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Solubility of FBC Ashes

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$CaSO_4$ and $Ca(OH)_2$ are the two main soluble phases in ash from the fluidized bed combustor (FBC) combustion of high-sulfur fuels with limestone addition. Their solubilities are of critical importance to several problems ranging from leaching to sorbent reactivation processes with liquid water. To determine these parameters, realistic models are necessary to estimate the activity coefficients of ionic components present. The current results indicate that the decrease of $CaSO_4$ solubility in the presence of $Ca(OH)_2$ is smaller than suggested in some earlier calculations, using more simplified assumptions. Experimental data from real FBC ashes have been obtained for comparison, and the current model predictions and experimental results are in excellent agreement.

1. Introduction

The low efficiency of limestone sorbent is a well-known problem in fluidized bed combustor (FBC) combustion; a substantial fraction of the available CaO remains unreacted. To improve efficiency, reactivation of the ashes has been investigated extensively, mainly by treatment with water or steam. During these treatments, the two main Ca compounds in the ash, calcium sulfate and calcium hydroxide, partially dissolve, producing ions Ca^{2+}, SO_4^{2-}, and OH^-. Because the two main compounds of the ashes are of low solubilities, the systems will evolve toward equilibrium of the two hydrated solid phases and the saturated ionic solution. A correct understanding of the thermodynamic equilibria is desirable, and it is the aim of this paper to clarify this subject. It should also be noted that although FBC ashes contain, in addition to the dominant compounds, a number of minor compounds, soluble and insoluble, their typical contributions to the ionic content of an aqueous solution is relatively small, and hence they are ignored in the following ionic considerations.

2. Solubility Equilibrium for a Single Component

For a single component of low solubility, let us say $CaSO_4$, the solubility equilibrium is given by the solubility product, P, which in the case of this compound is

$$P = a_{Ca^{++}} a_{SO_4^{--}} = \text{const.} \tag{2.1}$$

where a_i are the activities, in terms of molalities or molarities. In the solutions considered here (up to about 0.02 M), molarity and molality (molal concentration is the number of moles of a compound per kilogram of pure solvent, whereas molar concentration is the number of moles of a compound per liter of solvent) can only differ by a few tenths of a percent. This difference will be neglected for the following treatment, although subsequent calculations are done on the basis of molalities. In addition, the weak temperature dependence of the solubilities is not examined, and instead calculations are done at 25 °C.

Only for concentrations tending to 0, i.e., for infinitely dilute or ideal solutions, are the activities equal to the concentrations; otherwise, the concentrations must be corrected by activity coefficients, so that eq 2.1 can be written

$$P = a_{Ca^{++}} a_{SO_4^{--}} = c_{Ca^{++}} c_{SO_4^{--}} \gamma_{Ca^{++}} \gamma_{SO_4^{--}} = \Pi \gamma_{Ca^{++}} \gamma_{SO_4^{--}} \tag{2.2}$$

where c_i are the concentrations (whether in molalities or in molarities) and Π is the corresponding product of concentrations.

Defining the mean activity coefficient

$$\gamma_{\pm} = (\gamma_{Ca^{++}} \gamma_{SO_4^{--}})^{1/2} \tag{2.3}$$

and considering that the solubility, s, of $CaSO_4$ in pure water is given by

$$s = c_{Ca^{++}} = c_{SO_4^{--}} \tag{2.4}$$

eq 2.2 can be written as

$$P = s^2 \gamma_{\pm}^{\,2} \tag{2.5}$$

The relation between these three parameters, P, s, and $\gamma_{\pm}$, must be considered carefully. Their values are generally derived from physical determinations of a variety of properties (electromotive force of cells, vapor pressure, osmotic coefficient, freezing points, solubilities, etc.), from which the values of basic thermodynamic parameters can be determined. P can also be calculated from the change in the Gibbs free energy (or free enthalpy) for dissolution into an ionic solution from the solid phase. The solubility, s, can be directly determined. For $CaSO_4$, it is reliably close to 0.015 expressed in molality. In the present calculations, the value 0.01518 has been adopted.[1] Whatever the sources of the information, the relation (eq 2.5) should always be valid. However, very appreciable discrepancies are found in the literature between the values obtained from different

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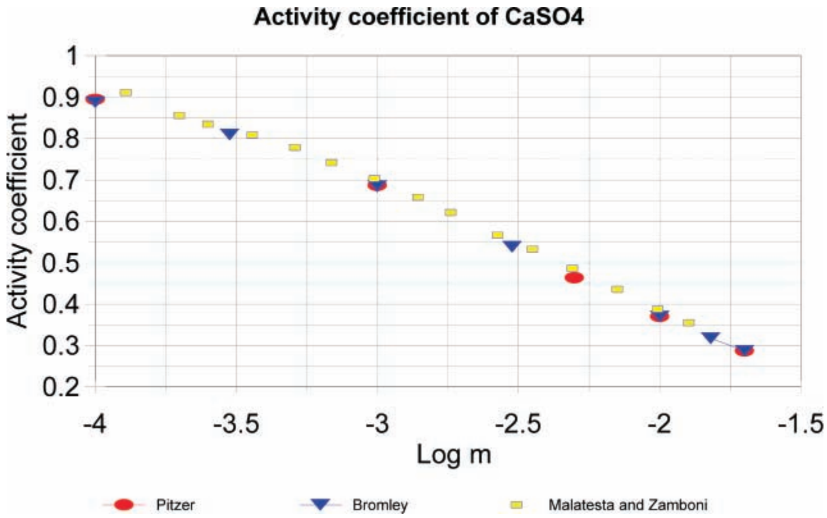

Figure 1. Activity coefficient of $CaSO_4$.

sources. Therefore, consistency in the values used for the calculations is an important consideration.

The expressions for the solubility product and the mean activity coefficient for $Ca(OH)_2$ are

$$P = a_{Ca^{++}} a_{OH^-}{}^2 = C_{Ca^{++}} C_{OH^-}{}^2 \gamma_{Ca^{++}} \gamma_{OH^-}{}^2 = \Pi \gamma_\pm{}^3 \quad (2.6)$$

$$\gamma_\pm = (\gamma_{Ca^{++}} \gamma_{OH^-}{}^2)^{1/3} \quad (2.7)$$

3. Calculation of Activity Coefficients

Along with direct derivation of activity coefficient values from experimental determinations, there have been various theoretical treatments and refinements of formulas to calculate them. The common starting point is the Debye−Hückel theory; here the simplest assumption is that the ions behave as point charges in a continuous medium with a given dielectric constant, i.e., the dielectric constant of the solvent. The theory leads to the so-called Debye−Hückel limiting law, which for a binary electrolyte with ions of charges z_+ and z_- is given by

$$-\ln \gamma_\pm = A_{z_+z_-} I^{1/2} \quad (3.1)$$

where A is the Debye−Hückel coefficient, and I is the ionic strength defined by

$$I = (1/2) \Sigma c_i z_i^2 \quad (3.2)$$

(c = concentration; the summation over all ions). For water at 25 °C, $A = 1.176$. Or, if using logarithms

$$-\log \gamma_\pm = Az_+z_- I^{1/2} \quad (3.3)$$

with $A = 0.511$.

A more elaborate formulation is provided by the extended Debye−Hückel expression

$$-\log \gamma_\pm = Az_+z_- \frac{I^{1/2}}{1 + BaI^{1/2}} \quad (3.4)$$

where a represents the effective average radius of the ions involved, given in Angstroms, and B is a function of temperature and dielectric constant of the solvent and is equal to 0.328 for water at 25 °C. Actually, $B{\cdot}a$ has been treated afterward as an empirically adjustable parameter chosen to reproduce as well as possible the activity coefficient values known for different electrolytes. In fact, $B{\cdot}a = 1$ appears to give reasonable approximations. Still this law can only represent adequately the values of activity coefficients for relatively dilute solutions (with ionic strengths not greater than, say, 0.1 m). To extend the validity to high concentrations (up to about 10 m), more terms must be added, with empirical parameters, some of them specific to each ion. The form of the terms and the values of the parameters are adjusted so that the semiempirical formulas adopted can accurately reproduce the values of the activity coefficients obtained from experimental measurements of thermodynamic properties.

For calculation of the mean activity coefficient for a given ionic compound (here, calcium sulfate) within a solution containing other ionic compounds as well (here, calcium hydroxide), appropriate methods must be followed because all the ions present influence the mean activity coefficient of each ionic compound.

Summaries of the main systems of formulas and procedures developed by different authors can be found in Zemaitis et al.[2] Here, formulas have been applied as given in the treatments by Pitzer and collaborators[3−10] and by Bromley.[11]

Figure 1 represents the values of the average activity coefficient of $CaSO_4$ obtained as a function of log m, where m is the molality, for solutions of $CaSO_4$ alone, in concentrations from $m = 10^{-4}$ to saturation ($m = 0.015$). The experimental results are from Malatesta and Zamboni,[12] using the electromotive force of liquid membrane cells. Data calculated with formulas from refs 3 and 11 are also shown in the graph, and they show excellent agreement with the experimental data. Bromley's system[11] has been used to calculate the mean activities of $CaSO_4$ in its saturated solution, of $Ca(OH)_2$ in its saturated solution, and of both compounds in a mixed solution saturated with respect to both compounds, all calculations being done for a temperature of 25 °C.

Bromley's general formula[11] is (after simplifying adjustments)

$$\log \gamma_\pm = \frac{A|z_+z_-|I^{1/2}}{1 + \rho I^{1/2}} + \frac{(0.06 + 0.6B)|z_2 z_1|I}{(1 + aI)^2} + BI \quad (3.5)$$

where A is the Debye−Hückel coefficient mentioned previously, with the value $A = 0.511$ for water at 25 °C (logarithms are being used); z_+ and z_- are the ionic charges of the ions; ρ is a general parameter that Bromley adjusted to $\rho = 1.0$ ($a|z_+z_-| = a(\sum m_i z_i^2)/(\sum m_i) = 1.5$, as adjusted to give satisfactory approximations, so that $a = 1.5/|z_+z_-|$); and B is a single specific parameter for each salt, given for a number of electrolytes in

Bromley's Table 1.[11] For other compounds not included in this table, B can be obtained in general from the values of two individual ion parameters, $B+$ and $\delta+$ for positive ions and $B-$ and $\delta-$ for negative ions, in Bromley's Table 2.[11] However, sulfates of divalent cations (such as $CaSO_4$) must be treated separately. A special term must be added to eq 3.5 (as is also done in the Pitzer system), and also the parameter B must be modified. The additional term is

$$-E\alpha I^{1/2}(1 - e^{-\alpha I^{1/2}}) \tag{3.6}$$

The parameter, α, is assigned the value 70, and B and E are adjusted, by Bromley using data from Pitzer[3] on divalent sulfates, to $E = 0.01143$ and $B = 0.4463$, so that $(0.06 + 0.6B) = 0.3278$. The expression for $\log \gamma_\pm$ for $CaSO_4$ finally becomes

$$\log \gamma_\pm = \frac{2.044 I^{1/2}}{1 + I^{1/2}} + \frac{1.311 I}{(1 + 0.375 I)^2} + 0.4463 I - 0.8 I^{1/2}(1 - e^{-70 I^{1/2}}) \tag{3.7}$$

The result from this equation was plotted in Figure 1. The value obtained for saturation (taken at $m = 0.01518$) is $\gamma_\pm = 0.318$. This would correspond to a solubility product

$$P = (s\gamma_\pm)^2 = 2.33 \cdot 10^{-5} \tag{3.8}$$

For $Ca(OH)_2$, eq 3.5 becomes

$$\log \gamma_\pm = -\frac{1.022 I^{1/2}}{1 + I^{1/2}} + \frac{0.1133 I}{(1 + 0.75 I)^2} - 0.0056 I \tag{3.9}$$

The solubility of $Ca(OH)_2$ at 25 °C in water is 0.0209 m.[13] Because $Ca(OH)_2$ is a strong electrolyte, $c_{Ca^{2+}} = 0.0209$ and $c_{OH^-} = 0.0418$, and the ionic strength of the saturated solution is $I = 0.0627$. Therefore, $\gamma_\pm = 0.633$ *and* $P = 4(s\gamma_\pm)^3 = 9.26 \cdot 10^{-6}$.

4. Calculation of Activity Coefficients in Multicomponent Solutions

The present problem is the calculation of activity coefficients for $CaSO_4-Ca(OH)_2$ in saturated multicomponent solutions. Calculations must be made on the basis of literature values of solubility products, which unfortunately display considerable variation. It is essential that the choice of values be consistent with the system of formulas that is used to predict activity coefficients. Here, Bromley's system of equations[11] is used; therefore, this requires the use of values $2.33 \cdot 10^{-5}$ and $9.26 \cdot 10^{-6}$ for the solubility products of $CaSO_4$ and $Ca(OH)_2$, respectively, as calculated in the previous section.

For convenience, in the following formulas, numeric sub-indices will indicate particular ions: cations with odd numbers and anions with even numbers. For the present case, 1 will indicate the only cation Ca^{2+} and 2 and 4 will indicate SO_4^{2-} and OH^-, respectively.

A single ion activity coefficient is written as follows

$$\log \gamma_i = -\frac{A z_i^2 I^{1/2}}{1 + I^{1/2}} + F_1 \tag{4.1}$$

where A, z, and I have the same meanings as in the previous sections and F is a function defined by the equation written above. In what follows, γ°_{ij} is defined as the mean activity coefficient for the ions from the salt ij if alone in solution at the same total ionic strength I. Here, the two following equations are considered.

(For $CaSO_4$)

$$\log \gamma^\circ_{12} = -\frac{A|z_1 z_2| I^{1/2}}{1 + I^{1/2}} + \frac{(906 + 0.6B_{12})|z_1 z_2| I}{\left(1 + \frac{1.5}{|z_1 z_2|} I\right)^2} + B_{12} I - E\alpha I^{1/2}(1 - e^{-\alpha I^{1/2}}) \cong -\frac{A|z_1 z_2| I^{1/2}}{1 + I^{1/2}} + B'_{12} I \tag{4.2}$$

(For $Ca(OH)_2$)

$$\log \gamma^\circ_{14} = -\frac{A|z_1 z_2| I^{1/2}}{1 + I^{1/2}} + \frac{(906 + 0.6B_{12})|z_1 z_2| I}{\left(1 + \frac{1.5}{|z_1 z_2|} I\right)^2} + B_{14} I \cong -\frac{A|z_1 z_2| I^{1/2}}{1 + I^{1/2}} + B'_{14} I \tag{4.3}$$

As in the previous sections
$B_{12} = B_{CaSO_4} = 0.4463$; $B_{14} = B_{Ca(OH)_2} = -0.0056$
z_i = charge of ion i
$E = 0.01143$; $\alpha = 70$

B_{12} and B_{14} are defined by the approximate equalities written above and are considered as approximately constant for varying I. This is true for $Ca(OH)_2$ because the denominator of the second term on the right of eq 4.2 changes slowly with I. For $CaSO_4$, however, the last term changes as $I^{1/2}$. When studying the change in the solubility of $CaSO_4$ due to the presence of $Ca(OH)_2$, the comparison will not involve very different values of the ionic strength, I, and the assumption of approximate constancy of B'_{12} can still be accepted. The above approximate equations, therefore, define

$$B'_{12} = \frac{(0.06 + 0.6B_{12})|z_1 z_2|}{\left(1 + \frac{1.5}{|z_1 z_2|} I\right)^2} + B_{12} - (1 - e^{-\alpha I^{1/2}})$$

$$B'_{14} = \frac{(0.06 + 0.6B_{14})|z_1 z_4|}{\left(1 + \frac{1.5}{|z_1 z_4|} I\right)^2} + B_{14} \tag{4.4}$$

The value of I for the saturated solution with respect to both $CaSO_4$ and $Ca(OH)_2$ is not known. This value will influence the values of B'_{12} and B'_{14}, particularly the former. Therefore, the calculation must be done by successive approximations, starting with reasonable values.

For the function F_1 for each ion i, Bromley[11] gives the following formulas, which take into account the interactions of oppositely charged ions but not those between ions with charges of the same sign. Higher-order interactions are also ignored (i.e., neglected as minor contributions). Here, where there is only one cation (1: Ca^{2+}) and two anions (2: SO_4^-, 4: OH^-)

$$F_1 = B'_{12} Z_{12}{}^2 m_2 + B'_{14} Z_{14}{}^2 m_4 = 4B'_{12} m_2 + 2.25 B'_{14} m_4$$

$$F_2 = B'_{12} Z_{12}{}^2 m_1 = 4\, B'_{12} m_1 \tag{4.5}$$

$$F_3 = B'_{14} Z_{14}{}^2 m_1 = 2.25 B'_{14} m_1$$

The charge factors (taken in absolute values) are $z_{ij} = (z_i + z_j)/2$, and m_i is the molality of ion i. The expression derived by Bromley[11] for the mean activity coefficient of a particular ionic compound, in this case calcium sulfate, is

$$\log \gamma_{12} = -(A|z_1 z_2|I^{1/2})/(1 + I^{1/2}) + \nu_1 F_1/\nu + \nu_2 F_2/\nu = -(A|z_1 z_2|I^{1/2})/(1 + I^{1/2}) + \{|z_1 z_2|/(z_1 + z_1)\}(F_1/z_1 + F_2/z_2) \quad (4.6)$$

where ν_1 and ν_2 are the number of [Ca^{2+}] and [SO_4^{2-}] ions present and ν is the total number of ions. Although many other ions may be present, the *i* ions of the formula refer only to those in the solution, which arise from the electrolyte whose activity coefficient is desired.

Initial Values for the Calculation. The solubilities of $CaSO_4$ and $Ca(OH)_2$ in pure water are $S_{12} = 0.015$ *m* and $S_{14} = 0.021$ *m*, giving an ionic strength in the mixture of $I = 0.144$. Considering that the relations, $s_{12} = m_2$, $s_{14} = m_4/2 = m_1 - m_2$, are valid yields the following starting values for a calculation at successive approximations: $m_1 = s_{12} + s_{14} = 0.036$; $m_2 = 0.015$; $m_4 = 0.042$; $I = 0.123$; $\gamma_{12} = 0.318$; $\gamma_{14} = 0.633$. From before, the solubility products are: $P_{12} = 2.33 \cdot 10^{-5}$ and $P_{14} = 9.26 \cdot 10^{-6}$. Furthermore, Π_{12} and Π_{14} will be defined by

$$P_{12} = \Pi_{12}\gamma_{12}^{\,2} = m_1 m_2 \gamma_{12}^{\,2};\ P_{14} = \Pi_{14}\gamma_{14}^{\,3} = m_1 m_4^{\,2}\gamma_{14}^{\,3} \quad (4.7)$$

Equilibrium Conditions. To solve the system constituted by the saturated solution, the following three parameters can be chosen as the unknowns: m_1, m_2, and m_4 (i.e., $m_{Ca^{++}}$, $m_{SO_4^-}$, m_{OH^-}). When their values are determined, the solubility of $CaSO_4$ and $Ca(OH)_2$ can be obtained from the relations $s_{CaSO_4} = m_2$ and $s_{Ca(OH)_2} = m_4/2 = m_1 - m_2$.

To find the equilibrium values of these three unknowns, a set of three independent equations is needed.

Charge balance

$$2m_2 + m_4 = 2m_1 \quad (4.8)$$

Solubility product of $CaSO_4$

$$P_{CaSO_4} = a_1 a_2 = m_1 m_2 \gamma_{Ca^{++}} \gamma_{SO_4^{--}} = \Pi_{12}\gamma_{12}^{\,2} \quad (4.9)$$

Solubility product of $Ca(OH)_2$

$$P_{Ca(OH)_2} = a_1 a_4^{\,2} = m_1 m_4^{\,2} \gamma_{Ca^{++}} \gamma_{OH^{--}} = \Pi_{14}\gamma_{14}^{\,3} \quad (4.10)$$

where γ_{12} and γ_{14} are the mean activity coefficients for $CaSO_4$ and $Ca(OH)_2$, respectively. Note that m_{H^+} does not appear in the charge balance equation, as it is many orders of magnitude smaller than the other terms of the equation and, therefore, totally negligible in the balance of charges. Incidentally, this makes it irrelevant to add the ionic product of water to the system of equations and the molality of H^+ as a fourth unknown.

Here, m_1 and m_2 are readily eliminated, leaving the following equation in the single unknown m_4

$$m_4^{\,4} + (\Pi_{14}/2\Pi_{12})m_4^{\,3} - \Pi_{14}^{\,2}/\Pi_{12} = 0 \quad (4.11)$$

This equation is solved numerically, giving the value of m_4. The values of m_1 and m_2 are then easily derived.

In this process, Π_{12} and Π_{14} are treated as constants, although they actually contain the activity coefficients of the ions, which depend on the ionic strength *I* and, therefore, on the values of the three ionic concentrations being calculated (cf. eq 3.2). This makes it necessary to proceed by a method of successive approximations. The solution obtained is given by the following values: $m_1 = 0.0248$; $m_2 = 0.0049$; $m_4 = 0.0398$; $I = 0.0793$; $\gamma_{12} = 0.438$; $\gamma_{14} = 0.618$. From the values of the concentrations (in molalities), the solubilities of $CaSO_4$ and $Ca(OH)_2$ in the saturated mixed solution are found to be

$$s_{12} = s_{CaSO_4} = m_2 = 0.0049;\ s_{14} = s_{Ca(OH)_2} = m_4/2 = m_1 - m_2 = 0.0199 \quad (4.12)$$

5. Experimental Determination of the Solubilities of $CaSO_4$ and $Ca(OH)_2$

Given the suggestion that $CaSO_4$ solubility may be suppressed by as much as an order of magnitude by the common ion effect, based on a calculation using a simplifying assumption of an activity coefficient of unity,[14] it was also decided to determine the solubilities of $Ca(OH)_2$ and $CaSO_4$ directly, using real ashes. This was done with saturated suspensions of bed ash and of fly ash in water, at three temperatures: 25 °C, 40 °C, and 85 °C.

The ashes originated in the Point Aconi (Nova Scotia Power) plant, obtained from the 165 MW circulating fluidized bed combustor (CFBC) burning a mixture of petroleum coke and Colombian steam coal. The solubilities are calculated on the assumption that Ca^{2+} ions are associated only with sulfate or hydroxyl ions. It was also assumed that the system essentially consisted of $CaSO_4$ and $Ca(OH)_2$ at saturation in water and that any effect of minor soluble components of the ash could be neglected. Direct scans revealed that the only cations in significant concentrations were K^+ (0 to 11 ppm) and Na^+ (3 to 7 ppm), with smaller amounts of Ba^{2+} (~0.3 ppm) and Sr^{2+} (~1.0 ppm). The bromide ion concentration was unexpectedly high and may have resulted from contamination in the water. Ca^{2+} was determined by ICP-ES, and anions were determined by ion chromatography.

Tests were carried out by placing 1.5 g batches of Point Aconi bed ash and fly ash in 30 mL of water and holding the mixture at 25 °C, 40 °C, and 85 °C for approximately 6 h, with stirring. Under these conditions, the water should become saturated with respect to the phases in question in the solid state. The ash suspensions were then filtered quickly, and the solutions were allowed to cool to room temperature. Higher temperatures were chosen, both because they are close to actual temperatures used in the authors' earlier studies of hydration[15,16] (one can more precisely control a temperature higher than room temperature) and because, over this range, the solubilities of both $CaSO_4$ and $Ca(OH)_2$ decrease with rising temperature (in the case of $CaSO_4$, the solubility falls below 25 °C, but insignificantly between 20 °C and 25 °C (*temp region of maximum solubility*)).[17] Thus, any cooling of the solutions should result in higher solubilities and prevent any precipitation. One should note that, because the Point Aconi ash used to produce the solutions analyzed was obtained from a CFBC burning a mixture of petroleum coke and coal, the question of the possible solubilization of Ca vanadates could arise. However, in other work, we have shown that, provided anhydrite and lime are not removed from the system, vanadates are not expressed in solution to any significant extent.[18] Table 1 gives the results of these measurements, with the solubilities of $Ca(OH)_2$ and $CaSO_4$ calculated on the assumption that Ca^{2+} ions are associated only with sulfate or OH^- anions.

The solubilities of $CaSO_4$ and $Ca(OH)_2$ in the FBC ash suspensions are quite close to those for the pure compounds in water, showing that the common ion effect is counteracted by the salt effect, associated with increased ionic strength and lower ion activity coefficients. The objection can of course be raised that these calculations ignored other cations and anions (see above) that affected the charge balance and ionic strength of the solution. However, these results are quite close to those of Taylor,[21] whose Table 6.6 gives the invariant points in the system CaO−alumina−sulfate−H_2O, at 20 °C.

It should be noted that in FBC systems firing high-sulfur coal and/or petroleum coke, the bed material tends to be primarily

Table 1. Concentrations of Ca^{2+} and Sulfate Ions in Aqueous Suspensions of CFBC Ashes[a]

ash	temp °C	Ca μm·mL^{-1}	SO_4 ion μm·mL^{-1}	$CaSO_4$ m·dm^{-3}	$Ca(OH)_2$ m·dm^{-3}	Br μm·mL^{-1}	Cl μm·mL^{-1}
FA	25	29.87 [29.93]	11	0.0110 {0.0144}*	0.0189 {0.0215}#	5.194	2.257
FA	40	25.05	11.17	0.0118 {0.0154}	0.0160 {0.0191}	5.181	1.974
FA	85	20.05	7.46	0.0074 {0.0131}	0.0127 {0.0122}	ND	2.257
BA	25	30.22 [29.22]	10.74	0.0107 {0.0144}	0.0194 {0.0215}	–	–
BA	40	29.13	11.79	0.0118 {0.0154}	0.0173 {0.0191}	5.131	1.974
BA	85	18.47	6.30	0.0063 {0.0131}	0.0122 {0.0122}	5.144	0.846

[a] [ ] replicate results; { } solubility data taken or interpolated from *Lide[19] and from #Perry et al.; [20] BA = bed ash; FA = fly ash.

Table 2. Experimental Solubilities (m·dm^{-3})

ash	$CaSO_4$	$Ca(OH)_2$
fly ash	0.0110	0.0188
bed ash	0.0107	0.0194

Table 3. Solubilities[a]

	$CaSO_4$	$Ca(OH)_2$
individual compound saturated in water	0.0152 m	0.0209 m
In Saturated Solution of Both Compounds		
(a) calculation based on Bromley's system[11]	0.0099 m	0.0207 m
(b) experimental results with real ashes	0.011 M	0.019 M

[a] *m*: molal; M: molar.

limestone-derived material. This arises for several reasons. The first is that in CFBC systems fuel ash is often fine and tends to report to the baghouse or electrostatic precipitator, leaving a bed that is primarily composed of limestone-derived materials, plus a few percent of shale and overburden from the coal.[22] Second, because of the high pH of the leachate (typically 12 to 13) resulting from the presence of free lime, most cations are present at only low levels in the leachate, without acid treatment (typically less than 100 mg·L^{-1}).[18,23] This means that, unless additives have been used to enhance the performance of the bed material, as might be done in the case of sorbent reactivation,[22] the main components in solution will usually be very similar to the materials examined here.

Finally, because of concerns over Br^- concentration in Table 1, two experiments were carried out in which pure $CaSO_4$ and limestone were calcined overnight at 850 °C, and $Ca(OH)_2$ and $CaSO_4$ were also heated at the same temperature. The two mixes were then placed separately in 40 °C water. For experiment one, the $CaSO_4$ solubility was 1.885 g·dm^{-3}, and for experiment two, the solubility was 1.77 g·dm^{-3}. In both experiments, the F^- ion concentration was 0.5 ppm, and that of Cl^- was 0.2 ppm for the first experiment and 3 ppm for the second (i.e., negligible). The Mg^{2+} concentration was below 0.01 ppm, and Na^+ concentration was 2.6 ppm and 2.9 ppm, respectively (i.e., also negligible). The Ca^{2+} contents were 1217 ppm and 1154 ppm. Therefore, making the assumption that, for a system with no other major cations or anions, what is not sulfate must be hydroxide, we can estimate the $Ca(OH)_2$ as 1.22 g·dm^{-3} and 1.17 g·dm^{-3}, respectively, which is quite close to the expected solubility of $Ca(OH)_2$ of 1.41 g·dm^{-3}. In this case, there was no potentially complicating effect due to high Br^- ion concentration, and one must conclude that both theory and measurement fail to support the idea of dramatically lower levels of SO_4^{2-} ions. In fact, they clearly show that assuming one can describe the solution in contact with an FBC ash based on Ca^{2+}, SO_4^{2-}, OH^-, and H^+ ions only, as if they were at infinite dilution, is inappropriate.

Here, only the results at 25 °C will be used to compare the results with those obtained in the previous calculations, although it is clear that depression of solubilities is significantly smaller than originally suggested by Scala et al.[14] The experimental results, summarized in molarities, are listed in Table 2.

Thus, with sufficient approximation, the solubilities determined were 0.011 M for $CaSO_4$ and 0.019 M for $Ca(OH)_2$.

Finally, Table 3 compares these experimental results (translated into molarities) with the solubilities of $CaSO_4$ and $Ca(OH)_2$ in pure water and in a mixed saturated solution of both compounds according to the previous calculations, in every case at 25 °C.

6. Conclusions

This paper has briefly reviewed the basic formulation and the development of semiempirical systems of formulas created to calculate activities of electrolytes at concentrations exceeding those at which the treatment of ideal solutions can be applied.

The particular problem considered ($CaSO_4$ and $Ca(OH)_2$ saturated in a mixed solution) is relatively simple, and it involves concentrations limited to relatively low values, at which the calculation of activity coefficients can be done with good approximation. However, the same systems of formulas and mathematical algorithms are applied in more complex systems and at much higher concentrations; such problems appear in industry and in multicomponent systems such as seawater.

Scala et al.[14] first looked at the problem of the solubilities of $CaSO_4$ and $Ca(OH)_2$ in a saturated solution containing both compounds and came to the conclusion that their solubilities were suppressed by an order of magnitude. However, these workers used the simplifying assumption that the activity coefficients were unity. According to the present calculations, following a more rigorous procedure, the effect of $Ca(OH)_2$ on the solubility of $CaSO_4$ is that the presence of saturated $Ca(OH)_2$ produces a decrease of only 35 % in the solubility of $CaSO_4$, which is a smaller effect than originally suggested. These conclusions assume the correctness of Bromley's treatment for multicomponent solutions as applied here. However, the measurements of $CaSO_4$ concentrations using FBC ashes provide further support for the present results given their excellent agreement with the calculated results.

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