Sorption Studies of Cd²⁺ on Calcite: Kinetics and Reversibility

방해석의 Cd²⁺ 흡착현상에 대한 연구

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ABSTRACT : The sorption of Cd²⁺ on calcite was studied in aqueous solutions of several electrolytes. The Cd²⁺ concentration, 10^{-8} M, was kept well below saturation with respect to CdCO₃(s). Sorption behavior of Cd²⁺ in different ionic strengths of NaClO₄ solutions shows that sorption is independent of ionic strength. This result suggests that Cd²⁺ sorption on calcite surface is of a specific nature, and adsorption is controlled by an inner-sphere type of surface complex. Two stages in the sorption behavior could be identified: an initial rapid uptake, followed by slower uptake reaching a maximum steady state by 145 hrs. No evidence was observed for surface precipitation, although it can not be entirely ruled out. Desorption of Cd²⁺ from the calcite surface after resuspension into Cd-free solution is initially very rapid, but depends partly on the previous sorption history. Desorption behavior of Cd²⁺ show that an initial rapid desorption followed either by slow uptake reaching a maximum, as in the adsorption experiments, or slowing desorption to reach a steady state minimum. This irreversible behavior of Cd²⁺ sorption and desorption may act as one of the controls for regulating the mobility of dissolved Cd²⁺ in natural aqueous systems. Calculated adsorption partition coefficients suggest that overall sorption and desorption process in the concentration range are controlled by a single mechanism.

Key words : calcite, sorption, ^{109}Cd, electrolytes, NaClO₄. desorption

요약 : 방해석 표면에 의한 Cd²⁺의 흡착연구를 하였다. 흡착실험에서 사용한 Cd의 농도는 10^{-8}M 로서 CdCO₃(s)의 침전농도 보다 낮은 농도를 유지하도록 조절하였다. NaClO₄를 전해질로 사용하여 이온농도 를 달리 한 실험 결과 Cd²⁺의 흡착은 용액의 이온세기와는 무관한 것으로 나타났다. 이는 Cd²⁺의 방해석 표면 흡착이 특징적인 성질을 갖고 inner sphere surface complex를 형성한다는 것을 암시한다. 흡착반응 은 초기의 매우 빠른 흡착시기와 후기의 지속적인 느린 흡착시기의 2단계로 구분되었다. 특히, 후기의 느 린 흡착시기에는 약 145시간 경과 후 최대정상상태 (steady state maximum)에 도달하였다. 본 연구에서 사용한 Cd²⁺의 농도가 낮아 방해석 표면에 CdCO₃(s)의 침전 형성에 의한 반응은 고려되지 않았다. 방해 석 표면으로부터 Cd²⁺의 탈착반응은 일정시간의 흡착 반응이 경과된 후 초기 흡착 실험 시와 같은 농도 의 과포화 용액을 사용하여 Cd²⁺을 흡착한 방해석이 새로운 용액에 재 평형을 이루도록 반응을 유도하였 다. 일반적으로 탈착실험에서는 새로운 과포화용액에 방해석을 넣자마자 매우 빠른 탈착반응을 보여준다. 그 이후는 2가지의 다른 경향성을 보여주며 새로운 평형에 도달하는 것으로 나타난다. 초기의 빠른 탈착 반응 시기 뒤 느린 흡착반응이 지속적으로 일어나 일정 시간 경과 후 다시 평형을 이루거나, 느린 탈착반

응이 계속적으로 지속되어 일정 시간 경과 후 새로운 평형을 이루는 2가지로 나타났다. 이러한 부분적으로 비가역적인 흡착 반응과 탈착반응은 실제 자연계에서 Cd^{2+}의 유동성을 결정짓는 매우 중요한 인자로 작용할 것으로 생각된다. 흡착 반응 및 탈착반응의 평형상수 값은 이들 반응이 서로 동일한 기작에 의하여 조절됨을 보여주었다.

주요어 : 방해석, 흡착반응, ^{109}Cd, 전해질용액, $NaClO_4$, 탈착반응

Introduction

Within aqueous systems, the fate of dissolved metal ions is strongly influenced by interactions with mineral surfaces. The removal of trace metals by solids is known as sorption. These sorption processes include adsorption, surface precipitation, and incorporation into the minerals (Sposito, 1986). Sorption and subsequent incorporation into carbonate minerals control the mobility and concentration of dissolved metal species in carbonate aquifers and in other systems.

Calcite, $CaCO_3$, is one of the most abundant minerals present in the Earth's hydrosphere. Its important role in regulating the concentrations of dissolved trace metals, such as Cd^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+} and Fe^{2+} in natural aqueous systems has been noted by many researchers (Curti, 1999; Davis et al., 1987; Fuller and Davis, 1987; McBride, 1980; Morse, 1986; Stumm and Morgan, 1996; Zachara et al., 1989, 1991). There have been numerous studies investigating sorption of divalent metal ions on calcite surfaces (Comans et al., 1991; Cowan et al., 1990; Davis et al., 1987; Dromgoole and Walter, 1990; Lorens, 1981; McBride, 1979, 1980; Morse et al., 1979; Zachara et. al., 1988, 1989, 1991; Watson, 1996). Metal sorption onto calcite has often been described as a two-step process: an initial rapid uptake, followed by a slow uptake. The initial rapid uptake generally occurs within the first 24 hrs, while in the second step metal sorption may continue slowly for several days (Morse, 1986).

Although sorption studies of Cd^{2+} onto calcite (Davis et al. 1987; Fuller and Davis, 1987) provided a better understanding of sorption behavior, the use of a complexing ligand

(EDTA) introduced additional complications, especially in solutions with low aqueous Cd^{2+} concentrations. Furthermore, Cd^{2+} sorption has usually been studied at high initial Cd^{2+} concentrations where precipitation of $CdCO_3$ could not be ruled out (McBride, 1979, 1980). The available data for Cd^{2+} sorption at high calcite loading do not show saturation of calcite surface sites, but indicate somewhat lower surface partitioning compared to sorption of Cd^{2+} of lower calcite loadings (Davis et al., 1987). An understanding of trace metal sorption reactions on calcite is required to predict geochemical behavior in calcareous environments. The kinetics of sorption and the reversibility of sorbed trace metals on calcite are poorly understood. The behavior of sorbed Cd^{2+} in different ionic strengths is also not clearly identified.

The purpose of this study is to examine the sorption behavior of one of these dissolved trace metals, Cd^{2+} onto calcite. We investigate the kinetics of Cd^{2+} sorption on calcite, and the effect of ionic strength in calcite suspensions of various electrolyte solutions. This study examined the possibility of separation of adsorption from surface precipitation, and the attainment of adsorption equilibrium. In order to resolve adsorption, surface precipitation, and incorporation in these experiments, the Cd^{2+} concentrations were maintained below saturation with respect to Cd-rich solid phases without introducing a controlling buffer (EDTA). The results of preliminary experiment demonstrated that the importance of using low calcite concentration as well as low Cd^{2+} concentration. Sorption reversibility was studied by desorption experiments. In order to study the reversible character of sorbed surface complexes, five different desorp-

tion initiating times were selected at various sorption stages, based on previous sorption history. Desorption of Cd^{2+} from the calcite surface was induced by replacing Cd^{2+} sorbed calcite into a solution of identical chemical compositions except being Cd^{2+} free.

Experimental

Calcite Suspensions

The cadmium sorption and desorption experiments were conducted with reagent grade calcite (J.T. Baker, Lot# 1294-01). Chemical analysis (provided by the manufacturer) indicated the following concentrations of contaminants: <0.0005% heavy metals such as Pb; <0.001% Fe; 0.001% Mg; 0.001% K; 0.004% Na; 0.01% Sr. The calcite particles have an average diameter of 11.4 μm. The BET surface area given by the manufacturer is 0.6 m^2/g. X-ray powder diffractometry showed no indications of the presence of aragonite. Before using the calcite, it was thoroughly washed with deionized water, and subsequently dried for at least three days at 60℃.

The calcite suspensions were prepared by dispersing the washed and dried calcite into a pre-equilibrated solution filtered through a 0.2 μm polycarbonate membrane filter (Nuclepore). The pre-equilibrated solution was prepared by equilibrating deionized water with respect to calcite, and atmospheric CO_2, $pCO_2=10^{-3.5}$ atm in the presence of electrolyte ($NaClO_4$, and $KClO_4$). During the preparation of this solution, the pH of the suspension was monitored periodically. The final pH was 8.28~8.34 after two months, which was in close agreement with calculated equilibrium values.

Sorption Experiments

The sorption experiments were performed in acid-cleaned 500 mL polymetalpropylene (PMP) flasks. The solution mass was recorded gravimetrically. Based on preliminary experiments,

the calcite loading, 100 mg of calcite per liter of solution (total surface area of 0.06 m^2/L) was chosen to obtain best distribution of Cd^{2+} between calcite and solution.

After the calcite suspensions, 45 mg of calcite per 450 mL of a filtered pre-equilibrated solution, were prepared, they were stirred gently for 2 hrs with a Teflon stir bar and allowed to sit for 15 to 20 hrs open to the air. No changes in pH were observed during this period. Then, 45 mL of a stable cadmium solution (ALDRICH analytical grade $CdCl_2$), 10^{-4} M, and 20 μL of a ^{109}Cd (carrier free cadmium chloride in 0.1 N HCl, obtained from AMERSHAM), 2.05×10^{-7} M, were added to the suspension to yield a final Cd^{2+} concentration of 10^{-8} M, of which 0.1% was radioactive. The Cd^{2+} concentration was kept well below saturation with respect to $CdCO_3(s)$. All bottles were then sealed, swirled, and periodically sampled. No indication of pH changes was observed.

The Cd^{2+} sorption on calcite was determined by measuring the ^{109}Cd concentrations in the suspension and on the particles following the protocol of Fisher et al. (1984). At regular intervals, two aliquots of the stirred suspensions 1 mL each were directly placed in a plastic counting tube, and two aliquots 10.0 mL were filtered through a 0.2 μm polycarbonate membrane filter (Nuclepore). During the filtration, identical solutions of filtered supernatant (0.2 μm filtered) were used to saturate the filter and to rinse off excess Cd^{2+} from the calcite surfaces. The filters were then removed for radioactive counting.

Radioactive samples were counted by gamma spectroscopy (COMMPUGAMMA-500) using a large well NaI(Tl) crystal. The ^{109}Cd photons were detected at 88 keV. Counting times were adjusted so that propagated counting errors could be less than 5%. Blank tests were carried out to measure ^{109}Cd sorption onto the reaction vessel wall and filtration apparatus. The results show that the PMP flasks adsorbed less than 1% of ^{109}Cd over a month. Throughout the experiments, we found sorption on PMP flasks

and plastic pipets were always less than sorption onto glass.

Desorption

To test the reversibility of Cd^{2+} sorption from the calcite surface, desorption was studied. Desorption was induced by re-equilibrating radiolabeled calcite after certain periods of sorption reaction.

Ten calcite suspensions 200 mL each were prepared according to the method described previously. Desorption was started after 1, 9, 24, 140, and 360 hrs of sorption. For each experiment, 200 mL of filtered $CaCO_3$ suspension was resuspended into 200 mL of 0.2 μm filtered, pre-equilibrated solution, identical in chemical composition, except for the absence of Cd^{2+}, as that used for the initial equilibration of calcite suspension. After the resuspension of labeled calcite into Cd-free solution, subsequent changes in the partitioning of Cd^{2+} between calcite and solution were monitored periodically.

Results

Sorption of Cd²⁺ on Calcite

The rate of Cd^{2+} uptake on calcite was measured in 0.1, 0.3, and 0.5 M $NaClO_4$ and 0.1 M $KClO_4$ solutions, and also with no supporting electrolytes ("zero ionic strength"). The overall Cd^{2+} sorption process can be divided into two stages on the basis of rate of uptake and summarized in Table 1. The first stage is characterized by an initial rapid uptake. Typically, about 15% of the Cd^{2+} are sorbed within the first 1 hr, and 20~25% within 5 hrs. After roughly 24 hrs, the rate of uptake begins to decrease sharply and a steady state maximum value is reached by approximately 145 hrs with no clear evidence of continued uptake. There is a continuous decrease in uptake rate between 24 and 145 hrs, and no clear distinction between the two stages is evident. In Fig. 1, it can be seen that sorbed Cd^{2+} values at 520 hrs are slightly higher than the steady state values between 145~460 hrs. The maximum Cd^{2+} sorption was 75~80% of total Cd^{2+} (Fig. 1).

There is essentially no difference in Cd^{2+} sorption in $NaClO_4$ of different ionic strengths. Moreover, no difference is found for Cd^{2+} sorption in 0.1 M $KClO_4$. Results of Cd^{2+} sorption with time for 0.1 M, 0.3 M, and 0.5 M $NaClO_4$ and 0.1 M $KClO_4$ solutions are shown in Fig. 1. It is evident that the sorption curves are similar within the error of the measurements.

Desorption

Desorption of Cd^{2+} was initiated after 1, 9, 24, 140 and 360 hrs of sorption, for suspensions at different ionic strengths in $NaClO_4$ solutions. The subsequent changes in Cd^{2+} sorption were normalized to the amount of Cd^{2+} adsorbed on the calcite surface before desorp-

Table 1. Calculated average Cd^{2+} sorption rates at different ionic strength solutions of $NaClO_4$, and $KClO_4$ (mol/m²/hr)

Ionic strength		Time (hr)			
		T < 0.5	0.5 < T < 24	24 < T < 145	145 < T
$NaClO_4$	0.1 0.3 0.5	0.57×10^{-7}	1.85×10^{-9}	0.34×10^{-9}	2.10×10^{-12}
$KClO_4$	0.1	0.55×10^{-7}	1.90×10^{-9}	0.32×10^{-9}	2.09×10^{-12}

· Averaged Cd^{2+} sorption rate= $\dfrac{(At_2 - At_1)/X}{t_2 - t_1}$, (mol/m²/hr)

· At_2, At_1: sorbed Cd^{2+} on calcite surface at time t_1 and t_2 respectively.

· t_1, t_2: time t_1, t_2 after sorption (hr).

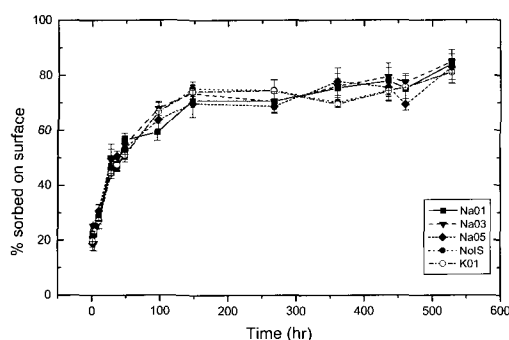· X: surface area of the calcite (0.06 m²/g in this study).

Fig. 1. Time-course experiments of Cd^{2+} on calcite in $NaClO_4$, $KClO_4$, and Zero ionic strength solutions. (Na01; $NaClO_4$ 0.1 M, Na03; $NaClO_4$ 0.3 M, Na05; $NaClO_4$ 0.5 M, K01; $KClO_4$ 0.1 M, NoIS; zero ionic strength of no electrolyte present).

tion was initiated (i.e., before resuspending the calcite into the Cd-free solution). The results of desorption experiments from this study are presented in Figs 3, 4, and 5.

Resuspension of the calcite was always followed by a rapid desorption and continued slow desorption (Figs. 3a, 4a, and 5a). Within five minutes after resuspension, approximately 30 to 50% of the sorbed Cd^{2+} were released into solution. It was characterized by a resumption of slow Cd^{2+} uptake after the initial rapid desorption, reaching a maximum. Desorption after 1, 145, and 360 hrs of sorption in 0.1 M $NaClO_4$ solutions and desorption after 1, 9, and 26 hrs of sorption in zero ionic strength solutions showed this type of desorption behavior (Fig. 3b, 4b, and 5b).

Discussion

Cd^{2+} Sorption Behavior

Relatively little is known about the detailed nature of sorbed species on calcite surfaces. Spectroscopic methods have been applied recently for direct study of sorbed species. However, certain aspects can be inferred from sorption trends. Parks (1990) describes two characteristic sorption behaviors, specific and non-specific, which are distinguished by the influence of

variables including pH, surface charge of the solids, and ionic strength. Of these variables, ionic strength dependency of sorption is a strong indication for distinguishing specific from non-specific sorption behavior. In specific sorption, increasing ionic strength, or the concentration of an indifferent background electrolyte, has little effect on sorption densities of the adion. However, in non-specific sorption, sorption densities of the adion are affected by the ionic strength of the solution, as increasing ionic strength decreases sorption densities.

In this study, changing the ionic strength, as shown by the comparative sorption in $NaClO_4$, $KClO_4$, and zero ionic strength solutions, had no effect on Cd^{2+} sorption on calcite surfaces (Fig. 1). The results also show no effect of the presence of different cations, such as Na^+ and K^+ on Cd^{2+} sorption. The independence of sorption behavior on ionic strength indicates a strong non-electrostatic interaction characteristic of specific sorption (James and Healy, 1972; Kinniburgh and Jackson, 1981; Papadopoulos and Rowell, 1988; Stumm and Morgan, 1996). This finding is consistent with other studies of Zn^{2+} sorption on calcite (Zachara et al., 1988), and Pb^{2+} sorption on hydrous oxide surfaces (Hayes and Leckie, 1987). Transition metal ions are commonly found to adsorb specifically (Hayes and Leckie, 1987; Hayes et al., 1987; James and Healy, 1972; Zachara et al., 1988).

Because of its stronger interaction with the surface, specifically sorbing metal ions are sometimes considered to form a surface complex in which the ion is close to the solid surface (i.e., an inner-sphere complex). Specifically sorbed inner-sphere complexes, as a result, should be more strongly bound to the surface than non-specific adions. However, it should be noted that a spectroscopic technique (e.g. EXAFS, XANES) is required to precisely differentiate the inner- or outer-sphere nature of an adion. And our experiments do not allow us to distinguish this character directly.

Kinetics of Cd^{2+} Sorption

Some aspects of Cd^{2+} sorption can be inferred from the behavior of similar divalent metal ions (Davis et al., 1987; Zachara et al., 1988). Trace metal sorption on calcite has been generally characterized as a two-step process (Davis et al., 1987; McBride, 1979; Zachara et al., 1988).

The rates of Cd^{2+} sorption in this study varied considerably over time. An initial rapid uptake decreases progressively with time, until after approximately 150 hrs, the rate is essentially zero (Table 1). It is almost certain that the initial rapid sorption is true adsorption on discrete surface sites on the calcite (i.e., high energy sorption sites, Davis et al., 1987; Farley et al., 1984). Much slower rates would be expected for surface precipitation or absorption (McBride, 1980). The apparently gradual decrease in rate further suggests that sorption is dominated by a single mechanism approaching a steady or equilibrium state. As noted earlier, there is no clear indication of continued sorption beyond approximately 150 hrs. This contrasts with previous work in which a slow Cd^{2+} sorption beyond 24 hrs was evident even after 190 hrs (Fuller and Davis, 1987). This slow and continuous Cd^{2+} uptake was interpreted as either a slow incorporation of Cd^{2+} into a $(Cd,Ca)CO_3$ solid solution during recrystallization (Davis et. al., 1987; Lahann and Siebert, 1982) or formation of a surface precipitate, where the composition of the solid varies continuously between that of calcite and a pure precipitate of the sorbing cation (Farley et al., 1984). In this study, however, no clear evidence indicating surface precipitation or absorption was found. Desorption experiments, discussed below, also support adsorption as the dominant, if not unique, mechanism. The lack of continued uptake in our experiments, which contrasts with previous work may reflect several features including low calcite loading for uniformed exposure of calcite surface area during sorption, and low metal concentration where the precipitation of pure solid phases were con-

trolled compared to the other studies (Davis et al., 1987; Fuller and Davis, 1987; McBride, 1979; Zachara et al., 1988, 1989, 1991).

Adsorption Partition Coefficient of Cd^{2+} Onto Calcite

Understanding the partitioning behavior of metal ions in natural systems is complicated by the observation that true thermodynamic equilibrium is commonly not obtained. However, laboratory measured partition coefficients from experiments can provide insight into the process governing the trace metal's interaction with solid surfaces. Partitioning of an adsorbate (Cd^{2+}) onto a solid surface can be represented by the distribution equation:

$$K_d = \frac{C_S}{C_L} \times 10^3 \text{ [mL/g]}$$

where C_S represents the adion's concentration on the solid surface [mol/g], obtained from d.p.m. (disintegration per minute) of radiotracer, and C_L represents the concentration of total metal dissolved in solution [mol/L].

Calculated adsorption partition coefficients (K_d) of Cd^{2+} between the calcite surface and the solution from this study are summarized in Table 2, and illustrated in Fig. 2. The desorption experiments (described below) show similar K_d's as the sorption experiments at maximum uptake. From these results, it appears that the overall surface processes, adsorption and desorption, are likely to be controlled by a single mechanism, and further that at maximum adsorption, equilibrium is likely obtained.

Reversibility of Sorption

It was anticipated that desorption experiments would show simple (and complete) reversibilty. Desorption behavior can be factored into at least two components, a rapid release of "labile" sorbed metals and a slower release of "nonlabile" sorbed metals (Karickhoff and Morris, 1985). Desorption can also be distinguished as

Table 2. Calculated adsorption partition coefficient (K_d) of Cd_{2+} on calcite in different solutions

Time (hrs)	Zero I. S.	NaClO₄ 0.1 M	NaClO₄ 0.3 M	NaClO₄ 5 M	KClO₄ (0.1 M)
1.58	516.3	289.4	340.2	234.5	246.2
4.00	658.4	284.4	234.5	317.5	302.8
10.0	730.6	400.6	363.8	443.9	372.3
28.3	890.2	874.8	999.3	986.4	795.8
37.0	810.6	885.9	924.9	1017	905.7
48.5	790.8	1299	1200	1139	1040
96.5	1471	1460	2120	1759	3001
146	2516	2433	2773	2314	2872
288	3079	2403	2381	2202	2906
360	3320	3068	3175	3508	2281
435	3427	3527	3866	3101	2882
460	3411	3056	3442	2264	3109
530	3456	5273	5686	4903	4308

· K_d(adsorption partition coefficient) $= \dfrac{C_S}{C_L} \times 10^3$ (mL/g)

· C_S : Cd^{2+} concentration on the solid, [mol/g], or d.p.m. (disintegration per minute) of radiotracer.

· C_L : Cd^{2+} concentration in the solution, [mol/L].

either true desorption or dissolution induced desorption by increased acidity, depending on the method of how the sorbed surface species were disturbed. Zachara *et al.* (1988) observed complete reversibility of adsorption in their desorption experiments, in which the bulk solution equilibrium was perturbed by lowering the system pH. Our desorption results, although achieved by different procedures, are also generally consistent with reversibility of adsorption. However, some desorption data are equivocal, and the desorption pathway toward the apparent equilibrium state is not always simple or direct. As described previously, all desorption experiments showed an initial rapid desorption, followed either by 1) slow uptake reaching a maximum, much as in the adsorption experiments, or 2) slowing desorption to reach a steady state minimum. Of those exhibiting slow uptake (1) K_d's calculated for maximum readsorption are essentially identical with those for adsorption. The K_d's calculated for the steady state minimum attained in the other experiments either agreed closely with adsorption values (Fig. 3a, 4a) or were slightly lower
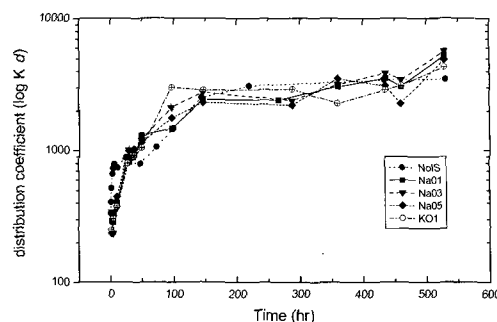

Fig. 2. Calculated adsorption partition coefficients of Cd^{2+} on calcite in different solutions. (Na01; NaClO₄ 0.1 M, Na03; NaClO₄ 0.3 M, Na05; NaClO₄ 0.5 M, K01; KClO₄ 0.1 M, NoIS; zero ionic strength of no electrolyte present).
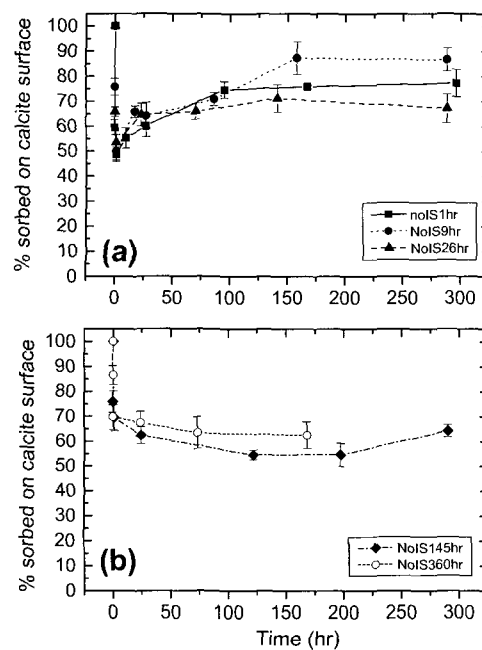

Fig. 3. Desorption data for Cd^{2+} in zero ionic strength solution. % values are normalized to the Cd^{2+} sorbed on the calcite surface before desorption was initiated (i.e., 100%). (a) The results of desorption experiments after 1 hr, 9 hrs, and 26 hrs of sorption. (b) The results of desorption experiments after 145 hrs, and 360 hrs of sorption.

(Fig. 5a). In the sense that similar K_d values were obtained for adsorption and most desorption experiments, the initial adsorption was reversed. This is apparently an equilibrium
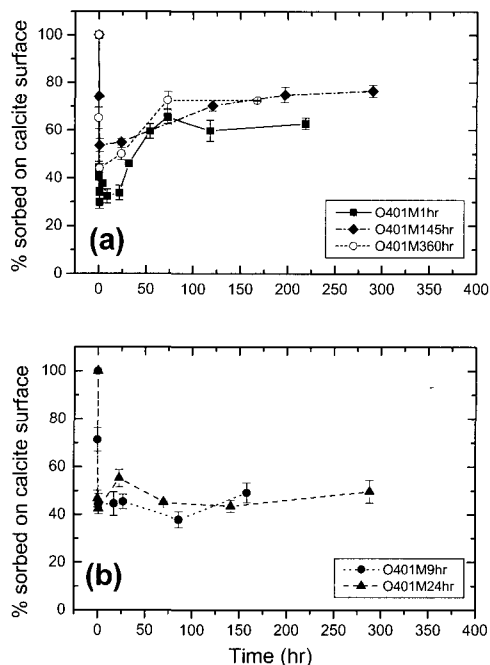
Fig. 4. Desorption data for Cd^{2+} in 0.1 M $NaClO_4$ solution. % values are normalized to the Cd^{2+} sorbed on the calcite surface before desorption was initiated (i.e., 100%). (a) The results of desorption experiments after 1 hr, 145 hrs, and 360 hrs of sorption. (b) The results of desorption experiments after 9 hrs, and 26 hrs of sorption.

Fig. 5. Desorption data for Cd^{2+} in 0.1 M NaCl solution. % values are normalized to the Cd^{2+} sorbed on the calcite surface before desorption was initiated (i.e., 100%). (a) The results of desorption experiments after 1 hr, 9 hrs, and 24 hrs of sorption. (b) The results of desorption experiments after 140 hrs, and 360 hrs of sorption.

adsorption value, and we again note that essentially the same value was obtained during the second spiking experiments(Ko, 1991). However, it should be noted that the final approach of the system to this apparent equilibrium was an adsorption stage in most, but not all, cases. We have no explanation for the few desorption results that produced K_d's lower than values determined for adsorption. We cannot entirely rule out the possibility that minor dissolution occurred during resuspension, thereby causing additional Cd^{2+} release from the surface. However, the solution used for resuspension was pre-equilibrated with respect to calcite, and no such dissolution was expected. On the other hand, the desorption experiments of Zachara *et al.* (1989) are far more likely to have been influenced by minor dissolution owing to the introduction of acid and the
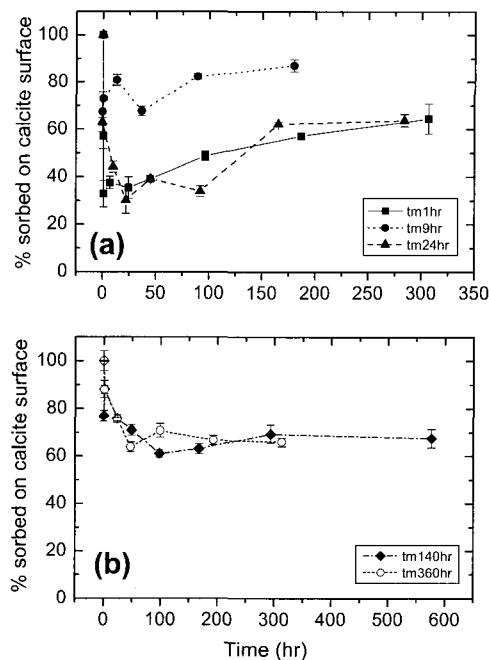
lowering of pH.

The initial rapid release of Cd^{2+} (40~70% of the total adsorbed on the surface) indicates that the Cd^{2+} surface complex is, at least in part, labile. Moreover, the rate of release is of the same order as (if not greater than) the initially rapid stage of adsorption. The generally comparable rates of the initial uptake and the initial release suggest that similar fundamental mechanisms may be involved in both adsorption and desorption.

Conclusion

The kinetics of Cd^{2+} sorption on calcite was investigated in a series of radiotracer experiments. Sorption behavior in different ionic strengths of $NaClO_4$ solutions shows that Cd^{2+} sorption on calcite is of a specific type. The

overall Cd^{2+} sorption on calcite was distinguished as one process, adsorption. The adsorption of Cd^{2+} on calcite shows an initial rapid uptake followed by decreasing rate leading to a sorption maximum.

Lability of sorbed Cd^{2+} species was investigated by desorption experiments in several different electrolyte solutions. Adsorption was generally found to be reversed following an initially rapid desorption, although different behaviors were noted.

Calculated partition coefficients for adsorption and desorption of Cd^{2+} on calcite in $NaClO_4$ solutions show similar results, which implies a single controlling mechanism for the overall processes. It is expected that sorption of Cd^{2+} on calcite surface may be controlled by the available free-Cd^{2+} within the system.

The overall Cd^{2+} desorption was characterized as irreversible, resuming sorption after initial rapid desorption. The irreversible behavior of Cd^{2+} sorption may act as one of the controls for regulating the mobility of dissolved Cd^{2+} in natural aqueous systems.

Acknowledgments

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