

Mineral Scale Management

Part II. Fundamental Chemistry

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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 modeled using the solubility product equilibrium constant. Although solubility product identifies the primary conditions that must 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. These equilibria are the primary control method to minimize or prevent scale in a bleach plant. Both the acid-base equilibria and solubility product equilibria are influenced by temperature and ionic strength. This paper reviews the chemistry of precipitation and acid-base equilibria. The Gibbs free energy expression is presented as a method to estimate equilibrium constants at temperatures in the bleach plant. The effect of ionic strength on ion activity and its influence on these processes are also discussed.

Application: Preventing scale problems requires an understanding of the solubility product equilibrium, the acid-base equilibrium of the scaling anion, and the effects of temperature and ion activity on these equilibria.

Some pulp mills have always experienced mineral scale buildup, but this problem has increased with efforts to comply with environmental requirements. The recycling of washer filtrates to reduce effluent volume has increased the concentrations of both cations and anions and with it the potential for mineral scale deposits. The switch from chlorine-initiated bleach sequences to the use of chlorine dioxide in the first stage has decreased the ability of the bleach plant to remove calcium and barium in the first stage. The result has been a significant increase in the frequency of calcium oxalate and barium sulfate scale deposits in the first bleach stage and an increase in calcium carbonate deposits in the first extraction stage. In particularly severe cases, the formation of calcium oxalate has also occurred in later bleach stages [1,2].

This paper is the second in a series on mineral scale management. A collection of case studies was presented in the first paper [3]. Most of these scale problems were resolved using the fundamental chemistry principles to be presented here. Several cases were more difficult, usually because of exceptionally high trace metal concen-

trations in the wood supply. Those cases required more detailed equilibrium modeling and will be handled in the third paper of the series on non-process elements in the paper industry.

OVERVIEW OF CHEMICAL PRECIPITATION

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; a few are listed here:

- In locations where precipitation is general and not directed toward a specific surface, fiber represents the largest surface area in the process. 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 cause problems.
- Precipitation is time and concentration dependent [4]. Under

conditions that barely exceed the saturation concentrations, it can take hours or longer for an obvious precipitate to form.

- Some salts can exceed the solubility by an order of magnitude or more without precipitating [4]. This supersaturation condition can be manipulated. One method of suppressing scale is to add chemicals that interfere with crystal growth or interfere with crystal nucleation [5,6]. Organic fragments may occur in bleach plant filtrates that behave in these ways to suppress precipitation.
- Numerous organic fragments can form complexes with trace metals. These complexes are in equilibrium with the free-solvated trace metal and the organic fragment. The net effect of these equilibrium processes is to reduce the concentration of free cations. 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. At present, we can not 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. Precipitation models that ignore these effects, however, represent a worst case analysis.

- Chemistry is often defined under unrealistic conditions. For example, what does “infinitely dilute” mean, and where can this condition be found 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 principles to the conditions in a mill are just approximations. Because of this, results are not absolutes and are subject to some interpretation.

TERMS AND GENERAL PRINCIPLES

Some common terms in aqueous inorganic chemistry are essential for understanding the chemical processes involved in scale formation:

- Anion—A molecule containing a negative charge. The typical scale-forming anions in the bleach plant are carbonate (CO_3^{2-}), oxalate ($\text{C}_2\text{O}_4^{2-}$), and sulfate (SO_4^{2-}).

- Cation—A molecule containing a positive charge. The trace metal nonprocess elements are all cations. The common cations in bleach plant scales are calcium (Ca^{2+}) and barium (Ba^{2+}).
- Monovalent and divalent—Terms that refer to the charge of an ion. Monovalent anions and cations 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 ions (ions containing three charges). Because the charge density of trivalent ions is so high, they rarely exist in the 3^+ or 3^- state in solution and often form charged molecules that are soluble.
- Molarity (M) and molality (m)—Molarity (M) is the molar concentration of a dissolved substance relative to a volume of 1 L. Molality (m) is the molar concentration relative to 1 kg of total mass. Activity (a) 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.

PRECIPITATION

More detailed explanations of precipitation and acid base equilibria can be found in any good analytical chemistry textbook[4]. 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,



The chemical equilibrium is usually written as

$$\frac{[\text{C}]^p [\text{D}]^q}{[\text{A}]^m [\text{B}]^n} = K \quad (1)$$

For solubility product, there is typically just one product. Following the equilibrium expression convention, the numerator is the concentration of the product. 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:



The solubility product expression is

$$[\text{A}]^m [\text{C}]^n = K_{sp} \quad (2)$$

For the common precipitates encountered in a bleach plant, the chemical equation and corresponding equilibrium equations are as follows:

For calcium carbonate (lime, calcite or aragonite),
 $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3$

$$[\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 4.8 \times 10^{-9} \quad (3)$$

For calcium oxalate,
 $\text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{CaC}_2\text{O}_4$

$$[\text{Ca}^{2+}] [\text{C}_2\text{O}_4^{2-}] = 2.3 \times 10^{-9} \quad (4)$$

and for barium sulfate (barite),
 $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{BaSO}_4$

$$[\text{Ba}^{2+}] [\text{SO}_4^{2-}] = 1.0 \times 10^{-10} \quad (5)$$

Assuming equal molar concentrations of anion and cation, all three precipi-

tate 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

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.

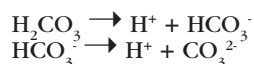
The general chemical equation for an acid equilibrium is written as $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$.

The resulting equilibrium expression is shown in Eq. 6:

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a \quad (6)$$

It is common to express H^+ as H_3O^+ , recognizing that the proton is heavily solvated and does not exist independent of the surrounding water. This convention has not been adopted here for simplicity. The choice as to how to represent this cation does not affect 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,

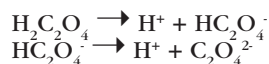


The corresponding equilibrium equations are presented in Eq. 7; Fig. 1 shows the pH dependence of the carbonates.

$$\begin{aligned} \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} &= 4.4 \times 10^{-11} \\ \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} &= 4.6 \times 10^{-7} \end{aligned} \quad (7a,b)$$

The carbonate ion dominates at pH above 10, but it is still measurable at pH levels down to 7. Bicarbonate dominates between pH 6 and 10, and carbonic acid dominates at pH below 6. Since many paper machines 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



$$\begin{aligned} \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}^+]}{[\text{HC}_2\text{O}_4^-]} &= 6.1 \times 10^{-5} \\ \frac{[\text{HC}_2\text{O}_4^-][\text{H}^+]}{[\text{H}_2\text{C}_2\text{O}_4]} &= 6.5 \times 10^{-2} \end{aligned} \quad (8a,b)$$

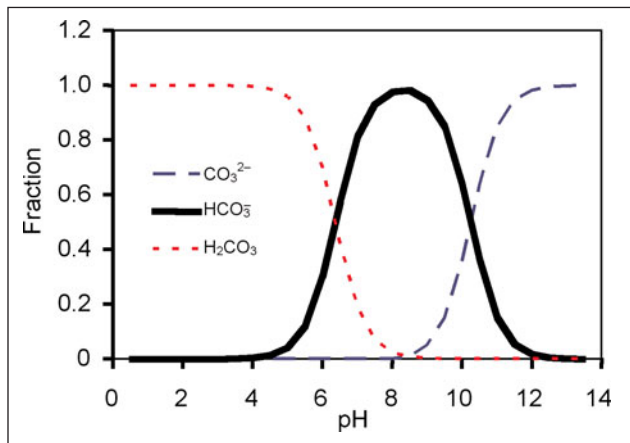


Figure 1. The pH dependence of carbonic acid, bicarbonate, and carbonate.

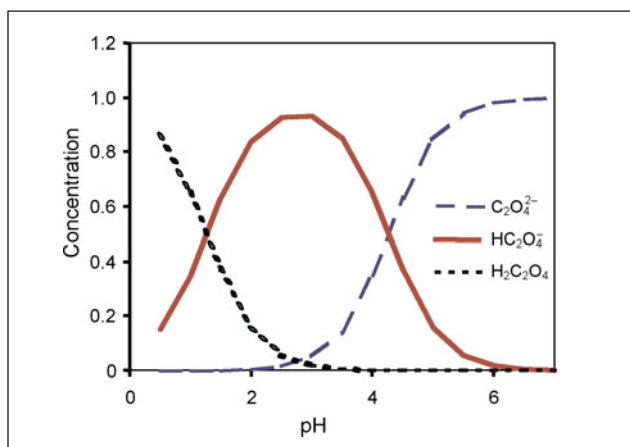


Figure 2. The pH dependence of oxalic acid.

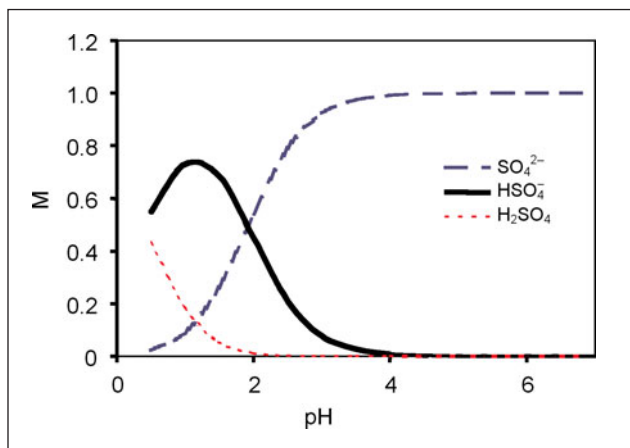


Figure 3. Speciation of sulfate and bisulfate relative to pH.

SCALE

The oxalate ion exists at any pH above approximately 2. It is the dominant form of oxalate at pH above 4. Figure 2 shows the acid-base speciation of oxalic acid.

Sulfuric acid is a strong acid. For practical purposes, when sulfuric acid is diluted with water, the first proton is always dissociated. Thus, only the second acid dissociation constant usually needs to be considered:



$$\frac{[\text{SO}_4^{2-}][\text{H}^+]}{[\text{HSO}_4^-]} = 1.2 \times 10^{-2} \quad (9)$$

Figure 3 shows the pH dependence of sulfuric acid and the sulfates. 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. Precipitation is likely only when the basic form, the divalent anion, and the cation combined exceed the solubility product. Figure 4 shows a calculation for precipitation of calcium carbonate. Precipitation starts at a pH of 8, about the same pH where the graph shows a measurable amount of carbonate. For this graph, carbonate was at 1 M and calcium at 0.01 mM. Calcium carbonate precipitation was determined using ESP equilibrium software from OLI Systems, Inc. (Morris Plains, New Jersey), and the scale for the precipitate was adjusted to make it fit on the graph.

A similar graph of calcium oxalate precipitation is provided in Fig. 5, in which the oxalate pH data are the same as those in Fig. 2, at a 1 M concentration. Calcium oxalate precipitation was calculated for a solution with a 1mM starting concentration of both calcium and oxalate.

These two graphs demonstrate the same point: 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 calcium scales in bleach plants.

Although solubility products and the acid-base chemistry of the precipitating anions have the biggest influence on when and where a process will develop mineral scale, other process variables also influence scaling. 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. However, the solubility of calcium carbonate decreases with temperature (Fig. 6). The temperature sensitivity of this equilibrium is the reason that calcium carbonate scale is common in digester heaters and other process heat exchangers. The temperature effect may also contribute to calcium oxalate and barium sulfate scale on washer wires. As the filtrate penetrates the mat and enters the drop leg, it cools a few degrees.

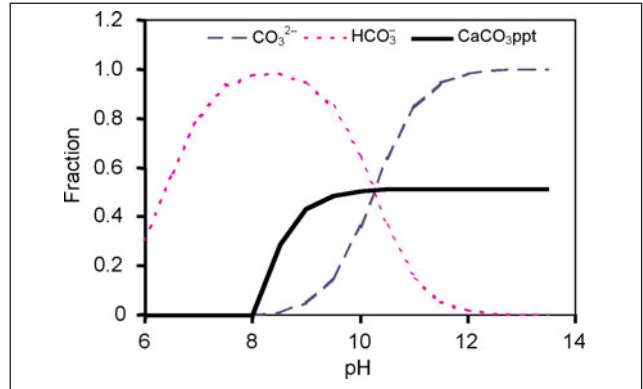


Figure 4. Effect of pH on precipitation of calcium carbonate. Carbonates at 1 M, Calcium at 0.01 mM.

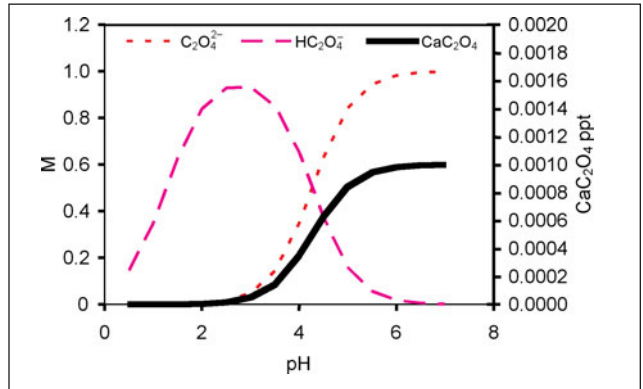


Figure 5. Calcium oxalate precipitation relative to pH. Calcium oxalate precipitation curve calculated for calcium and oxalate at 1 mM starting concentration.

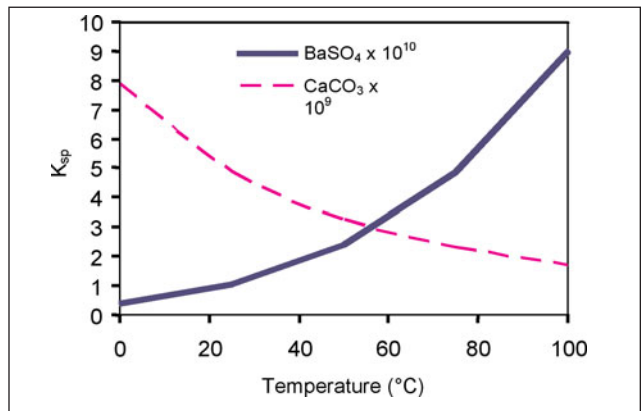


Figure 6. Change in solubility product with temperature. K_{sp} for barium sulfate has been multiplied by 10^{10} and calcium carbonate by 10^9 to fit both curves on the same graph. Notice that K_{sp} increases with temperature for barium sulfate, but decreases with temperature for calcium carbonate.

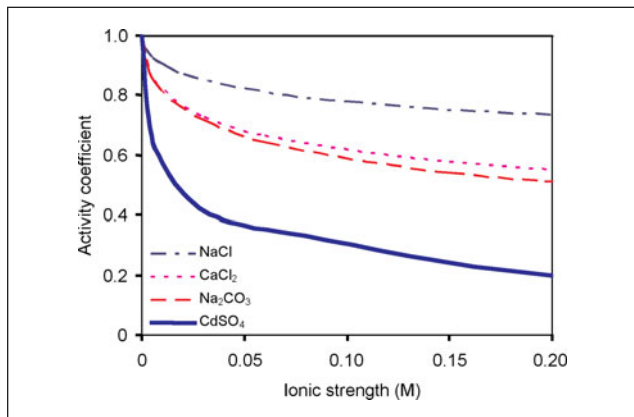


Figure 7. Measured activity coefficient for NaCl, CaCl_2 , Na_2CO_3 , and CdSO_4 .

ION ACTIVITY

The solubility product and acid-base equilibria presented thus far are accurate only for very dilute conditions. To move from the laboratory to conditions in the bleach plant, we must 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. Figure 7 shows activity coefficients for sodium chloride (NaCl), calcium chloride (CaCl_2), sodium carbonate (Na_2CO_3), and cadmium sulfate (CdSO_4). The ionic strength in the bleach plant is around 0.05 M in the first two stages and drops to about 0.02 M in the later stages. The activity of the monovalent ions ranges from 0.8 to 0.9 and that of the divalent ions from about 0.45 to 0.6. In practical terms, the real solubility of calcium carbonate, calcium oxalate, or barium sulfate is about five times the solubility as determined by the solubility product, without considering ion activity.

Most standard chemical references provide tables of activity coefficients suitable for evaluating the solubility limit for scale formation. For modeling purposes, it is useful to estimate the activity coefficient using the extended Debye-Hückel equation:

$$-\log(f) = \frac{Az^2\sqrt{I}}{1 + ba\sqrt{I}} \quad (10)$$

The values A and b vary slightly with temperature, but are around 0.5115 and 0.3291, respectively. The value of a is anion- and cation-specific. For calcium and manganese, a is

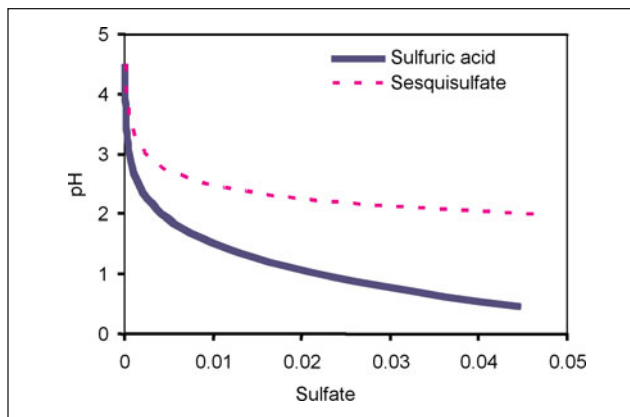


Figure 8. Concentration of sulfate produced when using sulfuric acid or sodium sesquisulfate for pH adjustment of water.

6 Å, and for barium and carbonate, 5 Å. 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

$$I = (C_i z_i^2 + A_i z_i^2)/2 \quad (11)$$

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

The extended Debye-Hückel equation is considered accurate to 0.05 molar ionic strength and provides sufficient accuracy for use in bleach plant equilibrium modeling. It is not accurate at the high ionic strengths found in the pulp mill and recovery. The Pitzer equations provide better estimates at high ionic strength and are more suitable for equilibrium modeling of these areas of the mill [7,8].

EFFECT OF TEMPERATURE

As shown in Fig. 6, solution equilibria are often influenced by temperature. Chemical equilibria are related to Gibbs energy by the expression

$$G = -RT \ln(K) = H - TS \quad (12)$$

where G , H , and S are the Gibbs energy of reaction, enthalpy of reaction, and entropy of reaction, respectively, 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 S/R and slope is H/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. As with activity coefficients, the free energy relationship is not always accurate, but the deviation from linearity is usually over extended temperature ranges or out-

side the range of interest in the bleach plant.

EXAMPLE OF PH CONTROL

As an example of the use of these equilibrium concepts, consider the use of sulfuric acid and sodium sesquisulfate for adjusting pH. Sodium sesquisulfate ($\text{Na}_3\text{HS}_2\text{O}_8$) 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 Eq. 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 it has been estimated with a pKa around 2. The reaction is



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

$$\text{H}^+ = 2(\text{SO}_4^{2-}) + \text{HSO}_4^- \quad (13)$$

$$\text{S}_T = \text{SO}_4^{2-} + \text{HSO}_4^- \quad (14)$$

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 SO_4^{2-} and HSO_4^- in terms of hydrogen and S_T :

$$\text{HSO}_4^- = 2\text{S}_T - \text{H}^+ \quad (15)$$

$$\text{SO}_4^{2-} = \text{H}^+ - \text{S}_T \quad (16)$$

Rewriting Eq. 9 with the ion activity coefficients added to the equation gives

$$\frac{[\text{SO}_4^{2-}] f_2 [\text{H}^+] f_1}{[\text{HSO}_4^-] f_1} = K_a \quad (17)$$

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 Eq. 16 for $[\text{SO}_4^{2-}]$ and Eq. 15 for $[\text{HSO}_4^-]$, Eq. 17 becomes

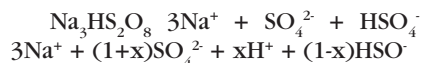
$$\frac{[\text{H}^+ - \text{S}_T] f_2 [\text{H}^+]}{[2\text{S}_T - \text{H}^+]} = K_a$$

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

$$\begin{aligned} ([\text{H}^+] - [\text{S}_T])[\text{H}^+] &= \frac{K_a}{f_2} (2[\text{S}_T] - [\text{H}^+]) \\ [\text{H}^+] - [\text{S}_T] [\text{H}^+] - \frac{2K_a}{f_2} [\text{S}_T] + \frac{K_a}{f_2} [\text{H}^+] &= 0 \\ [\text{H}^+] + [\text{H}^+] \left(\frac{K_a}{f_2} - [\text{S}_T] \right) - \frac{2K_a[\text{S}_T]}{f_2} &= 0 \end{aligned} \quad (18)$$

This is solved using the quadratic formula, providing the value of $[\text{H}^+]$ for any given total charge of sulfuric acid. Equations 15 and 16 can then be used to determine the solution concentrations of HSO_4^- and SO_4^{2-} .

Similarly, for sodium sesquisulfate, the chemical reaction is



This leads to the mass balance equations

$$\text{H}^+ = \text{Se} - \text{HSO}_4^- \quad (19)$$

$$2\text{Se} = \text{SO}_4^{2-} + \text{HSO}_4^- \quad (20)$$

where Se is used to indicate total sesquisulfate.

Solving for SO_4^{2-} and HSO_4^- as before gives

$$\text{HSO}_4^- = \text{Se} - \text{H}^+ \quad (21)$$

$$\text{and} \quad \text{SO}_4^{2-} = \text{Se} + \text{H}^+ \quad (22)$$

and substituting into Eq. 17 gives

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

Again, reorganizing this into a quadratic equation:

$$\begin{aligned} \text{Se}[\text{H}^+] + [\text{H}^+]^2 &= \frac{K_a}{f_2} \text{Se} - \frac{K_a}{f_2} [\text{H}^+] \\ [\text{H}^+]^2 + \left(\text{Se} + \frac{K_a}{f_2} \right) [\text{H}^+] - \frac{K_a \text{Se}}{f_2} &= 0 \end{aligned} \quad (23)$$

Figure 8 shows the results, where process pH is plotted against sulfate ion concentration when using sulfuric acid and sodium sesquisulfate for pH control. At pH above 4, sodium sesquisulfate results in four times the sulfate ion concentration of pH control with sulfuric acid. At pH 2.5, the sesquisulfate forms a buffer. The amount of sesquisulfate required increases the sulfate concentration to more than six times the sulfate concentration when using sulfuric acid. The two key issues raised by Fig. 8 are as follows:

1. Use of sodium sesquisulfate to control the pH substantially increases the concentration of sulfate in the bleach plant and with it the potential for encountering barium sulfate scale.

2. It is not possible to decrease the sulfate ion concentration and the potential for barium sulfate scale using sulfuric acid. The sulfate ion concentration continues to rise, even at very low pH.

CONCLUDING REMARKS

The chemical process that forms mineral scale in pulp mills and bleach plants is precipitation. 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. An evaluation of these equilibria demonstrates that calcium oxalate scale is unlikely to form at a pH of 2.5 and below, and calcium carbonate scale is unlikely to form at a pH below 8. A simplified solubility product cal-

ulation is a good starting point for understanding scale problems in a bleach plant, but both the solubility product and acid equilibrium constants are temperature dependent. In addition, the high dissolved ion concentration that exists in pulp mill bleach plants reduces ion activity. The effect of temperature and ion activity is to increase the solubility of calcium oxalate and barium sulfate by about one order of magnitude. These effects need to be included when performing a rigorous analysis of scale formation in a bleach plant.

In the third paper of this series[9], other factors that influence the solubility of trace cations in bleach plants will be discussed and a detailed equilibrium analysis performed for one of the mill case studies presented in part I of this series[3]. **TJ**

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This paper is also published on
www.tappi.org
and summarized in the June, 2006
Solutions! for People, Processes
and Paper magazine (Vol. 89 No. 6).



Received: June 29, 2005

Revised: April 11, 2006

Accepted: April 19, 2006

INSIGHTS FROM THE AUTHORS

An unanticipated outcome of the switch from chlorine initiated bleaching sequences to chlorine dioxide as the first stage bleaching agent was a considerable increase in the number of mills experiencing mineral scale deposits. After five years of effort eliminating scale deposit problems, it had become clear that there was not a general understanding of the basic chemistry controlling scale deposits in pulp mills and bleach plants.

This is a three-part series addressing mineral scale problems.

- The first paper related a series of case studies where scale has been eliminated. The process adjustment that succeeded in eliminating the scale problem is presented and the relevant chemistry discussed.
- The second paper in the series presented the solubility product equilibria for calcium carbonate, calcium oxalate and barium sulfate, and the acid equilibria for the precipitating anions. It uses the acid equilibrium for sulfuric acid to demonstrate the impact of using sodium sesquisulfate for pH control in a bleach plant.
- The third paper provides a detailed analysis of one case study showing how pH adjustment can eliminate calcium oxalate scale in a mill. This paper

uses the ion exchange, acid equilibrium for oxalate and solubility product for calcium oxalate to determine the likelihood of mineral scale problems for a specific set of conditions and a process change.

Most calcium oxalate scale problems can be resolved by adjusting the first chlorine dioxide stage terminal pH to 2.5. Many barium sulfate scale problems can be resolved by replacing ClO_x generator spent acid with commercial sulfuric acid.

This series of papers will help mill operators and process engineers to understand why these changes work and how to evaluate alternative when these simple solutions fail.

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