Fundamental Chemistry of Precipitation and Mineral Scale Formation

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Abstract

The mineral scale that deposits in digesters and bleach plants is formed by a chemical precipitation process. As such, it is accurately described or modeled using the solubility product equilibrium constant. Although solubility product identifies the primary conditions that need to be met for a scale problem to exist, the acid base equilibria of the scaling anions often control where in the process scale will occur and are the primary control method to minimize or prevent scale in a bleach plant. As equilibrium processes, both the acid/base equilibrium and solubility product are influenced by temperature and ionic strength. In this paper, the chemistry of precipitation and acid/base equilibria will be reviewed. The use of the Gibbs Free Energy expression that connects equilibrium constants to enthalpy entropy and temperature will be discussed. The affect of ionic strength on ion activity and how it influences these processes will also be presented.

Terms and general principals

There are some common terms used in aqueous inorganic chemistry that may need to be refreshed before starting. These terms are essential for understanding the chemical processes involved in scale formation. Their use may have been forgotten by those among us who have not worked with these concepts for several years.

- Anion is a molecule containing a negative charge. The typical scale forming anions in the bleach plant are carbonate (CO_3^{2-}), oxalate ($C_2O_4^{2-}$) and sulfate (SO_4^{2-}).
- Cation is a molecule containing a positive charge. The trace metal non-process elements are all cations. The common cations in bleach plant scales are calcium (Ca^{2+}) and barium (Ba^{2+}).
- Monovalent and divalent refer to the charge of an ion. Monovalent anions and cation contain a single negative or positive charge, divalent anions and cations contain two negative or two positive charges. Typically salts of monovalent anions and cations are quite soluble, salts containing a divalent anion or cation, and two monovalent ions of the opposite charge are also typically very soluble. But salts where both the anion and cation are divalent are typically sparingly soluble or insoluble. This trend cannot be extended to trivalent ion (ions containing three charges) because the charge density is so high, they rarely exist in the 3+ or 3- state in solution and often form charged molecules that are soluble.
- Molarity (M), molality (m) and activity (a): Molarity is the molar concentration of a dissolved substance relative to 1 liter volume. Molality is molar concentration relative to 1 kg of total mass. Activity is ion mobility and is related to both the concentration of the substance and the concentration of other dissolved ions. Ion activity is usually considered to be the product of concentration (either molarity or molality) and the appropriate ion activity coefficient (f). At "infinite" dilution and 25° C, molarity, molality and activity of a substance are all the same.

Introduction

Some pulpmills have always experienced mineral scale buildup, but with efforts to comply with environmental requirements, these problems have increased. The recycle of washer filtrates implemented to reduce effluent volume in the late 1970's and early 1980's increased the concentrations of both cations and anions and with it the potential for mineral scale deposits. Then the switch from chlorine initiated bleach sequences to the use of chlorine dioxide in the first stage decreased the ability of the bleach plant to remove calcium and barium in the first stage. The result was a significant increase in the frequency of calcium oxalate and barium sulfate scale deposits in the first chlorine dioxide bleach stage and an increase in calcium carbonate deposits in the first extraction stage. In particularly severe cases, calcium oxalate also forms in later bleach stages.[1,2]

Mineral scale formation is a chemical precipitation process. Although the chemical phenomenon of precipitation can identify where and when scale deposition is possible, it cannot determine that scale will definitely occur. The reasons are many, but to name a few:

- In locations where precipitation is general and not directed towards a specific surface, fiber represents the largest surface area in the process and precipitates that deposit on fiber are generally and at least temporarily harmless. These precipitates tend to stay with the fiber and carry trace elements further into the bleaching process where they often do cause problems.
- Precipitation is time and concentration dependant.[3] Under conditions that barely exceed the saturation concentrations, it can take hours or longer for an obvious precipitate to form. The first precipitates that form are very small nanometer sized particles. Over time, small crystals tend to dissolve and larger crystals grow, but this can take a long time before visible precipitates are observed.
- Some salts can exceed the solubility by an order of magnitude or more without precipitating.[4] This supersaturation condition can be manipulated and is one method of suppressing scale by adding chemicals that interfere with crystal growth or interfere with crystal nucleation.[5] There may be organic fragments in bleach plant filtrates that behave in these ways to suppress precipitation.
- There are numerous organic fragments that can form complexes with trace metals. These complexes contain physical bonds between the metal and organic fragment and form an equilibrium condition consisting of the complex, the free solvated trace metal and the organic fragment. The equilibrium expression for this complex is called a formation constant and these values are an indication of the strength of the complex relative to the independent molecules. For example, nearly all carboxylic acids have a weak attraction for calcium and barium. Fragments with two acid groups form much more stable complexes, but complexes with one or two appropriately placed alcohol groups can also form stronger complexes. For example, calcium and magnesium form very weak complexes with the acetate anion. The formation constant for these two complexes is around 5.[6] The formation constant of these two metals with lactate [$H_2C(OH)CH(OH)CO_2^-$] is about 5 times stronger at 25, and the formation constant of these two cations with the oxalate dianion ($O_2CCO_2^{2-}$) is 40 to 100 times stronger yet at 1000-2500. For a case where both the trace metal and complexing organic molecule are both at 1mM starting concentration, the complex represents less than 1% of the trace metal with a formation constant of 5, but 50% of the trace metal for a formation constant of 1000. Oxidized sugars like gluconic acid are much like the sugar fragment lactic acid and have formation constants with calcium and magnesium around 25.[7] It is not possible with current industry capabilities to catalog all the possible complexes and determine their formation constants. Fortunately in the bleach plant, organic fragments that can form strong complexes are usually at low concentrations, and fragments that are common tend to form weak complexes. It appears that both can largely be ignored in bleach plant environments. However, it needs to be recognized that precipitation models that ignore these effects represent a worst case analysis.
- The chemist error. Chemistry is defined under unrealistic conditions. For example, what is infinitely dilute supposed to mean and where can you find this condition in a pulp mill? The obvious answer is that whatever infinitely dilute means, it does not apply anywhere in a pulp mill or bleach plant. We need to understand that the approximations that allow us to extend chemical principals to the conditions in a mill are just approximations and because of this, the results are not absolutes and are subject to some interpretation.

Precipitation[8]

The scale that forms in digesters and bleach plants is basically a localized chemical precipitation process. As such it is usually described using the solubility product convention. For the generalized chemical reaction:

$$mA + nB \Leftrightarrow pC + qD$$

the chemical equilibrium is usually written as:

$$\frac{[C]^p[D]^q}{[A]^m[B]^n} = K$$ Equation 1

For solubility product, there is typically just one product and following the equilibrium expression convention puts the concentration of the product in the numerator. But – what is the concentration of a precipitate? By convention, the concentration or rather activity of the precipitate is defined as 1.0 and the equilibrium expression is inverted.

$mA + nC \Leftrightarrow A_mC_n$

The solubility product expression is

$$[A]^m[C]^n = K_{sp}$$ Equation 2.

This is the equivalent of writing the initial chemical equation as dissolving the solid.
For the common precipitates encountered in a bleach plant, the chemical equation and corresponding equilibrium equations are as follows:[9]

For calcium carbonate (lime, calcite or aragonite):[10]
$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3$

$$[Ca^{2+}][CO_3] = 4.8 \times 10^{-9}$$ Equation 3

For calcium oxalate:
$Ca^{2+} + C_2O_4^{2-} \Leftrightarrow CaC_2O_4$

$$[Ca^{2+}][C_2O_4^{2-}] = 2.3 \times 10^{-9}$$ Equation 4

and for barium sulfate (barite):
$Ba^{2+} + SO_4^{2-} \Leftrightarrow BaSO_4$

$$[Ba^{2+}][SO_4^{2-}] = 1.0 \times 10^{-10}$$ Equation 5

All three solubility products are quite small numbers. Assuming equal molar concentrations of anion and cation, all will cause precipitation at about a 10^{-4} molar concentration or about 4 or 5 parts per million. The typical pulp mill bleach plant receives over a ton of calcium a day in the unbleached pulp and all of this must be removed to avoid scale problems.

Acid Base Equilibria[11]

A key issue in precipitation is that the anions that participate in the precipitation process are the divalent anions, not HCO_3^-, $HC_2O_4^-$ or HSO_4^-. This means that the conditions for scale formation are strongly influenced by the process pH.[12]

The general chemical equation for an acid equilibrium is written as follows:

$HA \rightarrow H^+ + A^-$

Note, the equation is the reverse of the typical chemical equilibrium equation – the product in a chemical process involving an acid is considered to be H^+. The resulting equilibrium expression is shown in equation 6.

$$\frac{[H^+][A^-]}{[HA]} = K_a$$ Equation 6

It is common to express H^+ as H_3O^+, recognizing that the proton is heavily solvated in water and really does not exist independent of the surrounding water. This convention has not been adopted here for simplicity, but it is recognized that the solvated notation is a more accurate representation of the state of this ion. The choice as to how to represent this cation does not impact the equilibria or calculation to be discussed in this paper.

For all three cases contributing to scale, there are two acid dissociations to consider, but only the second of the two is important to the precipitation process. For carbonic acid:

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ and

$HCO_3^- \rightarrow H^+ + CO_3^{2-}$.

The corresponding equilibrium equations are presented below and a graph of the pH dependence of the carbonates is provided in Figure 1.

$$\frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 4.4\times10^{-11}$$
$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]} = 4.6\times10^{-7}$$ Equation 7 a and b[13]

The carbonate ion dominates at pH above 10 but is still measurable at pH levels down to7. Bicarbonate dominates between pH 6 and pH 10, and carbonic acid dominates at pH below 6. Since many papermachines operate with calcium carbonate filler at neutral pH, we know that lime scale is somewhat stable down to a pH of 7.

The chemical equations for oxalic acid are as follows:

$H_2C_2O_4 \rightarrow H^+ + HC_2O_4^-$

$HC_2O_4^- \rightarrow H^+ + C_2O_4^{2-}$

$$\frac{[C_2O_4^{2-}][H^+]}{[HC_2O_4^-]} = 6.1\times10^{-5}$$
$$\frac{[HC_2O_4^-][H^+]}{[H_2C_2O_4]} = 6.5\times10^{-2}$$ Equation 8 a and b

The oxalate ion exists at any pH above about 2 and is the dominant form of oxalate at pH above 4. The acid-base speciation of oxalic acid is shown in Figure 2.

Sulfuric acid is a strong acid and for practical purposes, when diluted with water, the first proton is always dissociated. So only the second acid dissociation constant usually needs to be considered.

$HSO_4^- \rightarrow H^+ + SO_4^{2-}$

$$\frac{[SO_4^{2-}][H^+]}{[HSO_4^-]} = 1.2 \times 10^{-2} \qquad \text{Equation 9}$$

The pH dependence of sulfuric acid and the sulfates is shown in Figure 3. The sulfate ion dominates at any pH above 2 and still exists at pH near 0.

When evaluating the likelihood of precipitation, both the acid/base behavior of the anion and the solubility product need to be considered. Only when the basic form, the divalent anion and the cation combined exceed the solubility product is precipitation likely. Figure 4 shows a calculation for precipitation of calcium carbonate. Precipitation starts at a pH of 8, about the same pH the graph shows a measurable amount of carbonate. For this graph, carbonate was at 1 M and calcium at .01mM. The calcium carbonate precipitation was determined using the ESP equilibrium software from OLI Systems, Inc. (Morris Plains, NJ) and the scale for the precipitate has been adjusted to make it fit on the graph. A similar graph of calcium oxalate precipitation is provided in Figure 5. In this graph, the oxalate pH data is the same as in Figure 2 and at a 1 M concentration. The calcium oxalate precipitation was calculated for a solution that had a 1 mM starting concentration of both calcium and oxalate. The two graphs display the same issue – precipitation does not usually occur at pH conditions where the divalent ion is at low concentration. For calcium carbonate, this pH is 7 - 8, and for calcium oxalate it is about 2.5. For sulfate, this would be a pH around 0.5. This feature makes pH control the most powerful tool for eliminating mineral scale in bleach plants.

Although solubility product and the acid/base chemistry of the precipitating anions have the biggest influence on when and where a process will develop mineral scale, there are other process variables that influence scaling processes. Temperature is probably the next in significance. Most salts become more soluble as the temperature increases and this is true for barium sulfate and calcium oxalate. But the solubility of calcium carbonate decreases with temperature (Figure 6). This is the reason that calcium carbonate scale is common in digester heaters and other process heat exchangers. This effect may also contribute to calcium oxalate and barium sulfate scale on washer wires. As the filtrate penetrates the mat, it enters the partial vacuum of the drop leg causing it to cool a few degrees. Of course, the partial vacuum also evaporates some of the water, causing the concentrations to increase as well.

Ion Activity

The solubility product and acid base equilibria presented so far are accurate only for very dilute conditions. To move from the laboratory to real situations, it is necessary to understand how other dissolved ions affect the equilibrium. As salts build up in solution, the anions and cations begin to organize to reduce repulsion of like charges. With increasing ionic strength, the weak organization of solution charges begins to strengthen and impede ion mobility. For a calcium cation to come into contact with a carbonate. anion it may need to "escape" a weakly attractive cage of chloride and hydroxide anions and the surrounding weakly repulsive cage of sodium, potassium and magnesium cations The influence of ionic strength is known as ion activity. Activity Coefficients for NaCl, $CaCl_2$, Na_2CO_3 and $CdSO_4$ are shown in Figure 7. At typical bleach plant concentrations, a salt of a monovalent anion with a monovalent cation has an activity coefficient around 0.8. That means the effective concentration in equilibrium calculations is just 80% of the actual concentration. For a salt of a divalent anion with a divalent cation, the mean activity coefficient under bleach plant conditions is about 0.35. In practical terms, this means the real solubility of calcium carbonate, calcium oxalate or barium sulfate is about ten times the solubility as determined by the solubility product without considering ion activity.

To apply the mean activity coefficient ($f_{(CaCO3)}$) to the solubility product, the product of the concentrations is multiplied by the activity of the salt raised to the power of the sum of the stoichiometries. Including the ion activity, the solubility product for calcium carbonate changes from equation 3 to equation 10 below..

$$\left[Ca^{2+}\right]\left[CO_3^{2-}\right]f^{\,2}_{(CaCO_3)} = K_{sp}$$ Equation 10

This form uses the mean molar activity coefficient for the salt. The mean molar activity coefficient is squared for a 1 to 1 salt and cubed for a 2 to 1 salt. It is possible to calculate the activity coefficient for the individual anions in which case, the concentration of each ion is multiplied by the activity coefficient raised to the power of the stoichiometric value of that ion. The individual ion activity coefficients are derived from the activity coefficient determined for the salt according to the equation:

$$f_{x_m y_n} = \sqrt[m+n]{f_x^{\,m} f_y^{\,n}}$$ Equation 11

There are suitable tables in several standard chemical references that provide measured activity coefficients suitable for determining if existing analyzed conditions exceed the solubility limit for scale formation. For modeling purposes, it is useful to estimate the activity coefficient using one of several model equations. The extended Debye-Hückel equation is typically the starting point for estimating activity coefficients.

$$-\log(f) = \frac{Az^2\sqrt{I}}{1+ba\sqrt{I}}$$ Equation 12

The value *A* varies slightly with temperature, but is around 0.5115, *b* also varies with temperature and is around 0.3291, and *a* is the hydrated radius of the anion or cation. For calcium and manganese this value is about 6, and for barium and carbonate this value is 5. Because of the log scale, the exact values do not have a large effect on f, and it is common to use 0.5 for *A* and either 1.0 or 1.5 for *ba*. I is ionic strength, defined as:

$I = (\sum C_i z_i^2 + A_j z_j^2)/2$ Equation 13

Where C_i represents the cations in solution, A_j the anions and z their respective charges. The sums are over all anions and cations in solution.

The basic form of the Debye-Hückel equation is an asymptotic decline from a value of 1 at zero ionic strength, to a low value at high ionic strength. Reality is far different. At high ionic strength, the same weak electrostatic order that limited mobility at low ionic strength begins to impose a pairing of charges that increases the effective activity. Most ions (or salts) reach a minimum activity coefficient somewhere between an ionic strength of 0.5 to 5 M, but there are also many cases where the minimum is outside this range. In general, this minimum is quite variable and appears to be unpredictable based on first principles. The form of the extended Debye-Hückel equation has no minimum – it cannot predict an increase in activity at higher ionic strengths. The solutions have been many, varied, and not altogether satisfactory. There have been numerous suggestions for adding or subtracting a term in ionic strength such as the Davies,[14] Guggenheim, and b-dot equations:

$$-\log(f) = \frac{Az^2\sqrt{I}}{1+ba\sqrt{I}} - b^* I$$ Equation 14

For the Davies equation, the recommended value of b^* is either 0.2 or 0.3 depending on the reference. For the b-dot equation, b^* is an ion-specific value. The effect of the added parameter is to multiply the activity coefficient estimated by the extended Debye-Hückel equation by a value of 10^{b^*I}. For $b^* = 0.2$ and an ionic strength of 0.5 M this increases the Debye-Hückel estimate by 1.25. I is ionic strength and is formally defined as

An example of the fit of both the extended Debye-Huckel and the Davies equations to the measured activity coefficient for the divalent salt copper sulfate is shown in Figure 8. A divalent salt was selected purposefully for this analysis since all the scale forming salts in the bleach plant are divalent cations with divalent anions. In general, the solubility of this 2-2 type salt is low and there is relatively little data

available in the literature for the specific scale-forming salts. This particular salt has not reached a minimum value at ionic strengths below 2 molar, but the Davies equation estimates a minimum value at an ionic strength of 0.6 molar (0.15 M $CuSO_4$ concentration). Similar results are obtained with the sulfate salts of cadmium, zinc, nickel, magnesium and beryllium. At ionic strengths up to about 0.5 molar, there is very little difference in the predicted value of the activity coefficients by any of these alternatives. At ionic strengths greater than 0.5 molar, the Davies equation matches experimental values for some ions better, but with the 2-2 salts, does not provide a good fit. For most bleach plant modeling, the extended Debye-Hückel equation provides sufficiently accurate activity coefficients and this is the method generally used in our bleach plant equilibrium modeling. However, this is not the situation in the pulp mill and recovery areas of the mill where concentrations are much higher. For these areas, the Pitzer equations provide reasonable accuracy and are more suitable for equilibrium modeling.[15]

The Impact of Temperature:

As shown in Figure 6, solution equilibriums are often influenced by temperature. Chemical equilibriums are related to Free Energy by the expression:

$$\Delta G = RT\ln(K) = \Delta H - T\Delta S \qquad \text{Equation 15}$$

Where □G, □H, and □S are respectively the free energy of reaction, the enthalpy of reaction and the entropy of the reaction. R is the gas constant and T is temperature in °K. Graphing ln(K) vs 1/T, provides a straight line relationship where the intercept is ΔS/R and slope is ΔH/(R). This provides a mechanism to estimate acid dissociation constants and solubility products for temperatures that have not been directly measured or are slightly beyond the range of convenient laboratory experiments.

A pH Control Example

As an example of the use of these equilibrium concepts, consider the use of sulfuric acid and sodium sesquisulfate for adjusting pH. Sodium sesquisulfate has the formula $Na_3HS_2O_8$ and is a bisalt of sodium bisulfate and sodium sulfate that can be obtained as the spent acid from some chlorine dioxide generators. The acid equilibrium was presented earlier as equation 9. Sulfuric acid is a strong acid and the first of the two protons is always dissociated under normal laboratory conditions. The second dissociation is still a strong acid, but has been estimated with a pKa around 2.
The reaction is:

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^- \leftrightarrow 2H^+ + SO_4^{2-}$$

Determining the amount of acid needed to reach a target pH using sulfuric acid, requires the following mass balance equations:

$$H^+ = 2(SO_4^{2-}) + HSO_4^- \qquad \text{Equation 16}$$
$$S_T = SO_4^{2-} + HSO_4^- \qquad \text{Equation 17}$$

Where S_T is the total amount of sulfuric acid added. Note that for simplicity, the square brackets indicating molar concentration have been dropped.

These two equations are solved to give the SO_4^{2-} and HSO_4^- in terms of hydrogen and S_T.

Reorganizing equation 17 gives:

$$SO_4^{2-} = S_T - HSO_4^-. \qquad \text{Equation 18}$$

Replacing the SO_4^{2-} in equation 16 with equation 18 gives:

$$H^+ = 2(S_T - HSO_4^-) + HSO_4^- = 2S_T - HSO_4^-$$

Reorganizing this gives:

$HSO_4^- = 2S_T - H^+$ Equation 19

Equation 17 can also be reorganized to solve for HSO_4^-:

$HSO_4^- = S_T - SO_4^{2-}$ Equation 20

Substituting equation 20 for HSO_4^- in equation 16 gives:

$H^+ = 2(SO_4^{2-}) + S_T - SO_4^{2-} = SO_4^{2-} + S_T$

Reorganizing this gives:

$SO_4^{2-} = H^+ - S_T$ Equation 21

Rewriting equation 9 with the ion activity coefficients added to the equation gives:

$$\frac{\left[SO_4^{2-}\right] f_2 \left[H^+\right] f_1}{\left[HSO_4^-\right] f_1} = K_a$$ Equation 22

Where f_1 is the activity coefficient for the monovalent bisulfate anions and proton (cation) and f_2 is the activity coefficient for the divalent sulfate. Writing the equation this way recognizes that the activity coefficients for the monovalent proton and bisulfate anion are nearly the same, and for practical purposes, equal within the accuracy of the formulas for estimating activity coefficients. They cancel.

Substituting Equation 21 for the $[SO_4^{2-}]$ and Equation 19 for $[HSO_4^-]$ in Equation 22 gives:

$$\frac{\left[H^+ - S_T\right] f_2 \left[H^+\right]}{\left[2S_T - H^+\right]} = K_a$$

Reorganizing into a quadratic and reinserting the square brackets gives the following:

$$\left(\left[H^+\right] - \left[S_T\right]\right)\left[H^+\right] = \frac{K_a}{f_2}\left(2\left[S_T\right] - \left[H^+\right]\right)$$

$$\left[H^+\right]^2 - \left[S_T\right]\left[H^+\right] - \frac{2K_a}{f_2}\left[S_T\right] + \frac{K_a}{f_2}\left[H^+\right] = 0$$ Equation 23

$$\left[H^+\right]^2 + \left[H^+\right]\left(\frac{K_a}{f_2} - \left[S_T\right]\right) - \frac{2K_a\left[S_T\right]}{f_2} = 0$$

This equation can then be solved using the quadratic formula, providing the value of $[H^+]$ for any given total charge of sulfuric acid, and then using equations 19 and 21, can determine the solution concentrations of HSO_4^- and SO_4^{2-}.

Similarly, for sodium sesquisulfate, the chemical reaction is

$Na_3HS_2O_8 \leftrightarrow 3Na^+ + SO_4^{2-} + HSO_4^- \leftrightarrow 3Na^+ + (1+x)SO_4^{2-} + xH^+ + (1-x)HSO^-$

This leads to the mass balance equations

$H^+ = Se - HSO_4^-$ Equation 24

$2Se = SO_4^{2-} + HSO_4^-$ Equation 25

Where Se is used to indicate total sesquisulfate.
Solving for SO_4^{2-} and HSO_4^- as before gives:

$HSO_4^- = Se - H^+$ Equation 26

And

$SO_4^{2-} = 2Se - HSO_4^- = 2Se - (Se - H^+) = Se + H^+$ Equation 27

and substituting into equation 22 gives:

$$\frac{\left[Se + H^+\right] f_2 \left[H^+\right]}{\left[Se - H^+\right]} = K_a$$

Again, reorganizing this into a quadratic equation.

$$Se\left[H^+\right] + \left[H^+\right]^2 = \frac{K_a}{f_2} Se - \frac{K_a}{f_2}\left[H^+\right]$$

$$\left[H^+\right]^2 + \left(Se + \frac{K_a}{f_2}\right)\left[H^+\right] - \frac{K_a}{f_2} Se = 0 \qquad \text{Equation 28}$$

Again, the equation can be solved with the quadratic formula and the concentration of the other ions determined using in this case, Equations 26 and 27. These equations were solved in Excel using the quadratic formula. The mass balance equations were used to determine the sulfate, bisulfate and proton concentrations for each charge concentration of either sulfuric acid or sodium sesquisulfate, and the ion activity estimated using the extended Debye-Hückel formula (Equation 12) using 0.5115 as the value for *A* and 1.5 as the value for *ba*. Ionic strength was calculated from the calculated concentrations of the three ions and factored into the quadratic as an iterative feedback loop. Since pH is proton activity, the solution to the quadratic equations needed to be multiplied by the activity coefficient for a monovalent ion to give final pH. Rather than plot the resulting pH against acid charge, we show pH against resultant sulfate concentration in Figure 9. At high pH, 4 and above, sodium sesquisulfate adds about 4 times the sulfate ions to solution as sulfuric acid. At pH 2.5, the sesquisulfate is forming a buffer and levels off. The amount of sesquisulfate required is diverging from the amount of sulfuric acid and now produces over six times the sulfate produced when using sulfuric acid.. Using sulfuric acid, the sulfate ion concentration continues to increase at a slower rate, and pHs levels below 2 are possible. The key issues this graph raises are that use of sesquisulfate to control the pH near 2.5 substantially increases the concentration of sulfate in the bleach plant and with it the potential for encountering barium sulfate scale. The second key issue is that it is not possible to decrease the sulfate ion concentration and potential for barium sulfate scale using sulfuric acid. This severely restricts the ability to use pH control to eliminate a barium sulfate scale problem.

Summary:

The chemical process that forms mineral scales in pulp mills and bleach plants is precipitation and the conditions that lead to scale formation are readily understood in terms of the solubility product for the precipitate and the acid-base behavior of the scaling anion. Both the solubility product and acid equilibrium constants are temperature dependant and these changes may need to be considered when evaluating the likelihood of scale formation. In addition, the high dissolved ion concentration that exists in pulp mill bleach plants reduces the ion activities. These last two factors (temperature and ion activity) can

increase the solubility of a salt by about one order of magnitude. Even with this level of error, a simple solubility product calculation is still a good starting point for understanding mineral scale problems. Given the normal process variation in a pulp mill or bleach plant, an order of magnitude safety factor is desirable to insure scale free operation. Thus even a simple solubility product provides a good first target for use in a mill to minimize deposition of mineral scale. In the second paper of this series, other factors that influence the solubility of trace cations in bleach plants will be discussed and a more detailed precipitation scenario evaluated using mill data.

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Session 1 of a tutorial on mineral scale

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What will we learn

- Scale is a chemical precipitation process
- Precipitation depends on
  - Chemical concentrations and solubility product
  - Acid/base equilibrium of the precipitating anion
  - Ion activities as affected by ionic strength
  - Temperature
- Solubility product, acid/base equilibrium and ionic strength are interdependent equilbria.
  - We will go through an acid/base equilibrium calculation for sulfuric acid and sodium sesquisulfate.

Changes relative to the preprint

- Use of free energy to determine K_{sp}
- Sulfuric acid vs sodium sesquisulfate
  - The calculation method assumes a known (or target) pH and determines the amount of sulfuric acid or sodium sesquisulfate needed.
  - This method results in a direct algebraic solution rather than a quadratic solution that results when determining pH by adding a known amount of these acids.

Major Sources

- Fundamentals of analytical chemistry (2nd edition) by D. Skoog and D. West, 1969.
- Quantitative chemical analysis (4th edition) by D. Harris, 1996.
- Lang's handbook of chemistry (14th edition), J. Dean, editor, 1992.
- The material in this session can be found in any good analytical chemistry textbook of traditional methods (as opposed to instrumental methods).

Terms (we just have to live with them)

- Cation: an atom or molecule containing a positive charge:
  - H^+, Na^+, Mg^{2+}, K^+, Ca^{2+}, Mn^{2+} and Ba^{2+} are all cations.
- Anion: an atom or molecule containing a negative charge:
  - Cl^-, OH^-, HCO_3^-, CO_3^{2-}, $HC_2O_4^-$, $C_2O_4^{2-}$, HSO_4^- and SO_4^{2-} are all anions.
- Monovalent: an atom or molecule containing just one charge.
- Divalent: an atom or molecule containing two charges

Concentrations

- Molar: (M) The concentration of a substance given in moles per liter of volume.
- Molal: (m) The concentration of a substance given in moles per kilogram total.
- Ion Fraction: $x_a = z_a M_a / (\Sigma\, z_i M_i)$.
  - Ionic fraction is used to express concentration in ion exchangers where $z_a M_a$ is the charge contribution of a particular counterion, and $\Sigma z_i M_i$ is the total fixed ion content of the ion exchanger.

Activity

- Activity : in either molar or molal basis, the activity is the apparent concentration in terms of equilibrium behavior. The term activity embraces the decrease in solution availability of ions when in the presence of other ions.
- $a_i = f_i[M_i]$
  - a_i is the activity, f_i is the activity coefficient that converts molar or molal concentration to activity.

Generalized Chemical Equilibrium

- mA + nB ↔ oC + pD

$$\frac{[C]^o[D]^p}{[A]^m[B]^n} = K$$

The equilibrium

- The equilibrium represents the minimum free energy for the system and therefore is the state the system will naturally trend towards.
- The rate at which a process achieves equilibrium is not addressed in the theory and cannot be predicted.
- We deal with non-equilibrium states all the time: Chlorine dioxide, and diamond. In scale, supersaturation is a non-equilibrium state.

Equilibrium expressions

- Solubility Product:
  - $A_mB_n \leftrightarrow$ mA + nB
  - The activity of the precipitate is assigned the value 1

$$[A]^m[B]^n = K_{sp}$$

- Acid dissociation:
  - $AH_m \leftrightarrow mH + A^{m-}$

$$\frac{[H]^m[A^{m-}]}{[H_mA]} = K_a$$

- Technically, all concentrations are activities

Example of solubility product

- Precipitation of calcium oxalate
- What typically is the need?
  - Do the concentrations of calcium and oxalate exceed the solubility?
  - At what pH will they no longer cause precipitation?
- Pertinent solubility product
  - $[Ca^{2+}][C_2O_4^{2-}] = 2.3 \times 10^{-9}$
- Pertinent acid dissociation
  - $[H^+][C_2O_4^{2-}]/[HC_2O_4^-] = 6.1 \times 10^{-5}$

The case data: pH 2.5

(mg/kg)/1000(mg/g) = g/kg ~ g/L. g/L/AMU = Molar or molal concentration.

Element	amu	mg/kg	Molar	z^2M
H^+	1.0		0.00316	.00316
Na^+	23.0	90.4	0.00393	.00393
Mg^{2+}	24.3	3.0	0.000122	.000488
Ca^{2+}	40	88.9	0.00222	.00888
Mn^{2+}	54.9	1.4	2.5×10^{-5}	1×10^{-4}
Ba^{2+}	137.3	1.6	1.2×10^{-5}	4.8×10^{-5}
				0.0166
Oxalate	88.0	12.5	0.000142	

Solubility Product Solution:

- Solve acid base equilibrium for divalent oxalate concentration.
- Determine the concentration product to see if it is less than the solubility product.
- This method involves the solution of just one equilibrium.

Solution

- Acid mass balance:
  - $[HC_2O_4^-] = Ox - [C_2O_4^{2-}]$ where Ox is total oxalate ion.
- Substitute in the acid dissociation:
  - $[C_2O_4^{2-}][H^+] = K_a(Ox-[C_2O_4^{2-}])$
  - $[C_2O_4^{2-}]([H^+] + K_a) = K_aOx$
  - $[C_2O_4^{2-}] = K_aOx/([H^+] + K_a)$
  - K_a is known, $H^+ = 10^{-pH}$ and Oxalate is obtained analytically.

Solution

- The calculated divalent oxalate is multiplied by the analytically determined calcium concentration to give the ion product. If this is greater than the solubility product, precipitation or scale is likely.
  - $[C_2O_4^{2-}] = KaOx/([H^+] + Ka)$
    $= (6.1 \times 10^{-5})(0.000142)/\{(0.00316)+6.1 \times 10^{-5}\}$
    $=2.69 \times 10^{-6}$
  - $2.69 \times 10^{-6} \times [Ca^{2+}] = 2.69 \times 10^{-6} \times 0.00222$
    $=5.9 \times 10^{-9} > 2.3 \times 10^{-9}$ so the condition could cause scale formation.

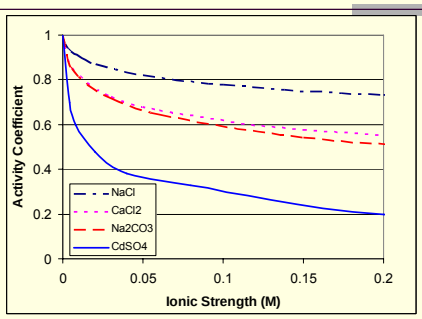
Other issues

- Temperature
  - At typical bleach plant temperatures, the solubility product is higher, but the acid dissociation favors more dissociation.
- Activity
  - At typical bleach plant concentrations, the activity of a divalent ion is approximately half of it's solution concentration, a monovalent ion about 85% of solution concentration.
- Complex formation

Ion Activity

- Opposites attract: The presence of other ions in solution forces additional order on dissolved anions and cations. This order makes it harder for them to move freely and typically reduces the probability of a reaction.
- At high ionic strength, this effect can reverse and ion mobility increases.
- Activity is the effective concentration after adjusting for ionic strength

Ion Activity: low ionic strength



Low ionic strength

- Activity for $CaCl_2$ and Na_2CO_3 are nearly the same.
  - Activity at low ionic strength is relatively simple and easily estimated.
- The activities shown are the mean activities for the salts. Monovalent ions have higher activities than divalent ions.
  - $f_{a,b} = (f_a^m f_b^n)^{(1/n+m)}$ where m and n are the stoichiometric coefficients of the salt.

Debye-Hückel Equation

$$\log(f) = \frac{-Az^2\sqrt{I}}{1+ba\sqrt{I}}$$

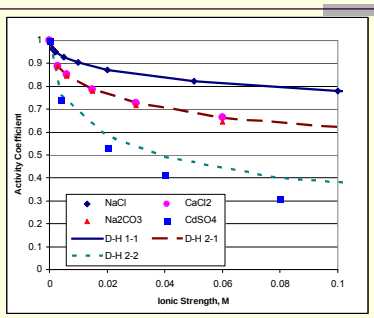
A and b are temperature dependant constants,
a is hydrated radius,
z is the charge of the ion and
I is ionic strength

Debye-Hückel Approximation

- A has the value 0.5115 at room temperature
- b has the value of 0.3291 at RT
- a is ion dependant, ranging typically from about 4 Å to 7Å.
- A good approximation of activity can be obtained from:

$$\log(f) = \frac{-0.5\sqrt{I}}{1+1.5\sqrt{I}}$$

Fit of Debye-Hückel at low ionic strength



Ionic strength: ~ 0.0167 M

- Technically, ionic strength is one half the sum of the cations, each times their charge squared, plus the sum of the anions times their charges squared.
- Anions are typically OH^-, SO_4^{2-}, CO_3^{2-}, Cl^-, and $C_2O_4^{2-}$. These are typically harder to analyze for than the cations.
- I usually use the ionic strength contribution of the cations as ionic strength and assume the mixture of monovalent and divalent anions is similar to the cations.

Activity Coefficients: Oxalate case

$$f_1 = 10^{\frac{-0.5115\sqrt{0.0166}}{1+1.5\sqrt{0.0166}}} = 0.88$$

$$f_2 = 10^{\frac{-0.5115(2^2)\sqrt{0.0166}}{1+1.5\sqrt{0.0166}}} = 0.60$$

- Ignoring the effect of hydrated radius, we can estimate the activity of the monovalent and divalent ions and use them in the acid dissociation and solubility product determinations.

Temperature: K_{sp}

- Can determine K_{sp} from ΔG
  - ΔH for $CaC_2O_4 \cdot H_2O$ is – 21.11 kJ/mole
  - ΔS for $CaC_2O_4 \cdot H_2O$ is 94.15 J/deg/mole
  - At 25° C, $\Delta G = \Delta H - T\Delta S$ = -21.11{kJ/mole} - (273+25){deg}(94.15{*J/deg/mole*}/1000{*J/kJ*}) = - 49.17 *kJ/mole*.
  - Ln(K) = $\Delta G/RT$

  = -49.17{*kJ/mole*}/0.008314{*kJ/deg/mole*}/298{deg} $\Rightarrow$ $K_{sp} = 2.4 \times 10^{-9}$
  - At 65° C, $K_{sp} = 6.6 \times 10^{-9}$

Temperature: K_a

- Lang's Handbook 14th Ed, pp. 8.72-8.79.
  - 4.272 (25°), 4.295 (30°), 4.349 (40°), 4.409 (50°).
  - $\text{Log}(K_a) = 498.59/T - 5.9468$ where T is in degrees Kelvin
  - Extrapolating to 65°: $pK_a \approx 4.493$, $K_a \approx 3.2 \times 10^{-5}$

Equilibrium expressions

- Solubility Product:
  $CaC_2O_4 \leftrightarrow Ca^{2+} + C_2O_4^{2-}$

$$[Ca^{2+}] f_2 [C_2O_4^{2-}] f_2 = K_{sp}$$

- Acid dissociation:
  $HC_2O_4^- \leftrightarrow H^+ + C_2O_4^{2-}$
  - Note that pH gives proton activity – not concentration.
  - Note that the f_1 cancels – but need to correct H^+ from pH for activity.

$$\frac{[H^+] f_1 [C_2O_4^{2-}] f_2}{[HC_2O_4^-] f_1} = K_a$$

Solution: activity and Temperature

- $[C_2O_4^{2-}] = (K_a/f_2)Ox/\{[H^+] + (K_a/f_2)\}$
  $= (3.2 \times 10^{-5}/0.60)(0.000142)/\{(0.00316/0.88) + (3.2 \times 10^{-5}/0.60)\}$
  $=2.1 \times 10^{-6}$
  - $(2.1 \times 10^{-6})f_2 \times [Ca^{2+}]f_2 = 2.1 \times 10^{-6} \times 0.00222 \times 0.60^2$
    $=1.7 \times 10^{-9} < 6.6 \times 10^{-9}$
  - At this level of analysis, the condition is no longer considered likely to cause scale.

Sulfuric acid vs Spent acid

- Determine how much sulfuric acid or sodium sesquisulfate is required to adjust 1 liter of water to pH 2.5.
- Pertinent acid dissociation:
  - $HSO_4^- \rightarrow H^+ + SO_4^{2-}$ $K_a = 0.012$
- By starting with a pH target and determining the acid required, the calculation is simplified.

Sulfuric acid

- Chemical equation:
- $H_2SO_4 \rightarrow H^+ + HSO_4^- \leftrightarrow 2H^+ + SO_4^{2-}$
- $a \cdot H_2SO_4 \rightarrow (a+b)H^+ + b \cdot SO_4^{2-} + (a-b)HSO_4^-$
- $(a+b)H^+ = 10^{-2.5} = 0.00316$
- $[SO_4^{2-}]/[HSO_4^-] = K_a/[H^+] = 0.012/0.00316$
  - $= 3.8$
- $b/(a-b) = 3.8 \Rightarrow b = 3.8a - 3.8b \Rightarrow 4.8b = 3.8a$
  - $b = 0.79a$

Sulfuric Acid

- b = 0.79a
- a+b = 0.00316
- a + 0.79a = 0.00316
- 1.79a = 0.00316
- a = 0.00176
- b = 0.00139
- H_2SO_4 = 0.00176 moles
- HSO_4^- = a – b = 0.00037 molar
- SO_4^{2-} = 0.00139 molar

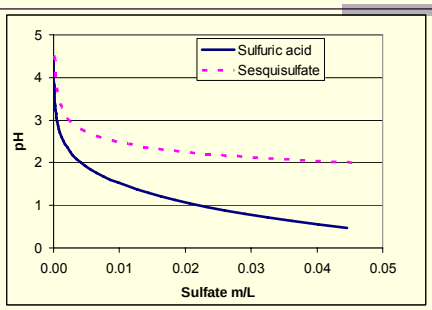
Sodium sesquisulfate

- Chemical Equation:
  - $a \bullet Na_3(SO_4)(HSO_4) \rightarrow 3a \bullet Na^+ + a \bullet SO_4^{2-} + a \bullet HSO_4^-$
  - $\rightarrow 3a \bullet Na^+ + (a+b) \bullet SO_4^{2-} + (a-b) \bullet HSO_4^- + b \bullet H^+$
  - $bH^+ = 0.00316$
  - $[SO_4^{2-}]/[HSO_4^-] = 3.8 = (a+b)/(a-b)$
  - $3.8a – 3.8b = a + b \Rightarrow 2.8a = 4.8\ b \Rightarrow a = 1.7b$
  - $b = 0.00316 \Rightarrow a = 0.00537$
  - $SO_4^{2-} = 0.0085$, $HSO_4^- = 0.00221$

The comparison

- SO_4^{2-} at pH 2.5 using sulfuric acid for pH control is 0.0014 Molar
- SO_4^{2-} at pH 2.5 using spent acid for pH control is 0.0085 Molar
- To control to this pH, spent acid adds 6 times more sulfate than sulfuric acid.

Entire pH range



Wrap up

- This session has reviewed the fundamental chemical equilibria involved in determining solubility product.
- This session has carried out example equilibrium calculations for acid base equilibria of oxalic acid and sulfuric acid.
- This session has carried out a solubility product calculation for solution concentrations of calcium and oxalic acid.

Preview of session II

- The next session of this tutorial will introduce the effect of wood fiber ion exchange on trace metal concentrations and will demonstrate the solubility product calculation for a case with wood fiber present.

In: Proceedings of the 2005 TAPPI engineering, pulping & environmental conference. 2005 August 28-31; Philadelphia, PA. Norcross GA: TAPPI Press: 10 p. CD ROM: ISBN 1-59510-095-4