CONF-8905356--1

PNL-SA--18360

DE91 005611

METAL CATION/ANION ADSORPTION ON CALCIUM CARBONATE: IMPLICATIONS TO METAL ION CONCENTRATIONS IN GROUNDWATER

J. M. Zachara
C. E. Cowan
C. T. Resch

May 1990

Presented at the
EPA Workshop on
Metal Speciation and
Transport in Groundwaters
Jekyll Island, Georgia
May 24-26, 1989

Work supported in part by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830
and the
Electric Power Research Institute
under Contract RP2485-03

Pacific Northwest Laboratory
Richland, Washington 99352

METAL CATION/ANION ADSORPTION ON CALCIUM CARBONATE: IMPLICATIONS TO METAL ION CONCENTRATIONS IN GROUNDWATER

John M. Zachara, Christina E. Cowan, and Charles T. Resch

May 1990

Environmental Sciences Department
Pacific Northwest Laboratory
P.O. Box 999, MSIN K3-61
Richland, Washington 99352

ABSTRACT

Calcite is a common mineral phase in groundwater zones. Calcite influences groundwater composition and pH, exhibits an appreciable surface area, and can function as a sorbent for metallic cations and anions. This chapter evaluates the sorption behavior of metallic ions on specimen calcite as a basis for determining the importance of calcite relative to other subsurface sorbents, such as layer silicates and oxides, in controlling metal ion concentrations in calcareous groundwaters. A review of the literature shows the sorption of both metallic cations and anions on calcite over ranges in pH and CO_2 partial pressure to be consistent with a surface-exchange process where cations exchange with surface Ca and anions exchange with surface CO_3. A general surface-exchange model was developed to account for the effects of Ca and CO_3 concentrations, pH, and calcite surface area on cation and anion sorption onto calcite. The model was applied to recently developed experimental sorption data of Zn and SeO_3 on specimen calcite in equilibrium $CaCO_3(aq)$ suspensions. The surface-exchange model was able to describe the effects of pH on both cation and anion sorption, and provided good predictions of the effects of variable $CO_2(g)$ pressure on Zn sorption and of PO_4 on SeO_3 sorption. The surface-exchange model, combined with sorption constants for other phases, was used to calculate Cd sorption to a hypothetical aquifer material containing a mixture of sorbents (i.e., calcite, amorphous iron, and smectite). The sorbent concentrations were fixed to those expected in groundwater zones. The multi-sorbent calculation documented the importance of calcite as a sorbent for metallic ions in groundwater.

1. INTRODUCTION

Calcite ($CaCO_3(s)$) is a common mineral phase in groundwater zones. Calcite is a matrix constituent of limestone aquifers such as the Floridan Aquifer (Plummer 1977) and is a secondary phase found in large regional aquifers, such as the Fox Hills-Basal Hell Creek Aquifer in the Dakotas (Thorstenson et al. 1979), the Snake River Aquifer in Idaho and Oregon (Wood and Low 1988), and the Columbia Plateau Aquifer in Washington State (Deutsch et al. 1982). Calcite is also a common constituent of small near-surface aquifers that often receive metallic and organic pollutants (Toran 1987, Fuller and Davis 1987, Morin et al. 1988, Barker et al. 1988, Garland et al. 1988). Calcite functions as a buffer for groundwater pH and influences groundwater composition via its precipitation/dissolution behavior (Langmuir 1971, Plummer 1977, Butler 1982, Morin et al. 1988).

Metal concentrations in calcareous groundwaters may be controlled by solubility or sorption processes (see, for example, Fuller and Davis 1987, Yanful et al. 1988a, 1988b, Morin et al. 1988). Groundwaters in contact with calcite are typically in near equilibrium with this solid, are elevated in pH (pH 6.5 to 10.0 depending on the $CO_2(g)$ partial pressure), and contain significant concentrations of bicarbonate and carbonate ions (Langmuir 1971, Plummer 1977). The concentrations of metal ions in these waters may be controlled by solubility equilibria with metal carbonate, hydroxy-carbonate, and hydroxide solid phases, because many of these solids exhibit low solubility and rapid precipitation-dissolution kinetics. Examples of such solid phases include otavite, $CdCO_3$ (Yanful et al. 1988a, Fuller and Davis 1987) and hydrozincite, $Zn_5(CO_3)_2(OH)_6$ (Zachara et al. 1989). When the total metal

concentration is insufficient to form a discrete metal-ligand solid phase or when the aqueous metal concentrations are below those maintained by these discrete solids, sorption to aquifer solids, including calcite, may regulate metal concentrations. Such conditions often exist in calcareous groundwaters that are downgradient or far-field from metal-containing waste sites.

Although calcite exhibits appreciable surface area in limestone and calcareous sediments (Holford and Mattingly 1975), its importance as a sorbent for metal ions in groundwater is not well recognized nor established through experiment. In this chapter, we review what is known about metal sorption reactions on calcite, develop and evaluate a generalized sorption model for metal cations and anions on calcite using recently measured sorption data, and perform calculations to evaluate the importance of calcite in hypothetical mixed sorbent materials containing calcite, smectite (a 2:1 clay), and amorphous iron oxide.

2. METAL SORPTION ON CALCITE

2.1 Surface Properties of Calcite

The surface of calcite develops charge in response to the surface excess of the potential determining ions, Ca^{2+} and CO_3^{2-} (Parks 1975, Foxall et al. 1979, Thompson and Pownall 1989). The point-of-zero charge (pzc) of calcite has been reported to occur at pCa = 4.4 (Foxall et al. 1979) with the surface exhibiting positive charge at Ca concentrations above this value and negative charge at Ca concentrations below this value. Calcite, therefore, carries predominantly positive charge below pH 9.0 in saturated calcium carbonate solutions in contact with atmospheric $CO_2(g)$ (pCO_2 = 3.5 atm.). Some

researchers have speculated that HCO_3^-, OH^-, $CaOH^+$, and $CaHCO_3^+$ exist as surface species on calcite and influence surface charge (Parks 1975, Somasundaran and Agar 1967, Siffert and Fimbel 1984), but recent studies using a streaming potential method suggest that Ca^{2+} and CO_3^{2-} alone are the dominant surface species and that other solution species, including H^+ and OH^-, have no significant effect on the surface charge (Thompson and Pownall 1989).

2.2 Sorption Behavior of Metallic Cations

A wide range of metallic cations have been shown to be sorbed onto calcite (Table 1). Sorption of metallic cations, Me^{2+}, on calcite (Figure 1) increases with increasing pH, paralleling a decrease in the aqueous concentration of Ca (Figure 2). The initial sorption of metallic cations on calcite appears, therefore, to occur by exchange with surface-associated Ca (Kornicker et al. 1985, Zachara et al. 1988), as depicted by the following reaction:

$$X\text{-}Ca + Me^{2+} \leftrightarrow X\text{-}Me + Ca^{2+} \quad (1)$$

and shown conceptually in Figure 2. X is considered to be a cation-specific surface site quantifiable by isotopic exchange with ^{45}Ca. Metal cation adsorption in equilibrium $CaCO_3$(aq) suspensions is influenced by 1) pH and pCO_2, which control aqueous Ca concentrations (Figure 2, Zachara 1988), and 2) calcite surface area, which determines the concentration of cation-specific surface sites (X, Figure 2). Low aqueous concentrations of Ca promote Me surface exchange in accordance with the mass action expression of equation (1).

While much of the data in Table 1 support the occurrence of a surface-exchange reaction (equation 1) for metallic cations, the molecular aspects of this surface reaction remain unresolved. For example, it is not known if the ion exchange occurs between dehydrated lattice ions or within a hydrated layer on the calcite surface with properties transitional between those of the crystalline lattice and the aqueous phase (Davis et al. 1987, Zachara et al. 1988). The adsorption data of Figure 1 indicate that metallic cations adsorb to calcite at pH and pCa levels where the surface carries positive charge, indicating that the $X\text{-}Me^{2+}$ surface complex is not simply electrostatic in nature, but is stabilized through chemical interaction (Lyklema 1989).

Following the surface-exchange reaction, which is usually completed within time periods of seconds to hours (Davis et al. 1987, Zachara et al. 1988), other phenomena specific to the metal cation sorbate and to the particular specimen of calcite have been observed to occur over time periods of hours to days. These latter phenomena involve changes in the chemical bonding of the Me^{2+} ion on the calcite surface, which influence the lability and reversibility of the surface complex (X-Me). Calcites with unstable particle energies and rapid recrystallization kinetics have been observed to trap the sorbed ions in a recrystallized surface phase or solid-solution (Lorens 1981, Davis et al. 1987, Zachara et al. 1989), limiting desorption and isotopic exchange (Zachara et al. 1988). In the absence of significant recrystallization, Cd and possibly Mn surface complexes appear to dehydrate forming a discrete Me^{2+} surface precipitate (e.g., $MeCO_3$) or Me^{2+} solid solution with $CaCO_3$ (e.g., $Me_xCa_{1-x}CO_3$) (McBride 1980, Davis et al. 1987, Zachara et al. 1990a). Other ions that do not precipitate readily as $MeCO_3$ solids,

including Zn, Co, and Ni, appear to remain as hydrated species on the calcite surface and are desorbable in the absence of recrystallization (Zachara et al. 1988, Zachara et al. 1990a).

2.3 Sorption of Inorganic Anions

The sorption of inorganic anions on calcite has not been extensively studied (Table 1). The sorption trend of the anion, SeO_3, on calcite (Figure 3, Cowan et al. 1990a) is inverse to that observed for cations (Figure 1), with the greatest sorption observed at lower pH. Anion sorption parallels increasing positive charge on the calcite sorbent and decreasing solution concentrations of carbonate ions (Figure 2). Analogous to metal cation adsorption, anion sorption is, therefore, consistent with a surface-exchange reaction between the aqueous anion (A^{2-}) and surface carbonate species as depicted by the following reaction:

$$X'\text{-}CO_3 + A^{2-} \leftrightarrow X'\text{-}A + CO_3^{2-} \qquad (2)$$

and shown conceptually in Figure 2. X' is an anion-specific surface site quantifiable by isotopic exchange measurements with $H^{14}CO_3$. Like metal cations, sorbed anions can also be incorporated into recrystallized surface layers on calcite (House and Donaldson 1986). Observations with phosphate, however, indicate that only a small fraction of the surface-associated anion that is associated with active crystal growth sites can be incorporated into the dehydrated crystalline structure (House and Donaldson 1986).

2.4 Surface Exchange on Calcite and Other Sorbents

The surface-exchange reactions postulated for metal cations and anions on calcite (equations 1 and 2, Figure 2) are consistent with many

experimental observations made using calcite and other salt-type solid phases. Auger analyses and isotopic exchange measurements have shown that the outer several atomic layers on the surface of calcite are in exchange equilibrium with the electrolyte solution with which it is in contact (Moller and Werr 1972, Moller 1973, Moller and Sastri 1974, Mucci and Morse 1985). Isotopic exchange measurements using lattice constituents are commonly made to estimate surface area of salt-type minerals (Inks and Hahn 1967, Kukura et al. 1972), suggesting that surface ions are exchangeable. Selective ion exchange reactions have been reported between the surfaces of sulfate and phosphate minerals and aqueous solutes in both trace and major concentrations (Lieser et al. 1966, Lin et al. 1981, Jonasson et al. 1988, Pate et al. 1989).

3. GENERALIZED SURFACE EXCHANGE MODEL

Although metal cation and anion sorption on calcite is consistent with a surface-exchange reaction between aqueous species and surface-associated Ca^{2+} and CO_3^{2-}, this hypothesis has not been evaluated using modeling techniques where the joint effects of solution speciation and the surface reaction could be assessed in relation to pH and Ca^{2+} and CO_3^{2-} concentrations. To further evaluate the plausibility of the exchange process as depicted conceptually in Figure 2, metal cation and anion sorption data on calcite over a range in pH were modeled using a computer code incorporating hydrolysis, acid dissociation, and aqueous complexation reactions as well as surface-exchange half-reactions. The objective of this modeling was to describe the initial reaction involved in the sorption of solute ions on the

calcite surface. No attempt was made, at this point, to include reactions that may follow surface exchange, such as surface precipitation or solid-solution formation. With the exception of House and Donaldson (1986), Davis et al. (1987), and Comans and Middelburg (1987), there have been no comprehensive attempts to model solute sorption reactions on calcite.

3.1 Metal Cation-Exchange Model

The cation-exchange model is based on exchange half-reactions that describe the surface reaction of the metal cation (Me^{2+}) or Ca^{2+} with the cation-specific surface sites, X, on the calcite. The exchange half-reactions for Ca^{2+} and Me^{2+} are given as

$$Ca^{2+} + X \leftrightarrow X\text{-}Ca \qquad K_{Ca}$$

and

$$Me^{2+} + X \leftrightarrow X\text{-}Me \qquad K_{Me}$$

respectively. The overall surface-exchange constant between Ca and the metal is calculated from the difference in the half-reaction constants; that is, $\log K_{ex} = \log K_{Me} - \log K_{Ca}$ in accordance with equation (1). No attempt was made to charge balance the half-reactions because the charge characteristics of the surface-exchange sites, X, and the surface-exchange complexes (X-Ca, X-Me) were not known. The overall exchange reaction is, however, charge balanced.

The details of the method used to determine the half-reaction constants for the metal cations shown in Figure 1 are given in Zachara et al. (1990a). The half-reaction constants were determined using the FITEQL program (Westall 1982a, 1982b), and the number of cation-specific exchange sites, X_t (3.42×10^{-6} mol/g), was estimated by isotopic dilution using isotopic exchange data

of ^{45}Ca on $CaCO_3(s)$ over a range in pH values (Zachara et al. 1990a). The effects of pH and solution speciation of Ca and the metal cation are accounted for by including solution complexation reactions and associated constants like those shown in Table 2 for Ca and Zn. The solution composition for each of the sorption experiments was assumed equal to that measured in calcite-saturated solutions of approximately the same pH. The activity of the Ca ion in solution was fixed (based on the measured aqueous Ca concentrations), and the ionic strength was set at its approximate analytical value (0.1 M). The half-reaction constant for Ca (i.e., log K_{Ca} = 15.5) was fixed to ensure that essentially all the surface sites were occupied by Ca or the metal cation and to ensure that the concentration of "free" or unoccupied sites (X) was very small.

The half-reaction model using Me^{2+} as the only sorbing species (e.g., reaction of the form X-Ca + Me^{2+} ↔ X-Me + Ca^{2+}) was able to quantitatively describe the pH-dependent sorption of all the metallic cations in Figure 1 (Ba, Sr, Cd, Mn, Co, and Zn) except Ni (Zachara et al. 1990a). An example is shown in Figure 4 for 10^{-7} M Zn (pCO_2 = 3.5 atm.). The overall exchange constant for the reaction at 10^{-7} M Zn (log K_{Me} - log K_{Ca}) was 2.45, and its positive value signifies strong preference of the $CaCO_3$ surface for Zn. In contrast, quantitative description of the sorption edge data of Ni required the use of two sorbing species (Ni^{2+} and $NiOH^+$), each with different exchange constants (Zachara et al. 1990a).

The robustness of the surface-exchange model was first evaluated by testing the ability of the exchange constant developed using the data in Figure 4 to predict the measured adsorption of 10^{-7} M Zn at 1) different partial pressures of $CO_2(g)$ and 2) different initial concentrations of X-Ca

(e.g., $CaCO_3$ solids concentration). The exchange constant from Figure 4 was able to closely predict the measured sorption of 10^{-7} M Zn on a second calcite specimen at three different levels of pCO_2 after the different surface area of the two calcite sorbents was taken into consideration (Figures 5a,b,c). The ability to predict the influence of $CO_2(g)$ based solely on mass action effects with Ca (e.g., $CO_2(g)$ effects on Ca activity through the $CaCO_3$ solubility constraint) and differing Zn aqueous speciation indicates that equation (1) is an accurate, first approximation of the exchange process. Electrostatic effects related to charge on the calcite surface appear to be second order. The exchange constant from Figure 4 also provided good predictions of Zn sorption at lower X-Ca (i.e., 10 g/L, Figure 6a), indicating constancy of the exchange constant over at least a limited range in Zn sorption density.

The ability of the exchange constants calculated for 10^{-7} M Zn to predict Zn sorption at 10^{-6} M initial concentration on a second calcite specimen was also evaluated as a further test of the exchange model. The 10^{-7} M Zn exchange constants accurately predicted the placement of the sorption edge at pCO_2 = 3.5 atm. (Figure 5d), but overpredicted sorption at pCO_2 = 2.5 atm. and 4.5 atm. (Figures 5e,f). Zn sorption at 10^{-6} M initial concentrations in a low surface area calcite suspension was also significantly overpredicted by the 10^{-7} M Zn constant (Figure 6b). A new exchange constant of lower intensity (log K_{ex} = 2.2) that was fitted to the 10^{-6} M sorption edge with pCO_2 = 3.5 atm. gave much-improved but still imperfect predictions of Zn sorption at different $pCO_2(g)$ levels and solids concentration (Figures 5e-g).

The discrepancies between predictions and experimental observations in Figures 5 and 6 are caused by decreasing selectivity of the $CaCO_3$ surface for

Zn with surface loading and are not indicative of a departure from equation (1). Zn sorption/exchange isotherms on calcite are nonlinear (Zachara et al. 1988, Zachara et al. 1990a), and conditional exchange constants calculated for 10^{-7} M Zn in Figure 4, therefore, greatly overpredict the sorption isotherm at initial Zn concentrations of 10^{-6} M and above (Zachara et al. 1990a). A power-exchange model requiring two constants is needed to describe Zn sorption over a range in surface loading (Zachara et al. 1988). This selectivity decrease is specific to Zn and is not observed for other metallic cations (Zachara et al. 1990a).

3.2 Metal Anion Exchange Model

Anion (A^{2-}) sorption on calcite can be described using a half-reaction approach based on equation (2) and analogous to that used for metallic cations. The reactions are

$$CO_3^{2-} + X' \leftrightarrow X'\text{-}CO_3 \qquad K_{CO_3}$$

$$HCO_3^{-} + X' \leftrightarrow X'\text{-}HCO_3 \qquad K_{HCO_3}$$

and

$$A^{2-} + X' \leftrightarrow X'\text{-}A \qquad K_A$$

where X' is an anion-specific surface site. The half-reaction approach for anions differs from one for metallic cations in that two surface-saturating species (CO_3^{2-} and HCO_3^{-}) must be explicitly considered to successfully describe anion sorption data (Cowan et al. 1990a). Thus, the surface exchange process is, at minimum, a ternary exchange reaction. Bicarbonate must be considered as a surface-reactive species and competitor with A^{2-} because it is the dominant carbonate solution species over most of the pH range of environmental interest (Figure 2). It is recognized, however, that

a recent study suggests that only Ca^{2+} and CO_3^{2-} exist as exchangeable species on the surface of calcite (Thompson and Pownall 1989). As performed for the metallic cations, the surface-exchange constants between CO_3^{2-}, HCO_3^-, and the anion (A^{2-}) are calculated from the difference in the half-reaction constants: that is, $\log K_{ex1} = \log K_A - \log K_{CO_3}$ and $\log K_{ex2} = \log K_A - \log K_{HCO_3}$.

An example of the half-reaction exchange approach described above is provided for SeO_3 sorption on calcite in the absence and presence of PO_4. The sorption data and modeling approach for this example have been presented in detail in Cowan et al. (1990a). The set of half-reactions for CO_3 and SeO_3 species that gave the best approximation to the sorption data of SeO_3 as a single sorbate in Figure 3 using the chemical equilibrium program FITEQL is given in Table 3. The fit of these half-reactions to the data is shown in Figure 7. For these calculations the total number of anion-specific surface sites, X'_t, for calcite in $CaCO_3$(aq) solutions (2.06×10^{-6} M/g) was estimated from isotopic exchange of $H^{14}CO_3$ (Cowan et al. 1990a). Because it was hypothesized that SeO_3 sorption was an exchange reaction with surface-associated carbonate, the value of the CO_3^{2-} exchange constant was chosen to ensure that all the surface sites would be occupied by either CO_3^{2-}/HCO_3^- or $SeO_3^{2-}/HSeO_3^-$ and that the concentration of "free" or unoccupied sites would be very small.

Removal of the effects of CO_3 or SeO_3 ionization from the exchange constants (Table 3) indicated that the exchange of HCO_3^- was stronger than the exchange of CO_3^{2-}, and the exchange of SeO_3^{2-} was slightly stronger than the exchange of $HSeO_3^-$. The difference between the exchange constants for CO_3^{2-} and HCO_3^- was significant because assuming equal selectivity between the two

surface CO_3 species resulted in inaccurate predictions of the measured sorption (not shown). However, assuming equal selectivity between the two SeO_3 constants did not result in significant differences in the predictions, suggesting that SeO_3 may exist on the surface as a single species. The HCO_3^- surface species ($X\text{-}HCO_3^-$) was calculated to predominate on the $CaCO_3(s)$ surface over the entire pH range (not shown). For both 10^{-7} and 10^{-6} M initial SeO_3 concentrations, the SeO_3^{2-} surface species accounted for most of the SeO_3 adsorption over the entire pH range, although the $HSeO_3^-$ surface species contributed at the lower pH values (Figure 7).

Like SeO_3, PO_4 sorption on calcite as a single sorbate could also be described as an exchange process between surface-associated HCO_3^-/CO_3^{2-} (Figure 8a, Cowan et al. 1990a). Unlike SeO_3, however, the dominant surface species of PO_4 was the complex $CaHPO_4$. House and Donaldson (1986) also concluded that $CaHPO_4$ was the dominant sorbing species. Phosphate is known to sorb strongly on highly energetic surface sites on calcite associated with crystal growth (Reddy 1977, Walter and Burton 1986, Busenburg and Plummer 1989). The surface-exchange approach used for PO_4 in Figure 8 requires no specific assumption or hypothesis regarding the degree of hydration or bonding in the surface complexes ($X'\text{-}PO_4$, $X'\text{-}CaHPO_4$).

Binary solute sorption experiments with mixtures of PO_4 and SeO_3 showed that PO_4 reduces SeO_3 sorption on calcite (Cowan et al. 1990a). The competitive sorption of the two anions is consistent with a mass action effect where both PO_4 and SeO_3 are binding to the same group of sites. The fitted exchange constants for PO_4, SeO_3, and CO_3 species on $CaCO_3(s)$ derived from single sorbate-sorption data (Table 3) were able to predict the resulting SeO_3 sorption in the presence of PO_4 quite well (Figure 8b). This good

agreement confirmed that exchange reactions involving the three components could explain the observed decrease in SeO_3 sorption in the presence of PO_4. Similarly, SO_4 was also found to reduce SeO_3 sorption, and its effects could also be predicted with single sorbate-exchange constants (Cowan et al. 1990a). The sorption of PO_4 did not result in 1:1 reduction in the sorption of SeO_3 because surface binding sites were in excess. The sorption of SeO_3 was reduced by only 1.5×10^{-10} mol/g, while the amount of sorbed PO_4 was 8.9×10^{-7} mol/g.

3.3 Exchange Versus Solid Phase Formation

The use of surface-exchange reactions to successfully describe the sorption of cations and anions on calcite does not presuppose a specific molecular nature of the surface complexes. Exchange reactions can be employed to describe replacement reactions between hydrated ions on layer silicates or between components of a solid solution (Sposito 1981), such as $CaCO_3(s)/CaSeO_3(s)$ or $CaCO_3(s)/ZnCO_3(s)$. As argued by Sposito (1984), the fact that the ion activity product (IAP) for a solution is below the solubility product of the pure phase and that the sorption conforms to an adsorption isotherm are not sufficient evidence to eliminate coprecipitation. In fact, both adsorption and co-precipitation can result in an IAP below the solubility product for the pure solid phase. The ability of two substances to form solid solutions is determined primarily by geometrical factors (Evans 1966). If two substances have similar structures and if the radii differ by no more than 15% of the smaller, then a wide range of solid solutions can occur (Evans 1966). Physically, SeO_3^{2-} and CO_3^{2-} are similar in structure and size, and thus could be readily exchanging and forming a solid solution

on the surface. Even if substances differ in structure, as do PO_4^{3-} and CO_3^{2-}, solid solutions can be formed, but their composition will be more limited (Evans 1966). Thus, although the sorption of these ions can be modeled by exchange reactions, this is not evidence for the presence of hydrated surface complexes on the $CaCO_3(s)$ surface.

4. IMPORTANCE OF CALCITE AS A SORBENT IN AQUIFER MATERIALS

Natural soils and aquifer materials are composed of a mixture of mineral and organic material spanning the clay, silt, sand, and gravel size range (Ainsworth and Zachara 1988 and references therein). Clay- and silt-sized materials typically dominate the sorptivity of an aquifer material for metallic anions and cations because most of the surface area of the porous media is associated with the smaller size fraction material (Zachara et al. 1989, Zachara et al. 1990b). Crystalline and amorphous oxides of Fe and Mn and layer silicates, such as smectites, illites, vermiculites, and kaolinites, have been consistently implicated as the clay or silt-sized material that dominates metal ion sorption in soil and aquifer sediments (Means et al. 1978, Bruggenwert and Kamphorst 1979, Jackson and Inch 1983, Sposito 1984, Stollenwerk and Grove 1985, Kent et al. 1988, Evans 1989, Loux et al. 1989). The relative importance of oxides versus layer silicates within a given aquifer material depends on many complex variables including sorbent site concentration (Luoma and Davis 1983), presence of strongly sorbed indigenous ions (Zachara et al. 1989), pH (Sposito 1984), electrolyte composition and ionic strength (e.g., Ca versus Na, Bowman et al. 1981, Elrashidi and O'Conner 1982, Hayes and Leckie 1987), as well as the

crystalline nature and chemical composition of the layer silicate and oxide sorbents (Ainsworth et al. 1989, Zachara et al. 1990b).

While this chapter has shown that specimen calcite sorbs both cations and anions, the importance of calcite as a sorbent relative to oxides and layer silicates remains in question. Most studies with natural materials containing calcite have implicated it as an important sorbent (Fuller and Davis 1987, Dudley et al. 1988, Goldberg and Glaubig 1988a, 1988b, Papadopoulos and Rowell 1988), while still others have suggested that calcite is not a major contributor to sorption (Ryan et al. 1984, Neal et al. 1987, Borrero et al. 1988). To evaluate the conditions under which calcite may be an important sorbent for metallic cations, model calculations were made for Cd sorption on a hypothetical aquifer material containing amorphous iron oxide, smectite clay, and calcite. The calculation was performed using 1) the calcite surface-exchange model discussed earlier in this chapter, 2) a non-electrostatic surface-exchange model for amorphous iron oxyhydroxide (Cowan et al. 1990b), and 3) an ion-exchange model for the basal plane sites on smectite (Zachara et al. 1990b, 1990c). All three models describe the sorption process in a conceptually similar manner using exchange half-reactions (see Table 4).

The sorbent site concentrations for the hypothetical aquifer material were a surface area of 2.2 m^2/g of calcite, a cation exchange capacity of 1.0 meq/100g as smectite, and a NH_2-HCl extractable amorphous iron oxide content of 0.01% and 0.001%. Calcite was assumed to exhibit a site concentration of 8.31×10^{-6} mol/m^2 (Moller and Sastri 1974), and the entire extractable amorphous iron oxyhydroxide surface was assumed to be available for Cd complexation and to exhibit a site density as reported by Davis and

Leckie (1978). The sorbent concentrations were not actual measurements on a single aquifer material, but were based on analyses of many relevant subsurface materials presented in Holford and Mattingly (1975), Borrero et al. (1988), Davis et al. (1987), and Loux et al. (1989). The aquifer material was assumed to have a bulk density of 1.5 g/cm^3 and a particle density of 2.65 g/cm^3. The test calculation is very sensitive to the assumed sorbent concentrations.

Cadmium was used for the test calculation because a consistent set of constants was available for its surface exchange on all three sorbents from high Ca electrolyte solutions where the competitive effects of Ca had been explicitly addressed. Cd is a very strongly sorbed ion on calcite (Davis et al. 1987, Zachara et al. 1990a), and its use in the test calculation will therefore demonstrate a maximum effect for the importance of calcite as a sorbent. While the surface exchange reaction for Cd on calcite given in Table 4 very accurately describes Cd sorption over a range in pH, it must be recognized that the surface-exchange complex apparently dehydrates rapidly, as Cd is poorly desorbable (Zachara et al. 1990a). The equilibrium calculation presented here must, therefore, be viewed within context of this irreversibility. The model calculations were performed with an initial Cd concentration of 10^{-5} M in equilibrium $CaCO_3$(aq) solutions over the pH range of approximately 7.0 to 9.5, with ionic strength of approximately 0.1 M (Table 5).

Cadmium was calculated to be strongly sorbed in this hypothetical calcareous aquifer material (Figure 9). Under the assumed conditions of the calculation, only calcite and amorphous Fe are important sorbents. Amorphous Fe is a dominant sorbent for Cd in the simulation in spite of the competition

with Ca, which has been shown to suppress Cd sorption (Cowan et al. 1990b). The high Na and Ca concentrations in the equilibrium $CaCO_3$ solutions suppress Cd sorption on smectite through ion-exchange mass action; similar results have been reported experimentally (Zachara et al. 1990b, 1990c). While both amorphous Fe and calcite sorb Cd (Figure 9), calcite out-competes the amorphous Fe for Cd at higher pH where Ca concentrations are low. The pH region where calcite predominates as a sorbent is related to its total site concentration (governed by its exposed surface area) relative to the total site concentration of amorphous Fe in the aquifer material. As shown in Figure 9a, amorphous Fe predominates as a sorbent over a greater range in pH when it is present in equal total site concentration to calcite. Calcite, in turn, is the dominant sorbent when its site concentration exceeds that of amorphous Fe (Figure 9b).

The multisorbent model calculation underscores the need for accurate site concentration measurements of different sorbents in a aquifer material to understand and predict metal ion sorption. Such measurements, which are currently problematic and often times ambiguous, are the focus of ongoing research. For example, while the total moles of amorphous Fe may be estimated by chemical extraction with NH_2OH-HCl (Chao and Zhou 1983), translating moles of extractable Fe into a site concentration is problematic because the effective surface area, accessibility, and surface site saturation of the amorphous Fe in the aquifer material are not known. Similarly, the site concentration of $CaCO_3$ in an aquifer material may be estimated by isotopic exchange with ^{45}Ca or $H^{14}CO_3$ (Holford and Mattingly 1975, Inks and Hahn 1967), but ambiguities arise because corrections must be applied for the

exchange of these same tracers on other mineral surfaces that may be present with greater surface areas (i.e., layer silicates and Fe, Mn, and Al oxides).

5. CONCLUSIONS

Both metallic cations and anions sorb on calcite. Their sorption behavior over ranges in pH and CO_2 gas pressure is consistent with an initial surface-exchange process, where cations exchange with surface Ca and anions exchange with surface carbonate. A general surface-exchange model containing exchange half-reactions was developed to describe the effects of Ca and CO_3 concentration, pH, and calcite surface area on metal ion sorption. The model is conceptually consistent with the surface reaction approach applied to oxide and layer silicate minerals, and can be readily incorporated into geochemical models such as MINTEQ. The model was able to describe the influence of pH on both anion and cation sorption, and provided good predictions of the effects of variable $CO_2(g)$ pressure on Zn sorption and of PO_4 on SeO_3 sorption. The model does not currently consider reactions such as metal dehydration, precipitation, or solid-solution formation that have been observed to follow the surface-exchange reaction for certain solutes (e.g., Cd and Mn) on calcite. These latter reactions, however, must be considered to accurately describe metal ion concentrations and migration in calcareous groundwater.

Model calculations in a ternary sorbent mixture containing calcite, amorphous Fe, and smectite clay documented that calcite can be an important sorbent in aquifer materials for metals that strongly associate with the calcite surface (i.e., Cd and Zn). Groundwater pH and the site concentration of calcite relative to other strongly sorbing phases such as Fe and Mn oxides

are the most important factors governing whether metal sorption to calcite is significant. Clearly, sorption reactions of both cations and anions to calcite will be important and potentially dominant in limestone or dolomitic aquifers, or in groundwater systems depleted of oxides. The model calculations presented here were based on sorption constants measured for specimen mineral phases. More accurate calculations should use sorption constants of natural carbonates, oxides, and layer silicates, as their sorptivity may differ significantly from specimen solids as a result of substitutional/compositional impurities and crystallinity differences. With specific regard to the carbonates, substitutions of Mg, Fe, and Mn, which are common in nature, affect calcite surface area and lattice dimension, which could significantly influence metallic cation and anion sorption.

Measurement of site concentrations of individual sorbents or sorbent classes in aquifer materials is needed to accurately describe metal sorption in both calcareous and non-calcareous groundwaters. The determination of sorbent mass or molar content alone is not adequate because the relationship of these parameters to site concentration has not been established. Even if the sorbent surface area is determined, the sorption magnitude may be inadequately predicted because the surfaces of oxide and calcite particles in subsoil or aquifer material may be modified by the sorption of natural organic compounds (humic substances, lower molecular weight organic acids) or strongly binding inorganic ions, such as Si, Al, or Fe, that may block or modify surface sites. Research to improve site concentration measurements on natural subsurface materials is a high priority.

Acknowledgments: This research was funded by the U.S. Department of Energy Subsurface Science Program within the Office of Energy Research under Contract DE-AC06-76RLO 1830 and the Electric Power Research Institute, Inc., under Contract RP2485-03, "Chemical Attenuation Studies," with Battelle Pacific Northwest Laboratories.

REFERENCES

Ainsworth, C.C. and J.M. Zachara. "Selection of Subsoils, Saturated Zone Materials, and Related Sorbents for Subsurface Research," DOE/ER-0390 U.S. Department of Energy, Office of Health and Environmental Research, Washington, D.C. (1988).

Ainsworth, C.C., D.C. Girvin, J.M. Zachara and S.C. Smith. "Chromate Adsorption on Geothite: Effects of Aluminum Substitution," Soil Sci. Soc. Am. J. 53:411-418 (1989).

Ball J.W., D.K. Nordstrom and E.A. Jenne. "Additional and Revised Thermodynamic Data and Computer Code for WATEQ2 -- A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters," WRI 78-116, U.S. Geological Survey, Menlo Park, CA (1980).

Bancroft, G.M., J.R. Brown and W.S. Fyfe. "Quantitative X-ray Photoelectron Spectroscopy (ESCA): Studies of Ba^{2+} Sorption on Calcite," Chem. Geol. 19:131-144 (1977).

Barker, J.F., J.E. Barbash and M. Labonte. "Groundwater Contamination at a Landfill Site on Fractured Carbonate and Shale," J. Contam. Hydrol. 3:1-27 (1988).

Bilinski, H., R. Huston and W. Stumm. "Determination of the Stability Constants of Some Hydroxo Carbonato Complexes of Pb(II), Cu(II), Cd(II), and Zn(II) in Dilute Solutions by Anodic Stripping Voltammetry and Differential Pulse Polarography," Anal. Chim. Acta 84:157-164 (1976).

Borrero, C., F. Pena and J. Torrent. "Phosphate Sorption by Calcium Carbonate in Some Soils of the Mediterranean Part of Spain," Geoderma 42:261-269 (1988).

Bowman, R.S., M.E. Essington and G.A. O'Connor. "Soil Sorption of Nickel: Influence of Solution Composition," Soil Sci. Soc. Am. J. 46:860-865 (1981).

Bruggenwert, M.G.M. and A. Kamphorst. "Survey of Experimental Information on Cation Exchange in Soil Systems," in Soil Chemistry B. Physics-Chemical Models, G. H. Bolt, Ed. (New York, Elsevier, 1979) pp. 141-203.

Busenberg, E. and L.H. Plummer. "Thermodynamics of Magnesian Calcite Solid-Solutions at 25° and 1 atm Total Pressure," Geochim. Cosmochim. Acta 53:1189-1208 (1989).

Butler, J.N. Carbon Dioxide Equilibria and Their Applications. (Reading, MA, Addison-Wesley Publishing Company, 1982).

Chao, T.T. and L. Zhou. "Extraction Techniques for Selective Dissolution of Iron Oxides from Soils and Sediments," Soil Sci. Soc. Am. J. 47:225-232 (1983).

Cole, C.V., S.R. Olsen and C.O. Scott. "The Nature of Phosphate Adsorption by Calcium Carbonate," Soil Sci. Soc. Amer. 17:352-356 (1953).

Comans, R.N.J. and J.J. Middelburg. "Sorption of Trace Metals on Calcite: Applicability of the Surface Precipitation Model," Geochim. Cosmochim. Acta 51:2587-2591 (1987).

Cowan, C.E., J.M. Zachara and C.T. Resch. "Solution Ion Effects on the Surface Exchange of Selenite on Calcite," Geochim. Cosmochim. Acta (In Press, 1990a).

Cowan, C.E., J.M. Zachara and C.T. Resch. "Cadmium Adsorption of Iron Oxides in the Presence of Alkaline Earth Elements," Environ. Sci. Tech. (In Press, 1990b).

Davis, J.A. and J.O. Leckie. "Surface Ionization and Completation at the Oxide/Water Interface. II. Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions," J. Colloid Interface Sci. 67(1):90-107 (1978).

Davis, J.A., C.C. Fuller and A.D. Cook. "A Model for Trace Metal Sorption Processes at the Calcite Surface: Adsorption of Cd^{2+} and Subsequent Solid Solution Formation," Geochim. Cosmochim. Acta 51:1477-1490 (1987).

Dekanel, J. and J.W. Morse. "The Chemistry of Orthophosphate Uptake from Seawater onto Calcite and Aragonite," Geochim. Cosmochim. Acta 42:1335-1340 (1978).

Deutsch, W.J., E.A. Jenne and K.M. Krupka. "Solubility Equilibria in Basalt Aquifers: The Columbia Plateau, Eastern Washington, U.S.A.," Chem. Geol. 36:15-34 (1982).

Dudley, L.M., J.E. McLean, R.C. Sims and J.J. Jurinak. "Sorption of Copper and Cadmium from the Water Soluble Fraction of an Acid Mine Waste by Two Calcareous Soils," Soil Sci. 45:207-214 (1988).

Elrashidi, M.A. and G.A. O'Conner. "Influence of Solution Composition on Sorption of Zinc by Soils," Soil Sci. Soc. Am. J. 46:1153-1158 (1982).

Evans, R.C. An Introduction to Crystal Chemistry. 2nd Ed. (Cambridge, Cambridge University Press, 1966).

Evans, L.J. "Chemistry of Metal Retention by Soils," Environ. Sci. Technol. 23:1046-1056 (1989).

Felmy, A.R., D.C. Girvin and E.A. Jenne. "MINTEQ, a Computer Model for Calculating Aqueous Geochemical Equilibria," NTIS-PB-84157148, National Technical Information Service, Springfield, VA (1984).

Foxall, T., G. Peterson, H.M. Rendall and A.L. Smith. "Charge Determination at the Calcium Salt/Aqueous Solution Interface," J. Chem. Soc. Faraday Trans. 75:1034-1039 (1979).

Franklin, M.L. and J.W. Morse. "The Interaction of Copper with the Surface of Calcite," Ocean Sci. Eng. 7:147-174 (1982).

Franklin, M.L. and J.W. Morse. "The Interaction of Manganese (II) with the Surface of Calcite in Dilute Solutions and Seawater," Marine Chem. 12:241-254 (1983).

Fuller, C.C. and J.A. Davis. "Processes and Kinetics of Cd^{2+} Sorption by Calcareous Aquifer Sand," Geochim. Cosmochim. Acta 51:1491-1502 (1987).

Garland, T.R., J.M. Zachara and R.E. Wildung. "A Case Study of the Effects of Oil Shale Operations on Surface and Groundwater Quality: II. Major Inorganic Ions," J. Environ. Qual. 17:660-666 (1988).

Goldberg S. and R.A. Glaubig. "Anion Sorption on a Calcareous, Montmorillonitic Soil-Selenium," Soil Sci. Soc. Am. J. 52:954-958 (1988a).

Goldberg S. and R.A. Glaubig. "Anion Sorption on a Calcareous, Montmorillonitic Soil-Arsenic," Soil Sci. Soc. Am. J. 52:1297-1300 (1988b).

Hayes, K.F. and J.O. Leckie. "Modeling Ionic Strength Effects on Cation Adsorption at Hydrous Oxide/Solution Interfaces," J. Colloid Interface Sci. 115:564-572 (1987).

Holford, I.C.R. and C.E.G. Mattingly. "Surface Area of Calcium Carbonate in Soils," Geoderma 13:247-255 (1975).

House, W.A. and L. Donaldson. "Adsorption and Coprecipitation of Phosphate on Calcite," J. Colloid Interface Sci. 112:309-234 (1986).

Inks, C.G. and R.B. Hahn. "Determination of Surface Area of Calcium Carbonate by Isotopic Exchange," Anal. Chem. 39:625-628 (1967).

Jackson, R.E. and K.J. Inch. "Partitioning of Strontium-90 Among Aqueous and Mineral Species in a Contaminated Aquifer," Environ. Sci. Technol. 17:231-237 (1983).

Jonasson, R.G., G.M. Bancroft and L.A. Boatner. "Surface Reactions of Synthetic, End Member Analogues of Monazite, Xenotime, and Rhabiophane, and Evolution of Natural Waters," Geochim. Cosmochim. Acta 52:767-770 (1988).

Jurinak, J.J. and N. Bauer. "Thermodynamics of Zinc Adsorption on Calcite, Dolomite, and Magnesite Type Minerals," Soil Sci. Soc. Am. Proc. 20:466-471 (1956).

Keeney-Kennicutt, W.L. and J.W. Morse. "The Interaction of $Np(V)O_2^+$ with Common Mineral Surfaces in Dilute Aqueous Solutions and Seawater." Marine Chem. 15:133-150 (1984).

Keeney-Kennicutt, W.L. and J.W. Morse. "The Redox Chemistry of $Pu(V)O_2^+$ Interaction with Common Mineral Surfaces in Dilute Aqueous Solutions and Seawater," Geochim. Cosmochim. Acta 49:2477-2588 (1985).

Kent, D.G., V.S. Tripathi, N.B. Ball, J.O. Leckie and M.D. Siegel. "Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments," NUREG/CR-4807, U.S. Nuclear Regulatory Commission, Washington, D.C. (1988).

Kitano, Y., N. Kanamori and S. Yoshioka. "Adsorption of Zinc and Copper Ions on Calcite and Aragonite and Its Influence on the Transformation of Aragonite to Calcite," Geochem. J. 10:175-179 (1976).

Kornicker, W.A., J.W. Morse and R.N. Damasceno. "The Chemistry of Co^{2+} Interaction with Calcite and Aragonite Surfaces," Chem. Geology 53:229-236 (1985).

Kukura, M., L.C. Bell, A.M. Posner, and J.P. Quirk. "Radioisotope Determination of the Surface Concentrations of Calcium and Phosphorous on Hydroxyapatite in Aqueous Solution," J. Phys. Chem. 76:900-904 (1972).

Langmuir, D. "The Geochemistry of Some Carbonate Groundwaters in Central Pennsylvania," Geochim. Cosmochim. Acta 35:1023-1045 (1971).

Lieser, K.H., P.H. Gütlich and I. Rosenbaum. "Die Tempuraturäbhangigkeit des Heterogenen Isotopenaustausches an der Oberfläche von Ionenkristallen," Radiochim. Acta 5:38-42 (1966).

Lin, J., S. Rayhavan and D.W. Fuerstenau. "The Adsorption of Fluoride Ions by Hydroxyapatite from Aqueous Solution," Colloids Surf. 3:357-370 (1981).

Lorens, R.B. "Sr, Cd, Mn, and Co Distribution Coefficients in Calcite as a Function of Calcite Precipitation Rate," Geochim. Cosmochim. Acta 45:553-561 (1981).

Loux, N.T., D.S. Brown, C.R. Chafin, J.D. Allison and S.M. Hassan. "Modeling Geochemical Processes Attenuating Inorganic Contaminant Transport in the Subsurface Region: Adsorption on Amorphous Ion Oxide," Proceedings of the First EPRI-EPA Research Conference. U.S. Environmental Protection Agency and the Electric Power Research Institute, Palo Alto, CA (1989).

Luoma, S.N. and J.A. Davis. "Requirements for Modeling Trace Metal Partitioning in Oxidized Estuarine Sediments," Marine Chem. 12:159-181 (1983).

Lyklema, J. "Discrimination Between Physical and Chemical Adsorption of Ions on Oxides," Colloids Surf. 37:197-204 (1989).

McBride, M.B. "Chemisorption and Precipitation of Mn^{2+} at $CaCO_3$ Surfaces," Soil Sci. Soc. Am. J. 43:693-698 (1979).

McBride, M.B. "Chemisorption of Cd^{2+} on Calcite Surfaces," Soil Sci. Soc. Amer. J. 44:26-28 (1980).

Means, J.L., D.A. Crerar, M. Borcsik and J.O. Duguid. "Adsorption of Co and Selected Actinides by Mn and Fe Oxides in Soils and Sediments," Geochim. Cosmochim. Acta 42:1763-1773 (1978).

Moller, P. "Determination of the Composition of Surface Layers of Calcite in Solutions Containing Mg^{2+}," J. Inorg. Nucl. Chem. 35:395-401 (1973).

Moller, P. and C.S. Sastri. "Estimation of the Number of Surface Layers of Calcite Involved in Ca-^{45}Ca Isotopic Exchange with Solution," Z. Phys. Chem. Neue Folge 84:80-87 (1974).

Moller, P. and G. Werr. "Influence of Anions on Ca^{2+} - Mg^{2+} Surface Exchange Process on Calcite in Artificial Seawater," Radiochim. Acta 18:144-147 (1972).

Morin, K.A., J.A. Cherry, H.K. Dave, T.P. Lin and A.J. Vivurka. "Migration of Acidic Groundwater Seepage from Uranium-Tailings Impoundments. 2. Geochemical Behavior of Radionuclides in Groundwater," J. Contam. Hydrol. 2:305-322 (1988).

Morse, J.W. "The Kinetics of Calcium Carbonate Dissolution and Precipitation," in Carbonates: Mineralogy and Chemistry, R.J. Reeder, Ed. (Mineralogy Society of America, 1983) pp. 227-264.

Mucci, A. and J.W. Morse. "Auger Spectroscopy Determination of the Surface-Most Adsorbed Layer Composition on Aragonite, Calcite, Dolomite and Magnesite in Synthetic Seawater," Amer. J. Sci. 285-306-317 (1985).

Mucci, A., J.W. Morse and M.S. Kaminsky. "Auger Spectroscopy Analysis of Magnesian Calcite Overgrowths Precipitated from Seawater and Solutions of Similar Composition," Am. J. Sci. 285:289-305 (1985).

Neal, R.H., G. Sposito, K.M. Holtzclaw and S.J. Traina. "Selenite Adsorption on Alluvial Soils: I. Soil Composition and pH Effects," Soil Sci. Soc. Am. J. 51:1161-1165 (1987).

Nelson, D.K., K.A. Orlandini and W.R. Penrose. "Oxidation States of Plutonium in Carbonate-Rich Natural Waters," J. Environ. Radioactivity 9:189-198 (1989).

Papadopoulos, P. and D.L. Rowell. "The Reactions of Cadmium with Calcium Carbonate Surfaces," J. Soil Sci. 39:23-36 (1988).

Parks, G.A. "Adsorption in the Marine Environment," in Chemical Oceanography, J.P. Riley and G. Skirrow, Eds. (Vol. 1, New York: Academic Press, 1975), pp. 241-308.

Pate, F.D., J.T. Hutton and K Morrish. "Ionic Exchange Between Soil Solutions and Bone: Toward a Predictive Model," Appl. Geochem. 4:303-316 (1989).

Plummer, L.N. "Defining Reactions and Mass Transfer in Part of the Floridian Aquifer," Water Resour. Res. 13:801-812 (1977).

Reddy, M.M. "Crystallization of Calcium Carbonate in the Presence of Trace Concentrations of Phosphorous Containing Anions. I. Inhibition of Phosphate and Glycerophosphate Ions at pH 8.8 and 25°C," J. Crystal Growth 41:287-295 (1977).

Ryan, J., D. Curtin and M.A. Cheema. "Significance of Iron Oxides and Calcium Carbonate Particle Size in Phosphate Sorption by Calcareous Soils," Soil Sci. Soc. Am. J. 48:74-76 (1984).

Sastri, C.S. and P. Moller. "Study of the Influence of Mg^{2+} Ions on Ca-^{45}Ca Isotopic Exchange on the Surface Layers of Calcite Single Crystals," Chem. Phys. Lett. 26:116-120 (1974).

Siffert, B. and P. Fimbel. "Parameters Effecting the Sign and Magnitude of the Electrokinetic Potential of Calcite," Colloids Surf. 11:377-389 (1984).

Somasundaran, P. and G.E. Agar. "The Zero Point of Charge of Calcite," J. Colloid Interface Sci. 24:433-440 (1967).

Sposito, G. The Thermodynamics of Soil Solutions. (Oxford, Oxford University Press, 1981).

Sposito, G. The Surface Chemistry of Soils. (Oxford, Clarendon Press, 1984).

Stollenwerk, K.G. and D.B. Grove. "Adsorption and Desorption of Hexavalent Chromium in an Alluvial Aquifer near Telluride, Colorado," J. Environ. Qual. 14:150-155 (1985).

Thompson, D.W. and P.G. Pownall. "Surface Electrical Properties of Calcite," J. Colloid Interface Sci. 131:74-82 (1989).

Thorstenson, D.C., D.W. Fisher and M.G. Croft. "The Geochemistry of the Fox Hills-Basal Hell Creek Aquifer in Southwestern North Dakota and Northwestern South Dakota," Water Resour. Res. 15:1479-1498 (1979).

Toran, L. "Sulfate Contamination in Groundwater from a Carbonate-Hosted Mine," J. Contam. Hydrol. 2:1-29 (1987).

Truesdell, A.H. and B.F. Jones. "WATEQ, a Computer Program for Calculating Chemical Equilibria of Natural Waters," J. Res. U.S. Geol. Survey 2:233-248 (1974).

Walter, L.M. and E.A. Burton. "The Effect of Orthophosphate on Carbonate Mineral Dissolution Rates in Seawater," Chem. Geol. 56:313-323 (1986).

Westall, J. "FITEQL, a Computer Program for Determination of Equilibrium Constants from Experimental Data. Version 1.2," Report 82-01, Department of Chemistry, Oregon State University, Corvallis, Oregon (1982a).

Westall, J. "FITEQL, a Computer Program for Determinatio of Equilibrium Constants from Experimental Data. Version 2.0," Report 82-02, Department of Chemistry, Oregon State University, Corvallis, Oregon (1982b).

Wood, W.W. and W.H. Low. "Solute Geochemistry of the Snake River Plain Regional Aquifer System, Idaho and Eastern Oregon," U.S. Geological Survey Professional Paper 1408-D (1988).

Yanful, E.K., H.W. Nesbitt and R.M. Quigley. "Heavy Metal Migration at a Landfill Site, Sarnia, Ontario, Canada. 1. Thermodynamic Assessment and Chemical Interpretations," Appl. Geochem. 3:523-534 (1988a).

Yanful, E.K., R.M. Quigley and H.W. Nesbitt. "Heavy Metal Migration at a Landfill Site, Sarnia, Ontario, Canada. 2. Metal partitioning and Geotechnical Implications," Appl. Geochem. 3:623-631 (1988b).

Zachara, J.M. "A Solution Chemistry and Electron Spectroscopic Study of Zinc Adsorption and Precipitation on Calcite," Ph.D. Dissertation, Washington State University (1988).

Zachara, J.M., J.A. Kittrick and J.B. Harsh. "The Mechanism of Zn^{2+} Adsorption on Calcite," Geochim. Cosmochim. Acta 52:2281-2291 (1988).

Zachara, J.M., J.A. Kittrick, L.S. Dake and J.B. Harsh. "Solubility and Surface Spectroscopy of Zinc Precipitates on Calcite," Geochim. Cosmochim. Acta 53:9-19 (1989).

Zachara, J.M., C.E. Cowan and C.T. Resch. "Surface Exchange and Precipitation of Divalent Metallic Cations on Calcite," Geochim. Cosmochim. Acta (Submitted, 1990a).

Zachara et al. "Sorption of Cd on Na-saturated Specimen and Natural Smectite: Selectivity Differences and Exchange Modelling," Soil Sci. Soc. Am. J. (Submitted, 1990b).

Zachara, J.M., C.E. Cowan and C.T. Resch. "Cadmium Exchange Sorption on Specimen and Natural Smectite in Ca and Mixed Electrolyte Solutions," Soil Sci. Soc. Am. J. (Submitted, 1990c).

Zirano, A. and S. Yamamoto. "A pH Dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium, and Lead in Seawater," Limnol. Oceanogr. 17:661-671 (1972).

TABLE 1. Metal Cation and Anion Sorption on Calcite.

Sorbate	Reference
Cations	
Ba^{2+}	Bancroft et al. (1977) Zachara et al. (1990a)
Cd^{2+}	McBride (1980) Davis et al. (1987) Papadopoulas and Rowell (1988) Zachara et al. (1990a)
Co^{2+}	Kornicker et al. (1985) Zachara et al. (1990a)
Cu^{2+}	Kitano et al. (1976) Franklin and Morse (1982)
Mg^{2+}	Moller (1973) Moller and Werr (1972) Mucci et al. (1985) Sastri and Moller (1974)
Mn^{2+}	McBride (1979) Franklin and Morse (1983) Zachara et al. (1990a)
Ni^{2+}	Zachara et al. (1990a)
$Np(V)O_2^{+}$	Keeney-Kennicutt and Morse (1984)
$Pu(V)O_2^{+}$	Keeney-Kennicutt and Morse (1985)
Pu^{2+}	Nelson et al. (1989)
Sr^{2+}	Zachara et al. (1990a)
Zn^{2+}	Jurinak and Bauer (1956) Kitano et al. (1976) Zachara et al. (1988) Zachara et al. (1990a)
Anions	
PO_4^{3-}	Cole et al. (1953) DeKanel and Morse (1978) House and Donaldson (1986)
SeO_3^{2-}	Goldberg and Glaubig (1988a) Cowan et al. (1990a)

TABLE 2. Aqueous Speciation Reactions with Associated Equilibrium Constants for Ca and Zn Experiments.

Reaction	log Kr
Ca	
$H_2O \leftrightarrow H^+ + OH^-$	-14.0[a]
$Ca^{2+} + H_2O \leftrightarrow CaOH^+ + H^+$	-12.6[a]
$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3^0$	3.15[b]
$Ca^{2+} + H^+ + CO_3^{2-} \leftrightarrow CaHCO_3^+$	11.3[b]
$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$	10.3[b]
$2H^+ + CO_3^{2-} \leftrightarrow H_2CO_3^0$	16.65[b]
$Na^+ + H^+ + CO_3^{2-} \leftrightarrow NaHCO_3^0$	10.08[a]
$Na^+ + CO_3^{2-} \leftrightarrow NaCO_3^-$	1.26[a]
Zinc	
$Zn^{2+} + H_2O \leftrightarrow ZnOH^+ + H^+$	-8.96[a]
$Zn^{2+} + 2H_2O \leftrightarrow Zn(OH)_2^0 + 2H^+$	-16.9[a]
$Zn^{2+} + 3H_2O \leftrightarrow Zn(OH)_3^- + 3H^+$	-28.4[a]
$Zn^{2+} + 4H_2O \leftrightarrow Zn(OH)_4^{2-} + 4H^+$	-41.4[a]
$Zn^{2+} + H^+ + CO_3^{2-} \leftrightarrow ZnHCO_3^+$	12.4[c]
$Zn^{2+} + CO_3^{2-} \leftrightarrow ZnCO_3^0$	4.76[d]

(a) Truesdell and Jones (1974)
(b) Ball et al. (1980)
(c) Zirano and Yamamoto (1972)
(d) Bilinski et al. (1976)

TABLE 3. Half-Exchange Reactions for Anionic Metal Exchange Model on the Calcite Surface and Fitted Constants. Source: Cowan et al. (1990a).

Reaction	log $^{*}K^{(a)}$	log $K^{(b)}$
$CO_3^{2-} + X' = X'\text{-}CO_3$	12.5	12.5
$H^+ + CO_3^{2-} + X' = X'\text{-}HCO_3$	27.06	16.76
$SeO_3^{2-} + X' = X'\text{-}SeO_3$	16.70	16.70
$H^+ + SeO_3^{2-} + X' = X'\text{-}HSeO_3$	24.96	16.92
$Ca^{2+} + H^+ + PO_4^{3-} + X' = X'\text{-}CaHPO_4$	32.34	17.26
$PO_4^{3-} + X' = X'\text{-}PO_4$	20.79	20.79

(a) The exchange constant for the half-exchange reaction in the first column with the anion exchange site, X'.
(b) The exchange constant with the effect of the complexation of the anion removed.

TABLE 4. Adsorption and Exchange Reactions with Constants for Modeling Adsorption of Cd on Aquifer Material.

Reaction	log K
Calcite	
$Cd^{2+} + CaX = X\text{-}Cd + Ca^{2+}$	-3.02(a)
$Fe_2O_3 \cdot H_2O$	
$SOH + H^+ \leftrightarrow SOH_2^+$	4.7(b)
$SOH \leftrightarrow SO^- + H^+$	-10.3(b)
$Cd^{2+} + SOH \leftrightarrow SO^-\text{-}Cd^{2+} + H^+$	-3.0(b)
$Ca^{2+} + SOH \leftrightarrow SO^-\text{-}Ca^{2+} + H^+$	-7.1(b)
$Na^+ + SOH \leftrightarrow SO^-\text{-}Na^+ + H^+$	-9.1(b)
Smectite	
$Cd^{2+} + CaZ_2 = CdZ_2 + Ca^{2+}$	-0.5(c)
$2CdOH^+ + CaZ_2 = 2CdOHZ + Ca^{2+}$	7.08(c)
$2Na^+ + CaZ_2 = 2NaZ + Cd^{2+}$	-3.62(c)

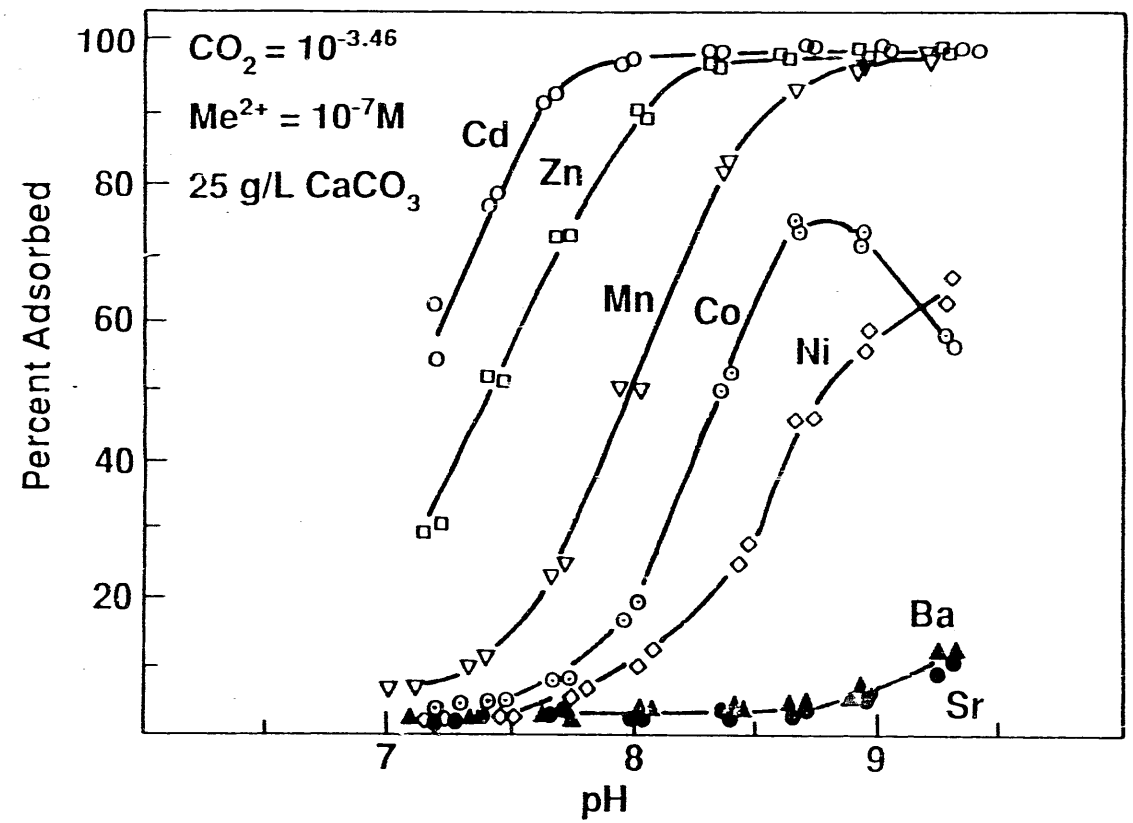
(a) Zachara et al. (1990a)
(b) Cowan et al. (1990b)
(c) Cowan et al. (1990c) and Zachara et al. (1990b)

TABLE 5. Composition of $CaCO_3$(aq) Solutions.

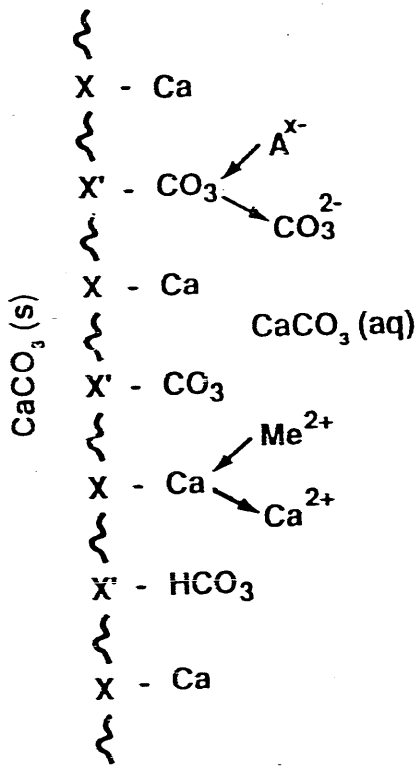
pH	Ca	Na	DIC	ClO_4	K	Mg	Si	Sr
	(mol/L)							
7.25	7.11E-2	5.87E-6	2.67E-4	1.29E-1	6.4E-5	6.58E-4	1.17E-4	4.0E-6
7.48	2.19E-2	6.35E-2	3.71E-4	9.59E-2	3.3E-5	2.01E-4	9.6E-5	1.4E-6
7.71	7.14E-3	8.57E-2	6.05E-4	9.53E-2	3.1E-5	7.0E-5	3.6E-5	4.3E-7
7.98	1.75E-3	9.44E-2	1.15E-3	8.61E-2	3.8E-5	9.9E-6	2.0E-5	1.4E-7
8.40	3.14E-4	9.35E-2	2.68E-3	8.58E-2	2.2E-5	BD(a)	2.6E-6	6.0E-8
8.60	8.21E-5	9.66E-2	5.39E-3	8.21E-2	2.6E-5	BD	2.0E-6	BD
8.88	3.27E-5	9.92E-2	1.03E-2	7.95E-2	3.3E-5	5.8E-6	3.6E-6	6.0E-8
9.22	1.21E-5	1.06E-1	2.25E-2	7.36E-2	2.6E-5	BD	3.2E-6	6.0E-8

(a) BD = below detection.

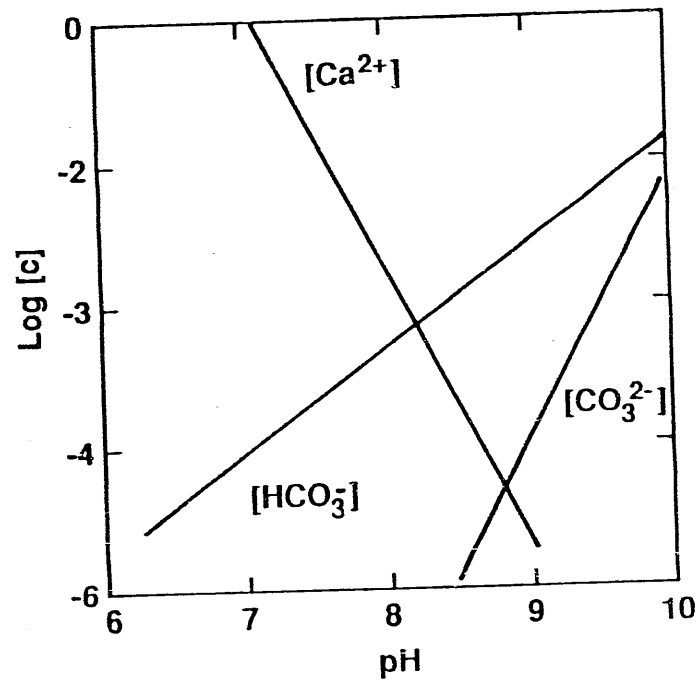
List of Figures:

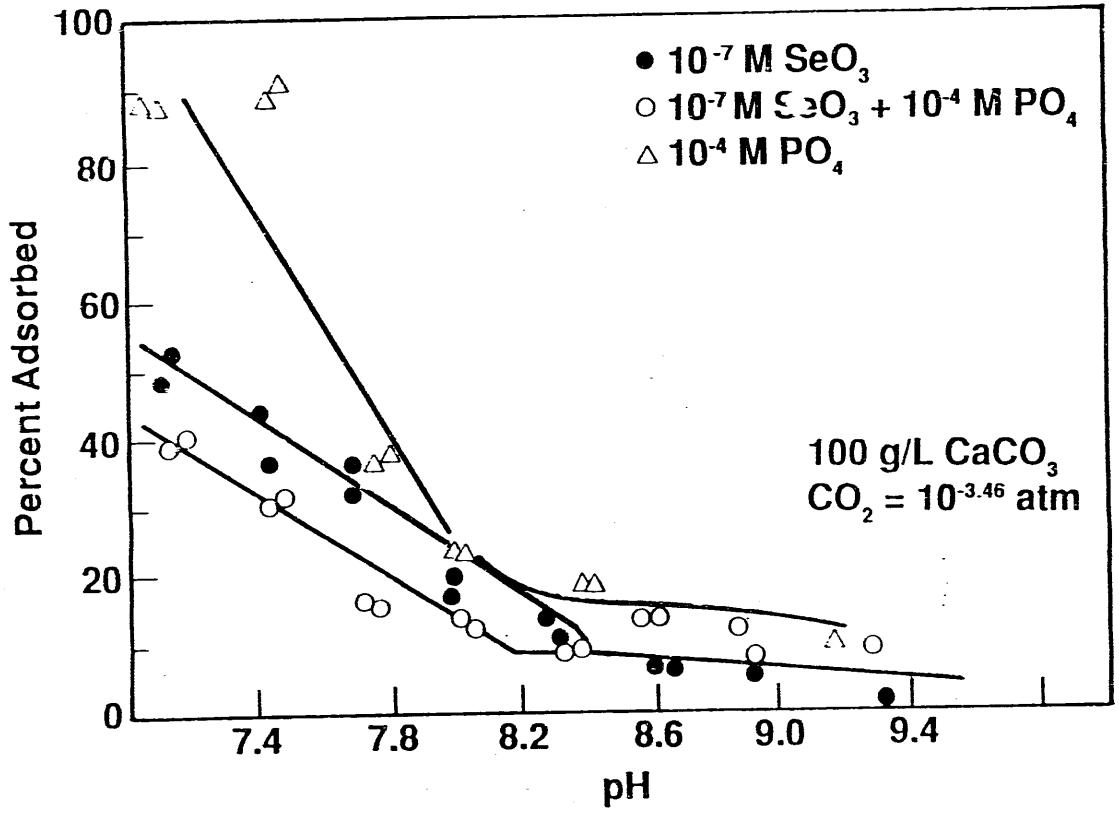

$CO_2 = 10^{-3.46}$
$Me^{2+} = 10^{-7}M$
25 g/L $CaCO_3$
Cd
Zn
Mn
Co
Ni
Ba
Sr
Percent Adsorbed
100
80
60
40
20
7
8
9
pH

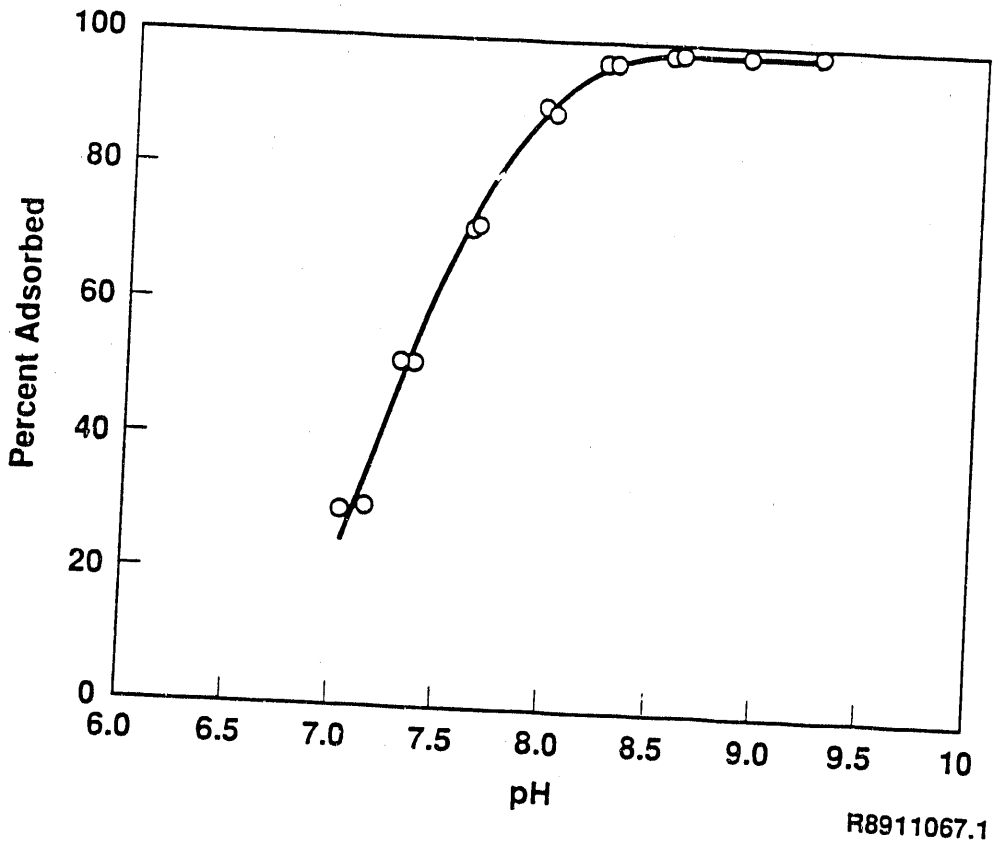
Surface Exchange

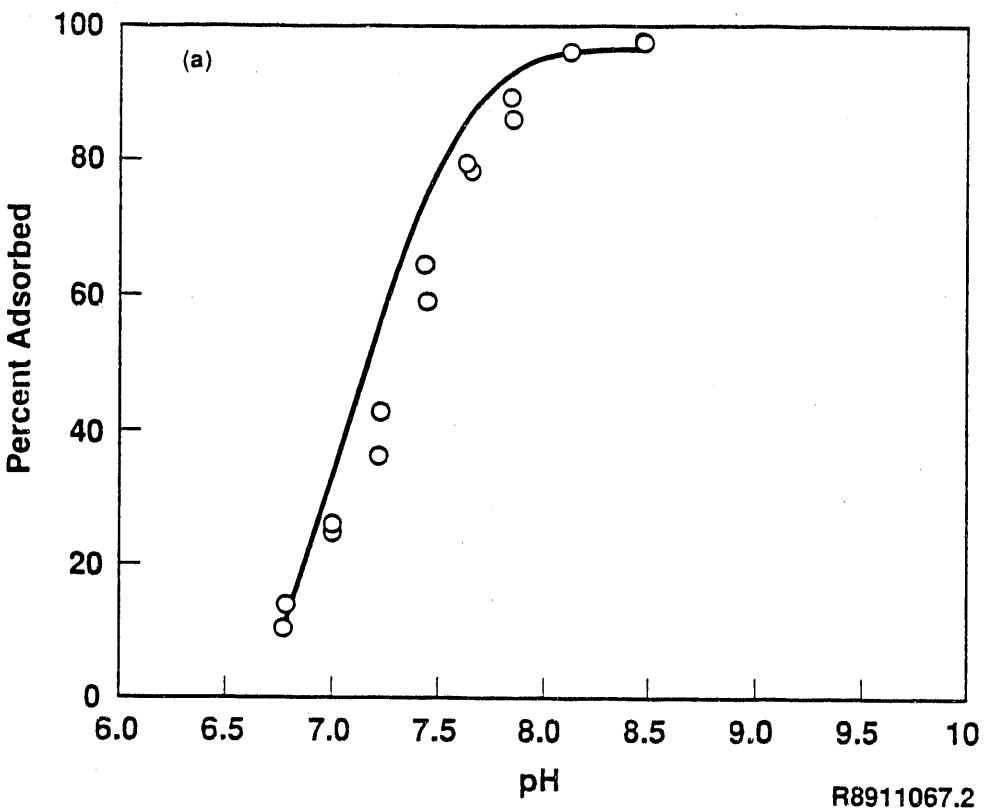


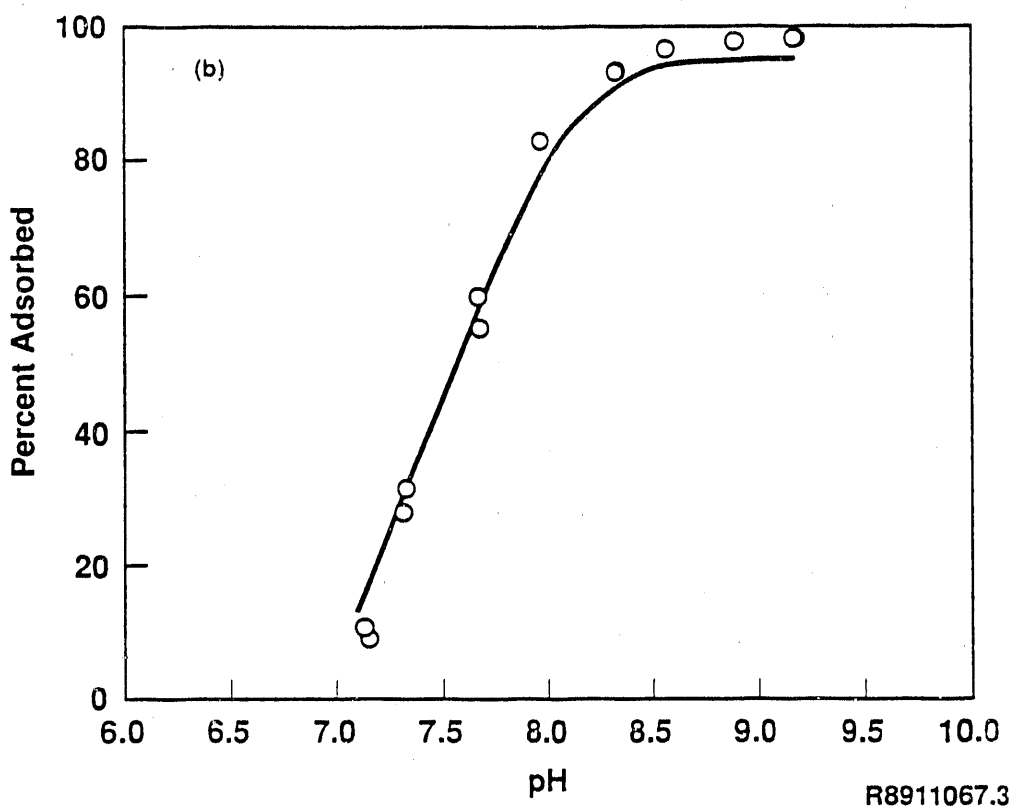
Solubility of $CaCO_3$ (s) $pCO_2 = 10^{-3.5}$ atm

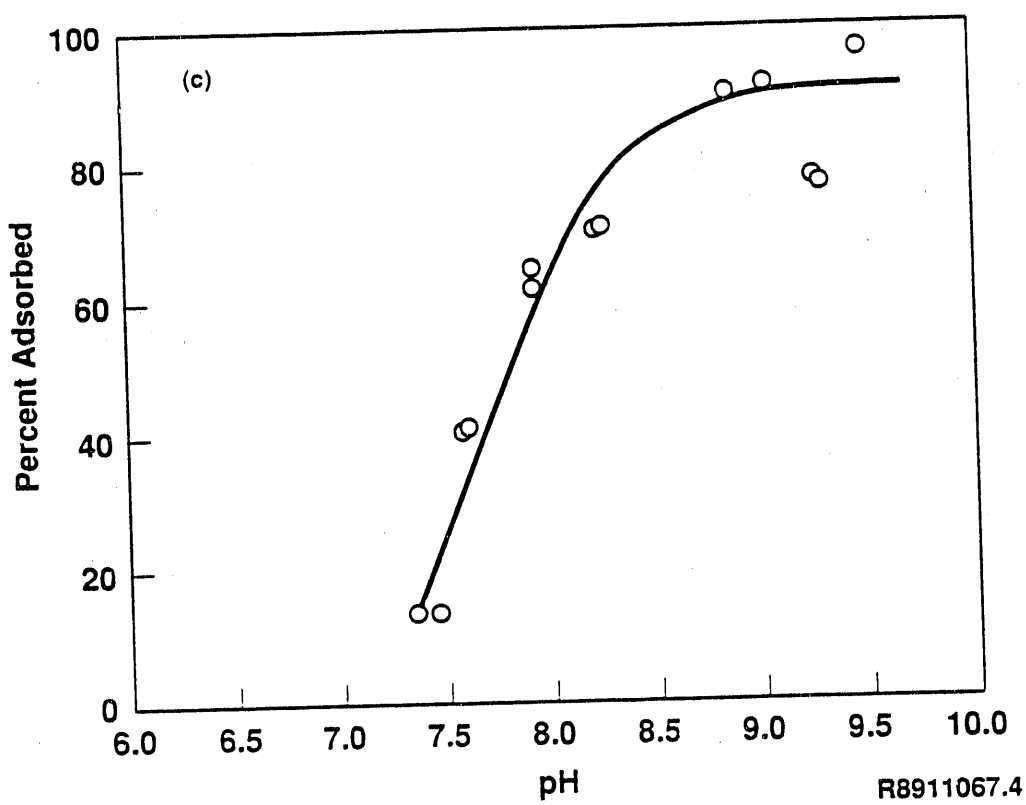


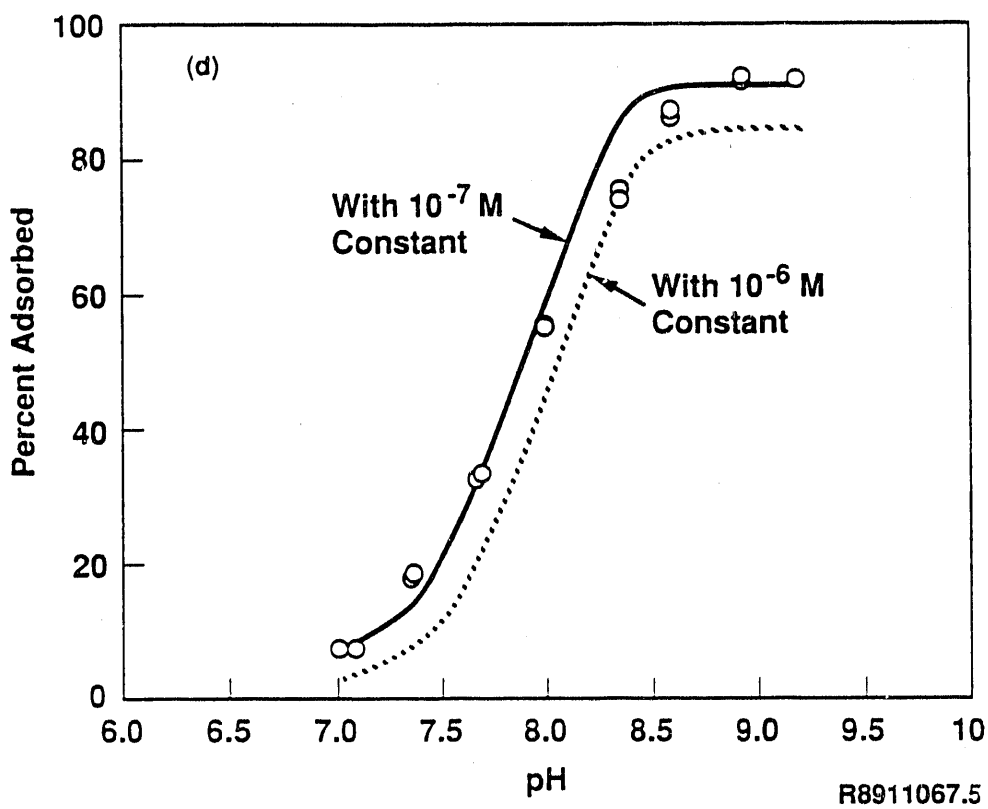

100
80
60
40
20
0
Percent Adsorbed
7.4
7.8
8.2
8.6
9.0
9.4
pH
● 10^{-7} M SeO_3
○ 10^{-7} M SeO_3 + 10^{-4} M PO_4
△ 10^{-4} M PO_4
100 g/L $CaCO_3$
$CO_2 = 10^{-3.46}$ atm

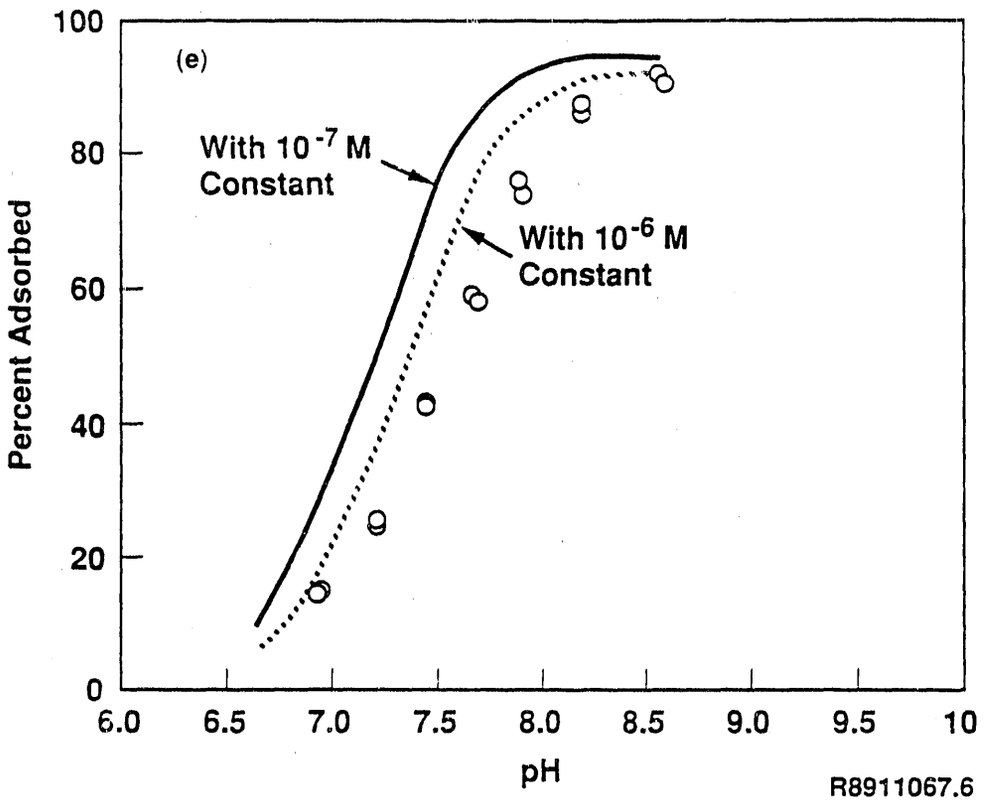

100
80
60
40
20
0
Percent Adsorbed
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10
pH
R8911067.1

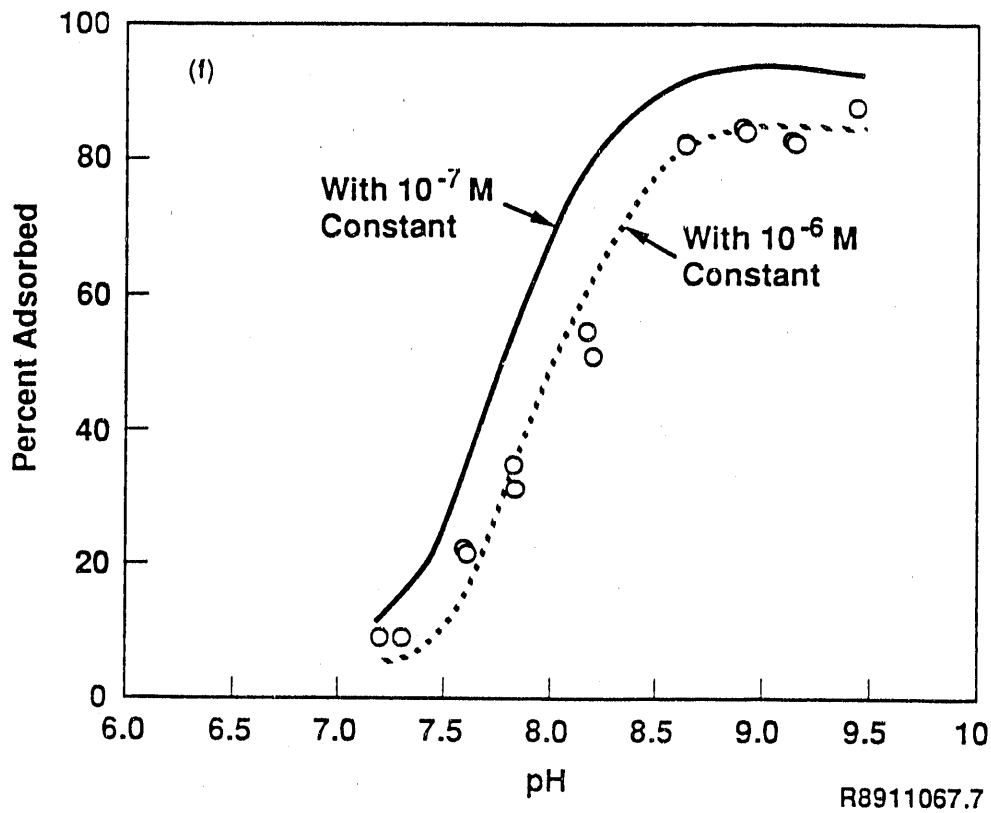

(a)
Percent Adsorbed
100
80
60
40
20
0
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10
pH
R8911067.2

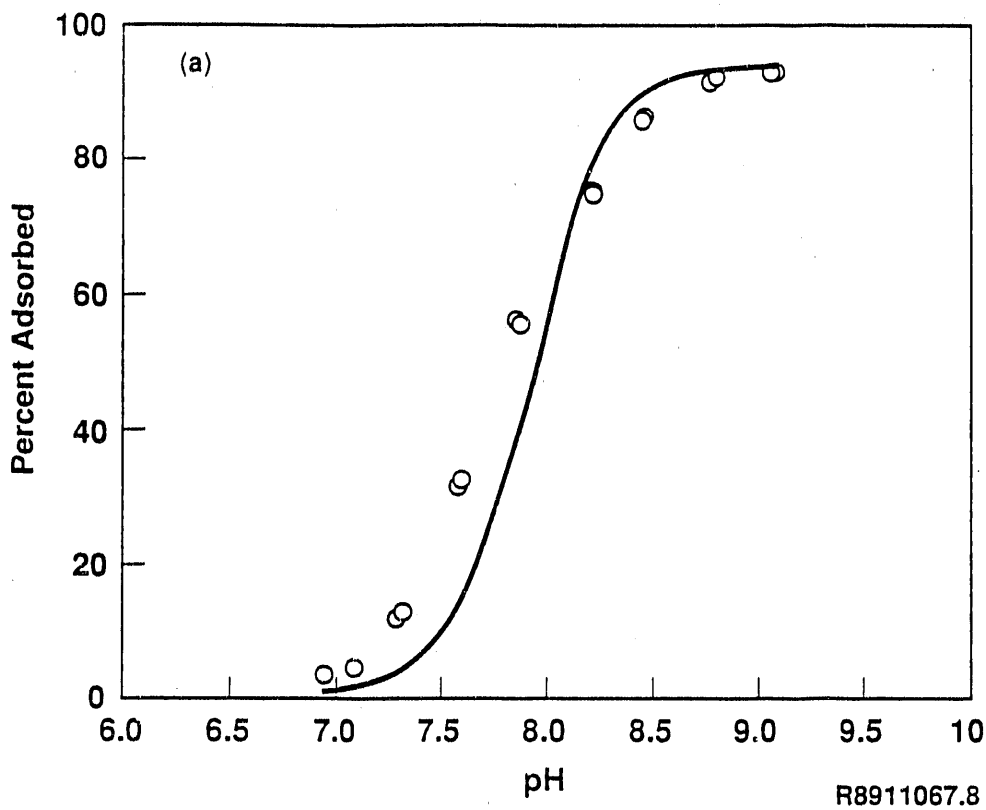

(b)
100
80
60
40
20
0
Percent Adsorbed
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
pH
R8911067.3

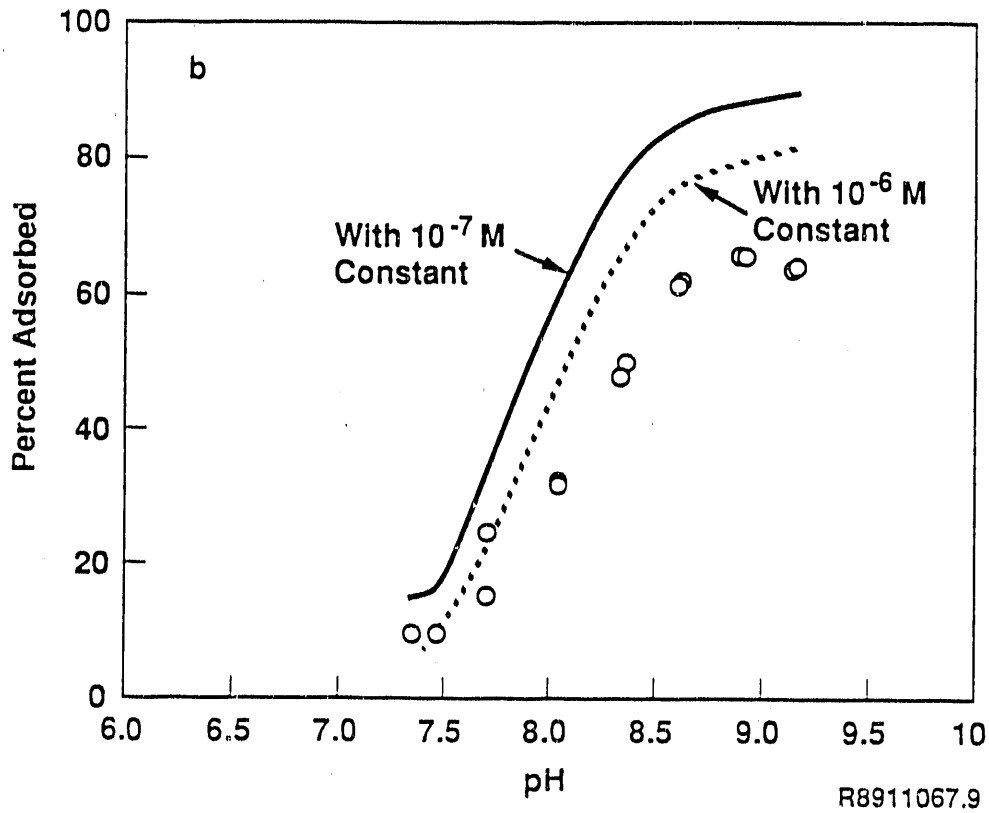

(c)
100
80
60
40
20
0
Percent Adsorbed
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
pH
R8911067.4

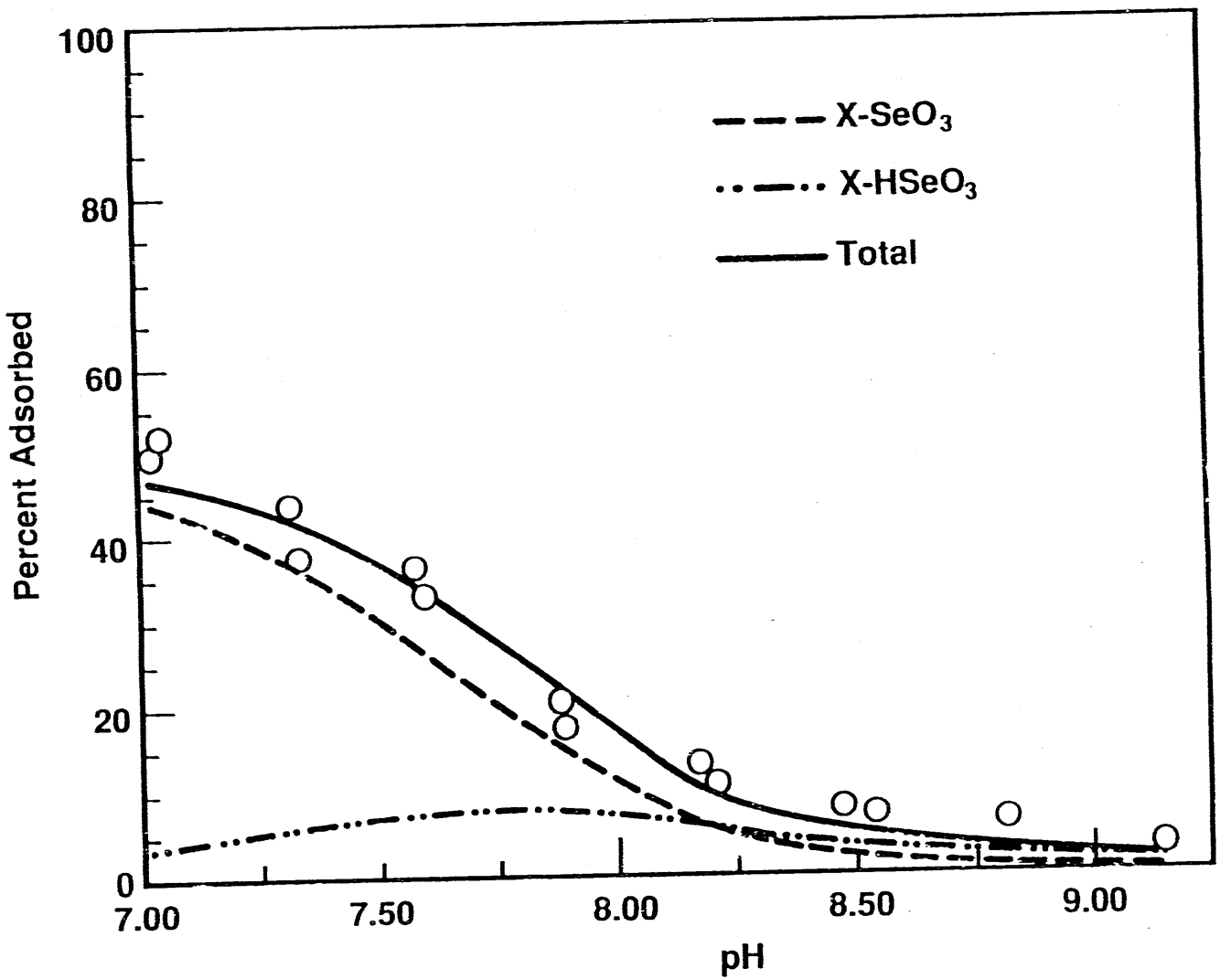

(d)
100
80
60
40
20
0
Percent Adsorbed
With 10-7 M
Constant
With 10-6 M
Constant
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10
pH
R8911067.5

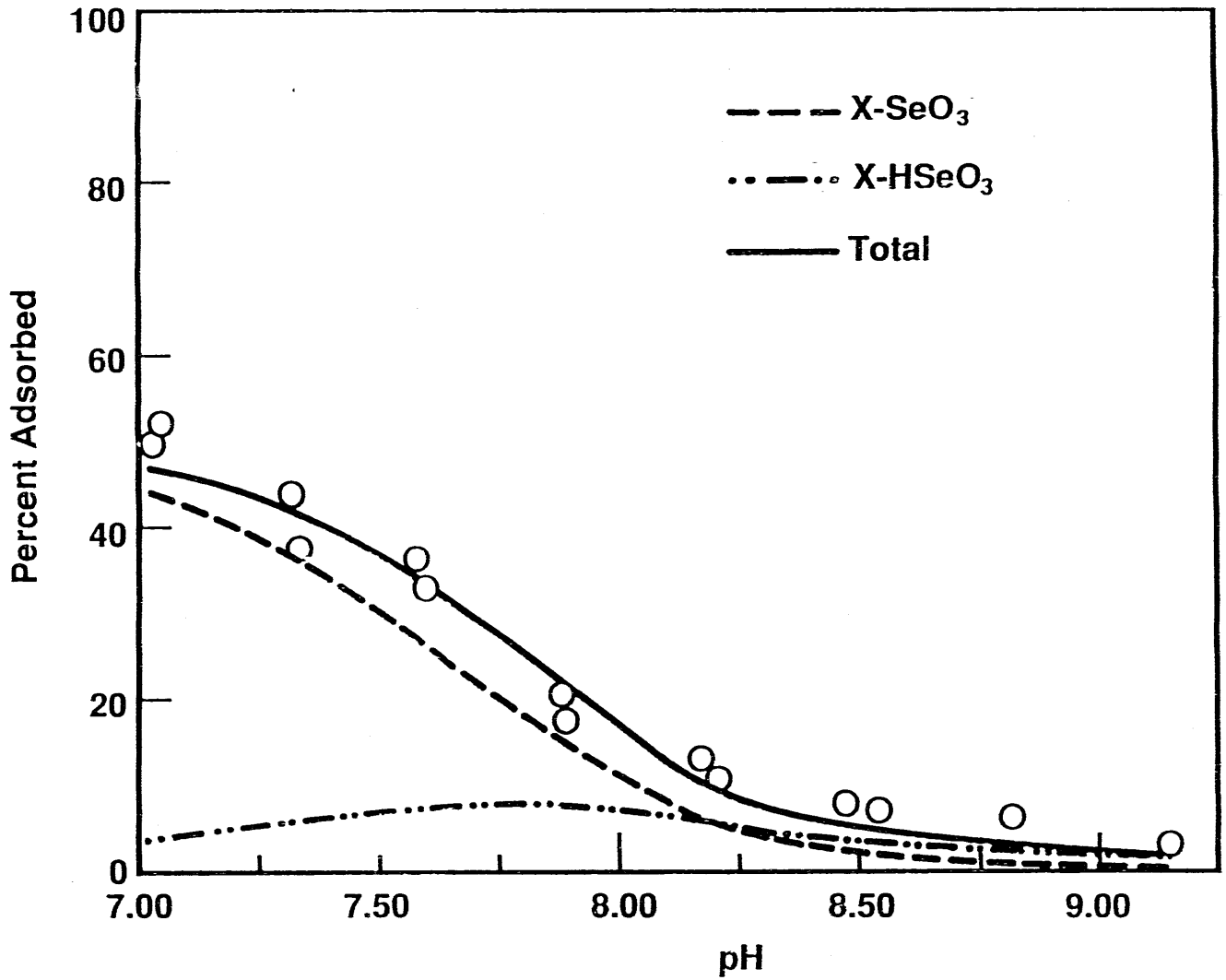

(e)
With 10^{-7} M Constant
With 10^{-6} M Constant
Percent Adsorbed
100
80
60
40
20
0
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10
pH
R8911067.6


100
80
60
40
20
0
(f)
With 10^{-7} M Constant
With 10^{-6} M Constant
Percent Adsorbed
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10
pH
R8911067.7

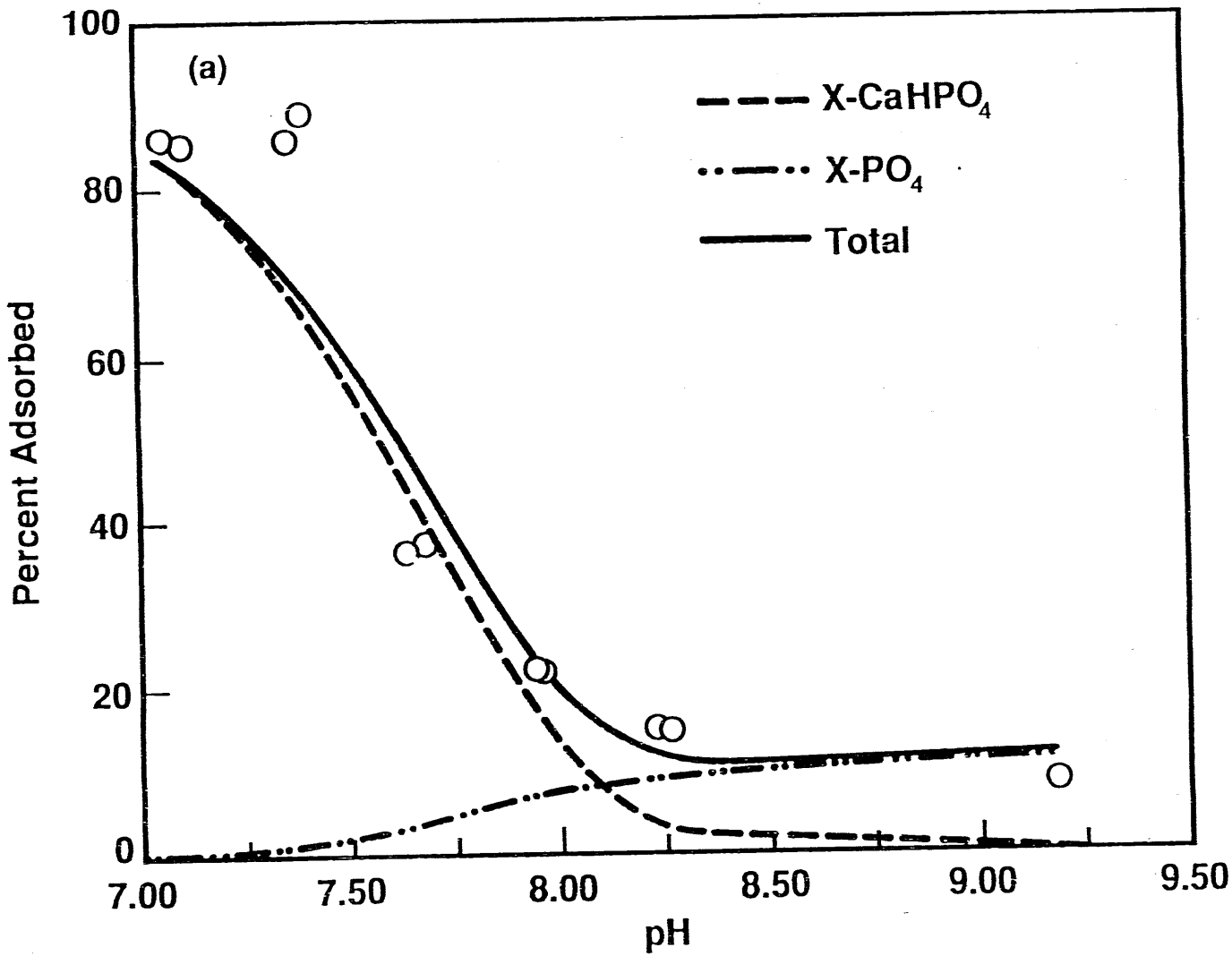

(a)
Percent Adsorbed
100
80
60
40
20
0
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10
pH
R8911067.8


b
100
80
60
40
20
0
Percent Adsorbed
With 10-7 M
Constant
With 10-6 M
Constant
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10
pH
R8911067.9

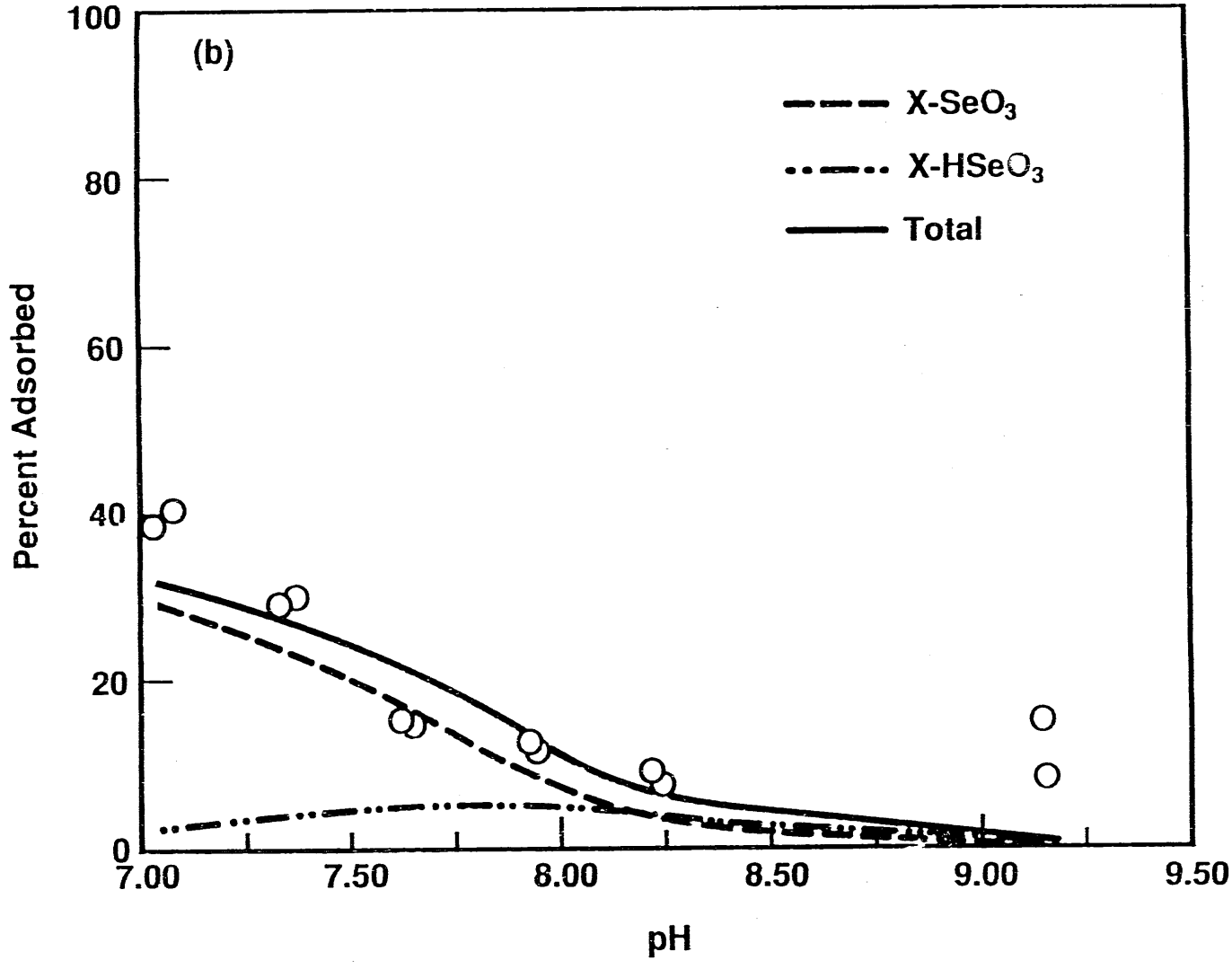

100
80
60
40
20
0
Percent Adsorbed
X-SeO3
X-HSeO3
Total
7.00
7.50
8.00
8.50
9.00
pH


100
80
60
40
20
0
Percent Adsorbed
X-SeO3
X-HSeO3
Total
7.00
7.50
8.00
8.50
9.00
pH

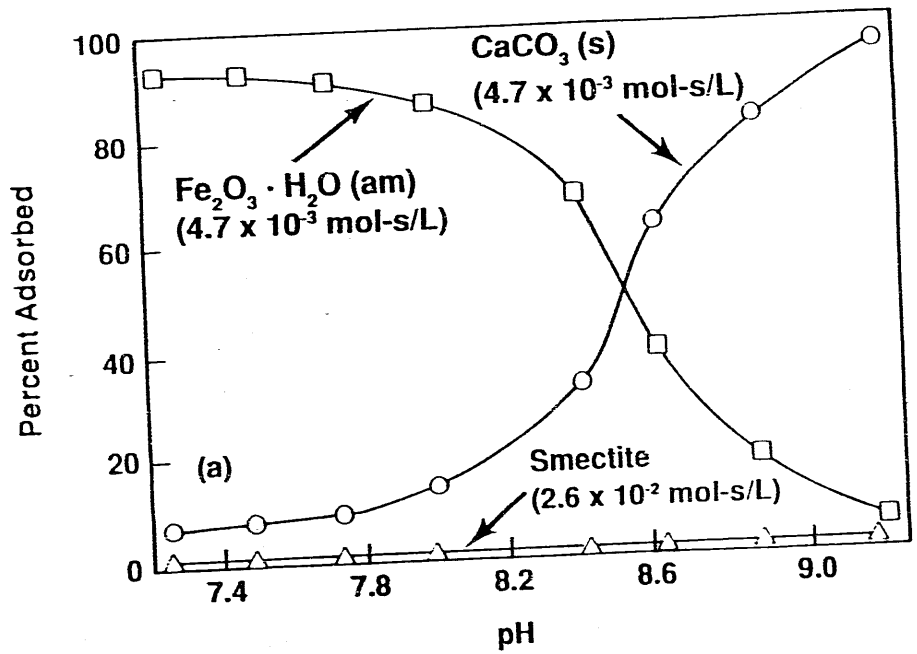
S8905039.5a

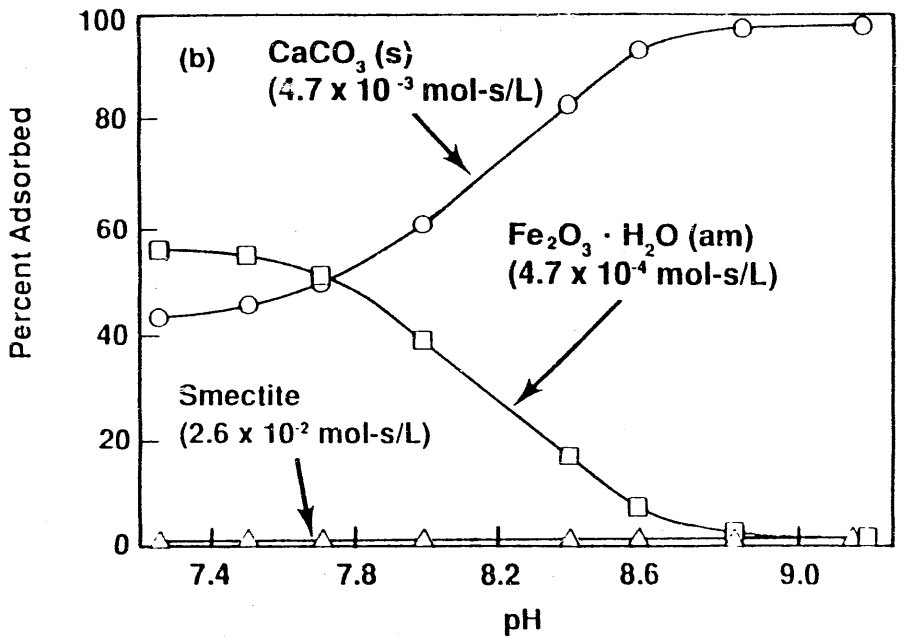

(a)
X-CaHPO4
X-PO4
Total
Percent Adsorbed
100
80
60
40
20
0
7.00
7.50
8.00
8.50
9.00
9.50
pH

S8905039.2a


(b)
X-SeO3
X-HSeO3
Total
Percent Adsorbed
100
80
60
40
20
0
7.00
7.50
8.00
8.50
9.00
9.50
pH

S8905039.4a


100
80
60
40
20
0
Percent Adsorbed
$CaCO_3$ (s)
(4.7×10^{-3} mol-s/L)
$Fe_2O_3 \cdot H_2O$ (am)
(4.7×10^{-3} mol-s/L)
(a)
Smectite
(2.6×10^{-2} mol-s/L)
7.4
7.8
8.2
8.6
9.0
pH


(b)
$CaCO_3$ (s)
(4.7×10^{-3} mol-s/L)
$Fe_2O_3 \cdot H_2O$ (am)
(4.7×10^{-4} mol-s/L)
Smectite
(2.6×10^{-2} mol-s/L)
Percent Adsorbed
100
80
60
40
20
0
7.4
7.8
8.2
8.6
9.0
pH

END

DATE FILMED

02 / 13 / 91