

**A COMPLEXATION MODEL TO EVALUATE  
CARBOXYMETHYL- $\beta$ -CYCLODEXTRIN  
(CMCD) FOR REMEDIATION OF  
CONTAMINATED SOIL  
AND GROUND WATER**

by

Magnus Sköld

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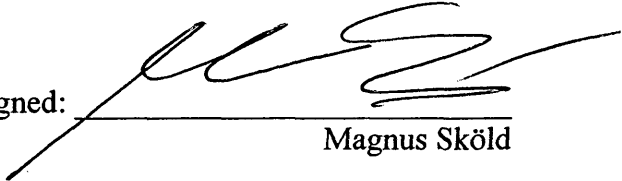
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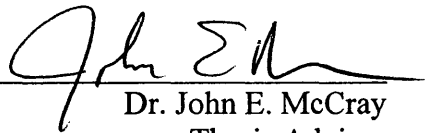
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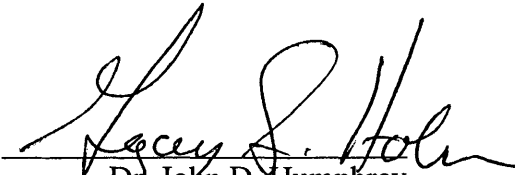
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## ABSTRACT

Carboxymethyl- $\beta$ -cyclodextrin (CMCD) is a non-toxic, sugar-based molecule that can enhance the solubility of metals and organic compounds simultaneously. Metals are bound to carboxyl groups on the outside of the molecule and organic compounds partition into the non-polar cavity in the center of the CMCD molecule. These mechanisms act independently of each other making CMCD attractive for remediation of sites co-contaminated with metals and organics. While research has quantified the strength of inclusion complexes between the cavity of cyclodextrin (CD) derivatives and various organic contaminants, only a few studies have investigated metal complexation by CMCD and only one has reported the formation constant for a CMCD-metal complex. Synthetic metal complexing agents, such as EDTA, form stronger interactions with metals than does CMCD and are therefore potentially more efficient remediation agents. However, these complexation agents are toxic and cannot typically be applied for in-situ remediation.

This study has three primary objectives. First, to demonstrate a practical, yet scientifically sound, complexation model that can be used to screen CMCD as a complexing agent for enhanced aquifer flushing of soil and ground water co-contaminated with metals and organic pollutants. Part of this objective is to present and utilize a statistical-based methodology to test the validity and relative quality of various geochemical conceptual models for metal complexation and to choose the most appropriate conceptual model. The second goal is to evaluate metal complexing properties of CMCD by determining conditional formation constants for selected important contaminant metals. The third objective is to investigate the impact of

contaminant mixtures (multiple metals, and metal-organic mixtures) on the solubility enhancing properties of CMCD.

The study determined conditional formation complexes for eight important contaminant metals (Ba, Ca, Cd, Ce, Ni, Pb, Sr, and Zn). To identify the most appropriate geochemical conceptual model, the effect of background ionic strength and increasing CMCD concentration on metal complexation was also investigated.

The modeling approach presented here, based on PHREEQC and UCODE\_2005, allows comparison of several conceptual models and statistical evaluation of uncertainties in estimated conditional stability constants. It can also be applied to evaluation of other metal complexing agents such as oxalic and citric acids. The use of PHREEQC and UCODE is recommended for determining thermodynamic constants from experimental data.

An evaluation of the complexation model indicates that it is able to correctly represent competitive complexation between CMCD and Pb, Sr, and Zn to within 15% for CMCD concentrations up to 100 g/l. Simultaneous perchloroethylene (PCE) and metal interactions have successfully been included in the model and it can be used for screening CMCD as a complexing agent for remediation of sites co-contaminated with metals and organics. Should CMCD-enhanced aquifer flushing be chosen as a remediation technique the model can also be used to optimize remediation performance.

The data presented in this dissertation will be useful for engineers and scientists who desire to remediate toxic metals or mixed waste from soils or ground water. While this research focused on common metal and organic contaminants that can be readily handled in the laboratory, the proposed methodology can be applied to any metal- and/or organic-

complexing remediation agent, and will be useful for screening complexing agents for subsurface remediation of mixed wastes.

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# CHAPTER ONE

## INTRODUCTION

A large number of sites in the U.S. are contaminated with both metals and organic pollutants, referred to as mixed waste hereafter in this dissertation. The different properties of the two contaminant classes make remediation of mixed-waste sites challenging. One approach that has been suggested to remove the contaminants is to use different techniques lined up in a treatment train. Another approach is to modify an existing technique so it can be applied to both contaminant groups. The research presented herein focuses on using a molecule that can form aqueous-phase complexes with both organics and metals, enabling removal of these co-contaminants from aquifers using enhanced pump-and-treat techniques. The approach detailed herein uses a combination of laboratory experimental data coupled to geochemical models to rapidly assess the potential of remediation agents. In particular, the dissertation addresses cyclodextrin-enhanced aquifer flushing and, especially, building conceptual and mathematical geochemical models to screen this agent for remediation of mixed waste sites.

### **Significance of research**

During the initial stage of this research project a thorough literature review was conducted on cyclodextrin (CD) enhanced flushing of contaminated soil and on remediation of mixed-waste sites (presented in Chapter 2). Also, the co-occurrence of metals and organic compounds at sites on the National Priority List (NPL) was evaluated by screening information about 134 sites in California, Colorado, New Jersey, and Pennsylvania. California, New Jersey, and Pennsylvania were chosen because these states

have the largest number of sites on the NPL; Colorado was chosen because it is the home state of the Colorado School of Mines. Information about the sites was gathered during the summer of 2003 from the data base CERCLIS (Comprehensive Environmental Response, Compensation, and Liability Information System) which is published by the U.S. Environmental Protection Agency (EPA). Both organic and inorganic contaminants were encountered at approximately 60% of the screened sites. The most commonly encountered metal pollutants were, in order of decreasing abundance: Pb, As, Cr, Cd, Zn, Cu, Hg, Ba, and Ni. It was not possible to determine if metals and organic pollutants were encountered at the same location or at separate places of the sites. However, the results clearly indicate that co-occurrence of metals and organic contamination is a challenge for remediation of many sites. Thus, there is a need for a remediation technique that can be used to clean-up mixed waste sites. Unfortunately, the literature on remediation of actual mixed-waste sites is sparse. Only a few articles present laboratory or theoretical studies on this topic. Thus, fundamental and applied studies on remediation of mixed waste is clearly a fruitful area for novel research. However, the literature study revealed no papers that presented field trials of mixed waste removal using any complexing agent.

The literature review revealed attempts to modify soil flushing for remediation of mixed waste by using aqueous-phase chemical agents that can enhance the natural solubility of both classes of contaminants. The flushing solution can be modified by using either a mixture of complexing agents and surfactants or cosolvents, or by using one agent that enhances the solubility of both organic and inorganic contaminants. One cyclodextrin derivative, carboxymethyl- $\beta$ -cyclodextrin (CMCD), has the ability to complex both organic and inorganic contaminants simultaneously. CMCD is the focus of this research. While other potential complexing agents are available, CMCD is selected because it is a sugar-based molecule, and is non-toxic in the environment. More discussion on the relative benefits of CMCD compared to other candidates is provided in subsequent chapters.

Several studies, including five field trials, have investigated the effectiveness of CD enhanced aquifer flushing for remediation of organic contaminants. However, only a handful of investigations (and no field trials) have been performed on metal removal using CMCD as a complexing agent. The understanding of CMCD-metal interactions is therefore limited. Investigating the CMCD complexation of relevant metal ions will thereby improve the knowledge of metal-CMCD complexation, as well as the fundamental knowledge on metal remediation via complexation, in general.

Aquifer remediation is an expensive endeavor. Thus, conducting laboratory experiments and mathematical modeling to evaluate and design remediation schemes prior to implementation in the field are imperative, though not always conducted. Geochemical modeling is a potentially powerful tool for predicting contaminant speciation during transport and remediation. A valid conceptual model and availability of thermodynamic constants for contaminant speciation are necessary to correctly model a potential remediation scenario. A geochemical model describing metal-CMCD interactions would enable screening and comparison of CMCD-enhanced aquifer flushing to other remediation techniques as a first step in the design of remediation efforts and would also facilitate cost-benefit analyses between different remediation techniques. This dissertation demonstrates the development of a CMCD-metal complexation model, derives the conditional formation constants for enhanced solubilization of solid-phase metals via complexation by aqueous-phase CMCD, uses the modified geochemical model to predict the behavior of CMCD in mixed waste systems, and, finally, compares the model results to experimental data from a synthetic mixed waste system.

Only a few studies have been carried out on metal remediation using CMCD, and only one study attempted to quantify the stability constant for complexation between CMCD and a single metal ion (cadmium). The overarching goal of this research is to attempt to

fill existing research gaps by evaluating the efficacy of CMCD to complex several important contaminant metals, to provide a means to screen CMCD-enhanced aquifer flushing as a remediation technique, and to evaluate whether CMCD complexation in contaminant mixtures is feasible. Specific objectives of this research, and the associated hypotheses, are provided below.

### **Objectives and hypotheses**

The first objective is to demonstrate a practical, yet scientifically sound, complexation model that can be formulated for CMCD-metals and organic complexation. Part of this objective includes demonstrating that a statistical-based methodology can be combined with inverse geochemical modeling (parameter estimation) to test the validity and relative goodness of various geochemical conceptual models for metal complexation and to choose the most appropriate conceptual model.

Second, evaluate metal complexing properties of CMCD by determining conditional formation constants for selected important contaminant metals (Ba, Ca, Cd, Ce, Ni, Pb, Sr, and Zn) from simple batch experiments.

Third, use the modified geochemical model to predict the performance of CMCD in a synthetic mixed-waste system (multiple metals, and metal-organic mixtures) and compare the results to experimental data.

Based on these three objectives the following hypotheses were formulated, respectively.

First, available and commonly used activity models and complexation formulations between specific species can be used to predict CMCD-enhanced solubility of metal salts and common organic contaminants.

Second, CMCD forms complexes with common metal contaminants and therefore significantly enhances the solubility of these contaminants.

Third, interactions between CMCD and contaminants in a contaminant mixture (multiple metals and metal organic-mixtures) can be predicted from the geochemical complexation model.

### **Structure of thesis**

The research presented in this dissertation is being submitted as five separate papers to peer reviewed journals. A discussion on how each paper is related to a chapter or appendix in this dissertation is described below. The submitted journal papers are listed as footnotes referenced in the discussion below. In addition, a brief discussion is provided to show which chapters are associated with each of the above objectives and hypotheses.

Chapter 2<sup>1</sup> provides an extensive literature review of previous work performed on the use of cyclodextrin derivatives for remediation of contaminated sites. Because most work has focused on remediation of organic contaminants, the literature review discusses the remediation of organic contaminants in more detail than metal remediation.

A lead-CMCD complexation model is presented in chapter 3<sup>2</sup>. The solubility of a lead oxalate was measured in batches at three different ionic strengths, each in the presence of various concentrations of CMCD to build a conceptual complexation model and to determine the conditional formation constant. Several conceptual models were evaluated

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<sup>1</sup> This chapter will be submitted as a literature review to a peer reviewed journal shortly after publication of this thesis.

<sup>2</sup> Skold, M.E., Thyne, G.D., Drexler, J.W., McCray, J.E., A geochemical model for lead complexation by carboxymethyl- $\beta$ -cyclodextrin (CMCD). Submitted to Journal of Contaminant Hydrology. In review.

by modeling experimental data using the computer programs PHREEQC and UCODE\_2005. The chapter describes and statistically justifies which conceptual models are appropriate. Research described in this chapter is associated with completion of objective 1 and testing of the 1<sup>st</sup> hypothesis.

Chapter 4<sup>3</sup> presents results on similar batch experiments that were performed for seven other metal salts to estimate conditional stability constants for metal-CMCD complexes. The same conceptual model developed for lead-CMCD complexation was used. Research described in this chapter is associated with completion of objective 2 and testing of the 2<sup>nd</sup> hypothesis.

The complexation model is evaluated in chapter 5<sup>4</sup>. Results from a set of batch experiments consisting of a mixture of PCE and three metal salts in the presence of CMCD were compared to predicted solubilities. This chapter is the component of this thesis directly dealing with remediation of mixed waste. Research described in this chapter is associated with completion of objective 3 and testing of the 3<sup>rd</sup> hypothesis, and also of completion of objective 1 and testing of the 1<sup>st</sup> hypothesis.

Appendix A<sup>5</sup> describes in detail how conditional formation constants were extracted from experimental data; parts of input files to the two computer programs (PHREEQC and

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<sup>3</sup> Skold, M.E., Thyne, G.D., Drexler, J.W., McCray, J.E., Solubility enhancement of eight metal contaminants using carboxymethyl- $\beta$ -cyclodextrin (CMCD). Submitted to Environmental Science and Technology. In review.

<sup>4</sup> Skold, M.E., Thyne, G.D., Drexler, J.W., McCray, J.E., Enhanced solubilization of a metal-organic contaminant mixture (Pb, Sr, Zn, and PCE) by cyclodextrin. This chapter will be submitted as a research paper to a peer reviewed journal shortly after publication of this thesis.

<sup>5</sup> Skold, M.E., Thyne, G.D., McCray, J.E., An example of using UCODE\_2005 and PHREEQC to determine thermodynamic constants from experimental data. Submitted as Computer Note to Ground Water. In press.

UCODE\_2005) that were used for this purpose are presented. Research described in this chapter is associated with completion of the 1<sup>st</sup> objective.



**CHAPTER TWO**  
**A REVIEW OF THE LITERATURE ON THE USE OF**  
**CYCLODEXTRIN (CD) DERIVATIVES FOR**  
**REMEDICATION OF CONTAMINATED**  
**SITES**

**Abstract**

Several properties of cyclodextrin (CD) make it an attractive in-situ remediation agent: CD is a non-toxic sugar, does not sorb significantly to most soil surfaces, has hydraulic properties similar to water, and enhances the solubilities of organic contaminants. In recent years, several field trials of CD enhanced aquifer flushing have demonstrated that the technique significantly enhances the removal rate of organic contaminants compared to conventional pump and treat. CD enhanced aquifer flushing is appropriate for treatment of source zones in combination with other long-term treatment strategies such as natural attenuation. In order for this innovative technique to be economically viable at commercial scales the flushing agent must be reused. This has been achieved using air stripping in a pilot test and can likely be implemented to larger projects with minor modifications. Because CD enhances the aqueous solubility of organic contaminants it also increases their biodegradation potential.

One specific CD derivative, carboxymethyl- $\beta$ -cyclodextrin (CMCD), has the ability to simultaneously complex metals and organics and has been suggested for remediation of mixed waste (metals and organics) sites. Laboratory experiments on artificially contaminated soil show great promise for enhanced dissolution of metals and organics.

However, CMCD forms less strong complexes with metals than do synthetic complexing agents and the metal removal efficiency of CMCD flushing will depend on site specific conditions such as metal speciation, pH, and extent of contamination.

## **Introduction**

Cyclodextrin (CD) is produced by microbial degradation of starch and can be classified as a sugar. Because the sugar molecule is non-toxic and has several properties of an ideal flushing agent it has been proposed as a complexing agent for in-situ remediation of contaminated soil and groundwater. The focus of most cyclodextrin research in remediation has been on removing organic contaminants from the subsurface. Many investigations have shown that the solubilities of organic contaminants increase significantly in the presence of cyclodextrin derivatives. These non-polar organic substances form inclusion complexes with the low-polar cavity in the center of the cyclodextrin molecule. However, several investigations have shown that one cyclodextrin derivative, carboxymethyl- $\beta$ -cyclodextrin (CMCD) also forms complexes with metal ions and consequently has potential for remediation of mixed waste, at sites co-contaminated with both metals and organic compounds.

A previous literature review on the use of cyclodextrin for remediation purposes was published by Boving and McCray (1998). Since then, many articles have been published that describe new applications and field trials. Thus, another review of the current literature is timely. This literature review attempts to improve our understanding of the use of cyclodextrin in remediation efforts by demonstrating new applications and principles, corroborating assumptions and knowledge previously supported by only one study, and include additional work published after 1998. Interactions with organic substances are discussed after a short description of cyclodextrin and its behavior in the subsurface. Finally, metal complexation and use of CD to improve other remediation techniques are discussed.

## Properties and Subsurface Behavior

Cyclodextrin is a non-toxic remediation agent that consists of glucose molecules in a ring structure which forms a relatively non-polar cavity in the center of the molecule (Figure 2-1). Typical derivatives include  $\alpha$ ,  $\beta$ , and  $\gamma$ -cyclodextrin which refers to the number of glucose molecules in the CD: 6, 7, and 8, respectively. The most common CD is composed of 7 glucose rings and if not otherwise noted all cyclodextrins discussed herein are  $\beta$ -CDs.

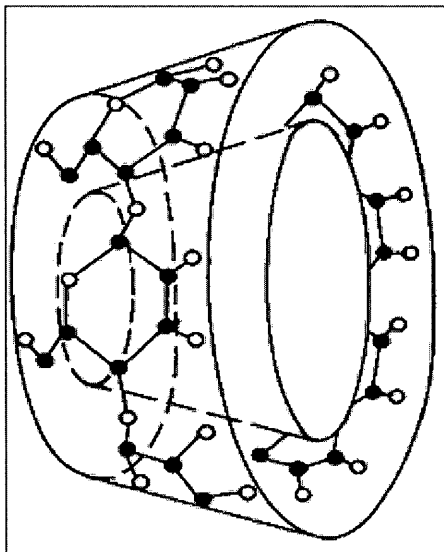


Figure 2-1. Structure of  $\beta$ -cyclodextrin (Loftsson, 1996).

CD with no functional groups substituted to the molecule is only slightly soluble in water. To increase its water solubility and to change other properties, functional groups are substituted on the outside of the molecule. Attaching functional groups to the CD molecule normally results in mixtures of CDs with different degrees of substitution and with functional groups in different positions on the CD (Müller and Brauns, 1986). For remediation of organic contaminants, the most commonly investigated CD derivatives are methyl- $\beta$ -cyclodextrin (MCD), hydroxypropyl- $\beta$ -cyclodextrin (HPCD), and

carboxymethyl- $\beta$ -cyclodextrin (CMCD). Among these CD derivatives, only CMCD complexes metals.

For in-situ remediation, it is important that the remediation agent does not appreciably interact with soil particles and that it reaches the entire hydrological compartment in the soil. McCray et al. (2000) reported physical properties of a 10 wt.% HPCD solution and concluded that the slightly higher density and viscosity, 2.4% and 19% higher than water, respectively, do not significantly affect the performance of an in-situ remediation system. Brusseau et al. (1994) investigated the transport of pyrene, anthracene, and trichlorobiphenyl through soil in the presence of aqueous-phase HPCD. Two different soils were used: a low organic carbon (0.3%) Borden sand and a fine grained (24% silt and 16% clay) organic carbon rich (13%) Mt. Lemmon soil. Comparison of breakthrough curves for HPCD and pentafluorobenzoate indicated that there was no measurable sorption, retardation, or pore exclusion of HPCD on either soil. Batch experiments confirmed that HPCD does not sorb to these soils. The retardation factors for 8 different organic compounds were significantly reduced in the presence of HPCD indicating that HPCD significantly enhances the transport of organic compounds. The transport of organic compounds was slower in the high organic soil but the presence of HPCD reduced the retardation by a factor of 2 to 8. Similarly, Ko et al. (1999) showed that HPCD does not sorb onto kaolinite. The authors argued that HPCD may have advantages over surfactants such as Tween and SDS because these agents have been found to sorb to the solid phase. However, Jozefaciuk et al. (2003) discovered that randomly methylated MCD strongly interacted with soils. Other scientist have obtained similar results to the ones presented by Jozefaciuk and co-workers. HPCD and a less polar CD derivative, heptakis-2,6-di-O-methyl- $\beta$ -cyclodextrin (DMCD), both enhanced the solubility of trinitrotoluene (TNT) and its amino derivatives (Sheremata and Hawari, 2000). The least polar CD was more efficient but sorbed to illite and to an organic topsoil. HPCD did not sorb significantly to either soil. The difference in behavior may be attributed to the

difference in polarity; MCD and DMCD are less polar than HPCD and are therefore more likely to interact with non-polar soil particles. Because CMCD is more polar than HPCD it is essentially non-reactive with most soil particles. It does, however, interact with iron oxide/hydroxide surfaces (Vulava and Seaman, 2000).

Mobilization of dense non-aqueous phase liquids (DNAPLs) is sometimes used as a remediation strategy. However, this is difficult to control and could result in a spread of NAPL contamination. Thus, it is usually not desirable. Mobilization may occur if the remediation agent partitions into the organic phase causing a lowering of the surface tension between the flushing solution and NAPL phase. In general, the less polar the complexing agent is the higher the risk for mobilization. Boving et al. (1999) compared the efficiency of MCD and HPCD at removing PCE and TCE from an artificially contaminated porous medium. In addition to measuring dissolved TCE and PCE breakthrough curves they measured surface tension between the pure contaminants and cyclodextrin solutions. NAPL mobilization was observed in a PCE-contaminated medium flushed with 5 and 10 wt.% MCD. Surface tension was lower for these solutions and capillary forces were not able to resist the viscous forces. The surface tension of HPCD only decreased 10% when the HPCD concentration varied from 0 to 70 g/l; no mobilization was noticed in HPCD experiments. In another study, NAPL mobilization was observed for 5 wt.% solutions of MCD, the anionic surfactants SDS and DOWFAX 8390 as well as for a 50 vol.% solution of ethanol (Boving and Brusseau, 2000). The authors concluded that low surface tension was responsible for the NAPL mobilization.

These results clearly indicate that the sugar based, non-toxic agents HPCD and CMCD do not experience pore exclusion, do not sorb significantly onto soil constituents, and do not cause mobilization of residual NAPL. However, the least polar cyclodextrin, MCD, interacts with soil and may cause NAPL mobilization and thus may not be suitable for in-situ remediation via enhanced dissolution. The mechanism responsible for CD-enhanced

solubility of organic contaminants, inclusion complexation, is discussed in the section below.

### **Inclusion complexation of organic substances**

The use of cyclodextrin in remediation of organic contaminants stems from its ability to form inclusion complexes with these pollutants, thereby increasing the total aqueous concentration. Several studies have shown that the complexation ratio of guest to host molecule is 1:1 (Wang and Brusseau, 1993; Hanna et al., 2003), Equation 2-1. In the derivation below of the stability constant for the inclusion complex, concentrations are expressed in units of mol/l and are written within brackets.

$$S_w + CD_w = CDS \quad (2-1)$$

[S<sub>w</sub>] is the aqueous uncomplexed concentration of the organic compound, [CD] is the concentration of the free cyclodextrin, and [CDS] is the concentration of the inclusion complex. The strength of the complex can be described by the stability constant, K, which has units of l/mol.

$$K = \frac{[CDS]}{[S_w] \cdot [CD]} \quad (2-2)$$

The total aqueous concentration of the contaminant is the sum of the aqueous solubility, [S<sub>w</sub>], and the complexed concentration and can be expressed as:

$$[S_{tot}] = [S_w](1 + K \cdot [CD_w]) \quad (2-3)$$

If a substantial amount of CD is complexed the free and total CD concentrations differ. In this case, inserting  $[CDS] = [CD_{tot}] - [CD_w]$  into Equation 2-2 and rearranging yields:

$$[CD_w] = \frac{[CD_{tot}]}{1 + K \cdot [S_w]} \quad (2-4)$$

Inserting Equation 2-4 into Equation 2-3 results in an equation for the total concentration of the organic compound as a function of CD concentration:

$$[S_{tot}] = [S_w] \cdot \left( 1 + \frac{K}{1 + K \cdot [S_w]} \cdot [CD_{tot}] \right) \quad (2-5)$$

Inclusion complexation can also be described as partitioning of the contaminant between water and CD (Chiou et al., 1986; Wang and Brusseau, 1993). Units of mass per volume (g/l) are used in the derivation of the partitioning constant,  $K_{CDW}$ , below. It is defined as:

$$K_{CDW} = \frac{S_{CD}}{S_w} \quad (2-6)$$

and has units of volume of water per mass CD.  $S_{CD}$  is the mass of solute partitioned into a unit mass of cyclodextrin and  $S_w$  is the aqueous solubility of the organic compound.

Thus, the partitioning coefficient is independent of concentration but the total mass of contaminant that partitions into CD,  $S_{CD-TOT}$ , is a function of the total CD concentration of the solution.

$$S_{CD-TOT} = S_w \cdot K_{CDW} \cdot CD_{tot} \quad (2-7)$$

The total aqueous solubility of the organic contaminant can now be expressed as:

$$S_{tot} = S_w \cdot (1 + K_{CDW} \cdot CD_{tot}) \quad (2-8)$$

It follows that the partitioning coefficient and the complexation constant are related, Equations 2-5 and 2-8. A unit conversion from mol/l to g/l is necessary to compare the two constants.  $MW_{CD}$  is the molecular weight of the CD.

$$K = \frac{K_{CDW} \cdot MW_{CD}}{1 - K_{CDW} \cdot MW_{CD} \cdot [S_w]} \quad (2-9)$$

The shape, size and polarity of the organic compound determine the degree of partitioning into the CD cavity. In general, the less polar the organic compound and CD derivative are, the stronger the interaction between host and contaminant. Size can be a limiting factor; if the organic compound is larger than the CD cavity the strength of the inclusion complex decreases significantly.

Wang and Brusseau (1993) investigated the enhanced solubility of five organic non-polar contaminants (TCE, chlorobenzene, naphthalene, anthracene and DDT) by HPCD in a series of batch experiments. The aqueous concentration (total solubility) of the test contaminants increased linearly from 0 to 70 g/l HPCD. The correlation between polarity of the organic compounds and their tendency to partition into HPCD was tested. The partitioning coefficients,  $K_{CDW}$ , were strongly correlated to the octanol-water partitioning coefficients,  $K_{OW}$ . The less polar the contaminant the stronger it partitioned into the HPCD cavity. However, one compound, DDT, did not conform to this trend. In addition, equilibrium between HPCD and DDT was slower than for the other contaminants. This phenomenon was explained by size exclusion. Only DDT has a diffusion molecular

volume larger than the volume of the HPCD cavity ( $0.346 \text{ nm}^3$ ). Thus, the DDT molecule does not completely fit inside the HPCD cavity. The non-polar part of the HPCD-DDT complex that protrudes into the aqueous phase decreases the stability constant of the complex. McCray et al. (2000), who measured the concentration of organic compounds in 10 wt.% HPCD, delivered a similar conclusion for 18 chlorinated solvents, aromatic hydrocarbons and long-chained alkanes. The authors noticed a linear relationship between  $K_{OW}$  and the  $K_{CDW}$  of the organic compounds.

Similarly, the stability constant for phthalic acid esters and  $\beta$ -CD polymer increased with increasing octanol-water partitioning coefficients (Murai et al., 1998). One exception was noticed. One ester with a branched alkyl chain had a lower stability constant than expected from its  $K_{ow}$ . The authors attributed this effect to steric hindrance of the branched alkyl chains. In the same way, PAH partitioning into  $\beta$ -CD and CMCD decreased when the PAH was larger than the CD cavity (Shixiang et al., 1988). The least polar CD,  $\beta$ -CD, enhanced the solubility more than CMCD (average carboxymethyl substitution was 1.3). However, the solubility of bromonaphthalene was not enhanced because the complex with  $\beta$ -CD formed a solid precipitate.

Wang and Brusseau (1995a) used cyclopentanol to attempt to enhance the PAH complexation by  $\beta$  and  $\gamma$  cyclodextrins. The solubility of straight PAHs in  $\beta$ -cyclodextrin decreased in the presence of alcohol whereas non-linear PAHs were more soluble in the presence of alcohol. It was deduced that shorter non-linear compounds fit inside the cavity and still leave space for cyclopentanol molecules to 'seal' the openings and render the complex more soluble with its hydroxyl group facing the aqueous solution. Linear PAHs on the other hand are too long to fit both cyclopentanol and the pollutant inside the  $\beta$ -CD cavity. Instead, the authors proposed that PAH and the alcohol compete for the cavity. The larger  $\gamma$ -CD was spacious enough for both the linear PAH and cyclopentanol

molecules. As a result, the solubility of all investigated PAHs increased in the presence of alcohol for this CD derivative.

The effect of pH on the polarity of an ionizable guest molecule and the consequence for inclusion complexation by several CD derivatives was evident from a study by Hanna et al. (2003 and 2004). These researchers studied complexation of pentachlorophenol (PCP) by  $\beta$ -CD, MCD, HPCD, and CMCD at pH 3 and pH 7. The average degree of substitution was 0.8-1, 1.6-2.0, and 1 for HPCD, CMD, and CMCD, respectively. The  $pK_a$  of PCP is 4.75 (Schwarzenbach et al., 1993). Thus, in acidic environment PCP is neutral ( $PCP^0$ ) but at pH 7 the deprotonated, and thus charged, form ( $PCP^-$ ) is the most prevalent. As expected, the aqueous solubility of PCP (the sum of both species) is much higher at pH 7 than at pH 3 (1300 mg/l and 5 mg/l, respectively). The study also showed that although the total solubility in the presence of CD derivates was higher at pH 7, the solubility enhancement was significantly more pronounced at low pH for all CDs.  $\beta$ -CD was an exception and the solubility enhancement was almost unaffected by pH. At low pH, PCP is less polar and therefore interacts more strongly with the CD cavity than the charged form prevailing at pH 7. The study also showed that the solubility enhancement decreased with increasing ionic strength ( $CaCl_2$ ). The authors attributed this effect to salting out and/or shifting of the guest-water or host-water interactions.

The solubility enhancement of PCP was similar for MCD and CMCD. These reagents complexed PCP more strongly than did HPCD. In addition, pH affected the solubility enhancement the most for HPCD. Thus, it seems that HPCD interacts more strongly with  $PCP^-$  than  $\beta$ -CD, MCD and CMCD. Other researchers have found that less polar CD derivatives ( $MCD < HPCD < CMCD$ ) form stronger complexes with organic contaminants. Not only does the type of CD derivative, i.e.  $\beta$ -CD, HPCD or CMCD, affect the partitioning of organic compounds, but the density of functional groups substituted to the CD molecule may inhibit diffusion into the cavity. Müller and Brauns (1986) found that

the solubility of several pharmaceuticals in 50 and 100 g/l HPCD decreased with increasing degree of hydroxypropyl substitution.

The results from the studies discussed above indicate that CD derivatives enhance the solubility of organic contaminants by inclusion complexation. In general, less polar compounds partition more strongly into the CD cavity. However, molecular size and steric effects may limit or inhibit inclusion complexation. The solubility enhancement is greater for low polarity compounds but because of their very low aqueous solubility the total aqueous concentration in the presence of CD is greater for more polar compounds. Thus, the use of CD derivatives in soil and groundwater remediation may show structural selectivity effects towards non-polar compounds. This may be especially important for remediation of NAPL mixtures where the compounds with the lowest solubility concentrate in the NAPL during enhanced aquifer flushing. Comparison of CD derivatives indicates that HPCD is generally the most appropriate CD for remediation of organic contaminants. This CD derivative does not interact significantly with soil, does not mobilize NAPL, and forms relatively strong complexes with organic contaminants. The use of CD derivatives for enhanced flushing for removal of organic compounds from soil is discussed below.

### **Cyclodextrin-enhanced flushing of organics**

Information presented in the two previous sections indicates that CD derivatives have properties that make them suitable for in-situ flushing of soil contaminated with organic compounds. However, there are other challenges during remediation of contaminated soil. For instance, NAPL solubility is commonly rate-limited, subsurface inhomogeneities may prevent the distribution of a remediation agent throughout the entire soil, recycling of the remediation agent is necessary to make CD-enhanced flushing economically viable, and CD may complicate post-remediation tracer tests designed to evaluate

remediation performance (Dugan et al., 2003). Further, non-ideal dissolution, NAPL mobilization, sorption of the agent to soil surfaces, and toxicity of the flushing agent are important factors as well. This section presents a summary of studies investigating CD enhanced flushing of soil contaminated with organic pollutants. Results from both laboratory and field investigations are presented.

TCE and PCE are two common organic contaminants that can be removed from soil by flushing with CD solutions. Boving et al. (1999) studied the removal of these pollutants from sand with low organic carbon content by equilibrium (batch) and column experiments. The performance of 50 and 100 g/l HPCD and MCD solutions were compared. The average degrees of substitution were not reported. Effluent concentrations in column experiments with HPCD as flushing solution were equal to equilibrium concentrations in the batch experiments until approximately 65-70% of the contaminant was removed. Subsequently, a transient period followed when the surface area of the residual NAPL phase was not sufficient to allow equilibrium concentration. The effluent concentration decreased steadily and flow interruption experiments confirmed that concentrations were lower than at equilibrium. As previously discussed, MCD partitioned into the NAPL phase causing retardation of TCE and PCE peak concentrations. However, because equilibrium concentrations were almost doubled in MCD compared to HPCD the contaminants were removed more rapidly during the MCD flush. Some of the removed NAPL was mobilized as droplets in MCD solutions. Thus, despite lower solubility enhancement HPCD is a safer flushing agent for DNAPL contaminated soil due to the risk of spreading the contamination.

Removal of other contaminants from soil has been studied as well. Fenyvesi et al. (1996) used artificially contaminated soils to examine desorption of PAHs and pesticides by various cyclodextrins (MCD, HPCD,  $\beta$ -CD polymer,  $\gamma$ -CD polymer) and 96 wt.% ethanol. The investigation showed that PAHs with less than 4 rings were more easily

desorbed with a solution of 15 wt.% randomly methylated cyclodextrin than with ethanol but larger PAHs were clearly more soluble in ethanol than in any of the cyclodextrins. This observation is in accordance with investigations showing that contaminants with molecular volumes larger than the CD cavity have smaller solubilities than would be predicted based on the hydrophobicity of the contaminant. Randomly methylated cyclodextrin (MCD) was generally the most effective of the investigated CDs at removing PAHs from soil. However, PCP was more soluble in 200 g/l HPCD than in 96% ethanol or 200 g/l MCD. The solution pH was not measured. As noted above, PCP is a weak acid that deprotonates and forms a charged species at slightly acidic pH. Because the charged form is more soluble in water than the neutral form, pH is an important variable for solubility of PCP.

Another study indicated that DMCD (heptakis-2,6-di-O-methyl- $\beta$ -cyclodextrin) and HPCD enhanced the desorption of 2,4,6-trinitrotoluene (TNT) from a contaminated soil (Sheremata and Hawari, 2000). MCD at 2 wt.% approximately doubled the TNT desorption compared to water but HPCD was significantly less efficient. Both CDs enhanced the biodegradation of 2,4-diamino-6-nitrotoluene, a TNT metabolite, in a top soil.

Ko et al. (1999) argued that HPCD flushing may be an alternative to surfactant-enhanced remediation of sorbed hydrophobic organic contaminants. Sorption to soil surfaces by the remediation agent may be more important for remediation of sorbed hydrophobic compounds than for NAPLs. Because some common surfactants such as SDS and Tween 80 interact with soil surfaces, Ko and Schlautmann (1998) suggested the use of HPCD. The rate of the complexation reaction between HPCD and phenanthrene and naphthalene was investigated and the adsorption to kaolinite was quantified. The complexation reactions were very fast with over 95% of complexation occurring within 10 minutes. Varying solution chemistry did not significantly affect the conditional formation constant

for phenanthrene complexation by HPCD, likely due to the non-polar characteristics of both contaminant and host. A comparison showed that phenanthrene was more strongly complexed by the cyclodextrin than was naphthalene. Compared to conventional micelle surfactants, HPCD has a somewhat lower partitioning capability but modeling with a one-dimensional sorption and transport model showed that HPCD could be more effective in remediation applications as HPCD does not sorb to kaolinite. This study demonstrates the choice of complexing agent should be evaluated based on site and contaminant characteristics.

Boving and Brusseau (2000) evaluated the efficiency of six different flushing agents for removal of residual TCE. The concentrations of humic acid, the surfactants SDS and DOWFAX 8390, and the CD derivatives MCD and HPCD were 5 wt.%. Ethanol (50 wt.%) was used as an example of co-solvent. Column experiments showed that the SDS and ethanol solutions removed TCE faster than all other solutions. However, a much higher concentration (10 times) of ethanol was used. When normalized by the mass of the flushing agent, SDS was the most efficient followed by humic acid and MCD. DOWFAX 8390 and HPCD were slightly less efficient. The only agents that did not mobilize any NAPL were humic acid and HPCD. Thus, the authors argued that CD derivatives are less efficient on mass basis than some common surfactants. However, NAPL mobilization is often not desirable.

This literature study revealed five projects where cyclodextrin derivatives were applied in the field. The first field trial was performed at Hill Air Force Base, Utah (McCray and Brusseau, 1998). At this site the contaminants consisted mainly of disposed fuels and solvents with densities lower than water. The test was performed in a 3 m by 5 m area enclosed by sheet piles. The subsurface consisted of fine to coarse sand interbedded with gravel and clay stringers. A horizontal flow field was induced by a line of four injection wells and three extraction wells.

A water flush (19 pore volumes) was performed prior to the 10 wt.% HPCD flush. As expected, the concentration of organic contaminants decreased substantially after the first days of water flush due to rate limited dissolution of the NAPL phase (McCray et al., 1999). The HPCD flush was initialized immediately after the water flush. The breakthrough of a conservative tracer occurred at the same time as the breakthrough of cyclodextrin suggesting that the HPCD was not retained by the soil (Brusseau et al., 1999). Flow interruption and comparison of field-measured and laboratory batch solubility showed that HPCD enhanced the dissolution rate of the organic contaminants (McCray and Brusseau, 1998 and 1999). The HPCD solution did not change the hydrodynamic conditions at the site and did not mobilize the NAPL.

HPCD enhanced the concentration from 39 to >10,000 times (McCray and Brusseau, 1998). The least polar compounds showed the greatest solubility enhancement but the compounds with highest aqueous solubility were removed more efficiently due to their higher total solubility. The initial concentration of TCE was 48 mg/l (an enhancement factor of 264) and the recovery after 10 days HPCD flushing (8 pore volumes) equated to more than one year of water pumping (350 pore volumes). Soil core samples taken before and after the experiment showed that 93% of the TCE was removed. Only three of the 12 target compounds showed removal of less than 70% of initial contaminant mass during the flush. Weighted mean mass removal calculated from two different methods, core samples and partitioning tracer tests, demonstrated that 41% and 44% of the NAPL was removed, respectively.

In a follow up article, the solubility enhancement and NAPL dissolution behavior from the field test were discussed (McCray and Brusseau, 1999). Ideal equilibrium concentrations of the contaminants were calculated based on Raoult's law at the start and at the end of the test. The ratios of ideal to measured concentrations were within a factor of two for most contaminants indicating that the assumption of ideal equilibrium was

adequate. The effluent concentrations of some of the target compounds decreased from the high initial concentrations to lower but stable concentrations after 3-5 days. Calculations showed that changes in NAPL composition were responsible for this effect. The NAPL mole fractions of the most soluble compounds decreased during the flushing which decreased the concentrations of these compounds at ideal equilibrium conditions. Thus, it was concluded that, for practical purposes, NAPL dissolution during the enhanced flushing test could be considered ideal in the sandy aquifer. This study also determined that aqueous concentrations at the start of the HPCD flush were near equilibrium, while the aqueous concentrations at the end of the water flush (which immediately preceded the HPCD flush) were generally well below the equilibrium concentration. Thus, the presence of HPCD evidently increased the NAPL dissolution rate. The authors hypothesized this was due to the combination of an increased concentration gradient driving force and an increased NAPL-water surface area caused by a slight decrease in NAPL-aqueous interfacial tension for the HPCD solution. In other words, the solubility enhancement compared to the water flush was much larger than the enhancement predicted from batch experiments. During the water flush, tailing due to rate-limited transfer of the contaminants from the NAPL phase to the aqueous phase was observed. No tailing was observed during the HPCD flush.

A second pilot-scale test of HPCD flushing was conducted in a TCE contaminated Superfund site in Tucson, AZ (Blanford et al., 2001). The site, Air Force Plant 44, had been treated by conventional pump-and-treat for 12 years. Vertical HPCD flushing was attempted to overcome challenges associated with heterogeneities in the subsurface; the aquifer consisted of silty sand with horizontal silt and clay layers. A vertical circulation well was installed to a depth of 56 m below ground surface and was screened at two intervals approximately 6.5 m apart. A bromide tracer test was performed prior to the 20 wt.% HPCD flush. Only 34% of the tracer was recovered indicating that only a small volume close to the well would be treated. The sugar was injected for 8.5 hours and was

followed by water flush for another 40 hours. By the end of the test approximately 54% of the HPCD was recovered. The HPCD solution enhanced the solubility of TCE three-fold to a concentration of 0.8 mg/l. Comparison between TCE solubility enhancement measured in laboratory and field showed that laboratory experiments correctly predicted the TCE concentration. A prior laboratory study indicated that TCE could be removed from the CD solution by standard air-stripping technology with greater than standard air-to-water ratios (Boving et al., 1998). This was corroborated during the field test. The cost of the HPCD solutions was about \$0.25 per liter.

At Dover Air Force Base, Delaware, PCE was injected into the subsurface under strictly controlled conditions. The PCE removal efficiency of HPCD flushing was evaluated by mass balance (Tick et al., 2003). One of the objectives of the study was to implement agent recovery and reuse. Seven pore volumes of water was initially flushed through the contaminated area followed by seven pore volumes of 15 wt.% HPCD solution. After the test, the cell was flushed with 2.5 pore volumes of water to remove remaining HPCD. The flow rate decreased from 2.4 l/min to 0.9 l/min when water was exchanged for HPCD solution. The lower flow rate was attributed to the higher viscosity of 15 wt.% HPCD compared to water. During the initial water flush, approximately 4% of the PCE was removed. In comparison, the HPCD flush removed 48% of the NAPL. At the peak PCE concentration in effluent wells the HPCD enhanced the concentration 22 times which was very close to the solubility enhancement estimated from laboratory data. After an initial phase of high PCE concentration (1300 mg/l) the PCE concentration decreased steadily to approximately 300 mg/l before the test was terminated compared to an average PCE concentration of 60 mg/l during the water flush. This study also indicated that in addition to enhancing the removal of contaminants, CD flushing may increase the bioavailability of PCE. Some effluent samples during the HPCD flush were screened for anaerobic biodegradation products and TCE and DCE were encountered at a few

milligrams per liter. The authors hypothesized that some biodegradation occurred during the test.

In the Tick et al. (2003) study, an air stripper was used to remove PCE from the HPCD solution. Using a test solution, PCE concentration decreased from 150 mg/l to below the detection limit of the analytical technique (15µg/l). The air stripper was operated effectively both with and without a defoaming agent. The flushing solution was successfully reused approximately 3 times during the duration of the HPCD flush. Kashiya and Boving (2004) investigated the effect of HPCD concentration on the apparent Henry's constant of TCE and were able to develop a relationship between gas flow rate, residence time, apparent Henry's constant, and TCE concentration that can be used to design an air stripping system.

Boving et al. (2006) reported a fourth HPCD field trial. The goals of the study were to compare conventional line-drive injection-extraction flushing (injecting the flushing solution in one well and extracting in a second well) to single-well push-pull remediation, to report costs for the remediation effort, and to test the performance of techniques to reuse the HPCD. The unconfined aquifer at the site (Naval Amphibious Base Little Creek in Virginia Beach, Virginia) was shallow and consisted of poorly sorted sand with lenses of clay, silt, and coarse sand. Injection followed by extraction in a single well (push-pull) performed better than conventional line-drive injection-extraction. Concentrations of extracted chlorinated solvents were 1.5-2 times higher during the push-pull test; more contaminant mass was removed from the ground per hour of operation; less over-extraction was needed during push-pull; and due to iron precipitation in and around the injection wells during line-drive injection-extraction, hydraulic containment was difficult to achieve. In addition, the flushing solution was more diluted during line-drive test, which was partly due to problems with hydraulic containment. During push-pull, the concentration of TCE and 1,1,1-trichloroethane (TCA) increased up to 5.6 and 9.6 times,

respectively, compared to water flushing. In comparison, during the line-drive test the maximum solubility was enhanced 2.9 and 10.4 times compared to water for TCE and TCA, respectively. However, due to significant dilution of the flushing solution these high concentrations were only maintained for a short period of time (less than 3 days). As a result of both techniques implemented over more than one week, the PCE concentration in reference wells declined between 38.5% and 99.4% (77.3% average) from their pre-CD flushing levels.

The Boving et al. (2004 and 2006) studies also showed that pollutants were successfully removed from effluent solutions with an air stripper. CD solution recovered from the subsurface was reused after treatment without indications of decreased removal effectiveness. An ultrafiltration system was capable of reconcentrating recovered CD solution from 5 wt.% to 20 wt.%. The researchers concluded that CD-enhanced flushing can remove considerable amounts of residual NAPL but is not able to lower contaminant concentrations in the groundwater to below MCLs. Other treatment approaches, such as monitored natural attenuation, are needed to achieve such clean-up goals.

A slug of cyclodextrin was injected into the subsurface to enhance biodegradation of chlorinated solvents at a former dry cleaning site in Denver, Colorado (Boving et al., 2005). The subsurface, comprising of relatively tight sand, clay, and silt, was previously fractured to enhance distribution of molasses to create reducing conditions for reductive dechlorination of solvents. Addition of cyclodextrin enhanced the aqueous-phase concentration of total chlorinated compounds by approximately 350%, thus enhancing the bioavailability of the contaminants. A pilot-scale study is planned for another commercial site in Colorado (Boving et al., 2005). Cyclodextrin will be injected in a push-pull scenario to lower the source zone concentrations of mixed solvents to allow monitored natural attenuation.

### **Cyclodextrin-enhanced biodegradation of organics**

Cyclodextrin can, under certain conditions, enhance naturally occurring biodegradation of organic contaminants. As will be discussed below, the effect of CD on enhanced biodegradation is twofold; CD-enhanced solubilization increases the bioavailability of the contaminants and CD can reduce the toxic effect of certain contaminants. In addition, injection of industrial grade CD with its impurities, which function as substrates for microorganisms, creates an environment where reductive dechlorination can occur. If no biodegradable compounds are co-injected with the CD the available oxygen concentration can be increased.

Gruiz et al. (1996) studied biodegradation of diesel oil, mineral oil, and polyaromatic hydrocarbons (PAH) in soil in the presence and absence of MCD. Soils treated with 0.1-5 wt.% MCD displayed higher activity (number of cells per gram of soil) of contaminant-degrading microorganisms than untreated soil. The extracted concentration of contaminant at the end of the experiment did not correlate to increased activity; the concentration of total extractable organic compounds increased in the presence of MCD. The authors hypothesized that MCD increased the removal and degradation of natural organic matter as well as contaminants. The root growth in diesel contaminated soil was also studied. Diesel oil (6,500-30,000 mg/kg) decreased root growth by approximately 90%. In the presence of 5 wt.% MCD, the root growth was less affected (decreased by 68%). It was suggested that inclusion complexation of organic contaminants by MCD decreased the toxic effects of diesel oil.

Oláh et al. (1998) found similar results in a study of wastewater treatment. Addition of CD alleviated toxic effects of pesticides on microorganisms in activated sludge. As expected, the acetate metabolizing activity decreased when pesticides were added to the activated sludge. Addition of  $\beta$ -cyclodextrin (up to 0.1 g/l) increased the activity of the

microorganisms and the authors concluded that  $\beta$ -CD improves the detoxification capacity of activated sludge.

Schwartz and Bar (1995) investigated the degradation of toluene and p-toluic acid by *Pseudomonas putida*. While liquid toluene was highly toxic to the microorganisms, they metabolized toluene vapor. Supplying toluene as vapor from a  $\beta$ -CD-toluene complex, rather than vapor from liquid toluene, enhanced the degradation of toluene vapors, likely due to decreased molecular toxicity and increased rate of phase transfer. In one experiment where a solution of *Pseudomonas putida* was shocked by adding 1.8 g/l of toluic acid, the presence of 15 g/l  $\beta$ -CD alleviated the toxic effect of toluic acid. No liquid phase toluene was present in the experiment. The authors suggested that toluic acid complexed with  $\beta$ -CD was less toxic than free aqueous toluic acid.

Inclusion complexation of organic contaminants increases their bioavailability. Wang et al. (1998) showed that the biodegradation of solid-phase phenanthrene in an aqueous solution increased significantly in the presence of 1 and 10 wt.% HPCD. Increasing the aqueous phase concentration of phenanthrene increased its bioavailability. It was not possible to determine if CD-complexed phenanthrene was biodegraded or if complexation increased the rate of phase transfer from solid to dissolved-phase phenanthrene. Evidence for biodegradation consisted of increased cell counts and decreased contaminant concentration in the presence of HPCD. Also, the effect of technical and analytical grade HPCD was compared. Technical grade HPCD contained 3.5% glycol that competed with phenanthrene in the high microbial number experiments. The effect of glycol in the field setting will depend on the target contaminant(s) present. Glycol biodegrades more rapidly than most contaminants and may consume available oxygen. This could result in reducing conditions which may be beneficial for chlorinated solvents but not for contaminants that undergo oxidative biodegradation.

Potential interactions between cells and CDs are important for biodegradation of contaminants; if CD is toxic to cells, degradation may be slow. If CD degrades rapidly in the presence of bacteria, reuse would not be possible. In one study, randomly methylated  $\beta$ -cyclodextrin was degraded by microorganisms in soil after approximately 2.5 months (Gruiz et al., 1996). The *Pseudomonas putida* used in Schwartz and Bar's experiment (1995) did not biodegrade CD. This strain was, however, chosen for its inability to metabolize starch. Thus, it appears that cyclodextrin will not biodegrade significantly during the extent of a CD-flush. Conversely, the effect of CD on cells is also important. CDs form complexes with phospholipids, the main constituents of cell membranes and could potentially be harmful to cells. Nevertheless, CDs are generally non-toxic to bacterial cells (Schwartz and Bar, 1995) because overall, the effect is to increase biodegradation (based on prior studies) and possibly reduce overall toxicity when contaminants are present.

The effect of CD-flushing on biodegradation was investigated at Hill Air Force Base, Utah (Alter et al., 2003). The CD-flushing experiment is discussed in separate articles (e.g. McCray and Brusseau, 1998; McCray and Brusseau, 1999) and is summarized in the section above. The sandy aquifer in the sheet pile enclosed cell was simultaneously flushed, before and after the CD-flush, with a conservative tracer (Br) and three biotracers (ethanol, hexanol, and benzoate). The tracer tests are described in Alter et al. (2003). The biodegradation potential was analyzed using breakthrough curves and mass balances of the tracers as well as change in cell biomass during the CD-flush. The mass balance of Br was close to 100% both before and after the CD flush, indicating that mass was preserved. Mass balance for all three biotracers prior to CD-flushing was approximately 80%. Consequently, about 20% of each of the organic tracer compounds was biodegraded during the first tracer test, which was performed prior to the CD flush. A larger percentage of the ethanol and hexanol was degraded during the biotracer test performed after the CD flush. Only 64 and 54% of the ethanol and hexanol was

recovered, respectively. Thus, the CD flush appeared to enhance the biodegradation potential for ethanol and hexanol. The difference in recovered benzoate was within experimental uncertainty, 82% compared to 79%. Hexanol, the compound with most carbons and therefore likely the most attractive substrate, had the lowest recovery rate. This behavior could potentially be explained by partitioning into the NAPL phase. Hexanol is the compound that partitions most strongly into the NAPL phase and, because the NAPL concentration decreased during the CD flush, its bioavailability would be higher during the second biotracer test than during the first. Alternatively, the most easily biodegradable may be most affected by the CD-flush. The microbial biomass concentration increased during the CD flush and it was concluded that CD-flushing enhanced the biodegradation potential of organic contaminants.

No distinction was made between aerobic and anaerobic degradation. Some contaminants are decomposed more rapidly in anaerobic environments, i.e. chlorinated solvents, whereas other substances, such as hydrocarbons, are more readily degradable under aerobic conditions. Thus, co-injecting an organic substrate with the CD solution may improve conditions for degradation of chlorinated solvents whereas co-injecting an oxygen source may further speed up degradation of other compounds. If co-injecting an oxygen source, problems such as precipitation of iron in and around the injection and extraction wells should be considered (Boving et al., 2006).

### **Cyclodextrin-enhanced flushing of metals and mixed contaminants**

Most cyclodextrin research on remediation has focused on clean-up of organic contaminants. Many fewer studies have been published on the use of CD for remediation of metals. As part of this work, Records of Decisions for 134 sites on the National Priority List (NPL) were screened during the summer of 2003 (EPA, 2003). The screening study indicated that both metals and organic contaminants are present at

approximately 60% of the sites on the NPL. It was not determined whether the two contaminant groups were present at the same location or if they were encountered at different locations of the sites. The large number of sites contaminated with metals and organic pollutants and the possibility of using CMCD for in-situ remediation of mixed waste has spurred research interest in CD-enhanced remediation of metals and mixed waste. CD has also been suggested for managing radioactive waste (Szente et al., 1999).

Functional groups containing electronegative elements such as oxygen, nitrogen, and sulfur can attract and form chemical associations with positively charged cations. Research on natural organic matter indicates that carboxyl and hydroxyl groups are responsible for associations between metal ions and organic matter (Dudal and Gerard, 2004; MacCarthy, 2001). Often, carboxyl groups form stronger interactions with metals than hydroxyl groups and can be substituted to the outside of the cyclodextrin molecule. This enables these CD derivatives to complex metals. Until now, CMCD is the only CD derivative that, in the remediation literature, has been shown to complex metal ions. Surely, with time, other, and maybe more strongly complexing, CD derivatives will be produced.

Wang and Brusseau (1995b) suggested for the first time that CMCD can be used for remediation of mixed waste. The study showed that CMCD can complex  $\text{Cd}^{2+}$  simultaneously with anthracene, biphenyl, and TCE. In their experiments, metal complexation did not affect inclusion complexation of organic compounds and, conversely, metal complexation was not affected by the presence of organic contaminants. A NAPL phase was not considered in these experiments. Cadmium complexation by CMCD was investigated with an ion-selective electrode at constant Cd concentration (10 mg/l) in batches with varying CMCD concentration (0-10 g/l). A conditional stability constant for the CMCD-Cd complex, based on data collected at CMCD concentrations below 1 g/l, was calculated to be  $10^{3.66}$ . The authors noted that the

complexation strength of CMCD is similar to that of fulvic acids and anionic biosurfactants. The influence on Cd complexation by pH variations and by competition with calcium was also investigated. CMCD-Cd complexation decreased with increasing  $\text{CaCl}_2$  concentration but a significant amount of Cd was still complexed at 1000 mg/l  $\text{CaCl}_2$ .

Proton activity can affect metal complexation by CMCD in two different ways. When pH is close to or below the  $\text{pK}_a$ s of the carboxylic acid groups, hydrogen ions will compete with the metal ions. At high pH, metal ions tend to form hydroxides which inhibit complexation to CMCD. In Wang and Brusseau's batch experiments, increasing pH from 6 to 8 did not significantly affect Cd complexation and only a slight decrease in  $\text{Cd}^{2+}$  activity was noted when pH was lowered to 5. The  $\text{pK}_a$  of the hydroxyl groups are lower than 5, explaining why Cd complexation capacities were similar between pH 5 to 8.

After showing that CMCD complexes metals and organic compounds simultaneously, Brusseau et al. (1997) continued their work by investigating elution of metals (Cd, Sr, and Zn) and phenanthrene from three soils. One soil consisted of pure sand (Borden), another was a clayey sand (4% silt and 10% clay; Hayhook), and the third was a silty clayey sand with 1% organic carbon content (18% silt and 4% clay; surface soil). The Borden and Hayhook soils contained less than 1% organic carbon. The soils were flushed with phenanthrene and cadmium to artificially contaminate the soils before eluting with 1 wt.% CMCD or HPCD/CMCD solutions. Elution from the low organic carbon clayey sand (Hayhook) was studied most intensively. During a 1% CMCD flush, the maximum Cd concentration was 20 to 25 times higher than the maximum concentration during a 10 mM  $\text{KNO}_3$  flush. The presence of phenanthrene had a relatively small impact on the Cd removal efficiency: a slight increase in Cd removal was noticed when phenanthrene was present. The phenanthrene removal efficiency increased in the presence of cadmium. The same results were found for experiments with the Borden sand. The authors speculated

that Cd complexation neutralized the outside of the CMCD making the molecule more available to inclusion complexation of phenanthrene.

During the 1 % CMCD flush the maximum phenanthrene concentration was 2.5 times higher than in the  $\text{KNO}_3$  flush. CMCD complexed phenanthrene less strongly than HPCD; the solubility enhancement using CMCD was lower than when the soil was flushed with 1 % HPCD. Thus, additional experiments with mixture of 0.5 wt.% CMCD and 0.5 wt.% HPCD were performed. In these experiments the maximum solubility enhancement of phenanthrene increased to 3.5. As expected, during the HPCD/CMCD experiments, the cadmium elution efficiency was approximately half compared to the CMCD experiment. This finding confirms that HPCD does not effectively complex metals.

The degree of cadmium and phenanthrene removal was similar in the high organic carbon soil (surface soil) as in the Hayhook soil. The measured maximum concentrations were close to expected concentrations based on previous batch experiments, suggesting that the system was at equilibrium at peak concentrations. Thus, relatively high clay (10%) and organic carbon content (1%) do not significantly affect the organic or metal removal efficiency of CMCD flushing. For all three soils, 80-90% of the cadmium was eluted after approximately 20 pore volumes. In addition, ageing did not affect the removal efficiency of either Cd or phenanthrene using 1 % CMCD/HPCD. In contrast, ageing had a significant impact on phenanthrene, but not Cd, removal during the  $\text{KNO}_3$  flush. In an additional experiment, cadmium, nickel, and strontium removal were compared. Cadmium was removed most efficiently and nickel was removed faster than strontium. In all three cases the removal rates were much faster than removal rates in  $\text{KNO}_3$  flushing; at least 85% of the metals were removed after flushing the columns with 1 wt.% CMCD for 20 pore volumes.

Mercury is a contaminant that sorbs very strongly to soil organic matter and to soil surfaces. Due to its strong association with soil constituents it is difficult to remove using regular pump and treat (extracting, treating, and subsequent discharging of ground water). Wang et al. (2004) compared the ability of CMCD, rhamnolipid and  $\text{CaCl}_2$  to remove Hg from an artificially contaminated sandy soil with low organic carbon content (0.1%). Batch and column tests showed that, on a mass and molar basis, CMCD was more efficient than rhamnolipid. Although  $\text{CaCl}_2$  was the least efficient per mass and per mole, 50 mM  $\text{CaCl}_2$  was more efficient than 2 mM CMCD (0.3 wt.%), 2 and 10 mM (0.1 and 0.5 wt.%) rhamnolipid. After 40 pore volumes, 80%, 57%, and 26% Hg was recovered using 50 mM  $\text{CaCl}_2$ , 3 g/l CMCD, and 5 g/l rhamnolipid, respectively. In comparison, 40 pore volumes of 10 mM  $\text{KNO}_3$  removed 21% of the Hg.

The authors compared geochemical modeling to previous literature findings and concluded that the most prevalent form of mercury,  $\text{Hg}(\text{OH})_2^0$ , forms strong inner and outer sphere complexes with soil surfaces and also form strong complexes with natural organic matter. The authors suggested that removal efficiency of mercury with CMCD and rhamnolipid was related to the number of carboxylic acid groups on the complexing agents. Because rhamnolipid contains fewer carboxyl groups than CMCD and because it is retained by soil it was less efficient at removing Hg. In contrast,  $\text{CaCl}_2$  is not retained by soil and forms inorganic complexes with mercury. These complexes are not strongly retained by soil particles and, subsequently,  $\text{CaCl}_2$  was an efficient flushing agent. The authors concluded that all three agents (CMCD, rhamnolipid, and  $\text{CaCl}_2$ ) can be used for remediation of mercury from sand with low organic carbon content. Due to strong interactions between mercury and organic matter the Hg remediation potential of these agents is questionable in high organic carbon soil.

Many industrial sites are contaminated with arsenic. In an attempt to develop a technique to remove arsenic from soil, Chatain et al. (2004) attempted to use four CD derivatives to

remove arsenic and lead from a soil collected at a French gold mining site. The soil consisted of 63% sand, 25% silt, and 12% clay and contained 27,700, 1,700, 800, and 400 mg/kg As, Cu, Pb, and Zn, respectively. All experiments were performed in batch mode. Initial experiments showed that CMCD was the only CD derivative that enhanced the removal of As compared to deionized water;  $\beta$ -CD, MCD, and HPCD did not enhance the solubility of either As, Cu or Fe. Consequently, CMCD was chosen for further experiments. The equilibrium concentration of all three inorganic contaminants increased linearly with increasing CMCD concentration. At approximately 120 g/l CMCD (80 mM), the aqueous concentration of As was 16 mg/l, equivalent to a solubility enhancement factor of 16 compared to pure water. The concentrations of Cu and Fe were higher, 36 and 34 mg/l, respectively. At their experimental conditions (pH approximately 6.5 and oxidation/reduction potential about 400mV versus normal hydrogen electrode), arsenic is thermodynamically stable as an anion, As(V), and may not form complexes with CMCD in the same manner as the cations Cu and Fe. Mineralogical characterization (XRD and SEM) showed that most of the arsenic was associated with amorphous (oxy)hydroxides. Thus, the authors hypothesized that arsenic was removed from the soil by enhanced dissolution of the iron (oxy)hydroxides. In the same study, Chatain and coworkers studied the simultaneous removal of inorganic contaminants and 2,3,4,6 tetrachlorophenol (TCP). Addition of CMCD to an artificially TCP contaminated soil enhanced the removal of TCP. The enhancement was not linear; at approximately 45 g/l CMCD the TCP concentration reached a plateau at about 70% removed PCE. The presence of 20 g/l arsenic did not affect the removal efficiency of TCP.

Vulava and Seaman (2000) compared the lead removal efficacy of EDTA (ethylenediaminetetraacetic acid) and CMCD from a surface and a subsurface soil. The two soils were artificially contaminated with lead and were subsequently eluted with either 10 g/l (1 wt.%) CMCD or 0.37 g/l (1 mM) EDTA. The lead contents, after contamination, were 650 and 63 mg/kg in the surface and subsurface soils, respectively.

The results showed that EDTA was considerably more efficient than CMCD at removing lead from the two soils.

A sorption study of EDTA and CMCD showed that at low concentrations EDTA and, especially, CMCD were retarded by the subsurface soil but not by the high organic surface soil. The soils differed in that the subsurface soil contained more iron hydroxides (0.74 g Fe/100 g soil) than the surface soil. Likely, the agents formed complexes with iron hydroxide surfaces. Due to strong interactions between lead and iron hydroxide surfaces, CMCD was not able to remove any significant amount of lead from the subsurface soil. Conversely, EDTA which forms very strong complexes with both Pb and Fe, removed both lead and some iron. Flushing the soil with approximately 15 pore volumes of EDTA removed nearly 80% of sorbed lead. Both complexing agents removed significant portions of lead in the surface soil. The maximum solubility enhancements of EDTA and CMCD were 18.5 and 6 and removal efficiencies were 100% and 56%, respectively. Unfortunately, EDTA is considered a toxic substance and is therefore not used for in-situ remediation.

Research on metal extraction by CMCD discussed above indicates that CMCD increases the solubility of metal contaminants and enhances elution of these contaminants from artificially contaminated soil. In addition, CMCD complexes metals and organic contaminants by separate mechanisms and were removed simultaneously in experiments on artificially contaminated soil. However, metal speciation in artificially contaminated soil may differ from speciation in field conditions. Neilson et al. (2003) used two aged metal contaminated soils to compare the removal efficacy of CMCD and ramnolipid to a synthetic complexing agent, diethylenetriamine pentaacetic acid (DTPA). The results showed that DTPA was considerably more efficient at removing the target contaminant (Pb) and the authors concluded that due to lower complexation strength, the use of

biological complexing agents would require prolonged soil washing making the use of biological agents economically questionable.

Two soils with similar soil composition were used; the sand, silt, and clay contents were 84-85%, 15-20%, and 6-9% clay, respectively. One soil originated from a former mine site (Coeur d'Alene, Idaho) and the other was contaminated with lead paint and lubricating oils (Camp Navajo, Arizona). Because lead paint contains lead carbonates the Camp Navajo soil was higher in lead carbonate than the Coeur d'Alene soil that contained more amorphous iron hydroxides. The Coeur d'Alene soil contained 3.8 g/kg lead and the Camp Navajo soil contained 24 g/kg lead. At concentrations of 2 mM all three complexing agents significantly increased lead removal compared to electrolyte solutions. However, two washes of 2 mM DTPA removed 40-44% of all lead in both soils whereas 10 washes with 2 mM ramnolipid and 2 mM CMCD only removed 14 and 5% from the Coeur d'Alene soil and 15 and 13% from the Camp Navajo soil, respectively. The amount of extracted lead did not decrease with subsequent washes suggesting that more metals could be removed with further washes. It was proposed that dissolving carbonates and other lead containing species enhanced the dissolution of metal contaminants.

### **Using cyclodextrin to enhance other physiochemical remediation techniques for metals and organics**

The most commonly suggested remediation application of cyclodextrin is as flushing agent for in-situ enhanced flushing but other applications have been suggested as well. Some researchers have recommended the use of cyclodextrin derivatives to enhance the removal or destruction efficiency of other remediation techniques. These applications include enhancing the availability of organic contaminants for destruction using zero-

valent iron and increasing the mobility of organic and inorganic contaminants for electrokinetic remediation techniques.

Bizzigotti et al. (1997) used HPCD to solubilize PCE for subsequent destruction by a permeable reactive barrier (PRB) composed of zero-valent iron. The results showed that HPCD enhanced the reductive dechlorination of PCE by the PRB. The HPCD solution was recycled and after passing through columns with zero-valent iron and no significant reduction in efficiency was noted indicating that HPCD was unaffected by the iron.

Other researchers have studied enhanced solubilization and destruction of phenanthrene (Ko et al., 2000) and PCP (Hanna et al., 2005) by addition of HPCD to electrochemical techniques. Maturi and Reddy (2005) attempted to further develop an electrochemical technique to simultaneously extract PAH and metals.

Hanna et al. (2005) extracted PCP from spiked soil with a 0.75 wt.% HPCD solution. The extract (HPCD and PCE) was subsequently treated with Fenton's reagent to decompose the PCP. A catalytic quantity of ferrous iron was supplied at the beginning of the electrolysis experiment. PCP was destroyed by hydroxyl radicals originating from Fenton's reaction ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2 = \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}$ ). By supplying a voltage across two electrodes submersed in the solution, ferrous iron was constantly regenerated ( $\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$ ). However, both HPCD and PCE were destroyed during electrolysis, thus, prohibiting reuse of the complexing agent. HPCD should be removed from the solution before hydrolysis for this technique to become economically viable. No in-situ application was discussed; the technique would be amended to CD-enhanced flushing.

Electrokinetic removal of contaminants employs an electrical field between two electrodes inserted into the subsurface. This creates two modes of mobilization: electromigration of dissolved ions to the anode or cathode, depending on the charge, and

electroosmotic flow of water and dissolved uncharged compounds. Consequently, the technique has potential to mobilize both metals and organic compounds and, because the soil is not hydraulically flushed, the technique is an alternative for low permeability soils. Ko et al. (2000) attempted to enhance the electrokinetic mobilization of phenanthrene by adding HPCD to a system with clay soil (kaolinite). Initial experiments indicated that HPCD did not affect the permeability of the clay. Electrolysis at the anode and cathode lowered the pH to close to the point of zero charge of the soil. This decreased the electroosmotic flow and decreased the removal efficiency of phenanthrene. Flushing the anode with a pH buffer mitigated this problem. Due to the solubility enhancing effect of HPCD phenanthrene was more efficiently removed in the presence of HPCD than in its absence.

The possibility of remediating nickel and phenanthrene contaminated kaolinite by a HPCD-enhanced electrokinetical technique was investigated by Maturi and Reddy (2005). Kaolin spiked with 500 mg/kg Zn and 500 mg/kg phenanthrene was treated in the presence of deionized water, 1 and 10 wt.% HPCD. More phenanthrene was removed in the presence of 1 wt.% HPCD than in water and 10 wt.% HPCD. However, due to limited desorption of the phenanthrene in 1 wt.% HPCD the removal efficiency was limited. At the higher HPCD concentration the electroosmotic flow and electrical current decreased drastically after one pore volume. It was hypothesized that lower dielectric constant and higher viscosity of HPCD compared to water was responsible for the reduced removal efficiency. However, significant phenanthrene mobilization was noticed during the first pore volume. As in the experiments by Ko et al. (2000) pH in all three experiments decreased significantly in the soil but increased close to the cathode. Zinc was mobilized in the soil column, migrated towards the cathode and precipitated as zinc hydroxide close to the cathode. Hydrogen ion activity (pH) was least alkaline close to the cathode in the 1 wt.% HPCD experiment and more zinc was removed than in the other two experiments. If a metal complexing agent would be used precipitation may decrease and zinc removal

may increase. For this purpose CMCD may be a better agent than HPCD. The authors hypothesized that if the original electroosmotic flow can be maintained and pH near the cathode can be controlled, significant mass of phenanthrene and zinc can be removed using this CD-enhanced electrokinetic method.

## **Conclusions**

Cyclodextrin (CD) derivatives enhance the solubilities of sorbed and non-aqueous phase liquid contaminants by forming inclusion complexes between organic compounds and the relatively non-polar cavity in the center of the cyclodextrin molecule. Several properties of cyclodextrin make this glucose-based complexing agent attractive for in-situ remediation: it is non-toxic, sorbs little or not at all to soil particles, experiences little or no pore exclusion in soil, and does generally not mobilize non-aqueous phase liquids. Increasing the aqueous concentration of contaminants can increase their biodegradation potential, thus, CD-flushing removes and also enhances biodegradation of some organic contaminants. In addition, one cyclodextrin derivative, carboxymethyl- $\beta$ -cyclodextrin (CMCD), forms complexes with metals and is a potential agent for remediation of metal-contaminated and mixed waste (metal-organic) sites.

Results from laboratory and field studies show that flushing pesticide, solvent and fuel-contaminated soil with hydroxypropyl- $\beta$ -cyclodextrin (HPCD) enhances the removal rate of these contaminants compared to conventional pump and treat. Generally, the solubility enhancement in a CD solution is most pronounced for the least polar compounds. However, less polar compounds normally have lower aqueous solubilities which limit their total solubilities.

HPCD flushing is an innovative remediation technique that is slowly being used for remediation of source zones at commercial sites. The use of CMCD for remediation of

metal and mixed waste contaminated sites is less developed. Experimental studies have demonstrated that CMCD complexes metal ions and, compared to water flushing, enhances the removal efficacy of metals from soil. However, the complexing strength of CMCD is lower than that of synthetic complexing agents such as EDTA. CMCD is therefore less effective at removing metals than synthetic complexing agents and the effectiveness of CMCD flushing of aged contaminated soil depends on the metal species present. Thus, individual site conditions will govern the effectiveness of CMCD flushing. The ability to model a potential metal remediation scenario would facilitate evaluation of CMCD flushing.

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# CHAPTER THREE

## A GEOCHEMICAL MODEL FOR LEAD COMPLEXATION BY CARBOXYMETHYL-B-CYCLODEXTRIN (CMCD)

### Abstract

Carboxymethyl- $\beta$ -cyclodextrin (CMCD) has been proposed for remediation of metal-contaminated sediments. This research presents stability constants for CMCD-lead interactions, and demonstrates a rigorous methodology for estimating stability constants for metal-complexing agents. The conditional stability constant for the lead-CMCD aqueous complex was determined to be  $10^{5.14}$  with the 95% confidence interval ranging from  $10^{5.10}$  to  $10^{5.18}$ . The best fit for experimental data was made by assuming a reaction between divalent  $\text{CMCD}^{2-}$  and  $\text{Pb}^{2+}$  and using the WATEQ activity coefficient formulation. The optimized value was derived from experimental data with the geochemical model PHREEQC coupled to UCODE\_2005, a parameter optimization program. Like FITEQL, UCODE has a built-in option to optimize parameter values by minimizing the weighted sum of squared residuals (WSSR). However, our approach not only allows rapid, automatic optimization of the stability constant, but also allows determination of uncertainties in estimated parameter values and statistical analysis to assess the appropriateness of the conceptual model. The automation of the process allows testing of multiple conceptual models and the final values produced are internally consistent with the PHREEQC database. In this case five different conceptual models to describe the metal complexation and protonation reactions of CMCD were considered.

## **Introduction**

Geochemical models can be used to simulate enhanced solubility of metal contaminants in the presence of a complexing agent. Such simulations can be very useful when evaluating potential remediation agents and techniques. These simulations require explicit chemical reactions that describe the stoichiometry and the strength of chemical associations between the complexing agent and the metal ion, i.e. stability constant(s). Because metal solubility depends on the activities of the involved aqueous species, the charged nature of the complexing agent and the ionic strength of the solution must be quantified to allow calculation of activity coefficients. This paper aims to demonstrate a technique to derive conditional stability constants from experimental data and incorporate those constants into the geochemical model PHREEQC using lead and carboxymethyl- $\beta$ -cyclodextrin (CMCD) as an example.

Research has indicated that cyclodextrin derivatives (CD) may be used as flushing agents to remediate sites contaminated with organic compounds (Blanford et al., 2001; McCray and Brusseau, 1999a, b; Wang and Brusseau, 1993). Other studies have shown that CMCD simultaneously enhanced the solubility of metals (Brusseau et al., 1997; Wang and Brusseau, 1995; Wang et al., 2003; Boving and McCray, 2000). The ability of CMCD to simultaneously complex metals and organics is the result of CMCD torus structure that has both hydrophobic and hydrophilic properties. Specifically, this large organic molecule has exterior carboxyl groups that can complex metal ions (Wang and Brusseau, 1995), and a non-polar interior cavity that can sequester smaller organic compounds. Thus, CMCD is a potential flushing agent for remediation of mixed waste sites, i.e. sites contaminated with both metals and organic compounds. In this paper, we investigate the lead complexing properties of CMCD and attempt to formulate a geochemical model that calculates equilibrium lead solubility in the presence of CMCD. In our view, a successful model should be as simple as possible, be scientifically sound,

and describe observed data well. For practical purposes, it is important that the model can easily be included in available geochemical software.

Geochemical computer models consist of non-linear algebraic equations that represent the aqueous reactions. The computer code solves the set of equations that represent the system at thermodynamic equilibrium. The equations' equilibrium values are based on experimental data or derived by calculation from thermodynamic properties. Analysis of experimental data to determine stability constants is done by either graphical means or use of a computer program such as FITEQL (Herbelin and Westall, 1999). For instance, Cabaniss and Shuman (1988) used a semi graphical approach to investigate Cu complexation by natural organic matter based on experimental data. In contrast, Fein et al. (1995) investigated Al and Ca complexation by malonic acid using solubility enhancement of gibbsite. The authors set up 12 conceptual models with varying stoichiometry for the metal ion-malonate-hydroxide complex. They calculated a stability constant for each experimental point and considered the average stability constant optimized for that particular conceptual model. The stoichiometry that yielded the smallest difference between observed and simulated gibbsite solubilities was considered the best model.

Thermodynamic equilibrium models require that analytical concentrations be expressed as chemical activities. While the electrostatic interactions of most inorganic ions can be accurately modeled by correcting the non-ideal behavior with ionic strength dependent activity coefficients, such formulations are poorly suited to model metal complexation with large organic molecules such as humic acid or CMCD. Metal complexation sites are generally assumed to be reactive functional carboxyl and hydroxyl groups separated by hydrophobic segments. As a result, metal complexation with natural organic matter has been modeled with reactions for the multiple protonation and complexation sites, but no explicit description of the hydrophobic nature of the rest of the molecule. In an analogous

fashion reactions of metal ions with organic matter are modeled using both discrete and continuous complexation site models. For instance, non-ideal behavior of large organic substance in the NICA-Donnan (continuous site distribution) and WHAM (discrete site distribution) models are accounted for by simulating metal ion accumulation in the diffuse layer around the natural organic matter (Dudal and Gérard, 2004).

Commonly, more than one conceptual model can be formulated for a system and it may be difficult, if not impossible, to determine which model most accurately describes the system. For example, what is the complexation stoichiometry between Pb and CMCD? Do all potential Pb complexation sites on CMCD have the same strength? The more accurate the geochemical model, the better it will describe various aspects of the actual field system such as changes in pH, ionic strength and solution composition.

Our goal is to build a functional model for metal interactions between a large organic molecule, CMCD, and lead ions that can be used for assessing the feasibility of metal remediation. The conceptual methodology could also be applied for any metal/complexing agent pair. Our conceptual geochemical models are formulated as a set of non-linear mathematical equations based on chemical reactions that describe Pb complexation with CMCD. Several geochemical computer programs are available to solve the system of chemical reactions including MINTQA2 (Allison et al., 1991), FITEQL (Herbelin and Westall, 1999), PHREEQC (Parkhurst and Appelo, 1999) and Geochemist's Workbench (Bethke, 1996). However, FITEQL is the only stand-alone code designed to estimate constants from experimental data, and thus is the normal computer method for deriving stability constants. The normal procedure is to formulate the appropriate equations and then iteratively change the parameter values, i.e. stability constant(s) and/or site concentration(s), until model results best match experimental data.

This iterative procedure can be performed by trial or error or, as with FITEQL, by automatically minimizing an objective function. An objective function is a measure of the fit between data observed in the field or lab, and values simulated by the model. The weighted sum of squared residuals (WSSR) is a commonly used objective function. But it is also important to evaluate the appropriateness of the conceptual model, a process that is not explicitly part of programs like FITEQL. Instead, the researcher uses his or her best judgment in formulating the conceptual model, and the accompanying mass action equations.

We propose to use UCODE\_2005 (Poeter et al., 2005; Poeter and Hill, 1998) in combination with PHREEQC to optimize parameter values and assess the uncertainties in the estimated values. In this process, the PHREEQC model is set up for the experimental system and UCODE\_2005 is given instructions to optimize input parameter values such that PHREEQC output best matches experimental data. There are several advantages of this technique including: (1) automated calibration frees up time and effort to consider problems with the conceptual model and formulate and test alternatives, (2) uncertainties in estimated parameter values can be reported, (3) the appropriateness of the chosen model can be assessed based on output statistics and residuals, (4) the best conceptual models can be chosen after comparison of several, (5) additional data needs can be identified which may facilitate experimental design, and (6) values for constants generated are internally consistent with the database used by the model.

## **Materials and Methods**

### Materials

Industrial grade carboxymethyl- $\beta$ -cyclodextrin (CMCD) was provided by Wacker, Inc. The compound was delivered as a sodium salt with unknown purity. All other chemicals

were +98% pure and nitrogen gas was of ultra high purity. Ion-exchange resin (Rexyn 101H) was purchased from Fisher Scientific.

#### Potentiometric titrations

The CMCD-Na salt was converted to its acidic form before titrating with NaOH. A CMCD-Na solution (100 g/l) was run twice through an ion exchange resin column. IR spectroscopy did not detect any Na after freeze-drying.

Potentiometric titrations were performed in a glass vessel at  $25.0 \pm 0.5^\circ\text{C}$  with 50 mM  $\text{KNO}_3$  as background electrolyte. The pH was measured with a combination electrode. Prior to titrating, the CMCD solution was bubbled with nitrogen gas for at least one hour at pH 3.3 or lower. Incremental volumes of 0.1 M NaOH were added to 50 ml CMCD solution to cause a pH change of approximately 0.1 pH unit. Each titration lasted approximately 40 minutes. Five solutions with concentrations between 0.50 and 1.5 g/l CMCD and three blank solutions consisting of only 50 mM  $\text{KNO}_3$  were titrated under identical experimental conditions.

#### Metal complexation experiments

Batch experiments aiming at determining the conditional stability constant between CMCD and Pb were performed in sealed 15 ml polypropylene centrifuge tubes submerged in a water bath. Temperature was controlled at  $25 \pm 1^\circ\text{C}$ . The activity of  $\text{Pb}^{2+}$  was controlled by adding lead oxalate salt (20-50 mg) to 10 ml CMCD stock solutions with 50, 100 and 300 mM  $\text{KNO}_3$ . Solid-phase lead oxalate was present in all tubes at the end of the experiment. The centrifuge tubes were rotated top over bottom for 7 days. The pH was measured immediately after filtering ( $0.45\mu\text{m}$ ) each sample and total aqueous Pb concentration was analyzed with ICP-OES.

### Modeling Techniques

Results from lead solubility experiments were modeled with UCODE\_2005 coupled to the batch version of PHREEQC. PHREEQC performs geochemical calculations and UCODE\_2005 optimizes parameters within the PHREEQC model. For all conceptual models described below, we attempted to estimate all unknown parameters. The standard PHREEQC thermodynamic database amended with reactions for the formation of aqueous lead oxalate complexes (Martell and Smith, 1977) was used in all calculations.

UCODE\_2005 is a program for parameter estimation, or inverse modeling. It was developed with groundwater engineering applications in mind but is universal in the sense that it can be applied to any program that produces numerical output. In short, the UCODE\_2005 code solves a set of equations by comparing simulated and observed data in the following steps: (1) executes the forward model, in our case the PHREEQC model, (2) sums the weighted squared residuals between simulated and observed values (WSSR), (3) determines how sensitive simulated values are to PHREEQC input-parameter values, i.e. determines the slope of the objective function surface, and (4) uses these residuals and sensitivities to adjust parameter values to obtain a better fit. Steps 1-4 are repeated using a modified Gauss-Newton procedure until the change in parameter values are less than the user-specified tolerance.

UCODE\_2005 produces several useful statistical tools to evaluate the model and to assess the uncertainty of estimated parameters. These tools include: calculated sensitivities of simulated values to estimated parameters, correlation coefficients between estimated parameters, and the 95% confidence intervals on estimated parameters. In addition, the output data is organized to easily create graphs for residual analysis. The sensitivities can be used to determine which model-input parameters are critical to estimate versus assume known, and to ensure that the conceptual model is not insensitive to known important input data. Correlation coefficients can reveal whether two or more

parameters can be estimated independently. If parameters are correlated but this is unknown, then model parameters determined from calibration may not be unique, and thus may be useless for prediction if their unique values (as opposed to their linear combination, e.g. ratio or sum) are important to the prediction. Confidence intervals provide a widely accepted statistical measure to assess the accuracy and reliability of the estimated parameters. However, confidence intervals on estimated parameters do not include uncertainties related to the conceptual model. Residual analysis can be used to assess the conceptual model. Residuals should ideally be random and belong to a normal distribution; bias or trends in residuals can uncover weaknesses in the conceptual model. Graphs of residuals versus dependent or independent values as well as normal probability plots of residuals are useful for detecting potential trends. Hill (1998) provides an excellent discussion on effective model calibration and explains how to use these statistical tools.

### **Conceptual Models**

One of the most difficult and important tasks in geochemical modeling is to choose the most appropriate complexation model(s). We first use chemical arguments to set up conceptual models that describe Pb complexation by CMCD. There are several conceptual uncertainties in modeling complexation between Pb and a large organic molecule such as CMCD. These include the choice of activity model and representation of charges on the large organic molecule and its Pb complex(es). In addition, the complexation ratio (the number of complexation sites per CMCD molecule) and the potential competition between the cation constituent of the background salt and Pb are unknown. Five conceptual models are constructed to address these uncertainties. While many more models could be hypothesized, we present five that we consider to be the most realistic and that are useful to illustrate our methodology. The five conceptual

models are summarized in Table 3-1 and are described below. First, we present some general information relevant to all the models.

Table 3-1. Summary of CMCD-Pb complexation models.

Model	Types of sites	Ligand	Activity model <sup>6</sup>	Log $K_{\text{CMCD-Pb}}$ <sup>7</sup>	$R^2$ <sup>8</sup>	WSSR <sup>9</sup>	Comment
A	One type	CDMC <sup>-</sup>	Davies	4.44 (4.36 – 4.52)	0.823	1989	
B	Weak / strong	CDMC <sup>-</sup>	Davies	NA	NA	NA	Model does not converge
C	One type	CDMC <sup>-</sup>	Davies	4.90 (4.71 – 5.09) 1.41 <sup>10</sup> (1.09 – 1.73)	0.976	625	K competition
D	One type	CDMC <sup>2-</sup>	Davies	4.96 (4.90 – 5.01)	0.915	912	
E	One type	CDMC <sup>2-</sup>	WATEQ	5.18 (5.14 – 5.22) -0.65 <sup>11</sup> (-0.84 – -0.44)	0.989	133	<sup>a</sup> <sub>CMCD2</sub> in WATEQ fixed to 3.50

We define a system of equations that share several common elements. First, we assume that the protonation of the carboxylic acid groups is fully described by potentiometric titrations. Results from base titrations showed that each CMCD has on average 4.27 carboxyl groups. All functional groups had the same  $pK_a$ , consistent with carboxyl groups being separated by several single C-C bonds. The fractional stoichiometry of the carboxyl groups may represent the fractional stoichiometry of CMCD caused by random substitution during synthesis, and/or may be a result of impurities that contain acid functional groups. The correction of analytical concentrations to chemical activities is dependent on solution ionic strength and the square of individual ion charge. However,

<sup>6</sup> Activity model of free ligand. The Davies equation is used for all other ions.

<sup>7</sup> Best estimate and 95% confidence interval when all data were modeled simultaneously.

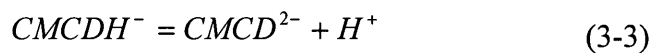
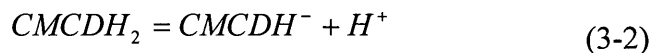
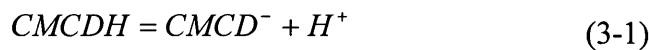
<sup>8</sup> Correlation coefficient between observed and simulated aqueous lead concentration.

<sup>9</sup> Weighted sum of squared residuals for optimized parameter values.

<sup>10</sup> Estimated stability constant for K complexation by CMCD<sup>-</sup>.

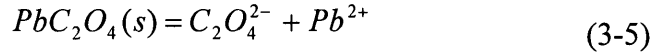
<sup>11</sup> Estimated value for <sup>a</sup><sub>CMCD2</sub> in WATEQ equation.

the applicability of the ionic strength equation to a solution with high concentration of a large organic molecule is uncertain; electrical attractions and repulsions are different between point charges and charges distributed over a large molecule. Thus, describing CMCD as an ionic species with a valence of -4 produces unrealistically high ionic strengths. Therefore, we explore two charge representations:  $CMCD^-$  and  $CMCD^{2-}$ . The protonation of the metal complexation portion of CMCD is modeled either by Equation 3-1 or by Equations 3-2 and 3-3, with the remaining carboxyl protonation reactions represented by Equation 3-4. When CMCD is represented as a monoprotic acid (Equation 3-1) the model contains 3.27 additional carboxyl groups per CMCD and when CMCD is represented as a diprotic acid it contains 2.27 additional carboxyl groups per CMCD. Both  $CMCD^-$  and  $COO^-$  are defined as independent basis species in PHREEQC, meaning these species are decoupled from the C, O and H in the model. By representing CMCD as a monoprotic or diprotic acid, the pH-dependence of Pb complexation is considered in the model, and the charge of CMCD is limited to one or two. All carboxyl groups, including the separate COOH groups and the one(s) on CMCD, are assigned identical  $pK_a$  values consistent with the base titrations.



Next, we can constrain the system by assuming that the dissolved concentration of  $Pb^{+2}$  is dictated by the dissolution of lead oxalate (Equation 3-5), where increased lead solubility

results from complexation (Equation 3-6 or 3-7). Equation 3-8 or 3-9 defines the stability constant of the reaction for the mono- and di-protic representation, respectively.



$$K_{CMCD-Pb^+} = \frac{\{CMCDPb^+\}}{\{CMCD^-\}\{Pb^{2+}\}} \quad (3-8)$$

$$K_{CMCD-Pb} = \frac{\{CMCDPb\}}{\{CMCD^{2-}\}\{Pb^{2+}\}} \quad (3-9)$$

Values within curved brackets represent activities. In this system of equations, the only unknown is the stability constant for the CMCD-Pb complex.

The above equations assume a 1:1 ratio between CMCD and the metal in the complex. Wang and Brusseau (1995) suggested a 1:1 complex for Cd-CMCD based on the relationship observed between CMCD concentration and complexed Cd. Our experiments had a very high CMCD:metal molar ratio (30:1 at 1 g/l CMCD), which further justifies an assumption of 1:1 stoichiometry. In addition, because the 1:1 complex has a less negative charge than un-complexed CMCD, the electrostatic attraction for the addition of another cation to form a 2:1 complex is less favorable than formation of another 1:1 complex.

Model A: One-site model, CMCD<sup>-</sup>, Davies-based activity coefficient

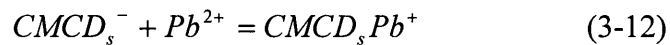
The simplest model assumes one complexation site per CMCD molecule with a complex stoichiometry of 1:1 (CMCD:Pb). The only unknown parameter is the stability constant for the CMCD-Pb complex,  $K_{\text{CMCD-Pb}}$ . Equations 3-1 and 3-4 to 3-6 describe the CMCD and Pb mass balances. The Davies equation is used to calculate activity coefficients for all charged aqueous species:

$$\log \gamma_i = -A \cdot z_i^2 \cdot \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3 \cdot \mu \right) \quad (3-10)$$

Where  $\gamma_i$  is the activity coefficient for ion  $i$ ,  $A$  is a constant that depends on temperature and pressure only,  $z_i$  is the charge of ion  $i$ , and  $\mu$  is the ionic strength.

Model B: Two-site model, CMCD<sup>-</sup>, Davies-based activity coefficient

In CMCD, the functional groups can be randomly substituted on one side of the torus on the cyclodextrin molecule (Bender and Komiyama, 1978). This makes it possible to have configurations where some of the carboxyl groups are closer to each other creating sites with different Pb complexation properties. Therefore we can envision a second model with a strong and a weak Pb complexation site, both with a 1:1 complexation ratio and only one complexation site CMCD molecule. Thus, the total number of complexation sites is the same as in model A.



All activity coefficients, as in model A, are calculated with the Davies equation and carboxyl groups and charges on CMCD are represented separately. This second model contains three unknown parameters: the percentage of weak and strong sites ( $f_{w/tot}$ ) and the conditional stability constants for the two complexes ( $K_w$  and  $K_s$ ).

Model C: One-site model,  $CMCD^-$ , Davies-based activity coefficient, Pb and K competition

This model considers the possibility that the cation,  $K^+$ , in the background salt may compete with  $Pb^{2+}$  for complexation sites on the CMCD. This competition can be taken into account by adding a complexation reaction between CMCD and K:



Other assumptions are identical to model A. This model contains two unknown parameters:  $K_{CMCD-Pb^+}$  and  $K_{CMCD-K}$ .

Model D: One-site model,  $CMCD^{2-}$ , Davies-based activity coefficient

The charge representation of CMCD affects the calculation of both ionic strength and activity coefficients; ionic strength is a function of the sum of squared charges of all individual ions and activity coefficients are calculated based on the squared charge of the particular ion. To explore the influence of charge representation on Pb complexation, we use the divalent representation of the CMCD ligand,  $CMCD^{2-}$ . This representation is consistent with a bi-dentate complex between free aqueous lead ion and two carboxyl groups on CMCD. However, it is not possible, based on our data and modeling, to distinguish between mono and bi-dentate complexation.  $CMCD^{2-}$  is an alternative formulation to try and better fit the experimental data.



The total acidity is taken into account by representing CMCD as a diprotic acid and distributing the total acidity between CMCD and carboxyl groups (Equations 3-2 to 3-4). The only unknown parameter is the conditional stability constant for the CMCD-Pb complex,  $K_{\text{CMCD-Pb}}$ .

Model E: One-site model, WATEQ-based activity coefficient,  $\text{CMCD}^{2-}$

The widely adopted Debye-Hückel theory for calculating activity coefficients assumes point charges, purely electrostatic interactions, and that the ions around any particular ion follow a Boltzmann distribution (Drever, 1997). Charges resulting from de-protonated carboxyl groups on the CMCD molecule do not fulfill these assumptions. Both the Davies and the WATEQ Debye-Hückel equations are based on the Debye-Hückel theory but the latter contains two more parameters that yield more flexibility in describing non-ideal behavior. In an attempt to better fit experimental data, model D was modified by using the WATEQ Debye-Hückel equation to calculate the activity coefficient for  $\text{CMCD}^{2-}$ .

$$\log \gamma_{\text{CMCD}^{2-}} = -A \cdot z_{\text{CMCD}^{2-}}^2 \cdot \left( \frac{\sqrt{\mu}}{1 + B \cdot a_{0,\text{CMCD}^{2-}} \cdot \sqrt{\mu}} \right) + b_{\text{CMCD}^{2-}} \cdot \mu \quad (3-15)$$

A and B are constants that depend on temperature and pressure only and  $a_{\text{CMCD-Pb},0}$  is, in theory, the hydrated radius of the ion. In practice, however,  $a_{\text{CMCD-Pb},0}$  and  $b_{\text{CMCD-Pb}}$  are used as fitting parameter to yield the best fit to experimental data. This model contains three unknown parameters:  $K_{\text{CMCD-Pb}}$ ,  $a_{0,\text{CMCD}^{2-}}$  and  $b_{\text{CMCD}^{2-}}$ .

## Results and Discussion

### Carboxyl group concentration

Results from five NaOH titrations indicate that CMCD contain on average 4.27 carboxyl groups, assuming CMCD is 100% pure. The 95% confidence interval range from 4.21 to 4.33 and the average error in blank base titrations is 1.4%. The titration curves show one inflection point with an average  $pK_a$  of 3.77 and a 95% confidence interval ranging from 3.77 to 3.84. Base titrations are considered more accurate than acid titrations because of slight dissolution of  $CO_2(g)$  at high pH. The titrations were modeled in PHREEQC using the experimentally derived values for  $pK_a$  and carboxyl concentration listed above (Figure 3-1). The good agreement between simulated and observed data indicates that acid-base behavior of CMCD can, for practical purposes, be modeled with carboxyl groups of identical strength.

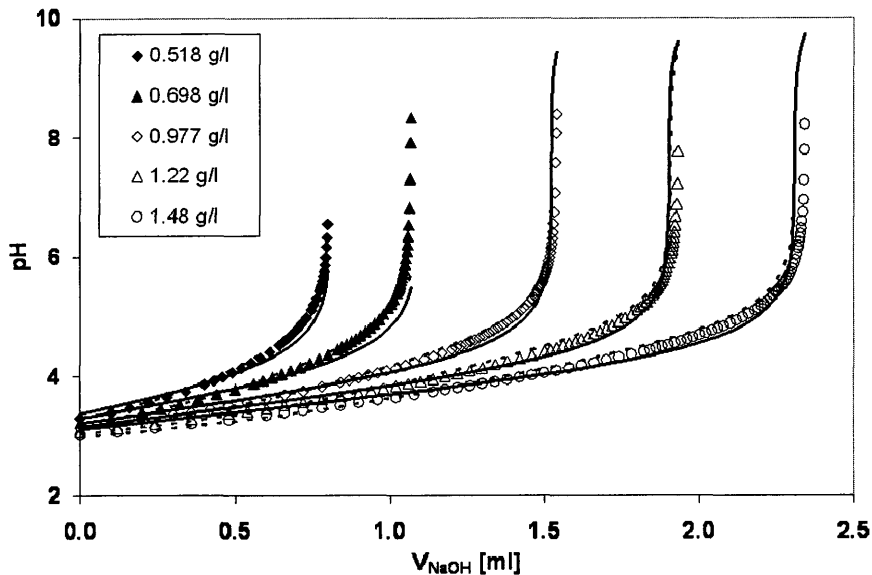


Figure 3-1. NaOH titrations of CMCD at 50 mM  $KNO_3$ . Symbols represent experimental data and lines PHREEQC model using experimentally derived constants.

### Lead solubility experiments

Pb solubility experiments were performed in 50, 100 and 300mM KNO<sub>3</sub> solutions. Aqueous lead concentration was analyzed in samples containing 0.1 to 20 g/l CMCD. Experimental results were modeled with five complexation models, described above.

#### Model A: One-site model, CMCD<sup>-</sup>, Davies-based activity coefficient

The single-site model fits observed data well only when Pb solubility at different ionic strengths are modeled separately; varying the conditional stability constant can compensate for a poor ionic strength model (Figures 3-2, 3-3 and Table 3-1). The optimized conditional stability constant decreases with increasing ionic strength. At 50mM KNO<sub>3</sub> log K is 4.65. It then decreases to 4.47 and 4.21 at 100, and 300mM KNO<sub>3</sub>, respectively. When all data are modeled simultaneously the model is not capable of correctly simulating the effect of varying ionic strength. Observed aqueous lead concentration decreases with increasing ionic strength while the model simulates the opposite behavior (Figure 3-2). This model is not robust with respect to changes in ionic strength, and should thus be discarded as a valid conceptual model.

#### Model B: Two-site model, CMCD<sup>-</sup>, Davies-based activity coefficient

Introducing a second Pb complexation site does not improve the model (Figure 3-2). In fact, the objective function lacks a unique minimum. Inherently, the minimum occurs at optimized parameter values but because the objective function is almost flat around its minimum a wide range of parameter values yield a similar fit to experimental data. Thus, the model is not unique. A flat objective function may result from the model containing correlated parameters or parameters that are not sensitive to observed data. Both cases may be signs of a poor model. Estimated aqueous lead concentrations were not sensitive to the distribution of sites between weak and strong sites,  $f_{w/tot}$ , and the parameter was highly correlated to the conditional stability constants. Thus, the fit of the model does not depend on the distribution of strong and weak sites. Figure 3-4 shows that with  $f_{w/tot}$  specified to 0.75 the minimum of the objective function occurs in a long trough with K

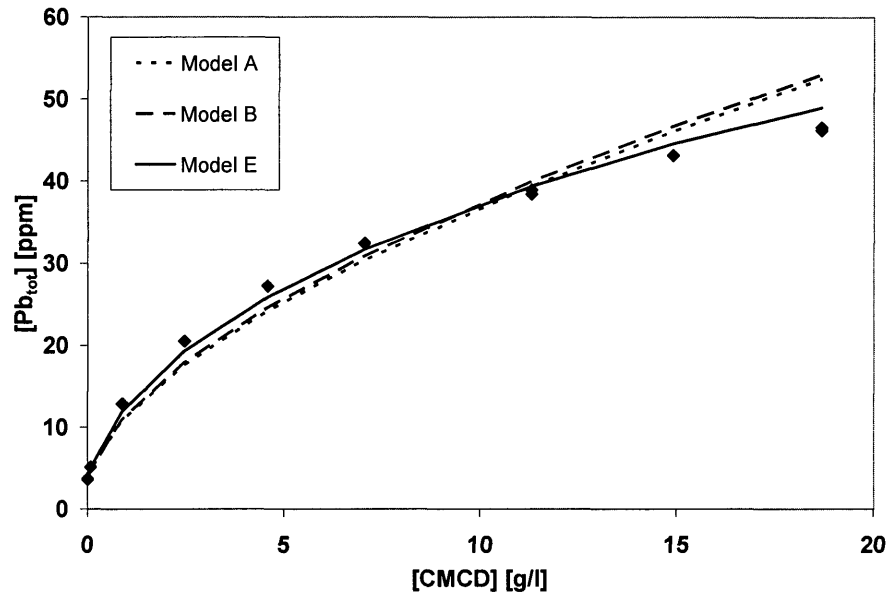


Figure 3-2. Comparison of models A, B and E using constants derived at 50 mM KNO<sub>3</sub> assuming 75% weak and 25% strong sites.

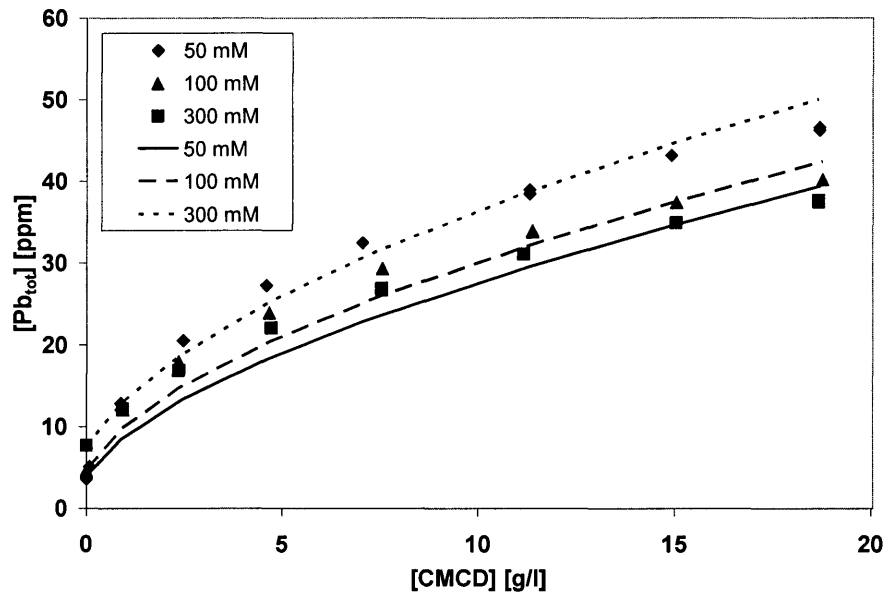


Figure 3-3. Fit of model A to experimental data. Symbols represent data and lines results from PHREEQC/UCODE model.

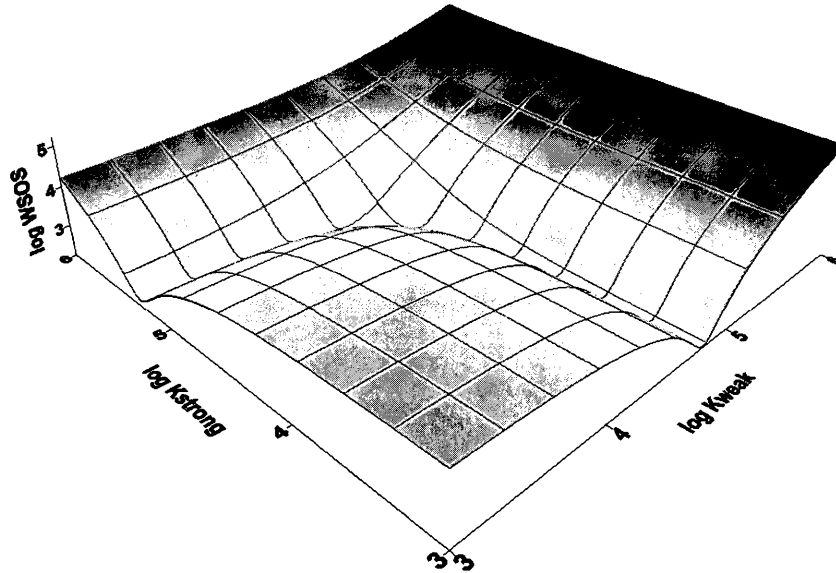


Figure 3-4. Objective function surface for model B at 75% weak and 25% strong sites.

values similar to the optimized K for the one-site model. In fact, the K values in the trough can be calculated from the K in model A and the distribution of strong and weak sites.

Introducing more fitting parameters generally allows more mathematical flexibility to fit data. However, in this case, introducing two more unknown parameters does not improve the fit. If several assumptions are made, a simple expression for total aqueous lead concentration can be derived. For simplicity, let us assume that the only reactions affecting total aqueous Pb concentration are the dissolution of  $\text{PbC}_2\text{O}_4(\text{s})$  and Pb complexation by CMCD, that pH is significantly higher than  $\text{pK}_a$ , and that all activity coefficients are unity. Then, for a one-site model total aqueous lead concentration can be described by

$$[Pb_{tot}] = \sqrt{K_{sp} \cdot (1 + K \cdot [L^-])} \quad (3-16)$$

and for a two-site model

$$[Pb_{tot}] = \sqrt{K_{sp} \cdot (1 + K_w \cdot [L_w^-] + K_s \cdot [L_s^-])} \quad (3-17)$$

$K_{sp}$  is the solubility product of  $PbC_2O_4(s)$ ,  $[L]$  is ligand concentration, and  $K$  is the stability constant. Subscripts  $w$  and  $s$  represent weak and strong sites, respectively. The sum of  $[L_w]$  and  $[L_s]$  is equivalent to  $[L]$ , or the total CMCD concentration.

A comparison between the one and two-site models reveal significant similarities. If both sites are equally important for Pb complexation ( $K_w \cdot L_w \approx K_s \cdot L_s$ ) Equation 3-17 approaches Equation 3-16. On the other hand, if  $K_w \cdot L_w \ll$  or  $\gg K_s \cdot L_s$  the products within the parentheses differ by a factor of 2. The difference can be adjusted for by increasing the conditional stability constant and/or the ligand concentration. The correlation between  $K$  and  $[L]$  explains why including a second site does not improve the model. UCODE\_2005 calculates a correlation coefficient close to 1, suggesting the parameters are highly correlated. Our experimental set-up, thus, does not allow us to distinguish between a one and a two-site model. It is possible that CMCD has two different complexation sites but for the purpose of enhanced dissolution of lead oxalate the distinction is not important. Because this conceptual model cannot produce a unique result, it is effectively useless for prediction purposes, and should therefore be discarded until data become available that can provide independently estimated parameters.

Model C: One-site model, CMCD<sup>-</sup>, Davies-based activity coefficient, Pb and K

Including competition between Pb and K for sites on CMCD improves the fit of the model to data (Figure 3-5a). The model simulates observed data well; aqueous lead

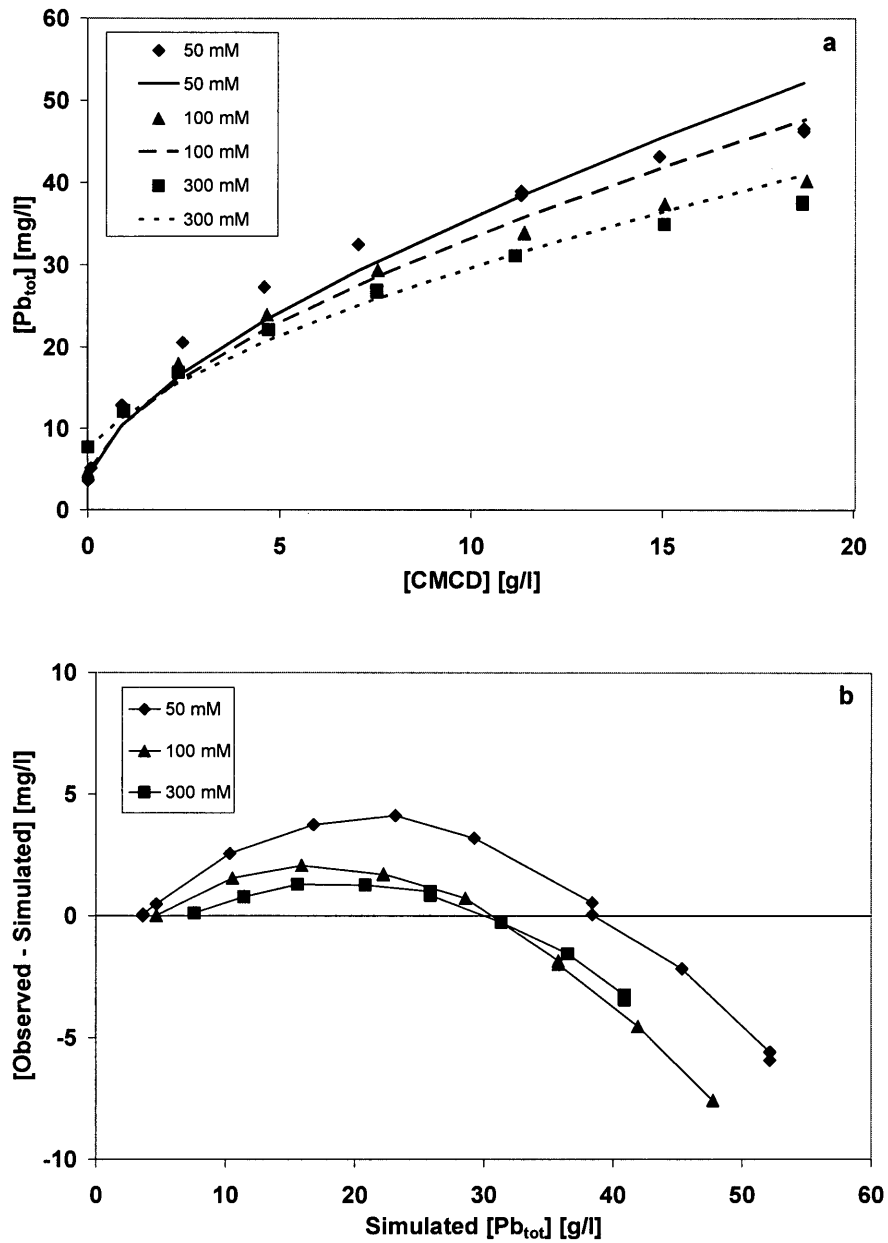


Figure 3-5. Fit of model C to experimental data. (a) Symbols represent data and lines represent results from PHREEQC/UCODE model. (b) Data are connected with lines.

concentration decreases with increasing KNO<sub>3</sub> and increasing CMCD concentration enhances Pb solubility at constant ionic strength. However, residual analysis reveals a systematic error at all three ionic strengths; the model under predicts the lead concentration at low CMCD concentrations and over predicts the lead concentration at high CMCD concentrations (Figure 3-5b). Despite this error, estimated aqueous lead concentrations are generally within 10% of observed concentrations.

The optimized conditional stability constant for Pb complexation is slightly higher compared to the one-site model (Table 3-1). Published complexation constants for other organic acids are lower than our estimated log K<sub>K</sub> for CMCD. For instance, citric acid and oxalic acid have log K<sub>K</sub> of 0.59 and -0.8, respectively, while published stability constants for Pb complexation by citric acid and oxalic acid range from 4 to 5 (Sillén and Martell, 1964). The comparably high conditional stability constant for K complexation raises concern over the chemical appropriateness of the model. Although the model fits the data well, the model is considered less than optimum because of the apparently unrealistic high stability constant for K complexation. In addition, the model is considered poor because of the systematic bias with respect to ionic strength (Figure 3-5); good conceptual models should exhibit random error bias (Hill, 1998).

Model D: One-site model, CMCD<sup>2-</sup>, Davies-based activity coefficient

This model is the same as Model A except CMCD is assumed to have a -2 charge. The representation of charges on CMCD affects both simulated ionic strength and activity coefficients of the free and complexed ligand. Equation 3-18 shows that, with the simplifying assumptions discussed above, simulated total aqueous lead concentration is a function of the ratio between the activity coefficients of the free and complexed ligand.

$$Pb_{tot} = \sqrt{\frac{K_{sp}}{\gamma_{Pb^{2+}} \cdot \gamma_{C_2O_4^{2-}}} \cdot \left( 1 + K_{CMCDPb} \cdot [CMCD^{2-}] \cdot \frac{\gamma_{Pb^{2+}} \cdot \gamma_{CMCD^{2-}}}{\gamma_{CMCDPb}} \right)} \quad (3-18)$$

Figure 3-6 shows that the model is not consistent with observed data; however, based on WSSR and  $R^2$ , the difference between model results and data is less pronounced when representing the ligand as  $\text{CMCD}^{2-}$ . Thus, while model D is not considered a good conceptual model, it has helped us to refine our conceptual model by demonstrating that a -2 charge improves the model fit.

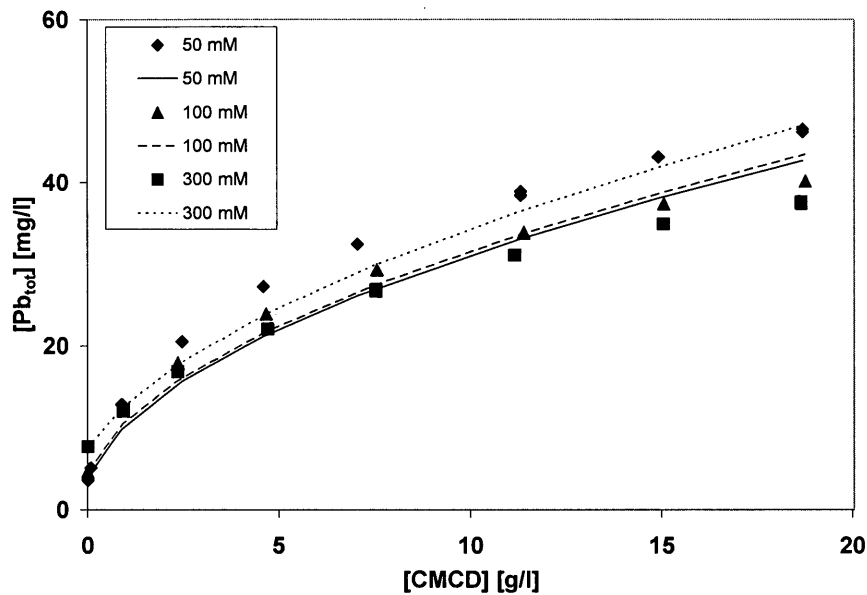


Figure 3-6. Fit of model D to experimental data. Symbols represent data and lines represent results from PHREEQC/UCODE model.

Model E: One-site model, WATEQ-based activity coefficient,  $\text{CMCD}^{2-}$

Based on the analysis of prior conceptual models, we can improve our conceptual model by proposing a model that might not have been obvious from the start. Experimental data show that CMCD becomes less efficient at complexing Pb at high ionic strengths (for instance Figure 3-6). This non-ideal behavior may be accounted for by an appropriate activity model. The WATEQ Debye-Hückel equation was evaluated because it provides a more flexible representation of the activity coefficient; it can simulate the observed

decreasing Pb solubility with increasing ionic strength. This conceptual model yields good results. Simulated aqueous lead concentrations are within 10% of observed values, and the shape of curves for specified values of  $\text{KNO}_3$  curves closely mimic experimental data (Figure 3-7a).

Initially, we attempted to optimize all three unknown parameters simultaneously. This resulted in non-unique solution to the regression problem; different starting values resulted in different optimized values of  $a_{0,\text{CMCD}2-}$  and  $b_{\text{CMCD}2-}$ . In addition, calculated sensitivities for  $a_{0,\text{CMCD}2-}$  were much lower than for the other two parameters, and  $a_{0,\text{CMCD}2-}$  and  $b_{\text{CMCD}2-}$  were highly correlated. Because the value of  $a_{0,\text{CMCD}2-}$  does not significantly affect the simulated Pb concentrations  $a_{0,\text{CMCD}2-}$  was fixed to 3.50 based on the recommendation of Stumm and Morgan (1996), while  $b_{\text{CMCD-Pb}}$  and  $\log K_{\text{CMCD-Pb}}$  were optimized simultaneously. The optimized value for  $\log K_{\text{CMCD-Pb}}$  was 5.18 with a 95% confidence interval ranging from 5.14 to 5.22. The activity coefficient parameter  $b_{\text{CMCD-Pb}}$  was estimated to -0.65 with 95% confidence interval ranging from -0.84 to -0.44. This conceptual model is robust for the observed conditions, provides the best WSSR, and is physically realistic. Thus, it is deemed a valid conceptual model that is appropriate for prediction. However, while this model is very good, it is not without weaknesses.

The 95% confidence interval is calculated assuming that residuals belong to a normal distribution and that they are randomly distributed around zero. Figure 3-7b shows that the assumption is not quite true. Uncertainty related to the conceptual model is not represented in the reported 95% confidence intervals.

The weakness of the model is that it is not capable of precisely simulating the magnitude of change in Pb solubility as a function of ionic strength, which is illustrated in

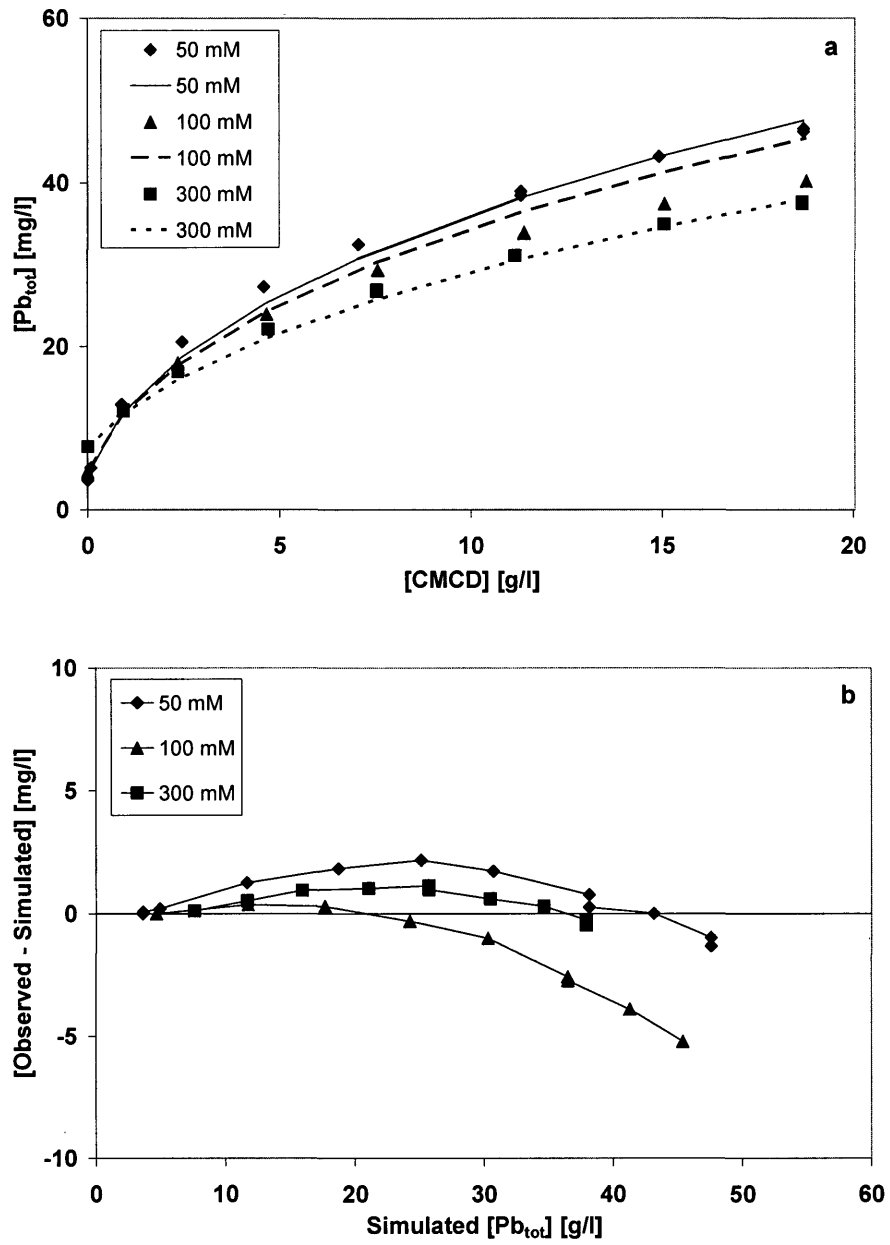


Figure 3-7. Fit of model E to experimental data. (a) Symbols represent data and lines results from PHREEQC/UCODE model. (b) Data are connected with lines.

Figure 3-7b. The largest difference in experimental data is between 50 and 100 mM while the model simulates the largest difference in Pb concentration between 100 and 300 mM. This shortcoming is due to either incorrectly calculated ionic strength and/or an imperfect activity model for CMCD. In addition, there is a trend within each solubility curve at a specific background ionic strength. The effect of adding CMCD on ionic strength is not very well understood.

Any model is a representation, and therefore an approximation, of reality. Because of the weaknesses in our models, the full truth is not included in any of our conceptual models. Akaike (1973) formulated a method for comparing several models based on the information lost when using a model to approximate the true reality. Using this method, Akaike's Information Criterion (AICc) is calculated for each model according to:

$$AICc = n \log(\sigma^2) + 2 \cdot k + \left( \frac{2 \cdot k(k+1)}{n-k-1} \right) \quad (3-19)$$

where n is the number of observations,  $\sigma^2$  is the estimated residual variance, and k is the number of parameters estimated in the model. Because the residual variance is always estimated, the parameter k is the number of unknown estimated parameters plus one. The model with the lowest AICc value is considered the most appropriate because it approximates the truth best among the selected models.

Generally, models fit experimental data more closely if more parameters are added to the models. However, as the number of parameters increases, precision decreases (Poeter and Anderson, 2005). The first term in Equation 3-19 accounts for goodness of fit (in our models the weighted, summed and squared residual lead concentrations) and the second and third terms penalize models for including additional parameters. Based on Akaike's

theory, several models can be ranked according to their AICc values and weighted by first computing simple differences,  $\Delta_i$ .

$$\Delta_i = AICc_i - AICc_{\min} \quad (3-20)$$

$AICc_{\min}$  is the AIC value for the most appropriate model. The weight for each model,  $w_i$ , can be used to predict CMCD-enhanced lead solubility based on several different models.

$$w_i = \frac{\exp^{-0.5\Delta_i}}{\sum_{j=1}^R \exp^{-0.5\Delta_j}} \quad (3-21)$$

The AICc values and weights calculated for our five conceptual models clearly show that there is much more evidence supporting model E than any of the other models (Table 3-2). Because model E has a weight of 1.00 it would dominate the predicted lead solubility

Table 3-2. Calculated values for Akaike's Information Criterion (AICc) and model weights.

Model	WSSR <sup>12</sup>	k <sup>13</sup>	n <sup>14</sup>	AICc	Weight
A	1989	2	28	125	1*10 <sup>-16</sup>
B	NA	NA	NA	NA	NA
C	625	3	28	95	1*10 <sup>-10</sup>
D	912	2	28	103	1*10 <sup>-12</sup>
E	133	3	28	52	1.00

<sup>12</sup> Weighted sum of squared residuals for optimized parameter values.

<sup>13</sup> Number of parameters estimated with UCODE\_2005. The parameter k includes the estimated error variance and equals the number of unknown parameters plus one.

<sup>14</sup> Number of observations used to estimate parameter values.

if several models and their weights were used for this prediction. Burnham and Anderson (2002) provide more information on this topic.

In summary, in addition to scientific soundness, we evaluate the models based on simplicity, how well they fit experimental data, whether they are physically realistic (i.e., believable), and on whether they can be included in available geochemical codes. All models discussed above are simple and can be included in the geochemical code PHREEQC. All 5 models have strengths and weaknesses. Models C and E fit observed data the best, and almost equally well, but because the high value of optimized  $K_{\text{CMCD-K}}$  and the stronger trend in residuals in model C, we argue that model E with the WATEQ activity coefficient formulation is the most appropriate among the models evaluated.

## **Conclusions**

Experimental data were analyzed using the geochemical model PHREEQC coupled to UCODE\_2005, a parameter optimization program, to derive the conditional stability constants for metal complexation of lead with a large sugar molecule, carboxymethyl- $\beta$ -cyclodextrin. The approach described in this paper determines stability constants from experimental data with associated uncertainties and compares several conceptual models. Evaluation of conceptual models is especially important because there are always uncertainties associated with any choice of a geochemical model, and even greater uncertainties when modeling solute reactions between metal ions and large organic molecules. The automated process with UCODE\_2005 was rapid, allowing evaluation of multiple models that are internally consistent with the database of the chemical equilibrium model. This is important because some of the models tested did not produce behavior consistent with observations. The model selected as the best conceptual model

separated the metal complexation reaction from the other carboxylic acid functional group reactions to minimize the effect on ionic strength calculations and activity models.

The complexation of lead ions with CMCD was strong at CMCD concentrations below 5g/L. However, the experimental data showed that the complexation reaction became less efficient at higher CMCD concentrations. A high concentration of CMCD affects the ionic strength of the solution which in turn affects the description of the non-ideal behavior of CMCD. The exact nature of this effect remains uncertain.

The main challenges in modeling enhanced lead solubility by CMCD appears to be the description of how a large organic molecule such as CMCD affects ionic strength and to correctly describe non-ideal interactions between CMCD and Pb. Activity models included in commonly used geochemical codes are based on the assumption of point charges. This assumption may not apply to organic complexing agents such as CMCD. To improve our ability to model remediation scenarios, work is needed to build an accurate activity model for large organic complexing agents. Despite this challenge we were able to model metal complexation by a large organic complexing agent using an existing activity-coefficient model (WATEQ). The model would be particularly useful for screening various metal remediation techniques. The combination of UCODE\_2005 and PHREEQC was indispensable in this endeavor.

### **Acknowledgments**

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**CHAPTER FOUR**  
**SOLUBILITY ENHANCEMENT OF EIGHT METAL**  
**CONTAMINANTS USING CARBOXYMETHYL- $\beta$ -**  
**CYCLODEXTRIN (CMCD)**

**Abstract**

Carboxymethyl- $\beta$ -cyclodextrin (CMCD) has been suggested as a complexing agent for remediation of sites co-contaminated with metals and organic pollutants. As part of an attempt to construct a geochemical complexation model for metal-CMCD interactions, conditional formation constants for the complexes between CMCD and 8 metal ions (Ba, Ca, Cd, Ce, Ni, Pb, Sr, and Zn) are estimated from experimental data. Stable metal concentrations were reached after approximately 1 day and estimated conditional formation constants range from  $10^{-3.2}$  to  $10^{-5.1}$  with confidence intervals within  $\pm 0.08$  log units. Experiments performed at 10°C and 25°C show that temperature affects the solubility of the metal salts but the strength CMCD-metal complexes are not affected by this temperature variation. The conditional stability constants and complexation model presented in this work can be used to screen CMCD as a potential remediation agent for clean-up of contaminated soil and ground water.

## **Introduction**

Organic and inorganic contaminant mixtures present at contaminated sites is one of the major challenges in remediating soil and ground. Due to the fundamentally different physiochemical properties of these contaminants, research has to a large extent focused on remediating organic and inorganic contaminants separately rather than with a single treatment. Two basic approaches to remediation are to wash (ex-situ) or flush (in-situ) the contaminated soil with an agent to increase solubility. If the complexing agent, or mixture of complexing agents, is chosen appropriately both organic and inorganic contaminants can be removed simultaneously. For instance, biosurfactants (Mulligan et al., 1999) and solutions of strong acids mixed with isopropyl alcohol (Semer and Reddy, 1996) have successfully been used in bench scale experiments. In both studies heavy metals were removed in the presence of organic compounds from a contaminated sand and sandy silt, respectively.

One potential complexing agent to clean up mixed waste is cyclodextrin (CD), a compound produced by microorganisms consisting of 6, 7 or 8 glucose molecules in a ring structure. The most common CD is the  $\beta$ -cyclodextrin which is composed of 7 glucose molecules. The ring structure creates a non-polar cavity enabling inclusion complexation of organic compounds (Wang and Brusseau, 1993). Chemical properties of interest such as aqueous solubility and metal complexation potential can be altered by substituting functional groups to the outside of the cyclodextrin. Laboratory and field studies have demonstrated that hydroxypropyl- $\beta$ -cyclodextrin (HPCD) has high aqueous solubility, strongly enhances solubility of organic compounds and is not retained by soil (Boving and McCray, 2000).

A field test at Hill Air Force Base, UT demonstrated that addition of 10 wt.% HPCD significantly accelerated the removal of organic contaminants via pump and treat (McCray et al., 1999; McCray and Brusseau, 1999). More TCE was removed over 10 days than would have been removed in 1 year with regular pump and treat. In addition, biotracer studies indicated that flushing with HPCD enhanced the biodegradation potential for ethanol and hexanol (Alter et al., 2003). Vertical flushing with HPCD of a contaminant source zone was attempted at another superfund site where the subsurface consisted of silt and clay layers. Despite rate limited transfer of TCE to the aqueous phase in this setting, 20 wt.% HPCD increased the TCE concentration in the extracted ground water threefold (Blanford et al., 2001). In a third field trial, enhanced flushing with HPCD increased effluent TCE concentration up to 22 times compared to water flush and the HPCD solution was recovered and reused after removing 99.99% of TCE with an air stripper (Tick et al., 2003). These studies show that HPCD is a potential complexing agent for remediation of organic contaminants.

Laboratory studies have shown that carboxymethyl- $\beta$ -cyclodextrin (CMCD) has the ability to complex heavy metals such as cadmium, nickel, strontium and mercury in the presence of various organic contaminants (Wang and Brusseau, 1995; Brusseau et al., 1997; Wang et al., 2003). A comparison between HPCD and CMCD showed that both CDs enhanced the solubility of organic compounds but that HPCD was the most effective (Brusseau et al., 1997). Thus, CMCD may be used to simultaneously enhance the solubility of organic and inorganic contaminants.

A literature review revealed only one study where the stability constant for a complex between a single metal (Cd) and CMCD was investigated (Wang and Brusseau, 1995), making quantitative evaluation of potential remediation performance and comparison to other complexing agents difficult. This study conducted a series of batch equilibrium experiments using remediation-grade CMCD to derive conditional stability constants for

aqueous complexes between CMCD and Ba, Ca, Cd, Ce, Ni, Pb, Sr, and Zn. Our data show that CMCD significantly enhances the solubility of all investigated metals salts. The transition elements form somewhat stronger complexes with CMCD than do group 2 elements. Thus, in a potential remediation scenario, the competition between common cations and metal contaminants will depend on the speciation and the concentration of metal contaminants as well as Ca and Mg. While temperature affects the inherent solubilities of metal salts, relevant temperature variations did not affect the strength of the CMCD-metal complexes.

## **Materials and Methods**

### Experimental techniques

Industrial grade CMCD was provided by Wacker, Inc. The compound was delivered as a sodium salt with unspecified purity. All other chemicals were +98% pure unless otherwise noted. The background ionic strength was controlled by  $\text{KNO}_3$  in the multi-day experiments, while  $\text{NaNO}_3$  was used in the 2-hour experiments. In all titrations, the solutions were purged with nitrogen gas (ultra high purity) prior to reaction and the pH was adjusted with sodium hydroxide solution. Ion-exchange resin (Rexyn 101H) was purchased from Fisher Scientific.

All metal salts (Ba, Ce, Cd, Ni, Pb, Sr, and Zn) were oxalates, except for  $\text{SrSO}_4$ . The purities of Cd and Ce oxalates were not reported. Zn and Ni oxalates were formed via precipitation from solutions of metal nitrates and oxalic acid as described in Donia (1997). XRD analysis showed that crystalline Ni and Zn oxalates formed (data not shown).

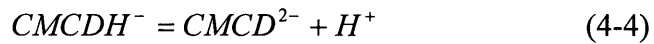
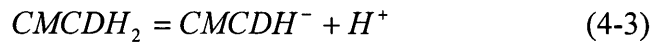
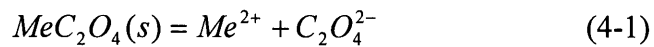
The acid-base behavior of CMCD was investigated by potentiometric titrations in a  $\text{CO}_2(\text{g})$  free atmosphere. Temperature was kept constant at  $25^\circ\text{C}$  and background ionic strength was  $50 \text{ mM KNO}_3$  while pH was increased by adding incremental volumes of  $0.1 \text{ M NaOH}$ . Before titrating cyclodextrin with  $\text{NaOH}$ , the CMCD- $\text{Na}$  salt was converted to its acidic form by passing  $50 \text{ ml}$  of a  $100 \text{ g/l}$  CMCD solution twice through a column containing an ion exchange resin.

Batch experiments aimed at determining conditional stability constants for complexation between CMCD and metal ions were performed in sealed  $15 \text{ ml}$  centrifuge tubes submerged in a water bath to control temperature at  $10 \pm 0.5$  or  $25 \pm 0.5^\circ\text{C}$ . Two separate sets of experiments were performed. A preliminary investigation at  $10$  and  $25^\circ\text{C}$  lasting  $2$  hours was performed prior to a second set of experiment at  $25^\circ\text{C}$  lasting  $7$  days. A small amount ( $20$ - $50 \text{ mg}$ ) metal salt was added to  $10 \text{ ml}$  solutions containing up to  $20 \text{ g/l}$  CMCD in  $50 \text{ mM}$  background ionic strength. In the preliminary experiments, background ionic strength was varied from  $0$  for  $20 \text{ g/l}$  CMCD solutions, to  $50 \text{ mM}$  at the lower CMCD concentrations. In the longer time experiments, the CMCD concentration ranged from  $0$  to  $100 \text{ g/l}$  and background ionic strength was held constant at  $50 \text{ mM KNO}_3$ . Hydrogen ion activity was adjusted to  $\text{pH } 6.0$  in all CMCD solutions before adding the metal salts. The centrifuge tubes were slowly rotated top-over-bottom throughout the experiment to ensure constant and gentle mixing.

#### Modeling techniques

In our batch experiments, the free metal ion activity is controlled by the presence of a sparingly soluble metal salt. CMCD complexes the free metal ion which causes more of the salt to dissolve (Equations 4-1 and 4-2). Previous systematic evaluation of experimental data for lead complexation by CMCD indicated the data is best modeled by representing  $3$  sets of mass action equations (Chapter 3). The CMCD has two protonation reactions and a complexation reaction with a  $1:1$  (metal ion:CMCD) stoichiometry

(Equations 4-1 to 4-4). Titrations indicated that each CMCD molecule has on average 4.27 titratable groups. Additional CMCD acidity (2.27 carboxyl groups per CMCD) is modeled as separate by carboxylic acid reactions (Equation 4-5). It is important to include the acid/base behavior of CMCD in the model because hydrogen ions and metal ions will compete for sites on CMCD at low pH. Also, the buffering capacity of CMCD will affect pH dependent dissolution of minerals when modeling a field application.



The activity coefficient for the species  $CMCD^{2-}$  is calculated using the WATEQ Debye-Hückel equation with  $a_{0,CMCD^{2-}} = 3.50$  and  $b_{CMCD^{2-}} = 0.65$  (Equation 4-6). The Davies equation was used to calculate the activity coefficients of all other species (Stumm and Morgan, 1995).

$$\log \gamma_{CMCD^{2-}} = -A \cdot z_{CMCD^{2-}}^2 \cdot \left( \frac{\sqrt{\mu}}{1 + B \cdot a_{0,CMCD^{2-}} \cdot \sqrt{\mu}} \right) + b_{CMCD^{2-}} \cdot \mu \quad (4-6)$$

The conditional stability constant for metal-CMCD complexation is calculated according to:

$$K_{CMCD-Me} = \frac{\{CMCDMe\}}{\{CMCD^{2-}\}\{Pb^{2+}\}} \quad (4-7)$$

Values within curved brackets represent activities. The geochemical modeling program PHREEQC (Parkhurst and Appelo, 1999) was used to model metal complexation by CMCD and the conditional stability constants were derived with the parameter optimization program UCODE\_2005 (Poeter et al., 2005; Poeter and Hill, 1998). The optimization process is described in Appendix A. Equations 4-1 to 4-7 were included in the PHREEQC model and the standard PHREEQC data base was amended with thermodynamic data for aqueous complexes between oxalate and metal ions, Table 4-1 (Martell and Smith, 1977). The optional Lawrence Livermore National Laboratory database in PHREEQC was used instead of the standard database when modeling cerium oxalate.

Table 4-1. Logarithmic constants for aqueous metal-oxalate complexes used in modeling (Martell and Smith, 1977).

	$MeC_2O_4$	$Me(C_2O_4)_2^{-2}$	$Me(C_2O_4)_3^{-4}$	$MeHC_2O_4^+$	$Me(HC_2O_4)_2$
Ba	2.31	NA	NA	NA	NA
Ca	2.54	2.69	NA	1.84	NA
Cd	3.89	5.66	5.06	NA	NA
Ce	6.52	10.48	11.30	NA	NA
Ni	5.16	NA	NA	NA	NA
Pb	4.91	6.76	NA	NA	NA
Sr	NA	NA	NA	NA	NA
Zn	4.87	7.65	NA	1.72	3.12

## **Results and discussion**

### **Potentiometric titrations**

Titration end-points and  $pK_a$ s were evaluated with half-point analysis. The analysis indicated an average carboxyl concentration of 4.27 functional groups per CMCD. This is equivalent to 0.610 substituted carboxymethyl groups per glucose ring. The 95% confidence interval ranges from 0.601 to 0.619. The molecular weight of CMCD was calculated to 1390 g/mol based on substitution ratio and its molecular structure. The average  $pK_a$  from five titrations was 3.80 with 95% confidence interval ranging from 3.77 to 3.84. This value compares well with published  $pK_a$ s of metoxyacetic acid and etoxyacetic acid, which have similar structure to functional groups on CMCD: 3.57 and 3.67, respectively (CRC, 2004). The calculations were performed assuming that CMCD was 100% pure.

The carboxymethyl groups are separated from each other by several single carbon-carbon bonds. Very little electron sharing is expected and we assume above that all carboxyl groups have identical strength. This assumption was investigated by comparing experimental data to a model based on experimentally derived acidity constants and assuming that all carboxyl groups have the same strength. The model fits experimental data well. The correlation coefficient between observed and simulated pH ( $R^2$ ) for all 5 titrations modeled simultaneously was 0.996. Experimental data show a slightly smoother pH transition than do calculated data. Subsequently, a model using two different  $pK_a$  values for the carboxyl groups was used to evaluate the data. This two-site model enhanced the fit somewhat but the improvement was not considered great enough to warrant the use of a more complicated model (Figure 4-1).

### **Transient metal solubilization**

In all experimental solutions, metal salts reached stable concentrations within

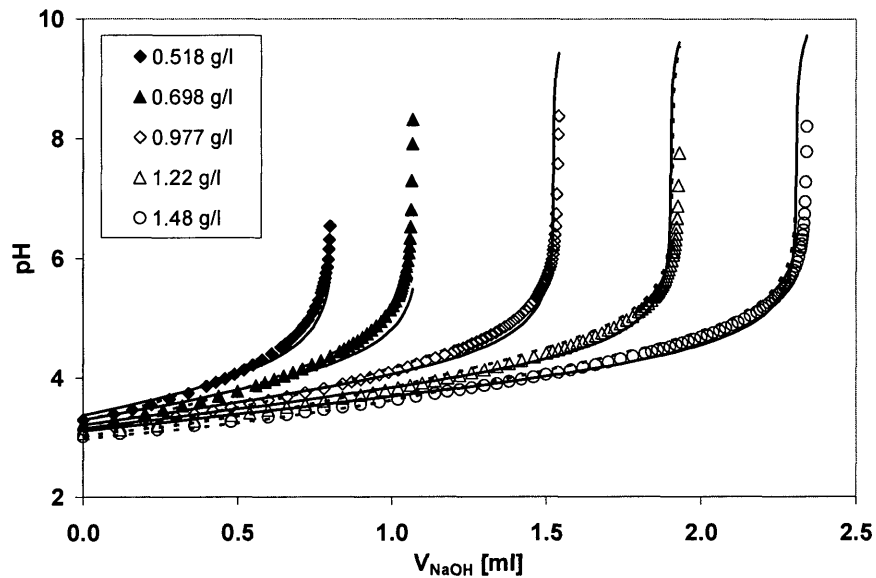


Figure 4-1. Base titrations of CMCD. Solid lines represent single-site model and dotted lines represent two-site model.

approximately one day (Figure 4-2). IR spectroscopy of CMCD solutions indicate that the large molecule does not decompose during the remaining experimental duration (data not shown). Ca, Sr, Ba, Pb, Ni, and Zn trends are stable over 7 days duration. In contrast, Cd and Ce show concentrations that decline with time in the presence of CMCD. The dissolution of all the salts was complete in less than a day except Ca-oxalate dissolution, which reached equilibrium after two days.

The trend of declining concentrations of Cd and Ce is not expected. The Cd salt concentration in the absence of CMCD is stable with time, while the Ce salt concentration, also in the absence of CMCD, decreases from approximately 1.5 to 0.3 mg/l over 7 days. This behavior is not well understood. For both elements, the metal-CMCD data show a downward trend.

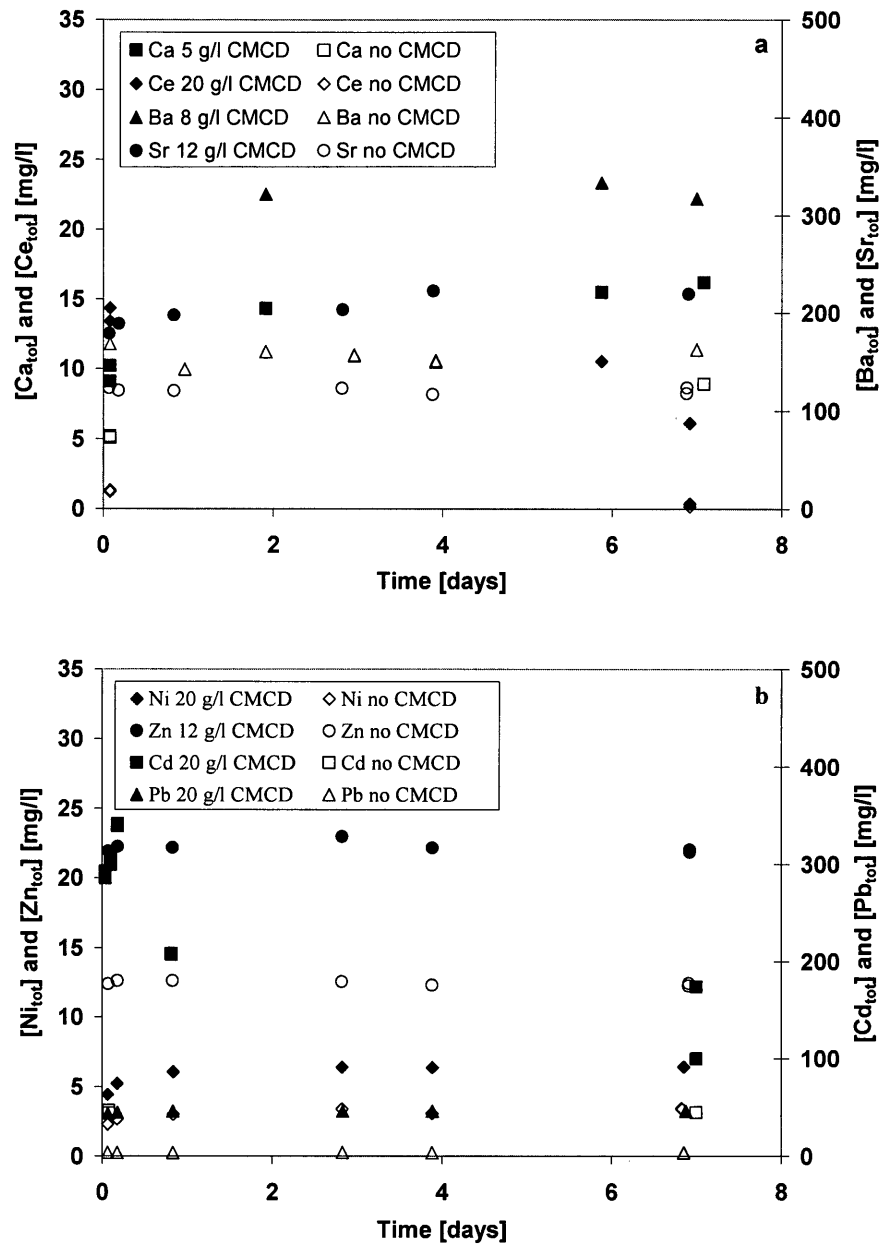


Figure 4-2. Aqueous metal concentrations as a function of time.

### Measured conditional stability constants

Results from batch experiments show that CMCD enhances the solubility of all the investigated metal salts. The calculated conditional stability constants for the CMCD-metal complexes were based on 7-day data at 25°C and range from 10<sup>-3.2</sup> to 10<sup>-5.1</sup> (Table 4-2). Ce is an exception and seems to form stronger complexes with CMCD than the other investigated elements. Estimated 95% confidence intervals are within ±0.08 log units for all elements but Cd and Ce. The Ce data are of lower precision and the calculated constant more uncertain.

Figure 4-3 shows that in most cases the agreement between experimental data and predicted solubilization based on the fitted conditional stability constants models is very good. The confidence intervals are estimated based on assumption of a correctly formulated conceptual model. Given the difficulty of modeling complexation reactions for multiple functional groups on organic molecules, this assumption may not be entirely correct. Although the difference between estimated and observed data is small, the true uncertainty is likely somewhat larger than the reported 95% confidence intervals because of uncertainties in conceptual model. Understanding the mechanism for the time dependent decrease in Cd concentration would help choosing the most appropriate experimental data to calculate the conditional formation constant. The solubility enhancement of Ce is not well understood either and we, thus, recommend that the KCMCD-Ce should be used with caution, if used at all.

Temperature affects the solubility of the salts. The concentrations of all metals, except Cd, increase with increasing temperature. The solubility product used to calculate the complexation was derived from the metal salt solutions. Table 4-2 shows the calculated solubility products are higher at 25°C than at 10°C but the estimated conditional formation constants do not change. Thus, it appears that the higher metal solubility in

warmer solutions is due to higher salt solubility rather than increased metal complexation by CMCD.

Table 4-2. Measured conditional formation constants and solubility products.

Metal salt	Temp.	t <sub>experimental</sub>	logK <sub>sp</sub> <sup>15</sup>	logK <sub>sp</sub> <sup>16</sup>	logK <sub>CMCDMe</sub>	95% C.I. <sup>17</sup>
BaC <sub>2</sub> O <sub>4</sub>	10°C	2 hours	-6.71	-6.79 <sup>18</sup>	3.60	3.54 – 3.66
	25°C	2 hours	-6.55		3.60	3.58 – 3.64
	25°C	7 days	-6.59		3.58	3.55 – 3.60
CaC <sub>2</sub> O <sub>4</sub>	10°C	2 hours	-8.76	-8.63 <sup>19</sup>	3.64	3.58 – 3.70
	25°C	2 hours	-8.49		3.67	3.59 – 3.75
	25°C	7 days	-8.03		3.56	3.47 – 3.64
CdC <sub>2</sub> O <sub>4</sub>	10°C	2 hours	-7.99	-7.85 <sup>20</sup>	5.14	4.76 – 5.52
	25°C	2 hours	-7.80		4.78	4.49 – 5.07
	25°C	4.5 hours	-7.80		4.95	4.75 – 5.16
	25°C	19 hours	-7.80		4.40	4.30 – 4.50
	25°C	7 days	-7.80		4.04	3.91 – 4.18
Ce <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	10°C	2 hours	-29.37	-25.5 <sup>21</sup>	6.36	6.29 – 6.44
	25°C	2 hours	-29.11		6.46	6.37 – 6.54
	25°C	7 days	-32.2		7.48	7.12 – 7.84
NiC <sub>2</sub> O <sub>4</sub>	10°C	2 hours	NA	-9.4 <sup>22</sup>	NA	NA
	25°C	2 hours	NA		NA	NA
	25°C	7 days	-9.73		3.48	3.44 – 3.51
PbC <sub>2</sub> O <sub>4</sub>	10°C	2 hours	-10.79	-9.32 <sup>23</sup>	5.21	5.13 – 5.30
	25°C	2 hours	-10.46		5.27	5.21 – 5.34
	25°C	7 days	-10.46		5.18	5.14 – 5.23
SrSO <sub>4</sub>	10°C	2 hours	-6.81	-6.46 <sup>24</sup>	3.49	3.29 – 3.69
	25°C	2 hours	-6.69		3.53	3.28 – 3.78
	25°C	7 days	-6.69		3.55	3.47 – 3.63
ZnC <sub>2</sub> O <sub>4</sub>	10°C	2 hours	NA	-8.86 <sup>25</sup>	NA	NA
	25°C	2 hours	NA		NA	NA
	25°C	7 days	-8.86		3.64	3.61 – 3.67

<sup>15</sup> Experimentally determined K<sub>sp</sub>.

<sup>16</sup> K<sub>sp</sub> values reported in Dean (1999).

<sup>17</sup> 95% confidence interval.

<sup>18</sup> Value for BaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O.

<sup>19</sup> Value for CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O.

<sup>20</sup> Value for CdC<sub>2</sub>O<sub>4</sub>·3H<sub>2</sub>O.

<sup>21</sup> Value for CeC<sub>2</sub>O<sub>4</sub>·9H<sub>2</sub>O.

<sup>22</sup> Value for NiC<sub>2</sub>O<sub>4</sub>.

<sup>23</sup> Value for PbC<sub>2</sub>O<sub>4</sub>.

<sup>24</sup> Value for SrSO<sub>4</sub>.

<sup>25</sup> Value for ZnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O.

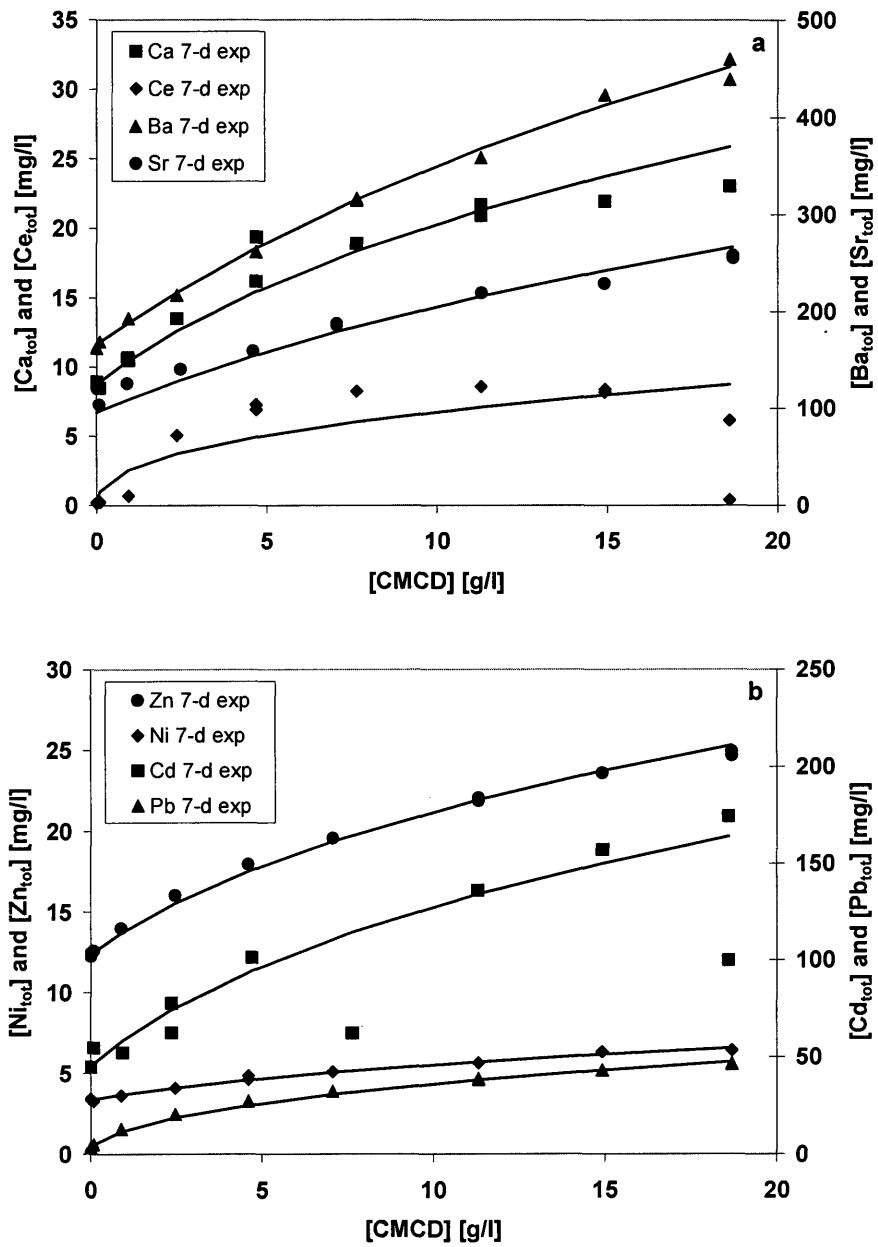


Figure 4-3. Enhanced metal solubility. Experimental data (symbols) compared to models (lines).

The conditional formation constants of the transition elements increase with increasing period and group in the periodic table (Figure 4-4). The heavier elements Cd and Pb have higher conditional formation constants than the lighter transition elements and the group 2 elements. Based on this trend, we hypothesize that other common metal contaminants such as Cu and Hg will also form relatively strong complexes with CMCD. While the solubility enhancement of some important metals not used in these experiments can be interpolated, such is not the case for all metals. For example, some metals of interest such as As and Se are normally oxy-anions in solution. Because anions do not form strong complexes with carboxyl groups, the behavior of these complexes can not be interpolated based on other elements but needs to be investigated separately. Indeed, Chatain et al. (2004) found that Cu and Fe were removed more readily from a mining contaminated soil with CMCD than was As.

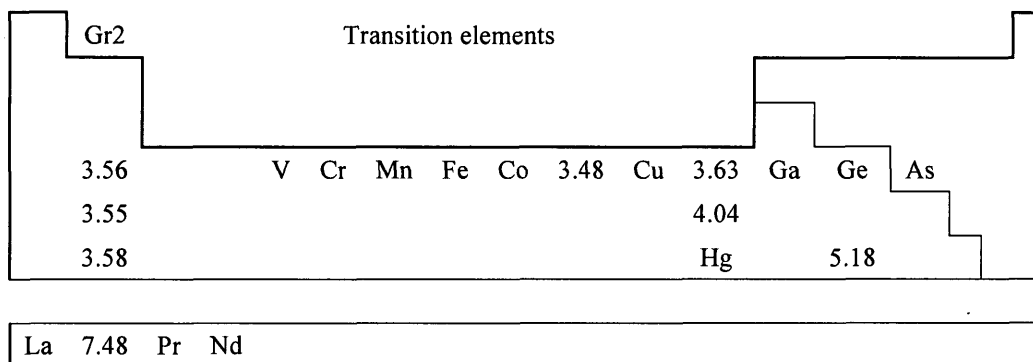


Figure 4-4. Logarithmic conditional formation constants calculated from data collected at 25°C, 50 mM KNO<sub>3</sub> and 7 days equilibration time. Constant for Cd-CMCD complex calculated from 4.5 hour data.

The effectiveness of metal remediation will be influenced by the presence of non-target cations, such as Ca and Mg. The extent of competition will depend on their concentrations and strengths of CMCD complexes. The slightly higher stability constants for the transition elements compared to the group 2 elements indicate that CMCD

preferentially complexes heavy metals. High concentrations of Ca and Mg may, however, lessen the solubility enhancement.

### **Conclusions**

Conditional formation constants for the complexes between CMCD and 8 metal ions (Ba, Ca, Cd, Ce, Ni, Pb, Sr, and Zn) range from  $10^{-3.2}$  to  $10^{-5.1}$  with confidence intervals within  $\pm 0.08$  log units. Temperature variation between 10°C and 25°C did not affect the metal complexation by CMCD, but significantly affected the solubility of the investigated metal salts. These conditional formation constants may be used to screen CMCD as a potential remediation agent. Evaluating CMCD flushing may be performed in a two-step process. First, solubility products for typical metal contaminants reported in the literature and the conditional formation constants reported in this study may be used to approximate metal solubility. In a second and more accurate step, results from metal solubility experiments on site specific soil should be used to model the solubility enhancement of metal contaminants. Several complexing agents can be evaluated and costs of various remediation agents compared to optimize remediation design.

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**CHAPTER FIVE**  
**ENHANCED SOLUBILIZATION OF A METAL-ORGANIC**  
**CONTAMINANT MIXTURE (Pb, Sr, Zn, AND PCE) BY**  
**CYCLODEXTRIN**

**Abstract**

Prior work has suggested that carboxymethyl- $\beta$ -cyclodextrin (CMCD) is capable of simultaneously enhancing the solubility of organics and metals but sparse experimental data and no theoretical models have been published on this process. A geochemical model for simultaneous metal and organic complexation by CMCD was formulated using PHREEQC based on conditional stability constants measured in single-metal and organic contaminant (PCE) experiments. Experiments to verify the application of the formulation to mixed waste systems were performed using solutions containing multiple metal salts (Pb, Sr, and Zn), and multiple metal salts and PCE simultaneously. The experimental data show simultaneous solubility enhancement of metals and PCE. The behavior in CMCD solutions can be described by independent mass action equations. For solutions up to about 50 g/l CMCD, the model accurately predicted the simultaneous solubility enhancement for PCE, Pb and Zn, while the difference between measured and predicted Sr concentration was accurate to within 15%. At CMCD concentrations greater than 50 g/l, the observed metal solubilities were greater than predicted (10% for Pb and Zn), probably due to the difficulty in accurately calculating the activity coefficient of uncomplexed CMCD and in calculating ionic strength of a concentrated CMCD solution. Because the largest discrepancy is only 15%, we conclude that the present model can be

used to evaluate CMCD-enhanced aquifer flushing as a remediation technology for sites co-contaminated with metals and organic contaminants.

## **Introduction**

A large number of sites in the U.S. are contaminated with both metals and organic pollutants. The different properties of the two contaminant classes make remediation of mixed-waste sites challenging. One approach that has been suggested to remove the contaminants is to modify an existing successful technique for one class of contaminants so it can be applied to both contaminant classes. The use of geochemical models to rapidly test potential remediation agents requires experimental data and appropriate mass actions equations consistent with standard thermodynamic formulations. The approach detailed herein uses a combination of laboratory experimental data coupled to geochemical models to rapidly assess potential remediation agents.

Carboxymethyl- $\beta$ -cyclodextrin (CMCD) is a non-toxic, glucose-based molecule that has been previously shown to simultaneously enhance the solubilities of metals and organic contaminants (Wang and Brusseau, 1995; Brusseau et al., 1997). The circular structure of the cyclodextrin molecule (CD) results in a non-polar cavity into which organic molecules can partition (Wang and Brusseau, 1993); carboxyl groups on the outside of CMCD allow complexation of metal ions. Other studies indicate that CMCD does not sorb significantly to soil (Brusseau et al., 1994) and does not experience pore exclusion in the soil (Hu and Brusseau, 1995). These properties make CMCD an attractive complexing agent for in-situ remediation of mixed waste sites, i.e. sites co-contaminated with organic and inorganic contaminants.

In comparison to synthetic complexing agents such as EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriamine pentaacetic acid), CMCD forms weaker metal complexes, and the metal removal efficiency of CMCD has been questioned (Neilson et al., 2003). Other researchers argue that because CMCD does not sorb significantly to soil

surfaces it may still be a viable complexing agent for in-situ remediation of metals (Chatain et al., 2004). However, Vuluva and Seaman (2000) reported that CMCD can be retarded by matrices with high content of iron oxide. Thus, site-specific conditions, including metal speciation, will determine the feasibility of CMCD-enhanced aquifer flushing. A geochemical model that describes metal complexation by CMCD would aid in screening the viability of CMCD for enhanced dissolution of metal ions.

Previously, we have estimated conditional formation constants for complexation between CMCD and eight metal ions (Chapter 4). These formation constants were derived in the presence of a single metal salt. The complexation model used to derive the conditional formation constants assumes identical complexation sites for all metals (Chapter 3). However, in field conditions where several metal ions are present, competition between metal ions may occur for these complexation sites. The complexation between ionic solutes and functional groups attached to large organic molecules, such as carboxyl groups on CMCD, is not well understood. For instance, activity coefficients are generally calculated based on assumption of point charges, which may not be correct for functional groups attached to a large molecule. Thus, it is not clear whether or not thermodynamic models can adequately simulate competition between several metal ions complexing with large organic molecules with multiple functional groups. In this study, one of our goals is to validate a multi-component mixed contaminant complexation model by comparing predicted and measured metal concentrations in the presence of three metals and an organic contaminant at various concentrations of CMCD.

Another goal of this work is to incorporate inclusion complexation of an organic compound into a geochemical model and to try and predict the concurrent solubility enhancement of organics and metals. We assumed that dissolved metal ions and organic compounds interact with different moieties of the CMCD molecule. Prior data suggests the interactions operate separately (Wang and Brusseau, 1995), but Brusseau et al. (1997)

suggested that metal complexation neutralizes charged groups on CMCD which may facilitate partitioning of organic compounds into the CD cavity. PCE (perchloroethylene) was chosen as the model organic compound because of the large number of sites contaminated with this solvent. Therefore, the enhanced solubilities of metal salts (lead oxalate, strontium sulfate, and zinc oxalate) were measured in the absence and presence of PCE to evaluate the full range of metal-PCE-CMCD interactions. This experimental data was used to evaluate the performance of the modified PHREEQC model.

## **Materials and methods**

### Materials

Enhanced metal and PCE solubility experiments were performed using industrial grade CMCD, which was provided as a Na salt by Wacker, Inc. Lead oxalate ( $\text{PbC}_2\text{O}_4$ ) and strontium sulfate ( $\text{SrSO}_4$ ) were +98% pure and zinc oxalate ( $\text{ZnC}_2\text{O}_4$ ) was made from analytical grade oxalic acid and zinc nitrate. PCE was +99.9% pure and potassium nitrate ( $\text{KNO}_3$ ), sodium hydroxide ( $\text{NaOH}$ ), and nitric acid ( $\text{HNO}_3$ ) were of analytical grade.

### Batch experiments

All solubility enhancement experiments were performed in glass vials with teflon lined caps at  $25 \pm 0.5^\circ\text{C}$  in 50 mM  $\text{KNO}_3$ . Prior to the experiments, the pH in CMCD standard solutions was adjusted to pH 6.0 with sodium hydroxide or nitric acid. Enhanced solubilities of metal salts and liquid-phase PCE were measured in 12 different CMCD solutions (0 to 100 g/l CMCD). The glass vials were rotated top-over-bottom for 7 days before being sampled.

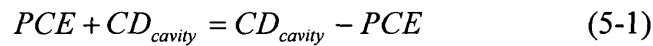
CMCD-enhanced PCE solubility was investigated in the absence and presence of three metal salts ( $\text{PbC}_2\text{O}_4$ ,  $\text{SrSO}_4$ , and  $\text{ZnC}_2\text{O}_4$ ). The samples were prepared and analyzed in a

random order. In the batch experiments, 250  $\mu\text{l}$  liquid PCE was added to glass vials containing 4.5 ml CMCD standard solutions ranging from 0 to 100 g/l CMCD. No or very little head space was allowed. To half of the samples, approximately 15 mg of each metal salt was added. After rotating for 6.5 days at  $25\pm 0.5^\circ\text{C}$  all samples were centrifuged at 2000 g for 5 min and left standing over night before 100  $\mu\text{l}$  of the aqueous phase was extracted into 2 ml glass vials containing 1.00 ml hexane. These vials were rotated top-over-bottom for 3 hours followed by centrifugation (2000 g for 5 min) and immediate analysis of the hexane phase on a gas chromatograph (Shimadzu GC-17A). Standards were analyzed prior to analyzing the samples ( $R^2=0.997$ , data not shown). All PCE batch experiments were performed in duplicate and each sample was analyzed in separate triplicate vials. Thus, for each CMCD concentration 6 GC analyses of PCE were performed with metals and 6 analyses without metals.

A separate set of batch experiments was conducted to investigate the CMCD-enhanced solubility for the inorganic contaminants with and without PCE. These samples were made in the same manner as the ones made for PCE analyses except that all samples contained metal salts but only half of the samples contained 250  $\mu\text{l}$  liquid PCE. Zinc oxalate was precipitated from 0.1 M solutions of oxalic acid and zinc nitrate as described in Donia (1997). XRD analysis confirmed that crystalline  $\text{ZnC}_2\text{O}_4$  was precipitated (data not shown). At the end of the batch experiments each solution was filtered (0.45 $\mu\text{m}$ ) to separate the aqueous phase. Solid metal salts remained in the vials at the end of all experiments. Immediately after filtering, the pH of the aqueous phase was measured and metal concentrations were subsequently analyzed by ICP-OES. The pH varied from 7.1 at low CMCD to 6.2 at high CMCD concentrations. Two separate enhanced metal solubility experiments were performed, in both the presence and absence of PCE. In the first experiment the CMCD concentration ranged from 0 to 20 g/l and in the second from 0 to 100 g/l. All other conditions were the same in the two experiments.

## Theory

We hypothesize that PCE and metal complexation by CMCD are independent. Therefore, in our model, metal and PCE complexing properties of CMCD are formulated as separate mass action equations. We model interactions between PCE and CMCD as formation of an inclusion complex ( $CD_{cavity}$ -PCE) between PCE and the single CMCD cavity ( $CD_{cavity}$ ).



The stability constant for the reaction,  $K_{CDPCE}$ , has units of l/mol and is defined by Equation 5-2. Values within curved brackets represent aqueous activities.

$$K_{CDPCE} = \frac{\{CD_{cavity} - PCE\}}{\{PCE\} \cdot \{CD_{cavity}\}} \quad (5-2)$$

We assume ideal interactions between the CD cavity and PCE, i.e. the activity coefficients for  $CD_{cavity}$ , PCE, and  $CD_{cavity}$ -PCE are therefore assumed to be unity.

An alternative formulation for CMCD-enhanced solubility of sorbed-phase or non aqueous phase liquid (NAPL) contaminants by CMCD is as a partitioning of the organic contaminant between the CD cavity and water. This partitioning is often reported as a CD-water partitioning constant,  $K_{CDW}$ , which has units of l/kg (Boving and McCray, 2000).

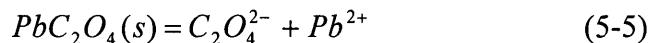
$$K_{CDW} = \frac{PCE_{CD}}{PCE_w} \quad (5-3)$$

$PCE_{CD}$  is the mass of PCE that partitions into the CD cavity (g PCE/kg CMCD) and  $PCE_w$  is the aqueous solubility (measured to 0.280 g/l) of PCE in the absence of CMCD. To facilitate comparisons to other studies, we convert our estimated stability constant to CD-water partitioning constant according to Equation 5-4,

$$K_{CDW} = \frac{1000}{MW_{CD} \cdot \left( \frac{PCE_w}{MW_{PCE}} + \frac{1}{K_{CMCDMe}} \right)} \quad (5-4)$$

where  $MW_{CD}$  and  $MW_{PCE}$  are the molecular weights of CMCD (1387 g/mol) and PCE (165.8 g/mol), respectively.

To model the metal complexation reactions we use standard mass action formulations. An example using Pb is provided below.

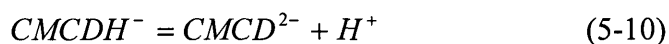
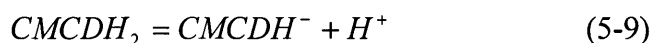


Previous evaluation of CMCD-Pb complexation showed that the activity coefficient for  $CMCD^{2-}$  produces the best fit to the experimental data when coupled to activity calculation using the WATEQ equation (Truesdell and Jones, 1974) with the coefficients a and b equal to 3.50 and 0.65, respectively (Chapter 3). In the model, all metal ions form complexes with the deprotonated cyclodextrin molecule,  $CMCD^{2-}$ . This creates competition between the metal ions for the CMCD.





Metals are believed to form complexes with carboxyl groups on CMCD (Wang and Brusseau, 1995). However, the carboxyl groups also act as acids producing or accepting protons. Therefore the model must represent both potential reactions. We describe the acid/base reactions of CMCD in equations 5-9 and 5-10.



Titration of CMCD showed that each CMCD contains on average 4.27 carboxyl groups (Chapter 3). Because the CMCD available for metal complexation reactions is represented as a diprotic acid, the additional acidity of the CMCD is separately represented by adding 2.27 separate carboxyl groups per CMCD to the model (Equation 5-11).



If the metal ions in a mixture interact in different ways or with different moieties of the CMCD molecule, this competition may not be correctly described by reactions 5-5 through 5-8. We test for competition between the metals by comparing theoretical simulations and experimental metal concentrations.

## **Results and discussion**

### Organic contaminant and CMCD

The computer program PHREEQC coupled to UCODE\_2005 (Poeter et al., 2005) was used to estimate the stability constant for the CMCD-PCE inclusion complex. In the absence of metal salts, the optimized stability constant was  $10^{2.075}$  with an estimated 95% confidence interval of  $10^{2.07}$  to  $10^{2.08}$  (Figure 5-1). Our experimentally determined stability constant (Table 5-1) compares well to published stability constant for PCE and hydroxypropyl- $\beta$ -cyclodextrin (HPCD). McCray et al. (2000) report a partitioning constant of 79.4 l/kg and our constant, measured in the absence of metals, converts to 71.4 l/kg. In their experiments, analytical grade HPCD was used; our experiments were performed on industrial grade CMCD. Other researchers have found that less polar CD derivatives are more efficient at complexing organic contaminants (Shixiang et al., 1988; Boving et al., 1999; Fenyvesi et al., 1996; Sheremata and Hawari, 2000; Boving and Brusseau, 2000). The slightly lower  $K_{CDW}$  measured in this study for the more polar CD derivative compared to the constant for PCE-HPCD reported in McCray et al. (2000) conforms to this trend.

### Measured and predicted metal concentrations in multi-metal solutions

The inorganic portion of the complexation model was evaluated for multiple metal solutions by first comparing the measured total aqueous concentrations of Pb, Sr, and Zn from the metal only experiments to those predicted with PHREEQC (Parkhurst and Appelo, 1999) using the theory presented in Equations 5-5 through 5-11 (see Figure 5-1). Conditional formation constants for CMCD-metal complexation previously determined from single-metal experiments (Chapter 4) were used to calculate metal concentrations for CMCD solutions containing the three metal salts. In those prior experiments, the metal salt solubility product,  $K_{sp}$ , was determined from the blank solutions (without CMCD).

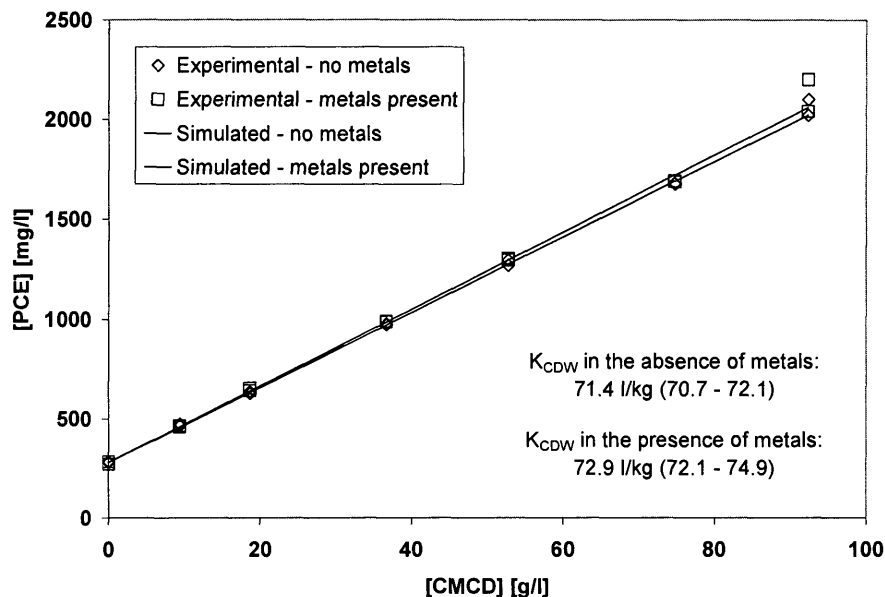


Figure 5-1. Comparison between observed and simulated enhanced PCE concentrations in the absence and presence of metals.

Table 5-1. Summary of partitioning constants derived in this study.

System	KCDW [l/kg]	95% C.I.
CMCD-PCE (no metals)	71.4	70.7-72.1
CMCD-PCE (with metals)	72.9	72.1-74.9

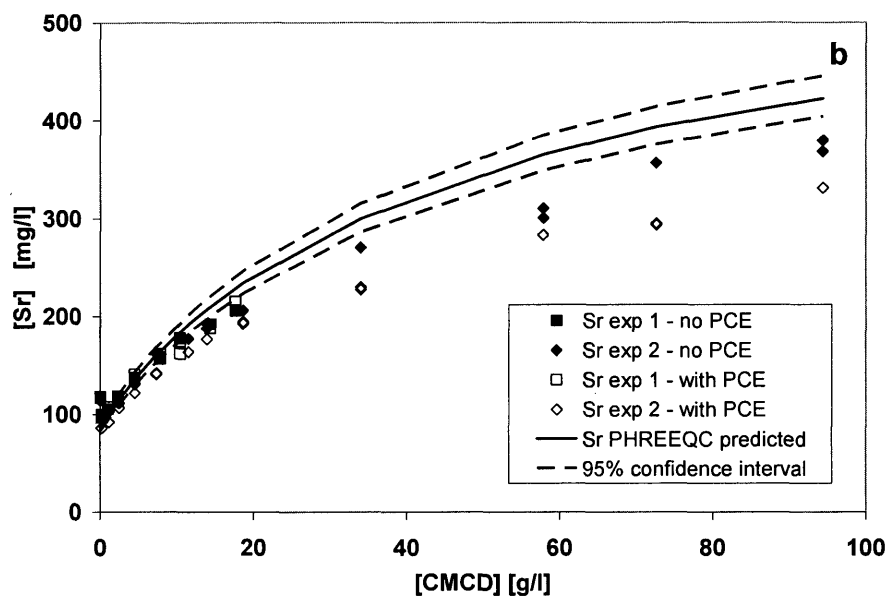
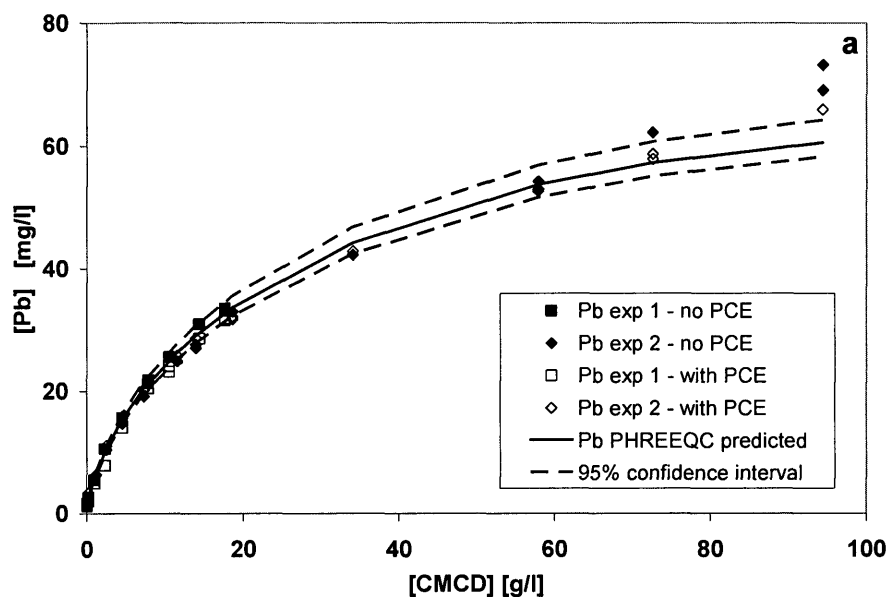
This method produces a consistent experimental dataset and avoids problems that arise from chemical impurities in reagents and analytical and experimental uncertainties associated with prior determinations of salt solubility. The same methodology was used in this study with the multi-metal solution blank. Because the measured solubility of  $\text{SrSO}_4$  was slightly lower in 0.1 g/l CMCD than in the blank  $\text{KNO}_3$  solutions, the  $K_{sp}$  for  $\text{SrSO}_4$  was based on Sr concentrations in the low CMCD solutions. The reason for the observed decrease in Sr concentration at low CMCD concentrations cannot be

determined with certainty from our data, but a phase transfer of SrSO<sub>4</sub> to a less soluble phase in the presence of CMCD would explain this observation.

The model accurately simulates the observed lead and zinc concentrations at CMCD concentrations up to about 50 g/l CMCD (Figure 5-2a and 5-2c). However, above 60 g/l predicted metal concentrations are less than the observed values. The simulated concentration curves flatten out whereas experimentally measured Pb and Zn increase in nearly linear fashion with CMCD. However, the model still predicts the metal concentrations to within 10%.

We believe this minor discrepancy between measured and simulated metal concentrations at high CMCD concentrations is related to uncertainties in ionic strength and activity coefficient calculations. In the model, ionic strength calculations include the CMCD<sup>-2</sup> ligand, which is the principle component of ionic strength at CMCD concentrations above 20 g/l. For instance, the calculated ionic strength increases from 50 mM in the pure electrolyte blank solution (KNO<sub>3</sub>) to above 400 mM in the 95 g/l CMCD solution. This causes the activity coefficients for Pb and Zn to decrease from 0.44 in the blank solutions to 0.26 in the 95 g/l CMCD solution. However, the model still performs surprisingly well considering the high ionic strength of the more concentrated CMCD solutions. For comparison, average seawater, which is challenging to simulate accurately with common geochemical models, contains 35,000 mg/l total dissolved solids and has an ionic strength of 670 mmol/l.

The model simulates CMCD-enhanced Sr solubilities less accurately than Pb and Zn. At low CMCD concentrations, enhanced Sr solubility is simulated well but at CMCD concentrations above 10 g/l simulated enhanced Sr solubility exceeds the measured solubility. Thus, Sr appears to compete less strongly with Pb and Zn for complexation sites than predicted from the single salt experiments. The difference between simulated



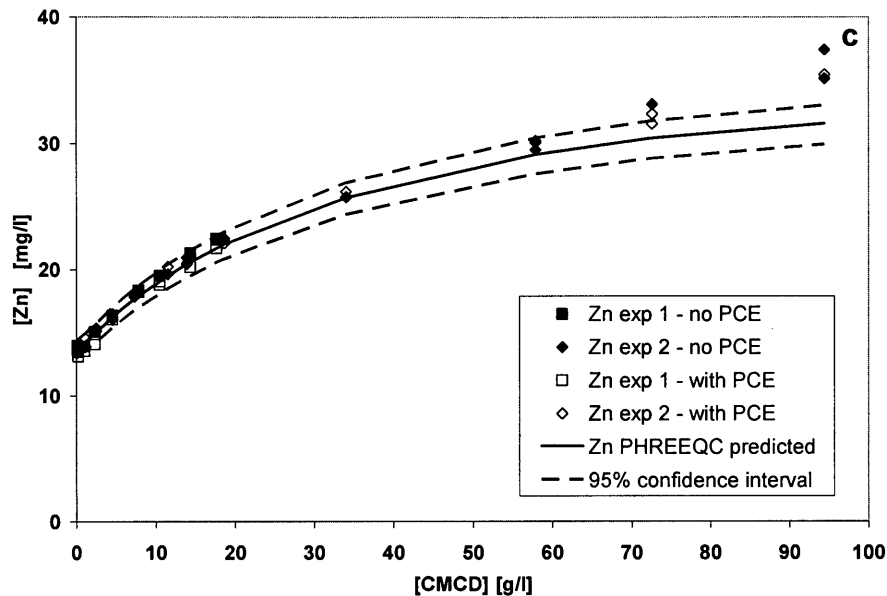


Figure 5-2. Comparison between observed and simulated enhanced metals concentrations in the absence and presence of PCE. Confidence intervals are calculated on predictions.

and measured Sr concentration increases with CMCD. At 95 g/l, the difference is approximately 15%. For the purpose of this model, to screen CMCD as a remediation agent, this accuracy is considered sufficient.

#### Mixed waste Systems - Effect of metals on enhanced PCE solubility

The solubility enhancement of PCE in the presence and absence of the three metal salts is shown in Figure 5-1. Each point on the graph represents the average PCE concentration from triplicate analyses. Consistent with prior work, the solubility enhancement is directly proportional to the CMCD concentration (Wang and Brusseau, 1993). The presence of metal salts did not affect the solubility enhancement of PCE significantly; the optimized stability constant for the metal + PCE experiments was  $10^{2.086}$  and the 95% confidence interval ranged from  $10^{2.08}$  to  $10^{2.10}$ . As mentioned above, the stability constant in the absence of metals was  $10^{2.075}$  ( $10^{2.07}$  to  $10^{2.08}$ ). Because the confidence

intervals overlap, there is no persuasive evidence that the presence of metals affects CMCD-enhanced PCE solubility. The average partitioning constant is 72.1 l/kg.

#### Mixed waste Systems - Effect of PCE on enhanced metal solubility

The enhanced Pb and Zn concentrations in the presence of PCE do not differ from the concentrations measured in its absence (Figure 5-2). Thus, PCE does not affect the CMCD-enhanced solubility of these metals. The effect of PCE on the solubility enhancement of SrSO<sub>4</sub> is less clear. The Sr concentration in experiment one is independent of the presence of PCE whereas the Sr concentration in experiment two decreases in the presence of PCE. At 95 g/l CMCD, the difference in Sr concentration in samples with and without PCE is approximately 10%, which is larger than observed experimental uncertainty based on duplicate samples. Thus, the influence of PCE on Sr solubility is practically negligible.

#### Conclusions

The CMCD-metal complexation model accurately predicts enhanced solubility of metal salts. Non-ideal interactions between CMCD and metal ions appear to be simulated accurately up to at least 60 g/l CMCD. Also, competition between the two transition elements Pb and Zn is simulated properly by the model. While the model over predicts the enhanced Sr solubility in the presence of Pb and Zn, the predicted metal concentrations are generally within 10-15% of the measured concentrations. We consider this discrepancy acceptable for screening CMCD flushing as a remediation technology for contaminated aquifers.

The presence of NAPL PCE did not appreciably influence the CMCD-enhanced solubilities of the three metal salts. The presence of metal salts did not affect the solubility enhancement of PCE by CMCD. Thus, the solubility enhancement of metals

and organic contaminants can be modeled simultaneously and the CMCD complexation model presented in this work is appropriate for screening CMCD as a complexing agent for remediation of sites co-contaminated with metals and organics.

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## CHAPTER SIX

### CONCLUSIONS

The following conclusions can be drawn based on the literature review, experiments, and modeling performed in this research.

- A literature study shows that cyclodextrin (CD) derivatives form inclusion complexes with organic compounds and have been used at pilot tests for in-situ remediation of soil contaminated with organic compounds. Hydroxypropyl- $\beta$ -cyclodextrin (HPCD) is the most appropriate CD derivative for CD enhanced aquifer flushing of sites polluted with organic compounds such as chlorinated solvents. CD enhanced solubility of organics also increases their bioavailability, which has been explored in field settings. A few previous studies also show that carboxymethyl- $\beta$ -cyclodextrin (CMCD) simultaneously complexes metals and organic compounds and suggest the use of CMCD for remediation of sites co-contaminated with metals and organics.
- A complexation model for CMCD-metal interactions is formulated from available geochemical activity models and complexation formulations between specific species and functional groups. For practical purposes, the model predicts non-ideal interactions between CMCD and metals well up to 100 g/l CMCD. However, the detailed effects of high CMCD concentrations on ionic strength and non-idealities are not completely understood. Available activity models assume point charges, which may not be entirely true for functional groups on a large organic molecule. In addition, the enhanced solubility of metal salts depends on both the activity model and on the charge representation of CMCD.

- A methodology was developed for determining conditional formation constants for metal complexation by CMCD. The method uses the two computer programs PHREEQC and UCODE\_2005 to optimize constants based on experimental data. The technique allows statistical comparison of several conceptual models and can be applied to other potential remediation agents. The conceptual model that best describes experimental data represents CMCD as a diprotic acid and uses the WATEQ equation to calculate the activity coefficient of the deprotonated ligand.
- CMCD complexes both group 2 and transition elements. However, CMCD forms slightly stronger complexes with heavier transition elements (Cd, Pb) than with group 2 elements (Ca, Ba, Sr). Based on an optimized conceptual model for CMCD-metal complexation, conditional stability constants for complexes between CMCD and eight metal ions are estimated.
- Temperature variations relevant for in-situ remediation influence the solubility of metal salts. Enhanced metal solubility experiments performed at 10°C generally exhibited lower solubility than experiments performed at 25°C. However, temperature does not affect significantly the strength of CMCD-metal interactions but rather the intrinsic aqueous solubility of the salts.
- The complexation model predicts competitive metal complexation well. It predicts CMCD-enhanced metal solubilities to within 15% of measured concentrations.
- Metal complexation to hydroxyl groups on the outside of CMCD and partitioning of PCE into the CD cavity can be modeled as independent interactions.
- The complexation model presented in this thesis can be used for screening CMCD as a complexing agent for remediation of sites co-contaminated with metals and organic pollutants.

**APPENDIX A**  
**AN EXAMPLE OF USING UCODE\_2005 AND PHREEQC TO**  
**DETERMINE THERMODYNAMIC CONSTANTS FROM**  
**EXPERIMENTAL DATA**

**Abstract**

This paper presents a method for estimating chemical thermodynamic constants from experimental data using the two computer programs UCODE\_2005 and PHREEQC. As an example, the conditional stability constant for lead (Pb) complexation by a remediation agent (carboxymethyl- $\beta$ -cyclodextrin, CMCD) is estimated, but the method can be applied to estimating other thermodynamic parameters such as sorption constants and degradation rate constants. Advantages of this technique include estimation of uncertainties associated with estimated parameters, evaluation of information content of observations, statistical evaluation of the appropriateness of the conceptual model, and statistical-based comparison of different models.

## **Introduction**

Chemical equilibrium constants can be determined from experimental data with graphical methods, by curve fitting, or with an optimization code such as FITEQL (Herbelin and Westall, 1999). These techniques have disadvantages; for instance, the uncertainties associated with the estimated parameters are difficult to quantify and comparison of different conceptual models is laborious and ultimately subjective. In contrast, ground water flow and contaminant transport models are commonly calibrated using parameter estimation codes such as PEST (Doherty, 2004) and UCODE\_2005 (Poeter et al., 2005). These codes find optimal values for system parameters (which are also model input parameters) such as transmissivity by adjusting the input parameters and repeatedly running the model until the best possible fit between observations and model-simulated values is achieved. There is no reason the same approach cannot be used for geochemical models. Some common geochemical codes that speciate aqueous solutions, simulate aqueous equilibria with solid phases and gases, and react aqueous species with surfaces are PHREEQC (Parkhurst and Appelo, 1999), MINTEQA2 (Allison et al., 1991), and the Geochemist's Workbench (Bethke, 1996).

In this paper we describe how to couple UCODE\_2005 to PHREEQC and demonstrate the procedure in an example that involves estimating conditional stability constants for aqueous species from experimental data. Our goals are twofold: (1) to describe the method with sufficient detail so the reader can duplicate the procedure and (2) to demonstrate the advantages of the procedure that include calculation of confidence intervals and generation of statistical criteria to help evaluate and compare multiple models.

## UCODE 2005

UCODE\_2005 is a universal parameter estimation modeling code that can be used to estimate unknown parameters in any code that is executed from a batch file and has text input and output files. Another requirement is that simulated values are continuous functions of the parameter values. The program is intended for use on any computer operating system. The first version of UCODE was released in 1998 (Poeter and Hill, 1998). An updated version (UCODE\_2005) was constructed using the JUPITER (Joint Universal Parameter Identification and Evaluation of Reliability) application programming interface conventions and modules (Banta et al., 2006). UCODE\_2005 includes six post-processing programs (Poeter et al., 2005).

UCODE\_2005 is always executed with one or more application models; the PHREEQC input files are created within UCODE\_2005 and the geochemical model is executed by UCODE\_2005. First, UCODE\_2005 runs PHREEQC with user supplied starting value(s) of the input parameter(s) to be estimated; the conditional stability constant (K) in our example. Second, the PHREEQC simulated values for the solution composition are compared to experimental data using a user-defined objective function that expresses the quality of the model fit (e.g., the weighted, squared, and summed differences (residuals) between observed and simulated aqueous Pb concentration is the objective function in our example below). Third, UCODE\_2005 changes the unknown parameter value(s) (conditional stability constant, K) slightly so the slope of the objective function (sensitivity) with respect to each parameter can be calculated. The residuals and sensitivities are used to calculate a better fitting parameter value(s) using a modified Gauss-Newton method. This new parameter value(s) is subsequently used in the geochemical system so the updated model and experimental data can be compared again. This iterative procedure of minimizing the difference between observed and simulated values (objective function based on residuals) is carried out until the parameter value(s)

change less than the user specified amount. The slope of the objective function is used to calculate a 95% confidence interval on the optimized parameter value(s).

### **Geochemical example problem**

Cyclodextrin derivatives have been used for clean-up of soil contaminated organic pollutants (Boving and McCray, 2000). We have previously investigated the Pb complexation properties of carboxymethyl- $\beta$ -cyclodextrin (CMCD) for the purpose of in-situ metal remediation (Chapter 3). In this example, we are using a subset of our experimental data to describe how we estimated thermodynamic stability constants from experimental data. Solubility enhancement was measured in batch experiments. Lead oxalate salt ( $\text{PbC}_2\text{O}_4$ ) was added to solutions of dissolved CMCD-Na salt with 50 mM  $\text{KNO}_3$  as background ionic strength. The total ionic strength ranged from 50 mM for the lowest CMCD concentration, to 100 mM for the 20 g/l CMCD solution. The samples were filtered after 7 days and pH and total aqueous Pb concentration were analyzed immediately after filtering the samples, Table A-1.

The acid-base properties of CMCD were investigated by base titration in a  $\text{CO}_2$ -free atmosphere. The results indicate that each CMCD contains on average 4.27 carboxyl groups and that all carboxyl groups can be assumed to have identical strength ( $\text{pK}_a = 3.77$ ). Our conceptual model for the CMCD acid-base and metal complexation reactions are expressed as a set of mass action equations:

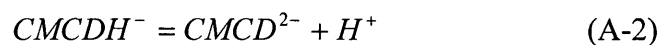
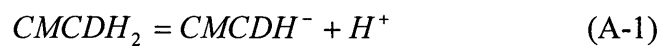


Table A-1. Composition of solutions in PbC<sub>2</sub>O<sub>4</sub>(s)-CMCD batch experiments.

Solution	[CMCD] [g/l]	[CMCD <sup>2-</sup> ] [mmol/l]	[COOH] [mmol/l]	[Na <sup>+</sup> ] [mmol/l]	[KNO <sub>3</sub> ] [mmol/l]	pH	[Pb <sub>tot</sub> ] [mg/l]
1	0	0	0	0	50	5.95	3.61
2	0	0	0	0	50	6.32	3.71
3	0.0839	0.0605	0.137	0.258	50	6.42	5.14
4	0.890	0.642	1.46	2.74	50	6.13	12.90
5	2.46	1.78	4.03	7.58	50	5.96	20.54
6	4.59	3.31	7.51	14.13	50	5.98	27.29
7	7.05	5.08	11.54	21.71	50	5.99	32.45
8	11.3	8.16	18.52	34.83	50	5.99	38.91
9	11.3	8.16	18.52	34.83	50	5.97	38.42
10	14.9	10.8	24.4	45.9	50	6.03	43.17
11	18.7	13.5	30.6	57.6	50	6.00	46.58
12	18.7	13.5	30.6	57.6	50	6.04	46.25

Additional acidity (2.27 carboxyl groups per CMCD) is modeled as separate carboxyl groups:



It is further assumed that each CMCD molecule complexes one Pb<sup>2+</sup>.



with the conditional stability constant of interest defined as:

$$K_{CMCD-Pb} = \frac{\{CMCDPb\}}{\{CMCD^{2-}\}\{Pb^{2+}\}} \quad (A-5)$$

The activity coefficients of all species but CMCD<sup>2-</sup> are calculated with the Davies equation which is the default option in PHREEQC. The WATEQ Debye-Hückel equation is used for the free CMCD ion:

$$\log \gamma_{\text{CMCD}^{2-}} = -A \cdot z_{\text{CMCD}^{2-}}^2 \cdot \left( \frac{\sqrt{\mu}}{1 + B \cdot a_{0,\text{CMCD}^{2-}} \cdot \sqrt{\mu}} \right) + b_{\text{CMCD}^{2-}} \cdot \mu \quad (\text{A-6})$$

where A and B are constants that depend on temperature and pressure only,  $z_{\text{CMCD}^{2-}}$  is the charge of  $\text{CMCD}^{2-}$ ,  $\mu$  is ionic strength, and  $a_{0,\text{CMCD}^{2-}}$  and  $b_{\text{CMCD}^{2-}}$  equal 3.50 and -0.65, respectively.

### **Procedure**

Building a PHREEQC/UCODE\_2005 model is performed stepwise in the following order. Each step is discussed in more detail in subsequent sections.

1. Create and execute a PHREEQC model. The program must be run from a batch file that can later be called from the UCODE\_2005 main input file. This can be accomplished by using the batch version of PHREEQC instead of a graphical user interface version.
2. Create the five UCODE\_2005 input files: (1) template file (filename.tpl), (2) main input file (filename.in), (3) instruction file (filename.instructions), (4) observation file (filename.obs), and (5) a batch file to run UCODE\_2005 (filename.bat).
3. Once the input files are created, execute UCODE\_2005 in forward mode. This step is necessary to verify that the PHREEQC input file is created correctly and that PHREEQC output is extracted properly.
4. Use UCODE\_2005 to calculate sensitivities to assess whether the observations contain enough information to estimate unknown parameter(s). Sensitivities are a measure of how important each observation is for the estimation of unknown parameter(s) and, conversely, how important the parameter value(s) are for

simulated values. If the sensitivities for estimated parameters differ significantly, it may not be possible to estimate the least sensitive parameters precisely.

5. Execute UCODE\_2005 in inverse mode to optimize unknown parameter(s). We refer to this step as the parameter-estimation mode.
6. Use UCODE\_2005 output to investigate residuals (differences between observed and simulated values) to assess the conceptual geochemical model (set of mass action equations) and to evaluate uncertainties associated with estimated parameters.

#### Step 1: Creating the PHREEQC model

First, create a geochemical model in PHREEQC by defining species that are not defined in the standard PHREEQC database. In our example, CMCD, carboxyl, and oxalate are defined as new solution master species in the PHREEQC input file. Solution master species are the basic building blocks in PHREEQC. In this formulation the new master species are not coupled to their elemental constituents, carbon, oxygen, and hydrogen. Figure A-1 shows selected parts of the PHREEQC input file. Non-executed comment lines start with the # sign. All input files are available upon request from the authors. Second, define the aqueous interactions between the species described by Equations A-1 through A-5 under the Solution\_Species data block. New solution species are defined directly under the Solution\_Species command followed by definitions of reactions involving these newly defined solution species. Third, define reactions with separate phases such as the dissolution of  $\text{PbC}_2\text{O}_4$  and the fictitious phase for pH buffering under the Phases data block. The solubility product of the  $\text{PbC}_2\text{O}_4$  used in the experiments was determined to be  $10^{-10.48}$ . Fourth, define the composition of the aqueous solutions that are to equilibrate with CMCD and  $\text{PbC}_2\text{O}_4$  under the Solution block. Lastly, instruct PHREEQC to react each solution with  $\text{PbC}_2\text{O}_4$  and CMCD under the Equilibrium\_Phases block.

```

# Definition of solutions master species not
# defined in the standard database.
SOLUTION_MASTER_SPECIES
Cmcd Cmcd-2 0.0 1390 1390
Carbox Carbox- 0.0 44.01 44.01
Oxalate Oxalate-2 0.0 88.018 88.018

# Definitions of new solution species.
SOLUTION_SPECIES
Pb+2 = Pb+2
log_k 0.0
-gamma 4.49 0

Cmcd-2 = Cmcd-2
log_k 0.0
-gamma 3.50 -0.65
# WATEQ equation for CMCD-2
# with a=3.50 and b=-0.65

# Acid/base reactions of CMCD.
Cmcd-2 + H+ = CmcdH-
log_k 3.80

CmcdH- + H+ = CmcdH2
log_k 3.80

Carbox- = Carbox-
log_k 0.0

Carbox- + H+ = CarboxH
log_K 3.80

# Pb/CMCD complexation.
Cmcd-2 + Pb+2 = CmcdPb
log_k 4.50

# Definition of oxalate and its reactions.
Oxalate-2 = Oxalate-2
log_k 0.0
-gamma 4.49 0

Oxalate-2 + H+ = OxalateH-
log_k 1.271

OxalateH- + H+ = OxalateH2
log_k 4.217

Oxalate-2 + Pb+2 = PbOxalate
log_k 4.91

2 Oxalate-2 + Pb+2 = PbOxalate2-2
log_k 6.76
-gamma 4.49 0

PHASES
Fix_H+
H+ = H+
log_k 0.0

PbOxalate
PbOxalate = Pb+2 + Oxalate-2
log_k -10.48

# Define solutions 1-11 by copying the following 7
# lines and adjust concentrations appropriately.
SOLUTION 12 #18.7 g/l CMCD
units mol/kgw
K 0.050
N(5) 0.050
Na 57.6E-03
Cmcd 13.5E-03
Carbox 30.6E-03
END

# Print aqueous Pb concentrations to selected
# output file.
SELECTED_OUTPUT
-file P_CMCD_Pb.sel
-high_precision false
-simulation false
-state false
-solution false
-distance false
-time false
-step false
-pH true
-pe false
-ionic_strength true
-molalities Pb+2 PbOxalate PbHCO3+ PbCO3 Cmcd-2

USER_PUNCH
-headings Pb_tot
-start
10 REM Convert Pb concentration to ppm.
20 PUNCH TOT("Pb")*207.2*1000
-end
PRINT
-selected_output true

# React solutions 1-11 at fixed pH with CO2 and Pb-oxalate.
USE SOLUTION 12
EQUILIBRIUM_PHASES
Fix_H+ -6.04 HNO3 10.0
CO2(g) -3.5
PbOxalate
END

```

Figure A-1. Selected portions of the PHREEQC input file. To save space, definitions and reactions of solutions 1-11 are not shown here.

In order to facilitate the extraction of simulated data with UCODE\_2005, write the total aqueous Pb concentration to a selected output file using the Selected\_Output and User\_Punch data blocks in PHREEQC. The conditional stability constant for the CMCDPb complex was initially set to  $10^{-4.50}$ . The PHREEQC simulated aqueous Pb concentration is shown in Figure A-2.

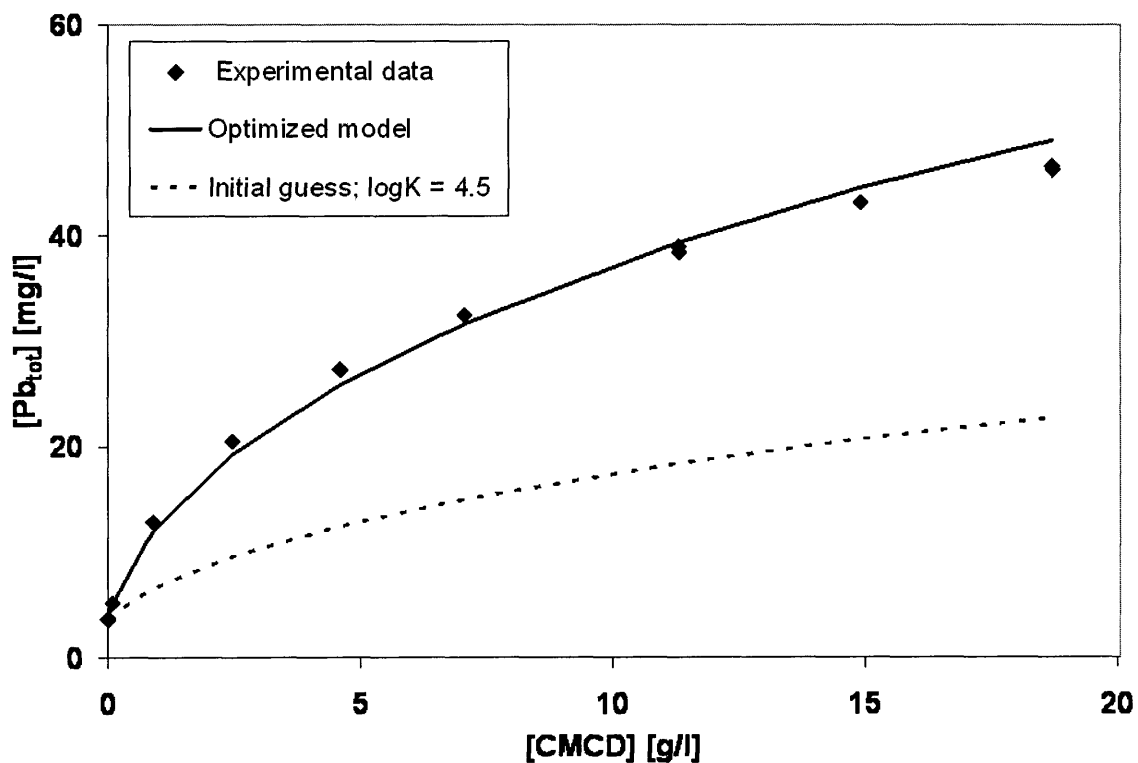


Figure A-2. Comparison of observed and simulated  $\text{PbC}_2\text{O}_4$  solubility in the presence of CMCD.

### Step 2: Creating UCODE\_2005 input files

After the PHREEQC model is built, the UCODE\_2005 input files should be created. Additional details on these input files are provided in the UCODE\_2005 manual (Poeter et al., 2005).

**Template file** The template file is a modified PHREEQC input file into which UCODE\_2005 inserts trial values of the parameters to be determined; the template file differs from the PHREEQC input file only (1) on the first line and (2) where values of unknown parameter(s) are defined. Thus, modify the PHREEQC input file by inserting “jtf @” (jtf is an acronym for Jupiter template file, and @ is the user selected symbol that will identify parameter names substituted with numerical values) on the first line and replace each parameter value by an @ followed by a parameter name, enough spaces so that UCODE\_2005 can insert the parameter value (always err in the direction of more spaces than needed to obtain a well-behaved regression), and then followed by another @ sign. We only estimate one parameter,  $\log K_{\text{CMCDPb}}$ , so, in addition to inserting the first line, only one substitution is necessary. In line 35 of Figure A-1,  $\log_k$  4.50 is replaced with @logK @.

**Main input file** The main input file controls the iteration process, it tells UCODE\_2005 what model(s) to execute, what parameter(s) to optimize, how to extract PHREEQC simulated values, and what observations to compare them to. The main input file used in our model is presented in Figure A-3. Explanations of its contents are given in comment lines in the file. UCODE options and inputs that are not specified in the main file defaults to values described in the UCODE\_2005 manual.

Only two parameters in the main input file need to be changed during a typical PHREEQC/UCODE\_2005 modeling project. In forward mode, the parameters ‘sensitivities’ and ‘optimize’ are specified to be ‘no’. In sensitivity-analysis mode, ‘sensitivities’ is changed to ‘yes’ and in parameter estimation mode both parameters must be specified to be ‘yes’.

```

# -----
# JCDDF INPUT - PHREEQC MODELING OF Pb COMPLEXATION BY CMCD
# -----
# Verbose determines what is printed to the main output file.
BEGIN Options KEYWORDS
  Verbose=4
END Options

# -----
# JCDDF-CONTROL INFORMATION
# -----
BEGIN UCDDF_CONTROL_DATA KEYWORDS
# These parameters control the optimization process.
  sensitivities=yes # calc. sensitivities yes (needed for param. optimization), no
  optimize=yes # estimate parameters: yes, no
END UCDDF_CONTROL_DATA

# -----
# COMMAND FOR APPLICATION MODEL (PHREEQC)
# -----
# Command defines the name of the process model batch file.
BEGIN MODEL_COMMAND_LINES
  Command=P_CMCD_Pb.bat
  CommandID=PHREEQC
END MODEL_COMMAND_LINES

#
# PARAMETER INFORMATION
# -----
# _list of parameter(s) to be optimized.
# The parameter name(s) must be identical to the name in the template file.
BEGIN PARAMETER_DATA TABLE
  NROW=1 NCOL=6 COLUMNLABELS
  ParamName StartValue LowerValue UpperValue Adjustable SensMethod
  logK 4.50 2.0 7.0 Yes 2
END PARAMETER_DATA

# -----
# OBSERVATION INFORMATION
# -----
# Observations are defined in a separate file called U_CMCD_Pb.obs
BEGIN OBSERVATION_DATA FILES
  U_CMCD_Pb.obs
END OBSERVATION_DATA

# -----
# APPLICATION MODEL INFORMATION
# -----
# _locates template file(s) to use to create the PHREEQC input file.
BEGIN MODEL_INPUT_FILES KEYWORDS
  ModInFile=P_CMCD_Pb.inp
  TemplateFile=U_CMCD_Pb.tpl
END MODEL_INPUT_FILES

# _instructs from where, and how, to extract simulations.
BEGIN MODEL_OUTPUT_FILES KEYWORDS
  ModOutFile=P_CMCD_Pb.se
  InstructionFile=U_CMCD_Pb.instructions
  Category=Obs
END MODEL_OUTPUT_FILES

```

Figure A-3. Main UCODE\_2005 input file.

**Instruction file** The instructions file (Figure A-4) tells UCODE\_2005 what values to extract from the PHREEQC selected output file, which is listed in the main input file (Figure A-3). It is convenient, but not required, to use the ‘StandardFile’ option to extract simulated Pb concentrations from the table in the selected PHREEQC output file. Create the instruction file by describing from where data should be extracted and list the observation names to which simulated values should be compared.

```
jif @
# Extract the 10 observations named below.
# Skip 3 lines and start at the 8th column.
# These comment lines (this file only) MUST
# be deleted before running UCODE_2005.
StandardFile 3      8      10
Soln_03
Soln_04
Soln_05
Soln_06
Soln_07
Soln_08
Soln_09
Soln_10
Soln_11
Soln_12
```

Figure A-4. UCODE\_2005 instruction file.

**Observation file** Create the observations file by, for each observation on a separate line, listing the observation name, observed value, uncertainty of estimated value, and measure used to assess uncertainty (Figure A-5). The observation names in the first column must correspond to the observation names defined in the instructions file. Columns three and four are used to weight the observed values. Weighting has two purposes. First, uncertainties in observations are quantified so that observations determined with less uncertainty are given more importance in the parameter estimation process than uncertain observations. Second, dividing each squared residual by the measurement of variance of the observation produces unitless values to sum in the objective function. This yields the advantage that different types of observations can be used to optimize unknown parameters. For instance, both measured pH and the concentration of one or more

elements can be used as observations. We assign a relative standard deviation, based on analytical uncertainty, of 2.5% for all our observations. Thus, all observed Pb

```
# Uncertainty in experimental data is expressed
# as 2.5% relative standard deviation, i.e.
# coefficient of variation (CV) = 0.025.
BEGIN OBSERVATION_DATA TABLE
  NROW=10  NCOL=4  COLUMNLABELS
  Obsname  ObsValue  Statistic  StatFlag
  Soln_03  5.14      0.025     CV
  Soln_04  12.90     0.025     CV
  Soln_05  20.54     0.025     CV
  Soln_06  27.29     0.025     CV
  Soln_07  32.45     0.025     CV
  Soln_08  38.91     0.025     CV
  Soln_09  38.42     0.025     CV
  Soln_10  43.17     0.025     CV
  Soln_11  46.58     0.025     CV
  Soln_12  46.25     0.025     CV
END OBSERVATION_DATA
```

Figure A-5. UCODE\_2005 observations file.

concentrations are equally important to the parameter estimation process. Changing the relative standard deviation equally for all observations does not change the optimized value but it does, however, affect the calculated standard deviation on the optimized parameter value.

### Step 3: Executing UCODE\_2005 in forward mode

Execute UCODE\_2005 in forward mode. This process creates the PHREEQC input file, executes PHREEQC one time, and extracts simulated Pb concentrations. At this point, it is recommended to compare the PHREEQC simulated values (selected PHREEQC output file) with the values that UCODE\_2005 extracts (main UCODE\_2005 output file). If the values are different, this suggests errors exist in the UCODE\_2005 input files. It is also a good habit to move or delete the PHREEQC input and output files and execute

UCODE\_2005 one more time to make sure that extracted values come from a new output file.

#### Step 4: Executing UCODE\_2005 in sensitivity-estimation mode

Execute UCODE\_2005 in sensitivity-estimation mode by setting the parameter 'sensitivities' to 'yes' in the main input file. In this mode, sensitivities are calculated, which can be extremely useful to evaluate whether observations contain enough information to estimate unknown parameters and to assess if any single observation dominates the parameter-estimation process. Ideally, dimensionless scaled sensitivities should be similar (within two orders of magnitude of the parameter with largest sensitivity) for all observations since they measure the effect of individual observations on estimated parameter values. Sensitivities can also be used to help plan additional experiments. For instance, as part of our research we may wish to investigate the effect of ionic strength on the non-ideal behavior of CMCD. We can create additional PHREEQC models for hypothetical experiments at various ionic strengths and use UCODE\_2005 to calculate sensitivities on these planned new observations.

In our model, dimensionless scaled sensitivities, calculated for the initial value of log K, range from 190 to 250. The sensitivity for the measured Pb concentration at 0.1 g/l CMCD was lower (90). Sensitivities of similar magnitude, such as 90-250, indicate that no observation is much more important than other observations for the estimation of the conditional stability constant.

#### Step 5: Executing UCODE\_2005 in parameter-estimation mode

Execute UCODE\_2005 in parameter estimation mode by changing the parameter 'optimize' to 'yes'. In our example, the conditional stability constant was successfully estimated to  $10^{5.20}$  with the 95% confidence interval ranging from  $10^{5.16}$  to  $10^{5.23}$ . The fit of the model to experimental data is shown in Figure A-2.

### Step 6: Evaluating the model

There are a number of statistical measures to evaluate the results of the automated parameter estimation. For instance, the confidence interval is calculated based on the assumptions that residuals are independent, belong to a normal distribution and are randomly distributed around a mean of zero. If these assumptions are not valid, the true uncertainty in the model is larger than indicated by the 95% confidence intervals. The first assumption is tested by the correlation coefficient between weighted residuals and normal order statistic,  $R_N^2$  (Poeter et al., 2005). Our data form a straight line on a normal probability graph ( $R_N^2=0.989$ ) suggesting that the residuals are independent and normally distributed (data not shown). The second assumption is generally tested using graphs of weighted and unweighted residuals vs weighted and unweighted simulated values. Ideally, there should be no correlation between residuals and simulated values. The uncertainties in our experimental data are directly proportional to the observations; the standard deviation is 2.5% of measured Pb concentration. Because of this direct relationship between observations and their weights the weighted observations are identical. Thus, in our example it was useful to graph unweighted residuals against CMCD concentration which reveals a trend in residuals (data not shown). Thus, the true uncertainty is larger than the 95% confidence intervals. Further measures are discussed in more detail by Hill and Tiedeman (2006).

In summary, simulated Pb concentrations differ from observed concentrations by less than 5%. However, the model is not perfect. At low CMCD concentrations the model under predicts the aqueous Pb concentration and over predicts at high concentrations. Other conceptual models may fit the data better and could be evaluated, compared and ranked using this automated technique (Poeter and Anderson, 2005).

## **Conclusions**

UCODE\_2005 coupled to PHREEQC can be used to automate the process of estimating parameters such as thermodynamic constants from experimental data. A similar approach can be used to estimate other parameters used in geochemical models such as sorption constants or degradation rates from experimental or field data. Besides automating the estimation procedure, advantages of this methodology include analysis of observation importance, estimates of uncertainties associated with the estimation and the comparative evaluation of multiple conceptual models.

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## APPENDIX B

### EXAMPLE PHREEQC INPUT FILE AND INPUT DATA

The following is an example of a PHREEQC input file for simulation of CMCD-Pb interactions. A summary of Solution\_Master-Species, Solution\_Species, and Phases that were amended to the standard PHREEQC data base is also included following the PHREEQC example input file.

TITLE CMCD-ENHANCED BaC2O4 SOLUBILITY, 50 mM KNO3. UCODE, WATEQ, CMCD-2,COO-, 25C.

SOLUTION\_MASTER\_SPECIES

Cmcd Cmcd-2 0.0 1387 1387  
Carbox Carbox- 0.0 44.01 44.01  
Oxalate Oxalate-2 0.0 88.018 88.018

SOLUTION\_SPECIES

Ba+2 = Ba+2

log\_k 0.0  
-gamma 4.49 0

Cmcd-2 = Cmcd-2

log\_k 0.0  
-gamma 3.50 -0.60

Cmcd-2 + H+ = CmcdH-

log\_k 3.80

CmcdH- + H+ = CmcdH2

log\_k 3.80

Cmcd-2 + Ba+2 = CmcdBa

log\_k 3.5774020e+000

Carbox- = Carbox-

log\_k 0.0

Carbox- + H+ = CarboxH

log\_K 3.80

Oxalate-2 = Oxalate-2

log\_k 0.0  
-gamma 4.20 0

Oxalate-2 + H+ = OxalateH-

log\_k 1.271

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GOLDEN, CO 80401

OxalateH- + H+ = OxalateH2  
log\_k 4.217

Oxalate-2 + Ba+2 = BaOxalate  
log\_k 2.31

PHASES

Fix\_H+  
H+ = H+  
log\_k 0.0

BaOxalate  
BaOxalate = Ba+2 + Oxalate-2  
log\_k -6.587

SOLUTION 1  
units mol/kgw  
K 0.0500  
N(5) 0.0500

SOLUTION 2  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 2.756E-04  
Cmcd 6.455E-05  
Carbox 1.465E-04

SOLUTION 3  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 2.875E-03  
Cmcd 6.733E-04  
Carbox 1.528E-03

SOLUTION 4  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 7.266E-03  
Cmcd 1.702E-03  
Carbox 3.863E-03

SOLUTION 5  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 1.444E-02  
Cmcd 3.381E-03  
Carbox 7.676E-03

SOLUTION 6  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 1.444E-02  
Cmcd 3.381E-03  
Carbox 7.676E-03

SOLUTION 7  
units mol/kgw

K 0.0500  
N(5) 0.0500  
Na 2.352E-02  
Cmcd 5.508E-03  
Carbox 1.250E-02

SOLUTION 14  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 2.352E-02  
Cmcd 5.508E-03  
Carbox 1.250E-02

SOLUTION 8  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 3.477E-02  
Cmcd 8.144E-03  
Carbox 1.849E-02

SOLUTION 9  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 4.595E-02  
Cmcd 1.076E-02  
Carbox 2.443E-02

SOLUTION 10  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 5.723E-02  
Cmcd 1.340E-02  
Carbox 3.042E-02

SOLUTION 11  
units mol/kgw  
K 0.0500  
N(5) 0.0500  
Na 5.723E-02  
Cmcd 1.340E-02  
Carbox 3.042E-02  
END

SELECTED\_OUTPUT

-file BaCD.sel  
-high\_precision false  
-simulation false  
-state false  
-solution false  
-distance false  
-time false  
-step false  
-pH true  
-pe false  
-ionic\_strength true  
-molalities Ba+2 BaOxalate BaHCO3+ BaCO3 Cmcd-2

USER\_PUNCH

```
-headings Ba_tot
-start
10 REM Print total Ba concentration in ppm to selected output file.
20 PUNCH TOT("Ba")*137.33*1000
-end
```

```
USE SOLUTION 1
EQUILIBRIUM_PHASES
Fix_H+ -8.40 NaOH 10
BaOxalate
CO2(g) -3.5
END
```

```
USE SOLUTION 2
EQUILIBRIUM_PHASES
Fix_H+ -8.28 HNO3 10.0
BaOxalate
CO2(g) -3.5
END
```

```
USE SOLUTION 3
EQUILIBRIUM_PHASES
Fix_H+ -7.32 NaOH 10.0
BaOxalate
CO2(g) -3.5
END
```

```
USE SOLUTION 4
EQUILIBRIUM_PHASES
Fix_H+ -7.22 NaOH 10.0
BaOxalate
CO2(g) -3.5
END
```

```
USE SOLUTION 5
EQUILIBRIUM_PHASES
Fix_H+ -6.88 NaOH 10.0
BaOxalate
CO2(g) -3.5
END
```

```
USE SOLUTION 6
EQUILIBRIUM_PHASES
Fix_H+ -7.08 NaOH 10.0
BaOxalate
CO2(g) -3.5
END
```

```
USE SOLUTION 7
EQUILIBRIUM_PHASES
Fix_H+ -6.62 NaOH 10.0
BaOxalate
CO2(g) -3.5
END
```

```
USE SOLUTION 14
EQUILIBRIUM_PHASES
Fix_H+ -6.88 NaOH 10.0
BaOxalate
CO2(g) -3.5
END
```

USE SOLUTION 8  
EQUILIBRIUM\_PHASES  
Fix\_H+ -6.51 NaOH 10.0  
BaOxalate  
CO2(g) -3.5  
END

USE SOLUTION 9  
EQUILIBRIUM\_PHASES  
Fix\_H+ -6.56 NaOH 10.0  
BaOxalate  
CO2(g) -3.5  
END

USE SOLUTION 10  
EQUILIBRIUM\_PHASES  
Fix\_H+ -6.70 NaOH 10.0  
BaOxalate  
CO2(g) -3.5  
END

USE SOLUTION 11  
EQUILIBRIUM\_PHASES  
Fix\_H+ -6.34 NaOH 10.0  
BaOxalate  
CO2(g) -3.5  
END

Table B-1. A summary of the Solution\_Master-Species, Solution\_Species, and Phases that were amended to the standard PHREEQC data base.

<b>Solution_Master-Species</b>	Cmcd-2
	Carbox-
	Oxalate-2
	Ba+2
	Ca+2
	Cd+2
	Ce+3
	Ni+2
	Pb+2
<b>Solution_Species</b>	Cmcd-2
	CmcdH-
	CmcdH2
	Carbox-
	CarboxH
	Oxalate-2
	OxalateH-
	OxalateH2
	Ba+2
	CmcdBa
	BaOxalate
	Ca+2
	CmcdCa
	CaOxalate
	CaOxalateH+
	CaOxalate2-2
	Cd+2
	CmcdCd
	CdOxalate
	CdOxalate2-2
	CdOxalate3-4
	Ce+3
	CmcdCe+
	CeO+
	CeO2-
	CeO2H
	CeOH+2

	Ce <sup>3+</sup> (OH) <sup>5+</sup>
	Ce(CO <sub>3</sub> ) <sup>2-</sup>
	Ce(CO <sub>3</sub> ) <sup>2-</sup>
	CeCO <sub>3</sub> <sup>+</sup>
	CeHCO <sub>3</sub> <sup>2+</sup>
	CeCl <sup>2+</sup>
	CeCl <sup>2+</sup>
	CeCl <sub>3</sub>
	CeCl <sup>4-</sup>
	CeNO <sub>3</sub> <sup>2+</sup>
	CeOxalate <sup>+</sup>
	CeOxalate <sup>2-</sup>
	CeOxalate <sup>3-3</sup>
	Ni <sup>2+</sup>
	NiOH <sup>+</sup>
	Ni(OH) <sub>2</sub>
	Ni(OH) <sup>3-</sup>
	NiCl <sup>+</sup>
	NiCl <sub>2</sub>
	NiNO <sub>3</sub> <sup>+</sup>
	NiCO <sub>3</sub>
	NiHCO <sub>3</sub> <sup>+</sup>
	CmcdNi
	NiOxalate
	CmcdSr
	Zn <sup>2+</sup>
	CmcdZn
	ZnOxalate
	ZnOxalate <sup>2-2</sup>
	ZnOxalateH <sup>+</sup>
	Zn(OxalateH) <sub>2</sub>
	CmcdPb
	PbOxalate
	PbOxalate <sup>2-2</sup>
<b>Phases</b>	Fix H <sup>+</sup>
	BaOxalate
	CaOxalate
	CdOxalate
	Ce <sub>2</sub> (Oxalate) <sub>3</sub>

	Ce(OH)3(am)
	Ce(OH)3
	Ce(CO3)3·8H2O
	Ce2O3
	NiOxalate
	Ni(OH)2
	NiCO3
	PbOxalate
	SrSO4
	ZnOxalate

The following reactions were included under the Solution\_Species input data block in the PHREEQC input files:

$\text{Cmcd-2} = \text{Cmcd-2}$

log\_k 0.0

-gamma 3.50 -0.60

$\text{Cmcd-2} + \text{H}^+ = \text{CmcdH-}$

log\_k 3.80

$\text{CmcdH-} + \text{H}^+ = \text{CmcdH}_2$

log\_k 3.80

$\text{Carbox-} = \text{Carbox-}$

log\_k 0.0

$\text{Carbox-} + \text{H}^+ = \text{CarboxH}$

log\_K 3.80

$\text{Oxalate-2} = \text{Oxalate-2}$

log\_k 0.0

-gamma 4.20 0

$\text{Oxalate-2} + \text{H}^+ = \text{OxalateH-}$

log\_k 1.271

$\text{OxalateH-} + \text{H}^+ = \text{OxalateH}_2$

log\_k 4.217

$\text{Ba}^{+2} = \text{Ba}^{+2}$

log\_k 0.0

-gamma 4.49 0

$\text{Cmcd-2} + \text{Ba}^{+2} = \text{CmcdBa}$

log\_k 3.5774020e+000

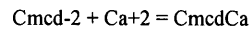
$\text{Oxalate-2} + \text{Ba}^{+2} = \text{BaOxalate}$

log\_k 2.31

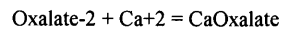
$\text{Ca}^{+2} = \text{Ca}^{+2}$

log\_k 0.0

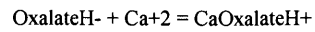
-gamma 4.49 0



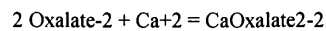
log\_k 3.5575770e+000



log\_k 2.54

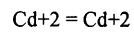


log\_k 1.84



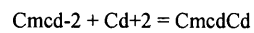
log\_k 2.69

-gamma 4.49 0

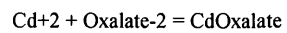


log\_k 0.0

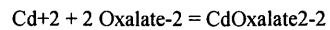
-gamma 4.49 0



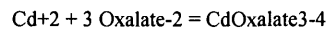
log\_k 4.0429490e+000



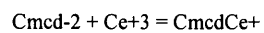
log\_k 3.89



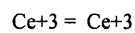
log\_k 5.66



log\_k 5.06

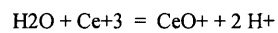


log\_k 7.4762730e+000



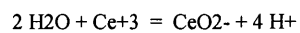
log\_k 0.0

-gamma 9.000 0.0



log\_k -16.4103

-gamma 4.0 0.0



log\_k -38.758  
-gamma 4.0 0.0

2 H2O + Ce+3 = CeO2H + 3 H+  
log\_k -26.1503  
-gamma 3.0 0.0

H2O + Ce+3 = CeOH+2 + H+  
log\_k -8.4206  
-gamma 4.5 0.0

5 H2O + 3 Ce+3 = Ce3(OH)5+4 + 5 H+  
log\_k -33.4754  
-gamma 5.5 0.0

2 HCO3- + 1 Ce+3 = Ce(CO3)2- + 2 H+  
log\_k -8.1576  
-gamma 4.0 0.0

HCO3- + Ce+3 = CeCO3+ + H+  
log\_k -2.9284  
-gamma 4.0 0.0

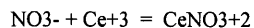
HCO3- + 1.0000 Ce+3 = CeHCO3+2  
log\_k 1.9190  
-gamma 4.5 0.0

Cl- + Ce+3 = CeCl+2  
log\_k +0.3086  
-gamma 4.5 0.0

2 Cl- + Ce+3 = CeCl2+  
log\_k 0.0308  
-gamma 4.0 0.0

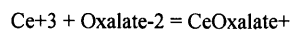
3 Cl- + Ce+++ = CeCl3  
log\_k -0.3936  
-gamma 3.0 0.0

4 Cl- + 1 Ce+3 = CeCl4-  
log\_k -0.7447  
-gamma 4.0 0.0

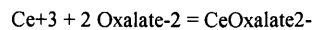


log\_k 1.3143

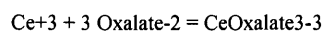
-gamma 4.5 0.0



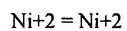
log\_k 6.52



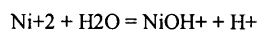
log\_k 10.48



log\_k 11.30



log\_k 0.0



log\_k -9.897

delta\_h 51.81 kJ

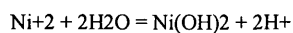
-gamma 0 0

# Id: 5403300

# log K source: NIST46.3

# Delta H source: NIST46.3

#T and ionic strength: 0.00 25.0



log\_k -18.994

delta\_h 0 kJ

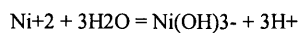
-gamma 0 0

# Id: 5403301

# log K source: NIST46.3

# Delta H source: MTQ3.11

#T and ionic strength: 0.00 25.0



log\_k -29.991

delta\_h 0 kJ

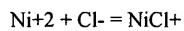
-gamma 0 0

# Id: 5403302

# log K source: NIST46.3

# Delta H source: MTQ3.11

#T and ionic strength: 0.00 25.0

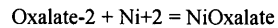


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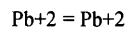
log_k    0.408
delta_h  2      kJ
-gamma   0      0
#         Id:    5401800
#   log K source: NIST46.3
#   Delta H source: NIST46.3
#T and ionic strength: 1.00 25.0
Ni+2 + 2Cl- = NiCl2
log_k    -1.89
delta_h  0      kJ
-gamma   0      0
#         Id:    5401801
#   log K source: SCD3.02 (1989 IPa)
#   Delta H source: MTQ3.11
#T and ionic strength: 0.00 25.0
Ni+2 + NO3- = NiNO3+
log_k    0.4
delta_h  0      kJ
-gamma   0      0
#         Id:    5404921
#   log K source: NIST46.4
#   Delta H source: MTQ3.11
#T and ionic strength: 0.00 25.0
Ni+2 + CO3-2 = NiCO3
log_k    4.5718
delta_h  0      kJ
-gamma   0      0
#         Id:    5401401
#   log K source: NIST46.3
#   Delta H source: MTQ3.11
#T and ionic strength: 0.70 25.0
Ni+2 + H+ + CO3-2 = NiHCO3+
log_k    12.4199
delta_h  0      kJ
-gamma   0      0
#         Id:    5401400
#   log K source: NIST46.3
#   Delta H source: MTQ3.11

Cmcd-2 + Ni+2 = CmcdNi
log_k    3.4757560e+000

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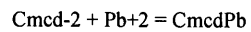


log\_k 5.16

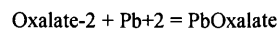


log\_k 0.0

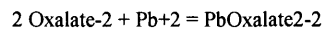
-gamma 4.49 0



log\_k 5.220845495666496E+000

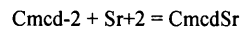


log\_k 4.91

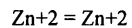


log\_k 6.76

-gamma 4.49 0

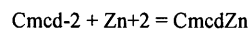


log\_k 3.5524530e+000

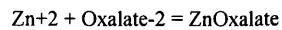


log\_k 0.0

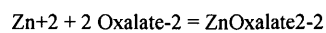
-gamma 6.00 0



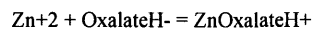
log\_k 3.6368680e+000



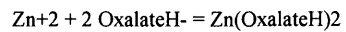
log\_k 4.87



log\_k 7.65



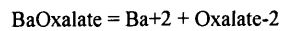
log\_k 1.72



log\_k 3.12

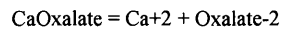
The following reactions were included under the Phases input data block in the PHREEQC input files:

BaOxalate



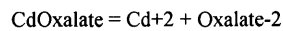
log\_k -6.587

CaOxalate



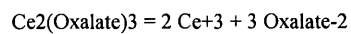
log\_k -8.029

CdOxalate



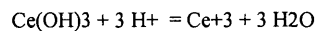
log\_k -7.80

Ce2(Oxalate)3



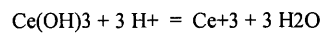
log\_k -32.2

Ce(OH)3



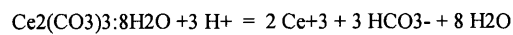
log\_k 19.8852

Ce(OH)3(am)



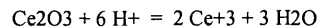
log\_k 21.1852

Ce2(CO3)3:8H2O



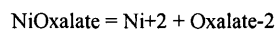
log\_k -4.1136

Ce2O3



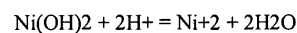
log\_k 62.3000

NiOxalate



log\_k -9.7335

Ni(OH)2



log\_k 12.794

delta\_h -95.96 kJ  
NiCO3  
NiCO3 = Ni+2 + CO3-2  
log\_k -6.87  
delta\_h -41.589 kJ

PbOxalate  
PbOxalate = Pb+2 + Oxalate-2  
log\_k -10.48

SrSO4  
SrSO4 = Sr+2 + SO4-2  
log\_k -6.69

ZnOxalate  
ZnOxalate = Zn+2 + Oxalate-2  
log\_k -8.8647