Pergamon

Cement and Concrete Research, Vol. 25, No. 5, pp. 1043–1053, 1995

0008-8846/95 $9.50 + .00

0008-8846(95)00099-2

MEASUREMENT AND PREDICTION OF PORTLANDITE SOLUBILITY IN ALKALI SOLUTIONS

J. Duchesne and E. J. Reardon
University of Waterloo, Dept. of Earth Sciences,
Waterloo, Ontario, Canada, N2L 3G1

(Refereed)
(Received August 8, 1994; in final form April 17, 1995)

ABSTRACT

The solubility of $Ca(OH)_2$ has been determined in sodium and potassium hydroxide solutions to 4 molal concentration at 25°C. These data and other solubility and EMF measurements in the Ca-K-Cl-OH-H_2O system have been used to refine Pitzer ion interaction parameter data for the $Ca(OH)_2$-H_2O system. Applications of these parameters to the results of 15 independent studies of portlandite solubility in pure water yield an average solubility product of $-\log K_{sp} = 5.19 \pm 0.04$. The resultant model yields an excellent representation of all available portlandite solubility data in $CaCl_2$, $CaSO_4$, NaCl, NaOH, KCl, Na_2SO_4 and K_2SO_4 solutions and their mixtures. The refined parameters will provide an improved representation of portlandite solubility in cement/water systems whose ionic strengths are typically beyond the limits for the application of Debye-Hückel based ion pairing equilibria models.

Introduction

Chemical equilibrium models can have an important role in representing the chemical composition of cement/water systems. An ion interaction model for electrolyte activity coefficients was developed by Pitzer and co-workers during the last two decades (1). The Pitzer model ascribes deviations of experimental data with those predicted using the Debye-Hückel theory to short-range electrostatic interactions between ions. The Pitzer equations for the osmotic or ion activity coefficients consist of the Debye-Hückel core to which are added a series of terms that contain the various ion interaction parameters to account for the ionic strength dependence of the short-range forces in electrolyte solutions. The ion interaction parameters describe the interactions between two ions of opposite charge in solution ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^{ϕ}), two ions of like charge (θ), two cations and one anion or two anions and one cation (ψ), and finally interactions of ions with a neutral species (λ). Other types of interaction such as interaction between three like ions or four ions are considered so unlikely to occur in solution that they are not included in equations for the osmotic or activity coefficients. Because it is based on experimental data, the Pitzer model allows the simulation of chemical equilibria between minerals and water to high concentrations. The strength of the model is its ability to accurately describe equilibria in multi-component solutions based on parameterization of data collected from simple binary and ternary salt/water systems. The ion interaction parameters are determined by regression analysis of thermochemical data such as isopiestic measurements, mineral solubility and EMF measurements in these systems. Although an extensive parameter database exists (1, 2, 3), many systems have not been described and there is often a need to refine a set of parameters as new thermochemical data become available.

Cement porewater can be described principally as a solution of Na^+, K^+, Ca^{2+} and OH^- ions, where portlandite ($Ca(OH)_2$) solubility controls Ca^{2+} concentrations. (SO_4^{2-} is an important ion in cement porewater only at early time.) However, there are few published solubility data of portlandite in KOH or NaOH solutions. The only data available are the 20°C measurements of Fratini (4) up to 0.2 molar (M) and Diamond (5) to 1 M. For these reasons, we have made additional measurements of $Ca(OH)_2$ solubility in sodium and potassium hydroxide solution up to 3.8 molal (m) at 25°C. New Ca-OH ion interaction parameters were regressed from our solubility data along with available solubility and EMF measurements in the literature. Parameterization of this system is important for the refinement of predictive models to describe the chemical composition in cement/water systems.

Materials and Methods

$Ca(OH)_2$ solubility measurements

Portlandite solubility measurements in sodium and potassium hydroxide solutions were made at 25°C. Solubility was approached from both under and supersaturation by dissolving excess reagent grade $Ca(OH)_2$ in NaOH or KOH solutions of various concentration varying from 0 to 3.8 m. The stock solutions were made with reagent grade NaOH and KOH. The concentrations of the stock solutions were verified by titration with standardized H_2SO_4. An excess of $Ca(OH)_2$, corresponding to ten times its solubility in pure water, was added to each solution in 30 ml high density polyethylene containers. The containers were mounted on a Plexiglas carousel that was suspended in a temperature bath maintained to within 0.1°C at 25°C. The carousel was rotated between 10 and 20 rpm for a period of 4 days. According to Johnston and Grove (6) and Kolthoff and Stenger (7), less than 24 hours was sufficient for equilibrium to be reached between portlandite and the solution. Yeatts and Marshall (8) and Bassett (9) reported equilibration times as low as one hour.

After the solutions were sampled at 25°C, the reaction vessels were returned to the bath and equilibrated at 13°C for 4 days. The purpose of this cooling was to force the solutions to become supersaturated relative to 25°C. Portlandite solubility is higher at lower temperature as indicated by a negative $\Delta H_R{}^o$ value for portlandite dissolution. The Van't Hoff equation was used to verify the ratio between portlandite solubility measurements at 25 and 13°C. The bath was then reset to 25°C to achieve solid phase equilibration from supersaturation conditions. A number of solutions were sampled and solubility values compared with the first set of experiments at 25°C. All solutions were filtered through 0.22 μm filters, diluted and acidified with 1:1 HCl solution, before analyses.

All solutions were analysed for calcium with a Varian Model 1475 atomic absorption spectrophotometer (AAS). Calcium determinations were carried out at a wavelength of 418 nm using an air-acetylene flame. A releasing agent consisting of 10% lanthanum chloride solution was added to avoid interferences from the presence of sodium and potassium. However, matrix interference from the presence of NaOH or KOH in the samples was observed despite the use of the releasing agent.

Matrix Interference

We observed that the absorbance response to calcium was reduced in the presence of high sodium or potassium hydroxide concentration as previously reported by Diamond (5) and Hobbs (pers. comm.). We evaluated the importance of the interference by measuring the AAS peak height of a 24 ml 1.6 ppm calcium standard solution with the sequential addition of five 1 ml aliquots of 1N NaOH solution. The absorbance markedly decreased with successive additions. With two additions, the AAS peak height measurement was 57% less than the initial measurement without NaOH addition while the dilution caused by adding 2 ml NaOH was only 8%. Further NaOH additions decreased the AAS peak height but to a lesser extent.

Because of this pronounced matrix interference, three standard solutions containing about 1, 2 and 4 mg/L of calcium and the same amount of NaOH or KOH, HCl, and lanthanum chloride as in the experimental samples were prepared. Three absorbance measurements were made by alternating the sequence of the standard and samples in order to minimize the effects due to machine drift. The three readings were averaged and an error of 0.77±0.13% was calculated as the mean error of the 68 sets of 3 peak height measurements. An individual calibration curve was constructed for each sample using the three standards which matched the sample matrix. The calcium concentration of the sample was calculated using a regression equation established from the calibration curve. This method of calculation was applied to each sample to correct for the matrix interference.

Results and discussion

$Ca(OH)_2$ solubility measurements

In this study, a value of 0.0222 m was measured for $Ca(OH)_2$ solubility in water at 25°C. A difference of less than 1% was observed between under and supersaturated runs. The measured solubility in pure water at 13°C was within 5% of that predicted using the Van't Hoff equation and heat of formation data. The addition of Na or K hydroxide markedly decreases the solubility of $Ca(OH)_2$. Indeed the solubility is two orders of magnitude lower at the highest NaOH and KOH concentration (~4 molal). Table 1 records the full set of solubility data determined in this study.

Table 2 presents $Ca(OH)_2$ solubility values measured in pure water by different workers at 25°C. This table shows some disagreement among reported values. The lowest value of 0.0198 m was measured by Johnston and Grove (6) for the solubility of large well-defined crystals of $Ca(OH)_2$, while a value of 0.0230 m was obtained by Bassett (9) for fine $Ca(OH)_2$ crystals. These observations indicate that $Ca(OH)_2$ solubility is dependent upon crystal size; presumably due to a high surface energy of portlandite particles in water. The surface energy of fine particles contributes to an overall increase in the ΔG^o_f of the compound and therefore an enhancement in its solubility. This solubility enhancement decreases over long time due to Ostwalt ripening.

TABLE 1
$Ca(OH)_2$ Solubility Measurements in KOH and NaOH Solutions at 25°C.

KOH solution		NaOH solution	
K^+ (m)	Ca^{2+} (m)	Na^+ (m)	Ca^{2+} (m)
0	0.0222	0	0.0222
0.0009	0.0220	0.0010	0.0217
0.0047	0.0210	0.0048	0.0209
0.010	0.0190	0.010	0.0197
0.019	0.0172	0.019	0.0172
0.047	0.0114	0.048	0.0111
0.094	0.00637	0.096	0.00573
0.190	0.00328	0.193	0.00330
0.482	0.00127	0.487	0.00126
0.991	0.00072	0.991	0.00065
1.965	0.00036	1.965	0.00042
3.860	0.00021	3.627	0.00023

TABLE 2
$Ca(OH)_2$ Solubility Data in Pure Water at 25°C.

Authors	Solubility (m)	Authors	Solubility (m)
Noyes & Chapin (11)	0.0202	Kolthoff & Stenger (7)	0.0214
Cameron & Bell (12)	0.0208	Bassett (9)	0.0202 (coarse)
Cameron & Robinson (13)	0.0210		0.0230 (fine)
Moody & Leyson (14)	0.0206	Bates et al. (10)	0.0229 (reagent)
Cameron & Patten (15)	0.0209		0.0204
Bassett & Taylor (16)	0.0205	Haslam et al. (18)	0.0209
Seidell (17)	0.0207	Linke (19)	0.0202
Johnston & Grove (6)	0.0120 (cryst.)*	Yeatts & Marshall (8)	0.0226 (reagent)

* large well-defined crystals

Pitzer Model Parameterization of the $Ca(OH)_2$-H_2O system.

Because of the low solubility of $Ca(OH)_2$ in water (0.02 m at 25°C), the single salt ion interaction parameters for $Ca(OH)_2$ cannot be derived simply from $Ca(OH)_2$/water system thermochemical data. This is a problem that is shared by all sparingly soluble salts. To obtain a robust set of parameters for a sparingly soluble salt, AX, it is necessary to include physicochemical measurements in solutions where A is in high concentrations (thus X is in low concentrations); and in solutions where X is in high concentrations (thus A is in low concentrations). This means that an ideal parameterized data set necessarily must include solutions that contain ions other than A and X. In deriving the interaction parameters for $Ca(OH)_2$, we chose K^+ and Cl^- to be these additional ions. Thus we assembled all thermochemical solution data in the Ca-K-Cl-OH-H_2O system for regression analysis. The analysis was performed using the Pitzer equations as given by

Harvie et al.(2) in a specially-prepared program, which allows regression of any selected number of parameters in multicomponent solution compositions. Ion interaction parameters for three salt/water systems; $KCl\text{-}H_2O$, $KOH\text{-}H_2O$, $CaCl_2\text{-}H_2O$ were used in the regression analysis to derive the single electrolyte parameters governing the interaction of two ions, Ca^{2+} and OH^- in solution. These data were obtained from the recent compilation of Pitzer (1). The system involved a total of 33 ion interaction parameters; 21 were known, 8 were found to have a negligible influence on the quality of the fit, and 4 were evaluated. The regressed parameters were $\beta^{(0)}$ $[Ca^{2+}\text{-}OH^-]$, $\beta^{(1)}$ $[Ca^{2+}\text{-}OH^-]$, $\beta^{(2)}$ $[Ca^{2+}\text{-}OH^-]$, and C^{ϕ} $[Ca^{2+}\text{-}OH^-]$.

Seven sources of literature data were assembled for the determination of the four parameters describing the interaction of Ca^{2+} and OH^- ions in solution. The ion interaction parameters were obtained by fitting simultaneously [1] data on the solubility of $Ca(OH)_2$ in 0.038 to 2.87 m KCl solution (6); [2] $Ca(OH)_2$ solubility in 0 to 3.86 m KOH solution (this study); [3] $Ca(OH)_2$ solubility in 0.476 to 4.39 m $CaCl_2$ solution (20); [4] individual $Ca(OH)_2$ solubility measurements in water (8, 10, 21); and, [5] emf measurements (22) of the cells

$$Pt: H_2\,(g),\ Ca(OH)_2,\ KCl \text{ or } CaCl_2,\ AgCl: Ag$$

for dilute $Ca(OH)_2$-KCl and $Ca(OH)_2$-$CaCl_2$ solutions. The potential of the cells are given by the expression

$$E = E^\circ - \frac{RT\ln 10}{F} \log (\gamma_{H^+}\gamma_{Cl^-} m_{H^+} m_{Cl^-})$$

where $E^\circ = 0.22234$ absolute volt at 25°C (23)
$R = 8.31439\ JK^{-1}mol^{-1}$
$F = 96493.1$ coulombs equivalent^{-1} (23)
$T = 298.16$ K

The data used to regress the parameters were selected up to the upper concentration limits recommended by Pitzer (1) for the application of its reported parameters. This was done to ensure that the values of the regression parameters derived in our analysis do not account for uncertainties in the known parameters used in the analysis. Consequently all solubility measurements were included only up to and including the first measurement above 4.3 m for $CaCl_2$, 4.8 m for KCl and 5.5 m for KOH solutions.

A total of 65 data were used to regress the $Ca^{2+}\text{-}OH^-$ ion interaction parameters. After the first regression analysis, the data of Johnston and Grove (6) (11 data) and three of the solubility data measured in this study (0.190, 1.965, and 3.86 m KOH solutions) were excluded from the parameterization since these values showed a deviation greater than two times the standard deviation of the predicted values. However, all of the data are used when comparisons of model predicted and actual experimental data are plotted. Figure 1 shows the observed divergence between predicted and measured values as a function of the square root of the ionic strength and indicates no substantive ionic strength dependence.

The four regressed parameters explain 99.95% of the variation of the data. The single parameter $\beta^{(0)}$ $[Ca^{2+}\text{-}OH^-]$ can explain 99.4% of the variation; however, the intercept value is significantly different from zero and more than six times higher than the intercept obtained by fitting with the four parameters. The results of the regression analysis of the 25°C solubility data are recorded in Table 3. This table also presents values for the 21 known parameters used in the regression

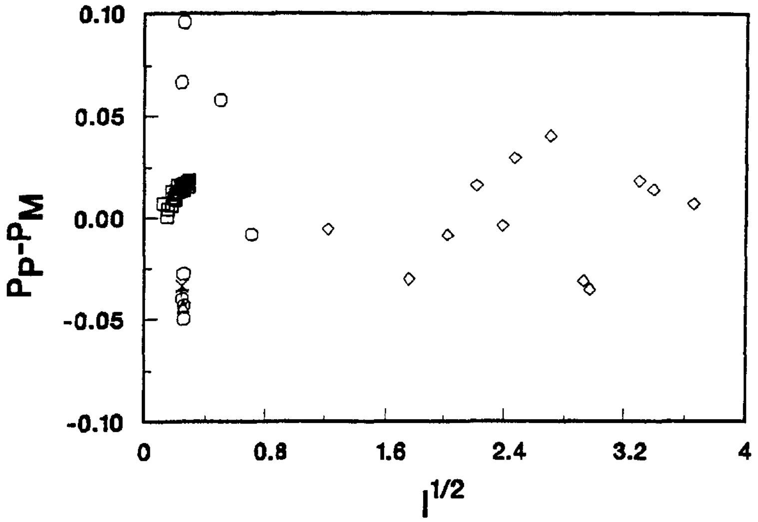

FIG. 1

Difference between predicted and measured values obtained from the fit of the Pitzer parameters. Open squares, circles, triangles, and diamonds are data from Bates et al. (22), this study, Schreinemakers and Figee (21), and Millikan (20), respectively. The plus and cross signs are from Johnston and Grove (6) and Yeatts and Marshall (8).

analysis from Pitzer (1). $\beta^{(0)}$ and $\beta^{(1)}$ together define the ionic strength dependence of the interaction of Ca^{2+} and OH^- in solution. The C^ϕ can be thought of as a parameter to account for three ion interactions at high concentrations. The $\beta^{(2)}$ parameter accounts for strong ion association in solution and acts in a similar way as would the association constant for $CaOH^+$in an ion pairing model. The $\beta^{(2)}$ parameter is important in fitting the low concentration data and has been related to the association constant (Ka) at infinite dilution by $\beta^{(2)} = -Ka/2$ (1). The ionization constant for calcium hydroxide ion pair ($CaOH^+$) at 25°C is reported to be between 0.04 and 0.07 mol kg^{-1} (8, 22, 25). This implies a $\beta^{(2)}$ value between -12.5 and -7.2. The regressed $\beta^{(2)}$ value of -11.05 obtained in this study is within this indicated range.

The average of all portlandite solubility measurements in Table 1 is 0.021±0.001. Application of the regressed parameters for Ca-OH interaction determined in this study yield a corresponding solubility product and standard deviation of $-\log K_{sp} = 5.19 \pm 0.04$. The results of the model fitted to the 25°C experimental data using $-\log K_{sp} = 5.19$ for portlandite are depicted in Figures 2 to 4 for the KCl, KOH, and $CaCl_2$ subsystems, respectively. The model for $Ca(OH)_2$ solubility is seen to accurately represent the regressed data. However, the strength of the Pitzer model has always been its predictive ability to represent equilibria in multicomponent and other salt/water systems not used in the parameterization. We now apply the derived parameters for $Ca(OH)_2$ to predict solubility relations in other systems and to compare them with published solubility data.

Figures 5 and 6 show a comparison of the model predictions with the experimental data in NaCl and NaOH solutions. It is important to note that these data were not used in the parameterization. The ion interaction parameters needed to describe sodium interactions in solution were obtained from the database given by Pitzer (1). In both systems, the agreement between the predicted and

TABLE 3

Ion Interaction Parameters for the Ca-K-Cl-OH System.

parameter	Pitzer (1)	Harvie (2).	this study	std dev.[a]
$\beta^{(0)}$ [Ca^{2+}-OH^-]	-	-0.1747	-0.1421[b]	0.0123
$\beta^{(1)}$ [Ca^{2+}-OH^-]	-	-0.2303	-0.3727[b]	0.1441
$\beta^{(2)}$ [Ca^{2+}-OH^-]	-	-5.72	-11.052[b]	1.392
C^{ϕ} [Ca^{2+}-OH^-]	-	-	-0.0092[b]	0.0277
$\beta^{(0)}$ [Ca^{2+}-Cl^-]	0.3053	0.3159	0.3053	
$\beta^{(1)}$ [Ca^{2+}-Cl^-]	1.7085	1.614	1.7085	
$\beta^{(2)}$ [Ca^{2+}-Cl^-]	-	-	-	
C^{ϕ} [Ca^{2+}-Cl^-]	0.00215	-0.00034	0.00215	
$\beta^{(0)}$ [K^+-Cl^-]	0.04835	0.04835	0.04835	
$\beta^{(1)}$ [K^+-Cl^-]	0.2122	0.2122	0.2122	
$\beta^{(2)}$ [K-Cl^-]	-	-	-	
C^{ϕ} [K^+-Cl^-]	-0.00084	-0.00084	-0.00084	
$\beta^{(0)}$ [K^+-OH^-]	0.1298	0.1298	0.1298	
$\beta^{(1)}$ [K^+-OH^-]	0.320	0.320	0.320	
$\beta^{(2)}$ [K^+-OH^-]	-	-	-	
C^{ϕ} [K^+-OH^-]	0.0041	0.0041	0.0041	
$\beta^{(0)}$ [H^+-Cl^-]	0.1775	0.1775	0.1775	
$\beta^{(1)}$ [H^+-Cl^-]	0.2945	0.2945	0.2945	
$\beta^{(2)}$ [H^+-Cl^-]	-	-	-	
C^{ϕ} [H^+-Cl^-]	0.00080	0.00080	0.00080	
θ [Ca^{2+}-K^+]	0.032	0.032	0.032	
θ [Ca^{2+}-H^+]	0.092	0.092	0.092	
θ [H^+-K^+]	0.005	0.005	0.005	
θ [Cl^--OH^-]	-0.050	-0.050	-0.050	
ψ [Ca^{2+}-H^+-OH^-]	-	-	-	
ψ [Ca^{2+}-H^+-Cl^-]	-0.015	-0.015	-0.015	
ψ [Ca^{2+}-K^+-OH^-]	-	-	-	
ψ [Ca^{2+}-K^+-Cl^-]	-0.025	-0.025	-0.025	
ψ [H^+-K^+-OH^-]	-	-	-	
ψ [H^+-K^+-Cl^-]	-0.011	-0.011	-0.011	
ψ [Ca^{2+}-OH^--Cl^-]	-0.025	-0.025	-0.025	
ψ [H^+-OH^--Cl^-]	-	-	-	
ψ [K^+-OH^--Cl^-]	-0.006	-0.006	-0.006	

(a) for this study only

measured values is excellent. Figures 6A and 6B present two different scales of the $Ca(OH)_2$ solubility in NaOH solution. Figure 6B shows that predicted values are only slightly above the experimental measurements at high NaOH concentration. Figures 7 to 10 compare the predicted solubility with experimental data in more complex systems. Figure 7 gives the predicted $Ca(OH)_2$ solubility in $CaSO_4$ solutions. The ion interaction parameters needed to describe sulfate interactions in solution were obtained from Hovey et al. data (26). The model is in good agreement with the experimental data. $Ca(OH)_2$ is only stable below 0.013 m $CaSO_4$; at higher concentrations it converts to gypsum ($CaSO_4 \cdot 2H_2O$). Figure 8 shows the predicted and experimental solution compositions in contact with $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ when K_2O concentration increases. Figures 9 and 10 present the $Ca(OH)_2$ solubility in solutions containing 1% KOH (Fig. 9) or NaOH (Fig. 10) given by mixing alkali oxide (K_2O or Na_2O) and alkali sulfates (K_2SO_4 or Na_2SO_4). Again, the model demonstrates considerable accuracy in predicting portlandite and gypsum solubility in different electrolyte solutions.

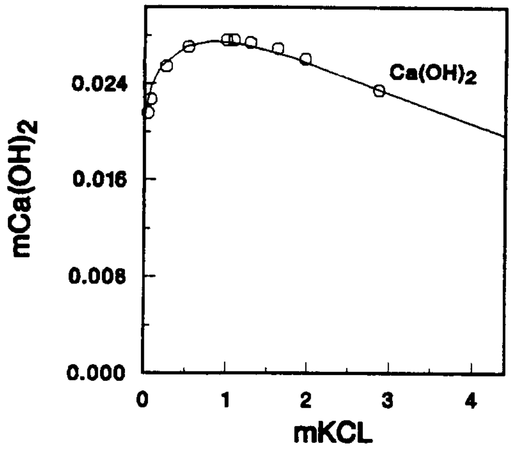

FIG. 2

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ solubility in KCl solution at 25°C. Data are from Johnston and Grove (6).

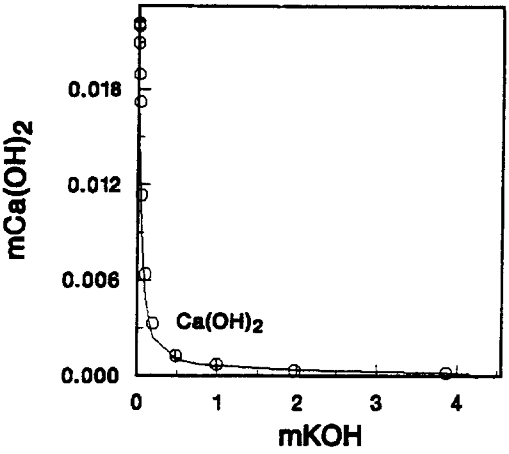

FIG. 3

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ solubility in KOH solution at 25°C. Circles are data from undersaturation while plus signs are from supersaturation.

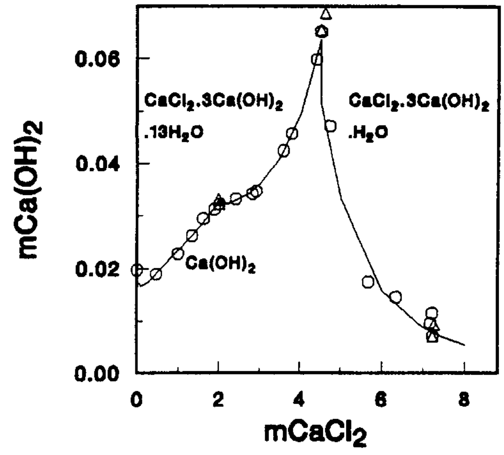

FIG. 4

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ solubility in $CaCl_2$ solution at 25°C. Data are from Millikan (20) (circles) and Schreine-makers and Figee (21) (triangles).

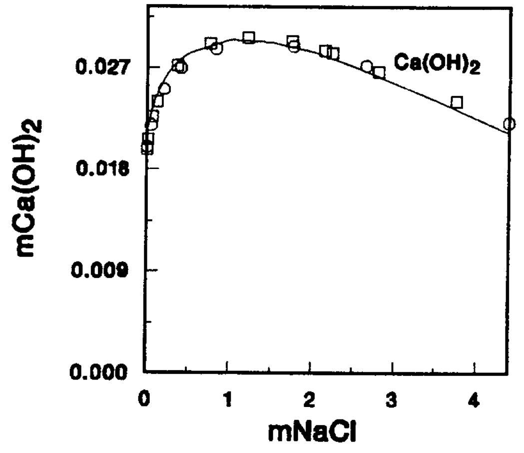

FIG. 5

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ solubility in NaCl solution at 25°C. Data are from Johnston and Grove (6) (squares) and Yeatts and Marshall (8) (circles).

The interaction parameters derived for $Ca(OH)_2$ in this study are quite different from those first reported by Harvie et al. (2) (see Table 3). Although their parameterization of $Ca(OH)_2$ only included portlandite solubility data to 0.8 molal KOH, solubility predictions based on their values yield similar results as our values. Nevertheless, we recommend the set of parameters reported in this study because the parameterization is based on more extensive data than used by Harvie et al. (2).

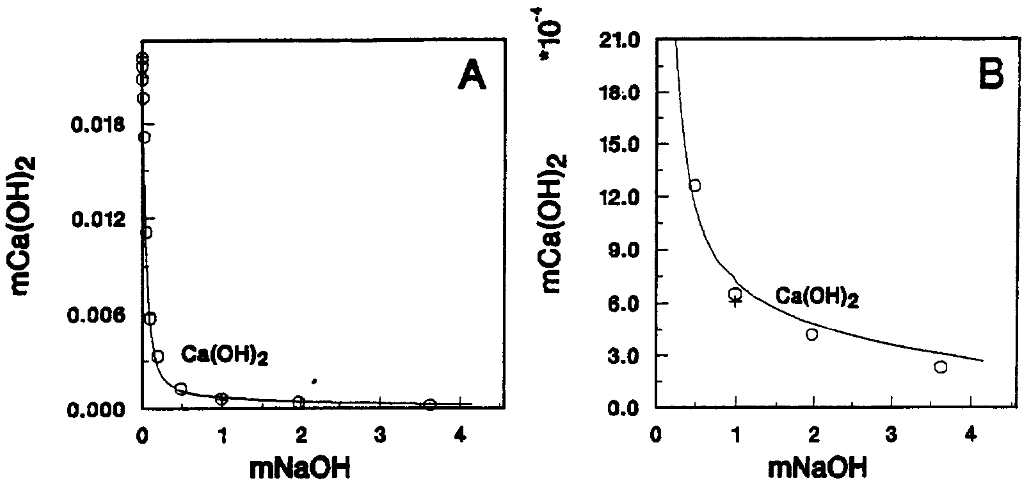

FIG. 6

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ solubility in NaOH solution at 25°C. Figures 6A and 6B present the same data but at two different scales. Circles are data from undersaturation while plus signs are from supersaturation.

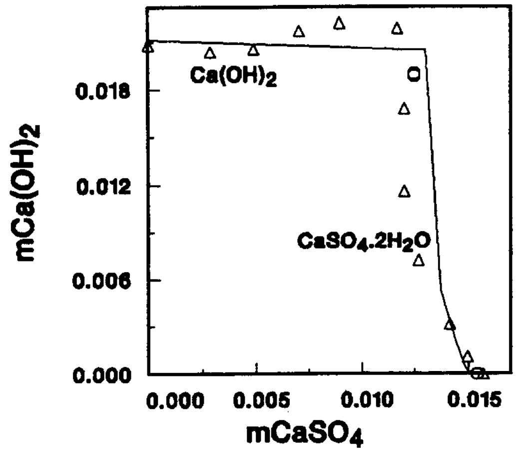

FIG. 7

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ solubility in $CaSO_4$ solution at 25°C. Data are from Cameron and Bell (12) (triangles) and Jones (27) (circles).

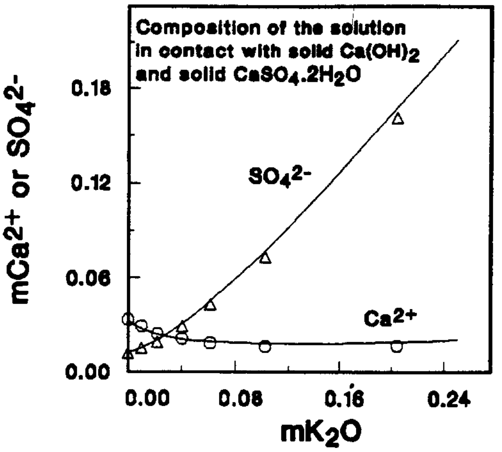

FIG. 8

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ and $CaSO_4{\cdot}2H_2O$ saturated solutions with increasing K_2O concentration. Ex-perimental data are from Hansen and Pressler (28).

Application to Cement/Water systems

The composition of a mature cement porewater is comprised principally of potassium and to a lesser extent sodium hydroxide. Total alkali concentrations are typically in the range of 0.5 to 1.0 molal (Page and Vennesland (31), Diamond (32), Larbi et al. (33), and Longuet et al. (34)). At these high ion concentrations, predicting equilibrium relationships with the traditional ion pairing

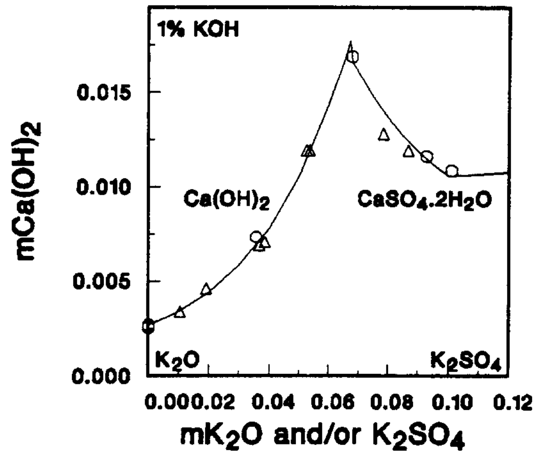

FIG. 9

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ solubility in 1% KOH solution made from different mixtures of K_2O and K_2SO_4 solutions at 25°C. Data are from Jones (29) (triangles are read from figure while circles are numerical data).

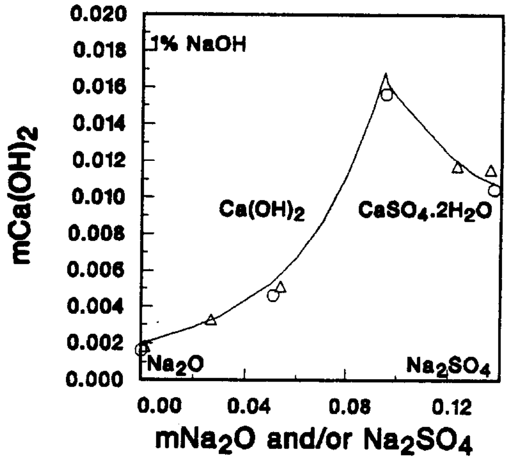

FIG. 10

Comparison of model-calculated and experimental measurements of $Ca(OH)_2$ solubility in 1% NaOH solution made from different mixtures of Na_2O and Na_2SO_4 solutions at 25°C. Values are from Jones (30) (triangles are read from figure while circles are numerical data).

approach, which uses the Debye-Hückel or Davies equation to predict ion activity coefficients, is inappropriate. The usual recommended limit for ion pairing models is 0.1 in ionic strength ($I = (\sum m_i z_i^2)/2$), although they are commonly applied to ionic strengths of 0.5. To illustrate the potential error in predicting solubilities at alkali concentrations typical of cement porewaters, we used two popular ion pairing-based equilibria models to predict portlandite solubility in KOH solutions. Both models yielded similar results and underestimated calcium concentrations compared to the Pitzer ion-interaction approach by a factor of 2.0 at 0.6, 3.5 at 1.2, and 5 at 2 molal KOH.

Conclusions

Portlandite solubility and EMF data in the Ca-K-Cl-OH-H_2O system obtained from the literature and new solubility data of portlandite in KOH solutions reported in this study have been used to refine Pitzer parameters for Ca^{2+}-OH^- interaction. The new values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ for $Ca(OH)_2$ have been applied to predict solubility relations in the aqueous mixtures of $Ca(OH)_2$ with $CaCl_2$, $CaSO_4$, NaOH, NaCl, Na_2SO_4 and K_2SO_4. In all cases, the predicted values are in excellent agreement with the experimental data attesting to the robust predictive capability of the ion interaction approach. Because of the typically high alkali content of cement porewaters, the Pitzer ion interaction model is recommended over the ion pairing model, which has often been used to describe equilibria in cement/water systems.

Acknowledgments

This research was funded by the National Science and Engineering Research Council of Canada. We would like to extend our appreciation to M. Hobbs for her helpful suggestions on analytical procedures and for identifying the alkali matrix interference problem on Ca analysis.

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