

HEAVY METALS IN WASTEWATER: THE EFFECT OF ELECTROLYTE COMPOSITION ON THE PRECIPITATION OF CADMIUM(II) USING LIME AND MAGNESIA

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Abstract. The effect of effluent composition on the efficiency of hydroxide precipitation of Cd(II), using both lime and magnesia as precipitants, has been modelled by the solubility domain approach in order to provide wastewater effluent treatment limits, and has been experimentally validated. Common anionic species such as Cl^- , SO_4^{2-} and CO_3^{2-} have been treated. Solubility domain calculations were based on those phases that were found to determine metal solubility for systems representing the upper and lower limits of potential effluent chemical compositions. The isolated phases were found to resemble their mineralized counterparts, although in several cases exhibited a lower degree of structural order. Experimentally determined Cd(II) solubilities were generally encompassed within the calculated solubility domains, indicating that solubility domain predictions provide effluent treatment quality assurance ranges for the hydroxide precipitation process. The formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcite (CaCO_3) at higher SO_4^{2-} and CO_3^{2-} concentrations as secondary precipitates using lime as the precipitant, and the hydroxy-sulfate $\text{Mg}_2(\text{OH})_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, nesquehonite ($\text{MgCO}_3 \cdot 4\text{H}_2\text{O}$), hydromagnesite [$\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$] and brucite [$\text{Mg}(\text{OH})_2$] when employing magnesia was shown to have little effect on the observed residual Cd(II) solubility, although $\text{Mg}(\text{OH})_2$ did promote β -Cd(OH)₂ formation in the Mg^{2+} -containing Cd(II)/ Cl^- and Cd(II)/ SO_4^{2-} systems.

Keywords: cadmium(II), carbonate, chloride, lime, magnesia, sulfate, wastewater

1. Introduction

Heavy metal species are some of the most common pollutants that are found in industrial wastewaters. Because of their toxicity, these species can have a serious impact if released into the environment as a result of bioaccumulation, and they may be extremely toxic even in trace quantities. One such heavy metal, cadmium, along with its compounds, is widely used in pigments, as heat stabilizers for plastics, for corrosion resistance of steel and cast iron, in soldering and brazing, and in the battery industry (Ni-Cd batteries). Cadmium is highly toxic and there is some evidence that it is carcinogenic (Hiatt and Huff, 1975). When ingested by human beings, cadmium that is not excreted immediately has a long half-life of several hundred days, so that a low dose exposure over a long period of time can lead to a high body burden. In view of its persistence as a cumulative poison and the low tolerance of the human body towards cadmium, it is of interest to develop schemes for the removal of

heavy metals from wastewaters prior to their disposal. Such disposal is, of course, subject to strict environmental regulation. In the case of cadmium, for example, the immobilization and remobilization of Cd(II) by ferrihydrite, and the effect of Cd(II) on the conversion of ferrihydrite to goethite and hematite has been reported previously (Lin *et al.*, 2003; Sun *et al.*, 1996).

A variety of specialized treatment processes for the removal of heavy metals prior to their discharge into the environment have been developed (Clifford *et al.*, 1986). Among them, the simple precipitation of metals as insoluble hydroxides, carbonates, or sulfides is used in about 75% of electroplating facilities to treat wastewater (Karthikeyan *et al.*, 1995). Of all the treatment techniques, heavy metal hydroxide precipitation is the most commonly employed because of its low cost and simplicity. This process is as simple as increasing the pH of the effluent using lime (CaO) or caustic soda (NaOH) to precipitate and hence immobilize the heavy metals as their respective hydroxides. However, the efficiency of hydroxide precipitation on heavy metal removal depends on a variety of factors. These include the nature of the actual solubility-limiting phase, the electrolyte composition of the effluent, the presence of soluble and/or insoluble products following reaction with complexing agents, ionic strength, electrical potential, temperature, and the time of reaction. Satisfactory hydroxide precipitation requires that all such parameters are identified and their manipulation understood. As the composition of industrial wastewater is highly variable, methods of providing wastewater treatment quality assurance are therefore highly desirable.

Several previous studies have investigated the application of hydroxide precipitation for the removal of Cd(II) from industrial wastewater effluents (Karthikeyan *et al.*, 1995; Brooks, 1991; Tünay *et al.*, 1991). However, little emphasis has been placed on generating guidelines for assuring an efficient hydroxide precipitation process with the variation of effluent composition. In our previous studies of other heavy metals, solubility domain predictions have been used successfully to account for the effect of anion type and concentration on the efficiency of hydroxide precipitation in the case of Zn(II), Pb(II), Cu(II) and Ni(II) using CaO or NaOH as a source of base (Baltpurvins *et al.*, 1995, 1996, 1997a,b; Lin *et al.*, 1998). This process involves calculating precipitation profiles (i.e. the residual metal concentration in solution versus pH) based on the solubility-limiting phases that represent the potential effluent composition limits. The area encompassed by the resulting profile, which is termed the solubility domain, represents the treatment efficiency range regardless of the effluent composition. Intersection of the discharge limit with the upper boundary of the solubility domain generates a pH range over which effluent treatment is assured. This approach has proved to be a useful way of systematically designing a treatment procedure for the removal of heavy metals in wastewater by hydroxide precipitation. However, such an approach to the immobilization of Cd(II) in wastewater has not been reported previously.

Secondary precipitation reactions, such as when lime is used as the source of base, do not always act to benefit the overall treatment performance. In cases of

high acidity where large amounts of lime are required for neutralization, significant quantities of a secondary precipitate (sludge) may be produced, such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). These secondary precipitates may increase the costs of sludge handling and its subsequent disposal. Moreover, these secondary precipitates can act as potential adsorbents, as well as acting to destabilize the primary heavy metal precipitate by inducing colloid formation, thereby making solid-liquid separation difficult (Glasner and Weiss, 1980). As an alternative to CaO and NaOH, the use of magnesia (MgO) to precipitate heavy metals from wastewater has been employed in recent years. Compared with CaO and NaOH, magnesia is reported to have the following advantages (ICI Watercare, 1996):

- (a) a lower neutralization rate providing for slower nucleation, thereby promoting enhanced crystal growth and better filtering capability,
- (b) a higher solids content in the resulting precipitate,
- (c) a lower residual sludge volume as a result of lower quantities of non-structural water trapped within the precipitate, and
- (d) the elimination of gypsum and calcite (CaCO_3) formation from sulfate- and carbonate-rich effluents.

While MgO does not change the solubility of the heavy metal precipitates, it modifies the treatment process by altering the physical parameters of the process. Moreover, industrial grade lime often contains substantial amounts of MgO. Thus dolomitic quicklime has an approximate composition of CaO·MgO. Up to now, few studies have focused on the effect of Mg(II) on the removal efficiency of heavy metals from industrial waste effluents by chemical precipitation (Baltpurvins, 1996; Wiechers, 1977). Moreover, as Mg(II)-hydroxy salts are known, the presence of Mg(II) may change the solid-aqueous phase characteristics, which in turn may effect the efficiency of heavy metal removal. This has yet to be investigated.

The present work examines the solubility domain approach to predict the efficiency of the Cd(II) precipitation process. Variation in the common electrolyte types Cl^- , SO_4^{2-} and CO_3^{2-} and their concentrations are considered in the determination of the precise precipitation profiles. The effect of lime and magnesia on the precipitation process, with the presence of both Ca^{2+} and Mg^{2+} being introduced as soluble Ca^{2+} and Mg^{2+} salts, is also examined. The addition of lime and magnesia to an aqueous medium results in spontaneous hydrolysis to produce their hydroxides and, depending on the concentration, insoluble $\text{Mg}(\text{OH})_2$. This can complicate the modelling process through difficulties associated with the control of the rate of dissolution, and subsequent nucleation of heavy metal hydroxides. It has been observed that the dissolution rate of magnesia is highly dependent on the nature of the supporting electrolyte (Mažuranić *et al.*, 1982). Therefore, kinetic factors related to the dissolution of brucite may control the nature of the solubility-limiting phases produced in these systems. The introduction of Ca(II) and especially Mg(II) as soluble salts can avoid such problems, and at the same time better represent the

precipitation process. This approach has been used successfully in previous studies (Mažuranić *et al.*, 1982; Baltpurvins *et al.*, 1997a,b). The investigation of multiple components in the solubility domain approach is an important extrapolation from previous studies and is of particular importance to industry.

2. Experimental Methods

2.1. SOLUBILITY DOMAIN PREDICTIONS

The geochemical modelling package Minteqa2, supplied by the U.S. Environmental Protection Agency (Allison *et al.*, 1991), was employed for all of the solubility domain calculations. Thermodynamic constants for both aqueous and solid phases were taken from the literature (Smith and Martell, 1976, 1989; Feitknecht and Schindler, 1962; Baes and Mesmer, 1976; Bilinski *et al.*, 1976; Minteqa2 database). Other values and references used for some constants are discussed below. Only those solid phases that were found to be solubility limiting were included in the models. Ionic strength and electrical potential were both left to “float” within the program, and were calculated only when equilibrium had been attained. The Davies equation approximation was used to adjust the thermodynamic constants for ionic strength, as this has been shown to be a valid method for ionic strengths up to 0.7 mol dm^{-3} (Robinson and Stokes, 1969). Calculations were performed at a fixed temperature of 298 K and the number of iteration cycles was constrained to 40. No contribution to pH from adsorbed CO_2 was included in the models, except for the CO_3^{2-} systems, for which it was fixed.

Solubility domains were calculated for the systems described in Table I. In the present study, the initial Cd(II) concentration was set at $0.001 \text{ mol dm}^{-3}$. The presence or absence of Ca^{2+} and Mg^{2+} in each of the systems is indicated by the symbols ‘+Ca’ if present or ‘-’ if absent for Ca^{2+} , respectively, and similarly in the

TABLE I
Composition of Minteqa2 model systems

Designation [$\text{M}^{2+}, \text{A}^{n-}$] ^a	[Cd^{2+}] mol dm^{-3}	[A^{n-}] ^b mol dm^{-3}	[Ca^{2+}] or [Mg^{2+}] mol dm^{-3}
[+Ca,+A]	0.001	$\text{Cl}^- = 0.100; \text{SO}_4^{2-}, \text{CO}_3^{2-} = 0.100$	0.100
[+Mg,+A]	0.001	$\text{Cl}^- = 0.202; \text{SO}_4^{2-}, \text{CO}_3^{2-} = 0.101$	0.100
[+Ca,-]	0.001	$\text{Cl}^- = 0.002; \text{SO}_4^{2-}, \text{CO}_3^{2-} = 0.001$	0.100
[-,+A]	0.001	$\text{Cl}^- = 0.100; \text{SO}_4^{2-}, \text{CO}_3^{2-} = 0.100$	0.000
[-,-]	0.001	$\text{Cl}^- = 0.002; \text{SO}_4^{2-}, \text{CO}_3^{2-} = 0.001$	0.000

^a $\text{M}^{2+} = \text{Ca}^{2+}$ or Mg^{2+} ; + and - refer to the presence or absence of added ion in the system under study.

^b A^{n-} corresponds to Cl^- , SO_4^{2-} or CO_3^{2-} .

case of Mg^{2+} , i.e. '+Mg' and '-'. The presence or absence of added anion ($A^{n-} = \text{Cl}^-$, SO_4^{2-} or CO_3^{2-}) are also indicated by the symbols '+A' and '-', respectively. Added (or not) cation and anion are given in the order $[\text{M}^{2+}, A^{n-}]$, where $\text{M}^{2+} = \text{Ca}^{2+}$ or Mg^{2+} , in Table I, and also when used in the text. In the Ca^{2+} systems the anion concentrations were varied from $0.001 \text{ mol dm}^{-3}$ for both SO_4^{2-} and CO_3^{2-} , and $0.002 \text{ mol dm}^{-3}$ for Cl^- , all on a charge balance basis, up to a maximum of $0.100 \text{ mol dm}^{-3}$ for each anion. In the Mg^{2+} systems the minimum values were the same as for the analogous Ca^{2+} systems, while maximum anion concentrations were $0.101 \text{ mol dm}^{-3}$ for both SO_4^{2-} and CO_3^{2-} , and $0.202 \text{ mol dm}^{-3}$ for Cl^- . The Ca^{2+} and Mg^{2+} concentrations were varied from 0.000 to $0.100 \text{ mol dm}^{-3}$. Calculations were carried out for all systems from pH 5 to 11, except for the CO_3^{2-} systems, for which the range was restricted to pH 7.5–11.

2.2. DETERMINATION OF PRECISE PRECIPITATION PROFILES

Precise precipitation profiles were determined experimentally using a computer-controlled "chemostat", which has been described previously (Baltpurvins *et al.*, 1996). The chemostat was used to control pH, temperature, reaction time, and both the extent and rate of precipitant dosage. Model solutions were prepared such that they contained a known concentration of Cd(II), along with the anion of interest (Cl^- , SO_4^{2-} or CO_3^{2-}) and, when included, Ca^{2+} or Mg^{2+} , in the molar concentrations given in Tables II and III, respectively. The salts $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used to introduce Cd^{2+} , Ca^{2+} and Mg^{2+} , respectively, whereas the anhydrous sodium salts of the anions were used to introduce the latter species in all precipitation profile determinations. The initial pH values of the solutions were adjusted to 3 using concentrated HNO_3 , except for the CO_3^{2-} systems, which were set to pH 7.5 to avoid evolution of CO_2 , which occurs at lower pH values. All chemostat experiments had an initial volume of 1 dm^3 . Carbon dioxide-free Millipore Milli-Q water was used for all profile determinations, and all reagents were of analytical reagent grade. Measurements were made at 298 K in the present study.

TABLE II

Model chemostat sample compositions and associated profile numbers for all Ca^{2+} systems (for use in Figures 1–3)

Profile number	$[\text{Cd}^{2+}]$ mol dm^{-3}	$[A^{n-}]^a$ mol dm^{-3}	$[\text{Ca}^{2+}]$ mol dm^{-3}
1–3	0.001	$\text{Cl}^- = 0.002$; SO_4^{2-} , $\text{CO}_3^{2-} = 0.001$	1 = 0.000, 2 = 0.010, 3 = 0.100
4–6	0.001	Cl^- , SO_4^{2-} , $\text{CO}_3^{2-} = 0.010$	4 = 0.000, 5 = 0.010, 6 = 0.100
7–9	0.001	Cl^- , SO_4^{2-} , $\text{CO}_3^{2-} = 0.100$	7 = 0.000, 8 = 0.010, 9 = 0.100

^a A^{n-} corresponds to Cl^- , SO_4^{2-} or CO_3^{2-} .

TABLE III

Model chemostat sample compositions and associated profile numbers for all Mg^{2+} systems (for use in Figures 4–6)

Profile number	$[\text{Cd}^{2+}]$ mol dm^{-3}	$[\text{A}^{n-}]^a$ mol dm^{-3}	$[\text{Mg}^{2+}]$ mol dm^{-3}
1	0.001	$\text{Cl}^- = 0.002; \text{SO}_4^{2-}, \text{CO}_3^{2-} = 0.001$	0.000
2	0.001	$\text{Cl}^- = 0.022; \text{SO}_4^{2-}, \text{CO}_3^{2-} = 0.011$	0.010
3	0.001	$\text{Cl}^- = 0.202; \text{SO}_4^{2-}, \text{CO}_3^{2-} = 0.101$	0.100

^a A^{n-} corresponds to Cl^- , SO_4^{2-} or CO_3^{2-} .

After addition to the reaction vessel of the chemostat, each solution was purged with N_2 gas for 15 minutes to remove dissolved CO_2 , with the exception of the CO_3^{2-} -containing systems, for which the reaction vessel was simply closed to the atmosphere. All reagent addition and sampling was subsequently performed under an atmosphere of nitrogen. Following the initial N_2 purge (with the exception of the CO_3^{2-} systems) a 20-cm^3 sample was taken, centrifuged at 2000 rpm for 15 minutes and filtered through a $0.45\text{-}\mu\text{m}$ cellulose nitrate membrane filter. The pH of each solution was then increased in 0.5 pH unit steps from 3 to 11, except for the CO_3^{2-} systems, for which the range was pH 7.5–11. An equilibration time of 40 minutes between pH adjustments was allowed before each sampling event. After sampling, centrifuging and filtering, as described above, the metal ion concentrations in the filtered solutions were determined by atomic absorption spectrophotometry using a Perkin Elmer AAS 3110 instrument under standard matrix matched conditions. Residual concentrations are considered to be accurate to within 5% in the region of minimum solubility and 0.5% for pH values outside of this region.

2.3. SOLID PHASE CHARACTERIZATION

Solid phases were generated from the chemical boundary systems given in Tables II and III. All solids were isolated at both pHs 9 and 11 to observe any pH-dependent precipitate transformation reactions. Samples were filtered through a $0.45\text{-}\mu\text{m}$ cellulose nitrate membrane filter, and dried at 20°C under vacuum for 24 hours. X-ray powder diffraction and thermogravimetric analysis was employed to characterize the solid phases. A Phillips PW 1710 Automated Powder Diffractometer System with a Philips PW1050 goniometer, employing graphite-monochromated $\text{Cu-K}\alpha$ radiation, was used to obtain the X-ray powder patterns of the solid phases. Thermogravimetric analysis was performed on a Stanton Redcroft TG-750 instrument coupled to a Eurotherm Model 94 temperature controller. Analyses used sample masses of about 10–30 mg, heating rates of $10^\circ\text{C}/\text{minute}$, and were performed in a static air atmosphere. Unless indicated, any mass loss below 100°C was attributed to adsorbed water and therefore not included in the mass loss calculations given below.

3. Results and Discussion

Previous studies (Lin *et al.*, 1998; Baltpurvins *et al.*, 1995, 1996, 1997a,b; Tünay *et al.*, 1991) have shown that the use of chemical speciation packages for the prediction of effluent treatment performance is highly dependent on the nature of the actual solubility-limiting (i.e. solubility-determining) phases. Thus factors such as stoichiometry, crystal size and degree of crystallinity must be taken into consideration. Moreover, the formation of solubility-limiting phases that are formed kinetically rather than the actual thermodynamically favoured phases must also be taken into account. It is therefore critical to establish the exact nature of these solubility-limiting phases for solubility domain calculations, instead of basing these calculations simply on the thermodynamically preferred phases. Furthermore, the presence of different electrolyte types and their concentrations influence the exact nature of the solubility-limiting phases (Baltpurvins *et al.*, 1995, 1996, 1997a,b). In the present study, a combination of X-ray powder diffraction (XRD) and selected thermogravimetric analysis (TGA) studies were employed to characterize the exact nature of the solubility-limiting phases for each individual system.

3.1. SOLUBILITY LIMITING PHASES

3.1.1. Cd(II)/chloride System (Ca^{2+} and Mg^{2+} Systems)

For all Ca^{2+} -containing systems, XRD on the solids that were isolated from the chemical boundaries of the Cd(II)/Cl⁻ system indicated that at low chloride ion concentrations, i.e. the [-,-] and [+Ca,-] systems, Cd(OH)Cl was the dominant solid phase isolated at pH 9, together with a small amount of β -Cd(OH)₂ in each case. At pH 11, however, significant transformation of Cd(OH)Cl into β -Cd(OH)₂ occurred in both systems, especially for [+Ca,-], based on changes in the relative intensities of the two XRD patterns. Not surprisingly, high chloride ion concentrations were observed to promote the formation of Cd(OH)Cl, at least at low pH values. Thus in both the [-,+A] and [+Ca,+A] systems at pH 9, Cd(OH)Cl was the major phase observed, along with a minor amount of β -Cd(OH)₂. At pH 11, however, some transformation of Cd(OH)Cl into β -Cd(OH)₂ was observed in the [-,+A] system, whereas extensive conversion occurred in the [+Ca,+A] system. The presence of Ca^{2+} would appear therefore to promote conversion of Cd(OH)Cl into β -Cd(OH)₂.

For the [+Mg,+A] system at pH 9, Cd(OH)Cl was the only phase observed, while at pH 11 only β -Cd(OH)₂ was observed, along with the secondary phase Mg(OH)₂ (brucite). Thus while Ca^{2+} promotes the conversion of Cd(OH)Cl into β -Cd(OH)₂ at both pH values, as indicated above, the presence of Mg^{2+} appears to result in enhanced conversion to β -Cd(OH)₂ at pH 11, as no Cd(OH)Cl was observed under these conditions.

It should be noted that in most of the Ca^{2+} - and Mg^{2+} -containing systems minor quantities of CdCO₃ were also detected by XRD, even after the careful exclusion of air from the chemostat titration system. The presence of CdCO₃ is attributed to

the uptake of CO₂ during the filtration and drying procedures. Similar observations have been made in previous studies (Baes and Mesmer, 1976).

Thermogravimetric analysis of the solid isolated from the [+Ca,+A] system at pH 9, which contains a mixture of Cd(OH)Cl and β -Cd(OH)₂ according to XRD analysis, exhibited a mass loss of 8.3% from 180 to 380 °C and 26.0% from 630 to 770 °C. These mass losses correspond to a combination of the dehydration reactions given by equations (1) and (2) for the lower temperature mass loss, and the reaction given in equation (3) at the higher temperature:



According to Duval (1963), Cd(OH)₂ dehydrates from 170 to 371 °C (a 12.3% mass loss), with the resulting CdO stable up to 880 °C. The mixed hydroxy-chloride, Cd(OH)Cl, for which no data is available, appears to dehydrate over a similar temperature range (with a theoretical 5.5% mass loss), resulting in the experimentally observed intermediate mass loss of 8.3% at 180–380 °C, which is consistent with the mixed product that is formed at this boundary. Duval (1959) has reported the thermal decomposition of anhydrous CdCl₂ in an air atmosphere. This study showed that CdCl₂ is stable up to 600 °C, after which CdO is formed. The mass loss observed above 630 °C in the present study is therefore in agreement with the previous work.

The TGA profile of the solid isolated from the [+Ca,+A] system at pH 11 showed a 7.3% mass loss on heating from 180 to 380 °C, and a further 6.7% loss from 630 to 770 °C. This is consistent with decomposition of β -Cd(OH)₂ as the main species present, along with the presence of some Cd(OH)Cl, in agreement with the XRD data.

For the [+Mg,+A] system at pH 11, a mass loss of ~10% was observed from 200 to ~300 °C, which corresponds to partial dehydration of β -Cd(OH)₂. This was then followed by a combination of further dehydration of β -Cd(OH)₂ and dehydration of Mg(OH)₂ to MgO and H₂O at higher temperatures (>300 °C). Duval (1963) has reported that Mg(OH)₂ begins to decompose about 280–290 °C, with the majority of water lost by 420 °C, followed by a continuous, slow mass loss to ~820 °C. The TGA profile obtained is consistent with the XRD result, and indicates that a mixture of β -Cd(OH)₂ and Mg(OH)₂ was present in the solid that was isolated under the above conditions.

3.1.2. Cd(II)/sulfate System (Ca²⁺ and Mg²⁺ Systems)

For both the Ca²⁺- and Mg²⁺-containing systems, CdSO₄·3.5Cd(OH)₂·xH₂O and β -Cd(OH)₂ were the only Cd(II)-containing phases that were observed in the present studies although, as in the Cd(II)/Cl⁻ systems described above, minor amounts of CdCO₃ were also observed by XRD. Again, this is attributed to adsorption of CO₂ during isolation of the solid phases.

For the $[-,-]$ and $[-,+A]$ systems at pH 9, the solid phases that were isolated were primarily $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, along with modest amounts of $\beta\text{-Cd}(\text{OH})_2$. Not unexpectedly, higher levels of sulfate promoted the formation of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ at pH 9, as indicated by an increase of the intensity of the XRD pattern of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ compared to that of $\beta\text{-Cd}(\text{OH})_2$ in the $[-,+A]$ system, relative to that in the $[-,-]$ system. At pH 11 in both of these two systems, however, $\beta\text{-Cd}(\text{OH})_2$ was found to be the major product, and only small amounts of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ were observed in each case.

For the $[+Ca,-]$ system at pH 9 only $\beta\text{-Cd}(\text{OH})_2$ was detected by XRD, along with a small amount of the secondary phase $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. In the $[+Ca,+]$ system, however, a little $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ was found to be present at pH 9 in addition to the major component $\beta\text{-Cd}(\text{OH})_2$, along with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. At pH 11 $\beta\text{-Cd}(\text{OH})_2$ was the only product observed in both the $[+Ca,-]$ and $[+Ca,+A]$ systems, again with the secondary phase $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The formation of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and/or $\beta\text{-Cd}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as separate phases suggests that no Ca^{2+} -Cd(II) multi-component solid species occur during the hydroxide precipitation of Cd(II) from a SO_4^{2-} -rich environment in the presence of Ca^{2+} . Moreover, the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ had little effect on the solubility of Cd(II), which is in agreement with previous observations in SO_4^{2-} -rich systems (Lin *et al.*, 1998; Baltpurvins *et al.*, 1996). These studies also demonstrate the effect that Ca^{2+} has on the nature of solid phases actually isolated. At both pH 9 and 11, the presence of Ca^{2+} introduces a competitive effect with Cd(II) for SO_4^{2-} , which leads to the change in the nature of the solid phase. This generally results in the formation of $\beta\text{-Cd}(\text{OH})_2$ at the expense of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, with the latter only appearing as a minor phase in the sulfate-rich $[+Ca,+A]$ system at pH 9. Compared to the previously discussed Cd(II)/ Cl^- systems, complete transformation of the mixed hydroxy-anion phase into $\beta\text{-Cd}(\text{OH})_2$ occurs more readily in the Cd(II)/ SO_4^{2-} systems.

In the $[+Mg,+A]$ SO_4^{2-} system, $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ was observed at pH 9, along with the secondary phase $\text{Mg}_2(\text{OH})_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, while $\beta\text{-Cd}(\text{OH})_2$ occurred at pH 11 along with $\text{Mg}(\text{OH})_2$. The conversion of both of the mixed hydroxy-sulfate solid phases, i.e. $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and $\text{Mg}_2(\text{OH})_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, to their respective hydroxides, $\beta\text{-Cd}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ at the higher pH value, was evident. Less conversion of the hydroxy-anion phase $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ to $\beta\text{-Cd}(\text{OH})_2$ occurred in the Mg^{2+} -containing system at pH 9 compared to the Ca^{2+} -containing system, probably because of competition for the OH^- by the secondary phase $\text{Mg}_2(\text{OH})_2\text{SO}_4 \cdot x\text{H}_2\text{O}$. However, there was no discernable difference between the effects of Ca^{2+} and Mg^{2+} at pH 11, unlike in the Cd(II)/ Cl^- system, as the presence of both cations resulted in the formation of $\beta\text{-Cd}(\text{OH})_2$. Notably, the secondary phase $\text{Mg}_2(\text{OH})_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ appeared only at pH 9, and was converted into $\text{Mg}(\text{OH})_2$ at pH 11, while $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ appeared in the $[+Ca,-]$ and $[+Ca,+A]$ phases at both pH values.

Thermogravimetric analysis of the solid isolated from the $[-,-]$ system at pH 9, which was pure $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ according to XRD analysis, showed a progressive mass loss from room temperature to $\sim 450^\circ\text{C}$. The mass loss may be attributed to a combination of strongly adsorbed water, water trapped in the lattice (with both producing a mass loss contribution above 100°C), and dehydration of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$. For the solid isolated from the $[-,+A]$ system at pH 9, which was a mixture of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and $\beta\text{-Cd}(\text{OH})_2$ according to XRD, there was a progressive mass loss ($\sim 7\%$) from room temperature to $\sim 250^\circ\text{C}$, followed immediately by a slow 11.3% mass loss from ~ 250 to 450°C . The two steps effectively overlapped at about 250°C , and were distinguished only by a small change in the rate of loss of mass. No further mass loss occurred above this temperature. The first mass loss is likely associated with strongly adsorbed water, water trapped in the lattice, and dehydration of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, as described above. It should also be noted that $\beta\text{-Cd}(\text{OH})_2$ would make some contribution to the mass loss above 170°C (see above). The second mass loss likely arises from further dehydration of the $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$, both of the water of hydration and from constitutional water, and also from dehydration of the $\beta\text{-Cd}(\text{OH})_2$. It has been reported that CdSO_4 itself becomes anhydrous above 320°C , and is stable up to 906°C (Duval, 1963).

The TGA profile of the solid isolated from the $[-,+A]$ system at pH 11 exhibited a sharp 8.4% mass loss from 190 to 270°C and a slow 4% mass loss from 270 to 380°C , which is consistent with dehydration of the primary component of the solid, which is $\beta\text{-Cd}(\text{OH})_2$, as well as dehydration of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$. The TGA mass loss profile of the solid isolated from the $[+Ca,-]$ system at pH 9 gave mass losses of 11% at 100 to 150°C and 7% at 180 to 380°C , respectively. The first mass loss may be attributed to dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to give anhydrous CaSO_4 (Lin *et al.*, 1998; Baltpurvins *et al.*, 1997a,b), while the second mass loss corresponds to dehydration of $\beta\text{-Cd}(\text{OH})_2$. For the solid isolated from the $[+Ca,+A]$ system at pH 11, mass losses of 15% and 2.2% occurred at 100 to 150°C and 180 to 380°C , respectively, with the first step involving dehydration of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and the second step dehydration of $\beta\text{-Cd}(\text{OH})_2$.

For the $[+Mg,+A]$ system at pH 11, an 8.4% mass loss was observed from 170 to 200°C , followed by a further 4% up to 300°C , and finally a sharp mass loss of 8% from 300 to 350°C . These correspond to overlapping dehydration steps of both $\beta\text{-Cd}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, with the former occurring over the complete mass loss range and the latter above 283°C (Duval, 1963), and is consistent with the XRD results.

3.1.3. *Cd(II)/carbonate System (Ca^{2+} and Mg^{2+} Systems)*

For the Ca^{2+} -containing system, the sole Cd(II)-containing solid phase detected at pH 9 for all of the four chemical boundaries was CdCO_3 (otavite). Even the presence of low amounts of CO_3^{2-} (i.e. no added CO_3^{2-}) lead to the formation of CdCO_3 . However, on increasing the pH from 9 to 11, $\beta\text{-Cd}(\text{OH})_2$ was found

to be a minor phase in all of the boundary systems, although CdCO_3 remained the dominant phase. This is in agreement with the previous observations of Baes and Mesmer (1976), that CdCO_3 is extremely insoluble and can be formed in the presence of air during the precipitation of $\beta\text{-Cd(OH)}_2$. Calcite (CaCO_3) was also observed as a secondary precipitate in the [+Ca,+A] system.

In the [+Mg,+A] system at pH 9 CdCO_3 was observed as the Cd(II)-containing phase, along with the secondary phase $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (nesquehonite). At pH 11, however, $\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$ (hydromagnesite) was observed in addition to CdCO_3 rather than $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. The formation of a hydroxy-carbonate phase of Mg^{2+} at the higher pH value is consistent with the increase in OH^- concentration. No evidence for $\beta\text{-Cd(OH)}_2$ was obtained at either pH value, unlike in the corresponding Ca^{2+} -containing system, where $\beta\text{-Cd(OH)}_2$ was observed as a minor product at pH 11. This can be attributed to competition for the OH^- with Mg^{2+} , with subsequent formation of insoluble $\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$, and/or to the difficulty in observing potentially small amounts of $\beta\text{-Cd(OH)}_2$ in the presence of both CdCO_3 and $\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$.

Thermogravimetric analysis of the solid isolated from the [-,-] boundary at pH 11 indicated a slow mass loss of $\sim 2\%$ from 100 to 340°C followed by a 17% mass loss from 330 to 470°C . According to Duval (1963), CdCO_3 is not stable when heated and its weight decreases progressively on heating until the temperature reaches 488°C . The two combined mass losses are thus attributed to the slow decomposition of CdCO_3 to CdO and CO_2 from 100 to 470°C , with dehydration of $\beta\text{-Cd(OH)}_2$ occurring during the middle stages of the overall mass loss. For the solid isolated from the [+Ca,+A] boundary system at pH 11, a slow, progressive mass loss of $\sim 8\%$ was observed up to $\sim 500^\circ\text{C}$, followed by a 21.3% mass loss from 600 to 850°C . The first mass loss is attributed to the decomposition of CdCO_3 , while the second mass loss involves decomposition of the secondary phase CaCO_3 to CaO and CO_2 , which has been shown to decompose above $600\text{--}675^\circ\text{C}$, being complete by $\sim 810^\circ\text{C}$ (Duval, 1963).

It should be noted that some slight variations existed between the XRD patterns that were observed experimentally for Cd(OH)Cl , $\text{CdSO}_4 \cdot 3.5\text{Cd(OH)}_2 \cdot x\text{H}_2\text{O}$ and $\text{Mg}_5(\text{OH})_2(\text{CO}_3)_4 \cdot 4\text{H}_2\text{O}$, and those given in their JCPDS files (JCPDS, 1989). This may be attributed to slight differences in the $\text{OH}^- : \text{A}^{m-}$ ratios (where $\text{A}^{m-} = \text{SO}_4^{2-}$ and Cl^-) in the solids and/or to the degree to which hydration occurred between the experimentally observed and the reported phases. Similar deviations have been observed in related studies of the solids formed in the Zn(II)-SO_4^{2-} , Zn(II)-CO_3^{2-} and Pb(II)-SO_4^{2-} systems (Baltpurvins *et al.*, 1996, 1997a).

3.2. THEORETICAL CALCULATIONS VERSUS EXPERIMENTAL RESULTS

In the absence of Cl^- and SO_4^{2-} , $\beta\text{-Cd(OH)}_2$ is known to form directly from solution on addition of OH^- to Cd(II) (Baes and Mesmer, 1976). However, in the present studies, in either the Cl^- and SO_4^{2-} systems, Cd(OH)Cl and

$\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ were formed, respectively, even at low anion concentrations. This is a reflection of relatively strong Cd(II)-anion complex formation in aqueous solution that subsequently influences solid phase formation following addition of OH^- . Previous investigations have indicated that Cd(II) and Zn(II) show a similar range of species in freshwater-seawater and freshwater-brine mixtures (Long and Angino, 1977). This was attributed to their similar cationic charges and valence orbital electron configurations ($4d^{10}$ and $3d^{10}$, respectively), despite the fact that there are significant differences in their ionic radii [crystal radii, 4 coordination: Zn(II), 0.74 Å; Cd(II), 0.92 Å (Shannon, 1976)]. The study revealed that both cations were strongly complexed by chloride ion, with Cd(II) complexed more strongly than Zn(II), and that the chemical speciation distributions of both ions were similar.

Baltpurvins *et al.* (1997a) have studied the precipitation behaviour of Zn(II) in the presence of both Cl^- and SO_4^{2-} , as well as the effects of added Ca^{2+} . Their results on the solubility-limiting phases indicated the formation of the hydroxy-anion phases $\text{Zn}_5(\text{OH})_8\text{Cl}_2$ and $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot x\text{H}_2\text{O}$ in the presence of Cl^- and SO_4^{2-} , respectively, at low pH values and at high anion concentrations, and showed that conversion to ZnO occurred at higher pH values. The latter presumably occurs by dehydration of $\text{Zn}(\text{OH})_2$ (Schindler *et al.*, 1967). It is not unexpected, therefore, given the similarities between Cd(II) and Zn(II), that mixed hydroxy-anion phases such as $\text{Cd}(\text{OH})\text{Cl}$ and $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ were formed in the present studies as solubility-limiting phases in the Cl^- and SO_4^{2-} systems. This was found to depend, however, on the pH of the solution, and has been discussed above. Notably, these mixed hydroxy-anion phases occurred irrespective or not of the presence of any added Ca^{2+} or Mg^{2+} , as no multi-component Cd(II)-containing complex species involving these cations were observed.

The present studies have shown that $\text{Cd}(\text{OH})\text{Cl}$ formed at both pH 9 and 11 in the Cl^- anion system irrespective of the presence of added Ca^{2+} , with some conversion to $\beta\text{-Cd}(\text{OH})_2$ at pH 11, but was found only at pH 9 in the presence of Mg^{2+} because complete conversion to $\beta\text{-Cd}(\text{OH})_2$ occurred at pH 11 in this latter system. In the SO_4^{2-} system, however, $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ was formed at pH 9, except in the [+Ca, -] system which produced $\beta\text{-Cd}(\text{OH})_2$, and the former species was also found at pH 11 in the absence of added Ca^{2+} . Conversion into $\beta\text{-Cd}(\text{OH})_2$ occurred in the presence of both Ca^{2+} and Mg^{2+} at pH 11. The different behaviour observed for the two anions is a reflection of the ability of Cd(II) to complex Cl^- more strongly than SO_4^{2-} . This is demonstrated by the relatively higher first formation constant between Cd(II) and Cl^- compared to Cd(II) and SO_4^{2-} than found for the analogous Zn(II)/anion systems, and also by the fact that Cl^- forms multiple complexes with Cd(II) (Table IV). A similar observation in the corresponding Zn(II)/ Cl^- and Zn(II)/ SO_4^{2-} systems was made by Baltpurvins *et al.* (1997a), and is evidenced by the respective formation constants of the two metal ions (Table IV). It should be noted in passing that the observed increase in the formation constants for anion association between the first and second Cl^- anions

TABLE IV
Stability (association) constants for Cd(II) and Zn(II) with Cl^- and SO_4^{2-} ^{a,b}

Metal Ion	Cl^-	SO_4^{2-}
Cd(II): $\log\beta_{11}$	1.98	2.46
$\log\beta_{12}$	2.6	
$\log\beta_{13}$	2.4	
$\log\beta_{14}$	1.7	
Zn(II): $\log\beta_{11}$	0.43	2.38
$\log\beta_{12}$	0.61	
$\log\beta_{13}$	0.5	
$\log\beta_{14}$	0.2	

^aSmith and Martell (1976).

^bSmith and Martell (1989).

to both Cd(II) and Zn(II) is likely caused by a change in metal coordination, as the $[\text{M}(\text{OH}_2)_6]^{2+}$ species ($\text{M} = \text{Cd}$ and Zn) are octahedral, while the $[\text{MCl}_4]^{2-}$ species are tetrahedral (Cotton and Wilkinson, 1988).

In the present study transformation of both the hydroxy-anion phases $\text{Cd}(\text{OH})\text{Cl}$ and $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ to $\beta\text{-Cd}(\text{OH})_2$ was observed on increasing the pH from 9 to 11, but this was complete at the higher pH value only in the Cd(II)/ SO_4^{2-} system in the presence of added Ca^{2+} or Mg^{2+} , and only in the Cd(II)/ Cl^- system in the presence of Mg^{2+} . In the case of added Ca^{2+} , the above precipitation behaviour for both the Cl^- and SO_4^{2-} anion systems is similar to that reported in previous studies on the related Zn(II) systems (Baltpurvins *et al.*, 1997a), except that in the Zn(II)/ Cl^- system, the zinc(II)-hydroxide-chloride precipitate, $\text{Zn}_5(\text{OH})_8\text{Cl}_2$, was only found at high chloride concentrations and low pH values (pH 8 and 9), and transformed completely to ZnO at pH 11. As the stability constants for Cd(II) and Zn(II) are relatively similar for an individual anion (Table IV), their precipitation behaviour with Cl^- is therefore expected to be relatively similar. The lower Zn(II)- Cl^- formation constants relative to the corresponding Cd(II)- Cl^- values account for the above difference in behaviour. In the presence of added Mg^{2+} , however, irrespective of the anion system, $\beta\text{-Cd}(\text{OH})_2$ was formed at pH 11, along with $\text{Mg}(\text{OH})_2$, suggesting that Mg^{2+} promotes the formation of $\beta\text{-Cd}(\text{OH})_2$ relative to Ca^{2+} . This is likely attributable to a significant nucleating effect of $\text{Mg}(\text{OH})_2$ at pH 11, as $\beta\text{-Cd}(\text{OH})_2$ is isomorphous and isostructural with $\text{Mg}(\text{OH})_2$ (both are hexagonal, with $a \approx 3.1$ and $c \approx 4.6 \text{ \AA}$) (Wells, 1976; JCPDS, 1989). While $\text{Ca}(\text{OH})_2$ is also isomorphous and isostructural with the above hydroxides, it is relatively soluble compared to $\text{Mg}(\text{OH})_2$ and was never observed as a precipitated phase, so that the corresponding effect did not occur with added Ca^{2+} .

Several studies have attempted to elucidate the stability intervals over which $\text{Mg}(\text{OH})_2$ formation in Cl^- and SO_4^{2-} -rich systems occurs (Janecky and Seyfried, 1983; Harvie *et al.*, 1984). In general, the formation of $\text{Mg}(\text{OH})_2$ is favoured at anion concentrations less than $\sim 0.5 \text{ mol dm}^{-3}$. Higher anion concentrations promote the formation of mixed Mg^{2+} -hydroxy-anion salts such as $\text{Mg}_2(\text{OH})_2\text{SO}_4$.

3.2.1. Solubility Domains in the Presence of Ca^{2+}

Based on the above results, for the Ca^{2+} -containing systems, $\text{Cd}(\text{OH})\text{Cl}$ and $\beta\text{-Cd}(\text{OH})_2$ were chosen as the solubility-limiting phases for the solubility domain calculations in the $\text{Cd}(\text{II})/\text{Cl}^-$ system, while $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and $\beta\text{-Cd}(\text{OH})_2$ were used in the $\text{Cd}(\text{II})/\text{SO}_4^{2-}$ system, for all four boundary systems. Transformation of both $\text{Cd}(\text{OH})\text{Cl}$ and $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ into $\beta\text{-Cd}(\text{OH})_2$ occurred at high pH values. In the $\text{Cd}(\text{II})/\text{CO}_3^{2-}$ system CdCO_3 was used as the solubility-limiting phase, with transformation to $\beta\text{-Cd}(\text{OH})_2$ again occurring at high pH values.

Solubility products ($\log K_{\text{sp}}$ values) given for $\beta\text{-Cd}(\text{OH})_2$ in the literature over the temperature range of 20–25 °C vary between -12.77 and -14.61 (Tünay *et al.*, 1991). These refer mainly to values corrected to zero ionic strength. The value of -14.29 given by Smith and Martell (1976), at an ionic strength of zero, was chosen for the solubility domain calculations in the present study. The solubility product for $\text{Cd}(\text{OH})\text{Cl}$ of -3.52 ($\log K_{\text{sp}}$ value) was taken from the Minteqa2 database. No literature values for the solubility product of $\text{CdSO}_4 \cdot 3.5\text{Cd}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ [i.e. $\text{Cd}_{4.5}(\text{OH})_7\text{SO}_4 \cdot x\text{H}_2\text{O}$] are available. However, for the related compounds of similar composition $\text{Cd}_4(\text{OH})_6\text{SO}_4$ and $\text{Cd}_3(\text{OH})_4\text{SO}_4$, $\log K_{\text{sp}}$ values of -28.40 and -22.56 , respectively, are given in the Minteqa2 database, and the former value was used given the closeness of the two formulations. The $\log K_{\text{sp}}$ values for the solubility product of CdCO_3 vary from -11.71 (Davis *et al.*, 1987) to -13.74 (Smith and Martell, 1976), which may represent freshly precipitated and aged materials, respectively, and their use will be discussed below.

The three-dimensional relationship between pH, $[\text{Ca}^{2+}]$ and residual $\text{Cd}(\text{II})$ in solution that is formed by the four composition boundary profiles may be projected onto a two-dimensional, residual soluble $\text{Cd}(\text{II})$ -pH plane as a solubility domain. Provided the pH, $[\text{Ca}^{2+}]$ and anion concentration are maintained within those values used to construct the solubility domain boundaries, the residual $\text{Cd}(\text{II})$ in solution must reside within the solubility range encompassed by the solubility domain. When derived in this way, the upper and lower boundaries thus represent absolute maximum and minimum solubilities predicted by any combination of the four precipitation profiles. More complex systems such as those containing, for example, the presence of additional complexing agents, require data for the extra species to be included in the solubility domain calculations.

The solubility domains and experimental profiles for the $\text{Cd}(\text{II})/\text{Cl}^-$ and $\text{Cd}(\text{II})/\text{SO}_4^{2-}$ systems, both involving added Ca^{2+} , are shown in Figures 1 and 2, respectively. For the $\text{Cd}(\text{II})/\text{Cl}^-$ system, the lower boundary of the solubility domain

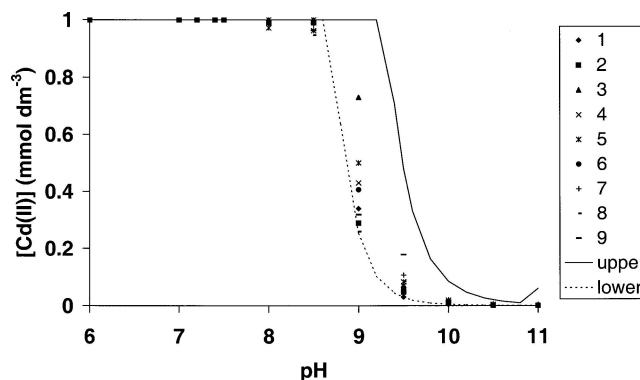


Figure 1. Calculated solubility domain and titration data for the Cd(II)/Cl⁻ system, with added Ca²⁺. Precipitation profile numbers are given in Table II. No precipitation occurs between pH 2 and 6.

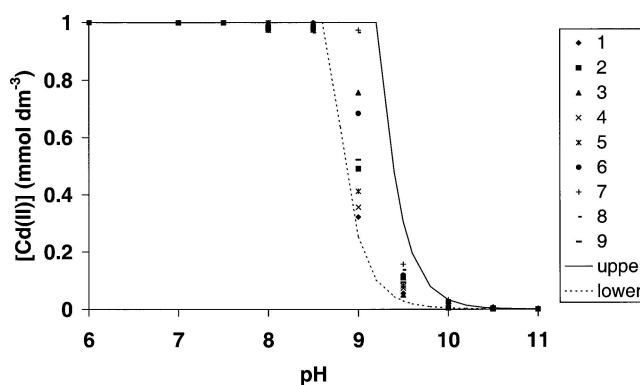


Figure 2. Calculated solubility domain and titration data for the Cd(II)/SO₄²⁻ system, with added Ca²⁺. Precipitation profile numbers are given in Table II. No precipitation occurs between pH 2 and 6.

was generated from the [-,-] system throughout the entire pH range, while the upper domain boundary was calculated from the [+Ca,+A] system, again independently of pH. Calculations of the boundary precipitation profiles were based entirely on the thermodynamic preferences of the systems.

The solubility domain for the Cd(II)/SO₄²⁻ system was generated from the thermodynamic preference for CdSO₄·3.5Cd(OH)₂·xH₂O and β-Cd(OH)₂. Transformation of CdSO₄·3.5Cd(OH)₂·xH₂O into β-Cd(OH)₂ was included in the high sulfate concentration systems. The lower boundary was calculated from the [-,-] system, while the upper boundary was calculated from the [-,+A] system throughout the pH range examined. Surface-enhanced precipitation or coprecipitation/adsorption interactions involving CaSO₄·2H₂O were not considered. No evidence could be found in the literature to suggest that these mechanisms act

to control Cd(II) solubility for systems in which Cd(II) concentrations exceed the aqueous ion activity product of the bulk precipitate phase, a conclusion also reached in the analogous Zn(II)/SO₄²⁻ system (Baltpurvins *et al.*, 1997a).

For both the Cd(II)/Cl⁻ and Cd(II)/SO₄²⁻ systems, all experimental precipitation profiles were sigmoidal in shape, which is typical of amphoteric hydroxides. In each case the onset of precipitation occurred at a pH of ~8–9, and effectively all of the experimental data are enclosed within the calculated solubility domains, as expected. The residual Cd(II) concentration minima occurred by pH 10.5, and no resolubilization was observed over the pH range studied. This is in agreement with previous studies (Tünay *et al.*, 1991), which showed that residual Cd(II) concentration only increased above pH 11.

The solubility domain and experimental precipitation profiles for the Cd(II)/CO₃²⁻ system, with added Ca²⁺, are shown in Figure 3. For the chemical boundaries of the Cd(II)/CO₃²⁻ system, the [–,–] system was used to generate the upper boundary while the lower boundary was generated from the [–,+A] system. The solubility-limiting phases were CdCO₃ at low pH and β-Cd(OH)₂ at pH 11. As indicated above, literature data for the solubility product (log *K*_{sp} values) of CdCO₃ vary from –11.71 (Davis *et al.*, 1987), which was obtained by equilibration of freshly precipitated CdCO₃ under CO₂ in nitrogen at 25 °C, to the value of –13.74 listed in Smith and Martell (1976). The former value was employed to generate the upper domain, while the latter value was used to calculate the lower domain in the present studies. This approach, using a range of solubility products, has been employed previously to calculate solubility domains for Ni(II) and Fe(III) systems (Lin *et al.*, 1998; Baltpurvins *et al.*, 1996).

Although adsorption of Cd(II) on calcite is known to occur (Davis *et al.*, 1987; Zachara *et al.*, 1991), no attempt was made to incorporate an adsorption mechanism into the solubility domain calculations. This is because previous studies have

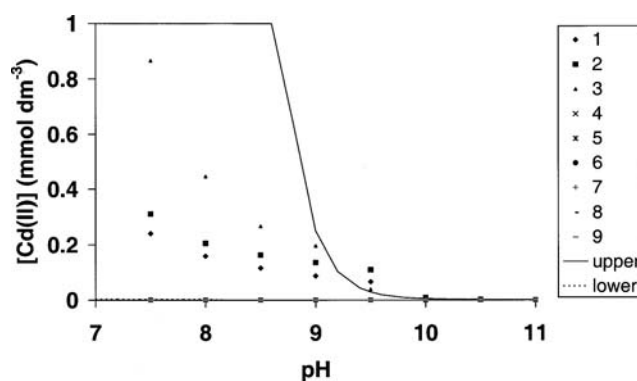


Figure 3. Calculated solubility domain and titration data for the Cd(II)/CO₃²⁻ system, with added Ca²⁺. Precipitation profile numbers are given in Table II.

indicated that adsorption of Cd(II) decreases substantially as pH increases (Davis *et al.*, 1987), and that adsorptive processes have been shown to have only a minimal effect on the residual metal ion concentration in the pH region of bulk precipitation (Comans and Middleburg, 1987). It is therefore expected that above pH 9, the adsorptive effects of calcite on residual Cd(II) concentration would be small.

The experimental results and the calculated solubility domain (Figure 3) indicate that the titration data are generally contained within the calculated domain. Significant variations in the residual Cd(II) concentration were observed in the experimental Cd(II)/CO₃²⁻ systems. The reason for this is that the solubility of Cd(II) is highly dependent on variations in the CO₃²⁻ concentration. Similar results were observed in previous studies in the Ni(II)/CO₃²⁻ system (Lin *et al.*, 1998). Importantly, however, the calculated upper and lower boundaries of the solubility domain essentially encompass the experimental precipitation results.

For all three systems, if an arbitrary discharge limit of, say, 1 mg/L of Cd(II) is assumed, then treatment efficiency based on the experimental data is assured within the range of pH ~9.9–11 for the Cd(II)/Cl⁻ system, ~10–11 for the Cd(II)/SO₄²⁻ system, and ~9.9–11 for the Cd(II)/CO₃²⁻ system. The treatment quality assurance range defined by the intercept of the arbitrary discharge limit with the actual upper boundary of the calculated solubility domain gives slightly reduced ranges for treatment efficiency in the Cl⁻ and SO₄²⁻ anion systems. While such treatment as described yields low Cd(II) concentrations, the minimum pH of the resulting treated wastewater may be too high for direct disposal, particularly into inland waters, according to local regulations. Following separation of the insoluble Cd(II)-containing material, the pH may be adjusted to lower values by subsequent treatment with acid prior to disposal. Some evidence of Cd(II) resolubilization was predicted from the theoretical upper solubility boundary in the Cd(II)/Cl⁻ system, presumably as a result of formation of soluble anionic hydroxy complexes, although this was not observed experimentally.

3.2.2. Solubility Domains in the Presence of Mg²⁺

For all Mg²⁺-containing systems, the solubility-determining phases were identical with the corresponding Ca²⁺-containing systems, with complete conversion into β -Cd(OH)₂ occurring at pH 11 with both Cl⁻ and SO₄²⁻ anions. In the Cd(II)/CO₃²⁻ system no conversion to β -Cd(OH)₂ at pH 11 was observed. The solubility products required in the solubility domain calculations were the same as those used above, along with log K_{sp} values for MgCO₃·3H₂O and Mg₅(OH)₂(CO₃)₄·4H₂O of -5.59 and -30.2, respectively (Langmuir, 1965). Previous investigations have indicated that the formation of MgCO₃·3H₂O and Mg₅(OH)₂(CO₃)₄·4H₂O are highly metastable with respect to Mg(OH)₂, and depend on the CO₃²⁻:OH⁻ ratio (Christ and Hostetler, 1970; Langmuir, 1965). It was also shown that the system was mainly kinetically controlled and that MgCO₃·3H₂O occurred over a very narrow pH stability region, with transformation to Mg₅(OH)₂(CO₃)₄·4H₂O occurring readily (Langmuir, 1965).

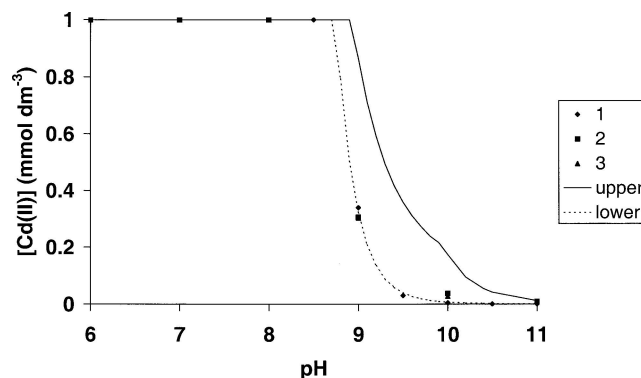


Figure 4. Calculated solubility domain and titration data for the Cd(II)/Cl⁻ system, with added Mg²⁺. Precipitation profile numbers are given in Table III. No precipitation occurs between pH 2 and 6.

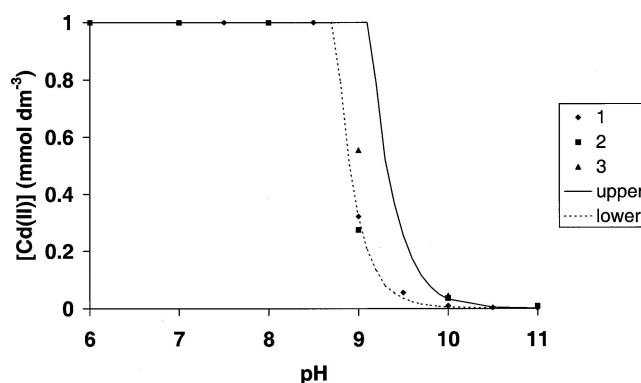


Figure 5. Calculated solubility domain and titration data for the Cd(II)/SO₄²⁻ system, with added Mg²⁺. Precipitation profile numbers are given in Table III. No precipitation occurs between pH 2 and 6.

The calculated solubility domains and experimental profiles for the Cd(II)/Cl⁻, Cd(II)/SO₄²⁻ and Cd(II)/CO₃²⁻ systems, all involving added Mg²⁺, are shown in Figures 4 to 6, respectively. The lower solubility boundary in all three cases was calculated from the [-,-] Cl⁻, [-,-] SO₄²⁻ and [-,-] CO₃²⁻ systems, respectively, while the upper boundaries of these systems were obtained from the [+Mg,+A] Cl⁻, [+Mg,+A] SO₄²⁻ and [+Mg,+A] CO₃²⁻ systems, respectively. Potential adsorption of Cd(II) onto secondary precipitates was not included in any of the calculations, as no evidence for Cd(II) adsorption onto any of the Mg²⁺-containing precipitates could be found in the literature. Effectively all of the experimental data resides inside the calculated domain, as expected. It is interesting to note, however, that in all three systems, particularly the Cl⁻ and SO₄²⁻ systems, the experimental data fall close to the lower boundaries of the calculated solubility domains. This

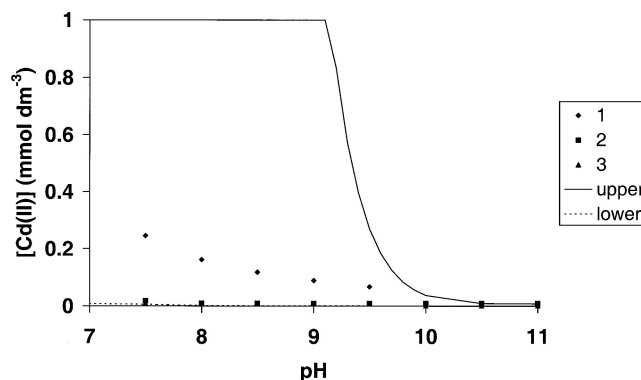


Figure 6. Calculated solubility domain and titration data for the Cd(II)/CO₃²⁻ system, with added Mg²⁺. Precipitation profile numbers are given in Table III.

is likely related to the choice of values for the β -Cd(OH)₂ and CdCO₃ solubility products. The former is known to vary significantly with ionic strength, while the latter shows a range of values, which may also depend on ionic strength, but for which data is not currently available.

As found for the analogous Ca²⁺-containing systems, the experimental precipitation profiles of the Cd(II)/Cl⁻ and Cd(II)/SO₄²⁻ systems were sigmoidal in shape. The onset of precipitation occurred at a pH of 8.5–9, and all of the experimental data are enclosed within the calculated solubility domains. The residual Cd(II) concentration minima in all three anion systems again occurred by pH 10.5, and no resolubilization was observed over the pH range studied. If an arbitrary discharge limit of, say, 1 mg/L of Cd(II) in solution is again assumed, as in the analogous Ca²⁺-containing systems, then treatment efficiency based on the experimental data is assured within the range of pH ~10.1–11 for the Cd(II)/Cl⁻ system, ~10.2–11 for the Cd(II)/SO₄²⁻ system, and ~9.9–11 for the Cd(II)/CO₃²⁻ system. Again the treatment quality assurance range defined by the intercept of the discharge limit with the upper boundary of the solubility domain gives slightly reduced ranges for treatment efficiency. Following separation of the Cd(II)-containing solids, the treated wastewater may have to be acidified slightly prior to disposal into, for example, inland waters to ensure compliance with local regulations.

4. Conclusions

The application of the solubility domain approach for the Cd(II)/Cl⁻, SO₄²⁻ and CO₃²⁻ systems provides a simple and effective means for predicting precipitation efficiency limits for Cd(II)-containing wastewaters using both lime and magnesia as a source of base. The solubility-determining phases have been found to be highly dependent on the nature of the electrolytes in the effluents. The presence

of secondary precipitates such as gypsum and calcite in the Ca^{2+} -containing systems had little influence on the overall treatment performance, making the observed limits dependent only on precipitation mechanisms.

For all systems, the nature of the counter-anion strongly influenced the removal of Cd(II) by formation of Cd(II) hydroxy-anion or Cd(II)-anion precipitates. However, for Cl^- and SO_4^{2-} -containing systems, their influence on the control of precipitation was limited to low pH values (~ 9) with transformation into $\beta\text{-Cd}(\text{OH})_2$ occurring, to a greater or lesser extent, in all of the systems at high pH (~ 11). The onset of precipitation of Cd(II) also varied significantly. This can be attributed in part to the metastable nature of fresh precipitates, with the degree of polymorph transformation being dependent on the solution composition.

The physical advantages obtained by the use of magnesia rather than lime have been detailed in the Introduction. However, there also appears to be a further advantage, in that the presence of $\text{Mg}(\text{OH})_2$ at high pH values promotes the formation of the highly insoluble $\beta\text{-Cd}(\text{OH})_2$, probably as a result of a nucleating effect as $\text{Mg}(\text{OH})_2$ and $\beta\text{-Cd}(\text{OH})_2$ are isomorphous and isostructural. A similar effect has been observed in the related $\text{Co}(\text{II})/\text{Cl}^-$ and $\text{Co}(\text{II})/\text{SO}_4^{2-}$ systems with the formation of $\beta\text{-Co}(\text{OH})_2$ being promoted at higher pH values, at the expense of $\alpha\text{-Co}_2(\text{OH})_3\text{Cl}$ and $\alpha\text{-Co}_2(\text{OH})_2\text{SO}_4$ (Lin, 1998).

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