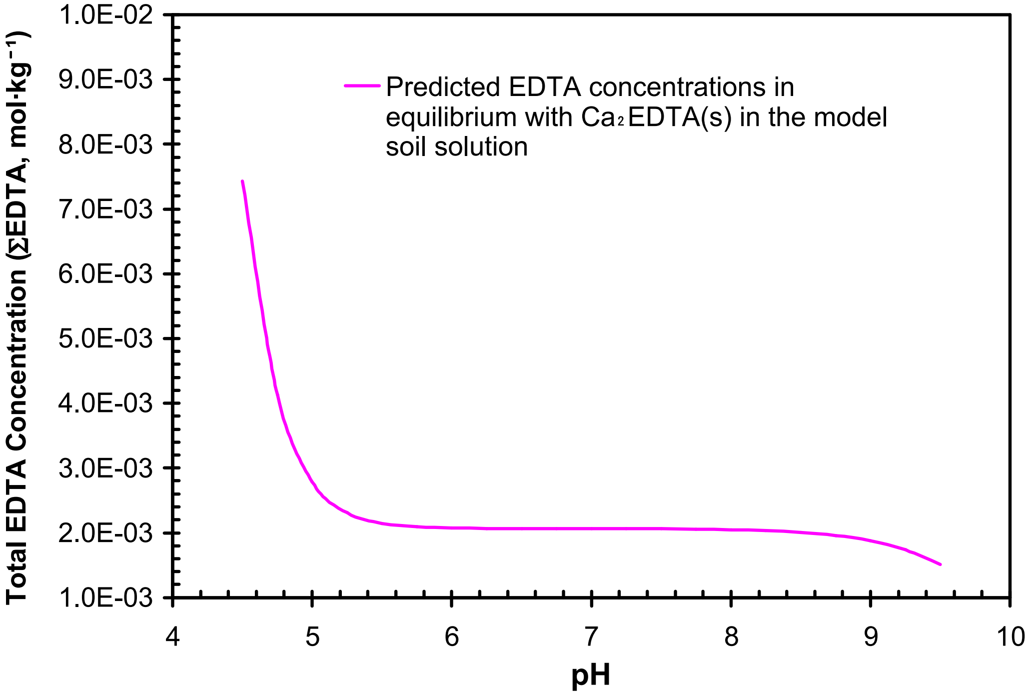

Total EDTA Concentration (ΣEDTA, mol·kg⁻¹)
1.0E-02
9.0E-03
8.0E-03
7.0E-03
6.0E-03
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
4
5
6
7
8
9
10
pH
Predicted EDTA concentrations in equilibrium with Ca₂EDTA(s) in the model soil solution

Figure 6.