Mineral scale management Part III. Nonprocess elements in the paper industry

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ABSTRACT: Efforts to comply with effluent standards have led to a situation where mills have little leeway in managing trace metals without developing mineral scale deposits. In most cases, the trace metals can be managed with minor process changes and siitable levels of process control. The principal tools available to the mill are pH and good washing in the first chorine dioxide stage washer. In some cases, mills may need to change shower sources on washers or upgrade the Do washer. By determining the chmical equilibrium for critical points in the process and in some cases modeling the chemical eqilibrium-mass balance, it is possible to identify operating conditions that will eliminate mineral scale buildup in nearly all mill situtaitons. This paper provides information on hwo trace metals enter the mill and how pulp ion exchange influences where the metals go in the bleach plant. It also demonstrates how a fundamental chemical analysis of the effect of pH on anion speciation and solubility product on scale formation can be used to troubleshoot and prvent scale problems.

Application: This paper provides a detailed equilibrium analysis of conditions in a mill that was experiencing calcium oxalate scale and describes the process adjustments that eliminated the problem. The analysis determeinds how ion exchange ion activity, and the acid-base equilibrium effect free ion concentrations of calcium and oxalate and how these free ion concentrations are used to determine the potential for mineral scale formation.

With the discovery of dioxins in bleach plant effluents in 1987, mills converted their first chlorination stage to a chlorine dioxide stage. This change resulted in scale problems in many mills that had never previously experienced mineral deposits. Initially, many mills set the D_0 stage pH target at 4.0, the same as the typical target for a D_1 or D_2 stage. Later research showed that D_0 was much less pH sensitive and that the optimum was anywhere between pH 2 and 4 [1, 2]. This is readily observed in the bleach response data shown in **Fig. 1.** This pH region is very active for barium sulfate and calcium oxalate precipitation [3, 4]. Mills targeting the pH 4 side of the operating window ran the risk of calcium oxalate scale forming in their D_0 stage. Mills adding enough sulfuric acid to drive the pH down to 2.5 increased the potential for barium sulfate scale.

At pH 4, half the pulp ion exchange sites are active in the anion form and exchanging trace metals **(Fig. 2).** This helps carry trace metals into the extraction stage and further into the bleach plant. The result is that managing a bleach plant to avoid mineral deposits becomes a much more challenging task. Meeting this task requires an understanding of the chemistry and mechanisms of scale formation and trace metals management. In the first paper of this series, we reported on seven mill case studies in which scale problems were eliminated and the chemical basis of the solution was well understood [5]. The second paper presented the fundamental chemistry of precipitation and the acid-base chemistry of the scale-forming anions [3]. This third paper demonstrates the chemical principles needed to determine chemical equilibria in a mill.

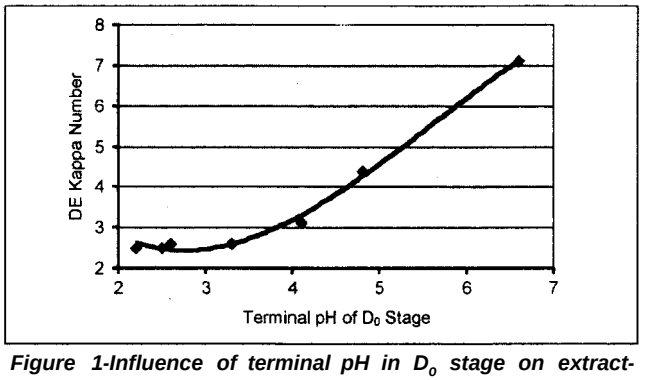

Figure 1-Influence of terminal pH in D_0 stage on extracted kappa.

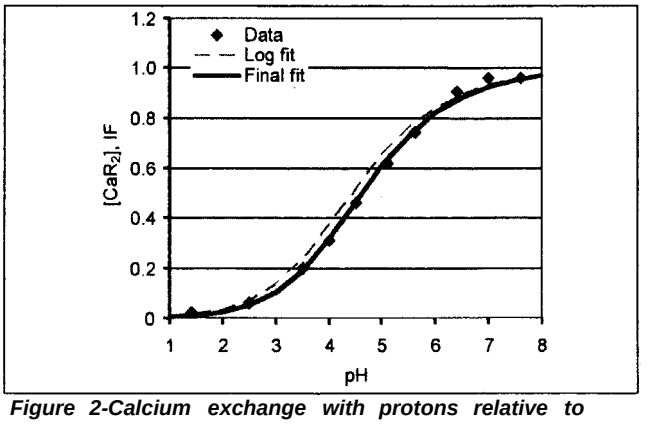

Figure 2-Calcium exchange with protons relative to solution pH. Solid line is best fit; dashed line is linear fit to Eq. (1).

ION EXCHANGE CAPACITY OF WOOD PULP

The ion exchange behavior of wood pulp has been known for about 40 years and has been fairly well understood for at least 10 years [6, 7]. The acids in wood pulp are primarily carboxylic acid groups from oxidized end groups, the hydrolyzed esters of uronic acid groups, and oxidized fragments of lignin. A typical kraft brownstock pulp contains about 100 milliequivalents per kilogram (meq/kg) of ion exchange capacity. This decreases to about 50 meq/kg in the partially and fully bleached pulp (Fig. 3). Most carboxylic acid groups have pKa values that fall between about 3.5 and 4.5 [8] (see also Fig. 2). At a pH around 4, about 50% are anions, the dissociated form, and about 50% are protonated, the acid form. Following typical equilibria, at a pH around 5, about 90% of the acid groups are dissociated, and at a pH around 3, only about 10% are dissociated. Figure 2 shows an example of the PH-controlled exchange of protons and calcium. Although still showing the characteristic step function of an equilibrium, the transition from the acid to the base state is not as sharp as a typical acid-base titration curve. By plotting log data, the equilibrium expression becomes a linear function with the intercept equal to log(K) and the slope equal to the stoichiometric coefficient of the reaction. Equation (1) shows this for an equilibrium involving the calcium ion and protons with an unspecified organic group R.

$$\frac{[CaR_2][H^+]^2}{[HR]^2[Ca^{2+}]} = K \qquad (1)$$

$$\log\left(\frac{[CaR]}{[Ca^{2+}]}\right) - 2\log\left(\frac{[HR]}{[H^+]}\right) = \log(K)$$

The equilibrium presented in Fig. 2 is shown again as a log plot in **Fig. 4.** The linear fit gives a slope of 0.67, not the slope of 2 expected. This deviation from ideal was probably first recognized by Towers and Scallan [7], and has been evaluated in detail by Laine et al [8]. The evidence is quite strong that the deviation from ideal is caused by the presence of several carboxylic acids slightly different acid dissociation constants. Some of these acids seem to be associated with lignin. The results is that the slope of the line in the log ratio plot is lignin concretration dependent [8].

In an ion exchange material, the fixed ionic groups must have thier charge neutralized by opposing charges [9]. In wood pulps, the fixed charge groups lose a proton to become anions and the fiber develops a net negative charge. The negative charge attracts cations from solution until the net charge is near neutral, and just enough remains to maintain the concentration difference between the fiber and the bulk solution [9]. The basics of this mechanism are contained in the Donnan equilibrium theory developed to explain the electrolyte imbalance common in dialysis. This process accounts for the ability of ion exchange materials to collect ions at internal concentrations that exceed the concentration in the external solution and the ability to collect ions like sodium and potassium that rearely form chemical complexes.

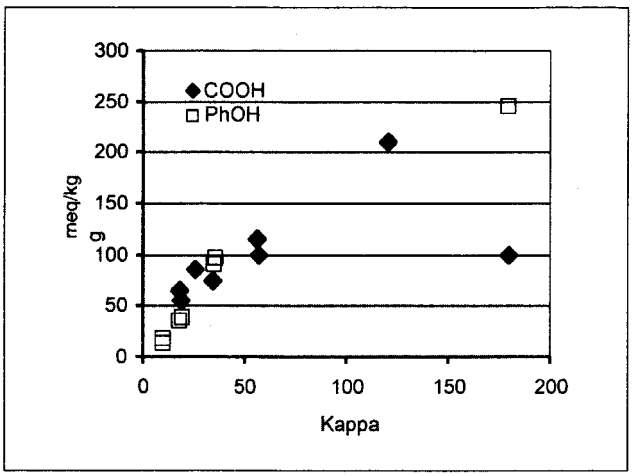

Figure 3-Acid groups measured in pulp relative to pulp kappa number [8, 14-16].

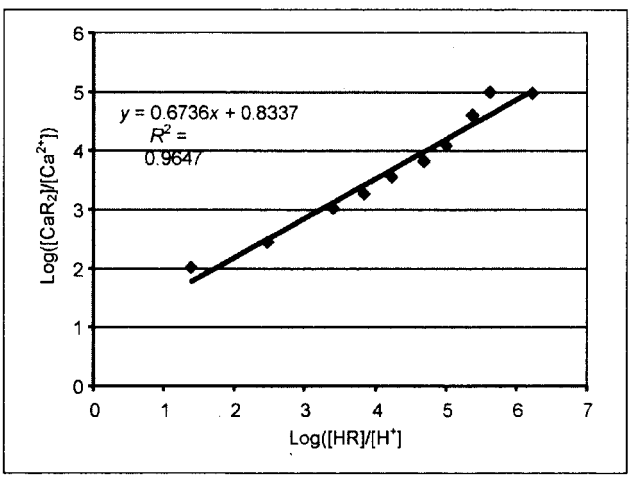

Figure 4-Log fit of calcium ion exchange data as in Eq. (1b).

In the Donnan theory, ion attraction to the ion exchange material is based solely on charge and can be described by the relationship shown in Eq. (2) [7,9].

$$\lambda = \frac{[M^+]_B}{[M^+]_F} = \sqrt{\frac{[D^{2+}]_B}{[D^{2+}]_F}} \qquad (2)$$

In Eq. (2), $[M^+]_F$ refers to the concentration of monovalent cations free in solution, and $[M^+]_B$ the concentration of "bound" monovalent cations in the cation exchange resin. $[D^{2+}]_F$ and $[D^{2+}]_B$ are the same for divalent cations. In the Donnan equilibrium, the bound state concentration is the ion concentration within the solvent-swollen ion exchange particles. This is not always an easy parameter to measure and is dependent on the cations present in solution and

the concentration difference between the internal and external solutions.An alternative that will be used here is to use mole fraction to define the concentration of cations in the internal solution. With this approach, the effect of fiber swelling is contained in the Donnan distribution constant A.

The Donnan approach provides an adequate account for the distribution of ions between the solution and bound states, but the distribution coefficient A is not really constant.The Donnan theory also does not account for specific complex formation. which has to be handled as an addtional equilibrium. The formation constants for most divalent cations with acetic acid are fairly small, and sodium is normally regarded as completely dissociated in nearly all solutions. But protons are a different story, and the formation of a complex between protons and an anion is exactly why acid is weak rather than storong. So, for ion exchange processes involving a weak fixed acid such as the carboxylic acid groups in pulp, the Donnan equilibrium method connot andle the stibution or partion of protons very well, and it is limited in accuracy on other cations by any complex formation.

An alternative model is the selectivity coefficient formalism. The selectivity coefficient method closely parallels solution chemistry but recognizes a difference int the concentration basis for the solution and bound states [9]. for the ion exchange reaction,

$$Ca^{2+} + 2NaR \rightarrow 2Na^{+} + CaR_2$$

Using the same notation as used for the Donnan equilibrium, the selectivity coefficient expression is

$$\frac{[Na^+]_F^2 [Ca^{2+}]_B}{[Ca^{2+}]_F [Na^+]_B^2} = K_{Na}^{Ca} \quad (3)$$

This formalism is nearly identical to the chemical equilibruim formalism expressed in Eq. (1), except for the important distinction that the bound and free ion concentration basis is not the same. Note that the selectivity coefficient and Donnan equilibruim are effectively the same when the selectivity coefficient constant has the value 1. The selectivity coefficient has several advantages over the Donnan equilibrium. It does account for specific ion interactions such as complex formation. The similarity to solution equilibria makes it an easy fit into solution equilibrium software, and the similarity to solution equilibria means that it can also be modeled according to the Gibbs free energy expression. But it greatly complicates calculating the process chemical equilibrium. For simplicity, this paper uses the Donnan theory.

EFFECT OF ION EXCHANGE (AND PRECIPITATION)

The basic effect of the pulp ion exchange is to prevent trace cations from being washed out of the pulp at modestly acid to alkaline pH. In brownstock washing, this is the sorbed sodium effect that places a limit on soda recovery. In the bleach plant, the ion exchange effect can carry cations such as calcium and barium through the initial chlorine dioxide stage and into the D_1 and D_2 stages. Some of these cations will be removed in these later stages. Metals will be added back into these stages where D_1 and D_2 filtrates are used as wash water on the first extraction or initial chlorine dioxide stages. At an acid content of 100 meq/kg of pulp and 10% pulp consistency, the ion exchange can account for a calcium concentration of 200 mg/kg in brownstock or D_0 stage pulp. Nonprocess elements (NPE) data from bleach plants show the pulp off the D_0 stage washer contains 200-300 mg/kg of calcium. Due to other factors, the ion exchange is only responsible for about a quarter of this total. This will be shown in detail in an equilibrium analysis later in this paper.

Limited washing and precipitation are the other major issues contributing to carryover of metals into the later stages of the bleach plant. Even good washing in bleach plants is typically limited to a displacement ratio of about 0.8. That means 20% of the calcium would carry into the extraction stage even with distilled water for wash water. Many mills operate with displacement ratios closer to 0.6. Even more important is the evidence that scale is just the tip of the iceberg. Where there is calcium oxalate scale in the D_0 stage, there is even more calcium oxalate attached to fibers. In many cases, mills just analyze for cations and ignore the anions. Under these conditions, precipitated calcium cannot be distinguished from adsorbed calcium. It makes sense that much of the oxalate would get trapped on fiber. Compared to the surface area of the pumps, piping, and towers, the fiber surface area is huge.

SUPERSATURATION

Supersaturation is a phenomenon whereby ions are known to exceed the solubility product and do not precipitate as expected. Supersaturated conditions can exceed the solubility product by an order of magnitude or more [10]. This regarded as a nonequilibruim status and eventually a precipitate will form. The presence of dissolved organic fragments and oligomers in bleach plant filtrates may support supersaturation because some of these fragments are surface active and can mimic the activity of scale inhibitors [11].

Given the typical process variation that exists in a mill, that possibility of a supersaturation condition persisting for an extended period is very low. That means that a persistent supersaturation condition is considered unlikely. Once the supersaturated state is broken and scale has formed, the existing scale will grow at the rate that new ions are transported to the surface. The supersaturation condition serves only to prevent harmless precipitation in solution and on fibers and to accelerate the growth rate of the scale.

CALCULATION OF TRACE METAL EQUILIBRIUM

Consider the case study for the hardwood bleach line in Mill D of the first paper in this series [5]. This mill operated with a D_0 terminal pH between 3 and 3.5 and suffered from scale buildup on the wash press. The concentrations of trace elements and anions are given in the third

column of **Table 1.** These data are determined as total concentration reported on an ovendried pulp basis. As such, the data include the bound cations and precipitated cations as well the cations contained in solution. In addition, column 4 of Table I adjusts the NPE concentration to the 7.5% consistency of the wash press headbox, column 5 expresses NPEs in molar concentration, column 6 records the monovalent cation contributions to λ^2, and column 7 records the divalent cation contribution. The final column shows the individual cation contribution to ionic strength ($C \cdot z^2$).

With a few simplifying assumptions, the Donnan approach provides a direct solution that is sufficiently accurate for many purposes. Typically, unbleached kraft pulps have about 100 meq/kg acid functional groups. The fraction of acid functional groups subject to ion exchange can be estimated from Fig. 2. At pH 3.5, this is approximately 20% or 20 meq/kg. This residual ion exchange capacity is satisfied by the process (Na^+) and the nonprocess cations (Mg^{2+}, K^+, Ca^{2+}, Mn^{2+}, and Ba^{2+}) in the solution. Remember, the proton concentration in the fibers has already been accounted for.

The equilibrium has three interdependent parts: ion exchange, acid-base equilibrium of oxalic acid, and precipitation of calcium oxalate. The ion exchange influences the concentration of free calcium in solution, and that value is critical to determine if precipitation is likely. The acid equilibrium of oxalic acid determines how much divalent oxalate is present in solution. That also affects the likelihood of precipitation. But when the pH is known, the acid equilibrium and ion exchange equilibrium have little direct effect on each other. It is also not necessary to consider the effect of the solubility product to determine if the concentrations of calcium and oxalate exceed the solubility product. This means the acid equilibrium and ion exchange equilibrium can be calculated independently, greatly simplifying the analysis. This is not the case if the goal is to determine how much calcium precipitates, because the solubility equilibrium will affect both the ion exchange and acid-base equilibria and then all three need to be determined simultaneously.

Adding specific cations to the Donnan relationship in Eq. (2) results in the following equation:

$$\lambda = \frac{[Na^+]_B}{[Na^+]_F} = \frac{[K^+]_B}{[K^+]_F} = \frac{\sqrt{[Mg^{2+}]_B}}{\sqrt{[Mg^{2+}]_F}} = \frac{\sqrt{[Ca^{2+}]_B}}{\sqrt{[Ca^{2+}]_F}} = \frac{\sqrt{[Mn^{2+}]_B}}{\sqrt{[Mn^{2+}]_F}} = \frac{\sqrt{[Ba^{2+}]_B}}{\sqrt{[Ba^{2+}]_F}} \quad (4)$$

Squaring both sides of each equality and rearranging Eq. (4), we get

$$\lambda^2 = \frac{[Na^+]_B^2}{[Na^+]_F} \Rightarrow \lambda^2 [Na^+]_F^2 = [Na^+]_B^2 \quad (5.a,b,c)$$

$$\lambda^2 = \frac{[K^+]_B^2}{[K^+]_F^2} \Rightarrow \lambda^2 [K^+]_F^2 = [K^+]_B^2$$

$$\lambda^2 = \frac{[Ca^{2+}]_B}{[Ca^{2+}]_F} \Rightarrow \lambda^2 [Ca^{2+}]_F = [Ca^{2+}]_B$$

Obviously, there are similar equations for Mg, Ba, and Mn. By adding the right-side equalities of Eq. (5) and converting to the summation notation, we get

$$\lambda^2 [Na^+]_F^2 + \lambda^2 [K^+]_F^2 + \lambda^2 [Ca^{2+}] = [Na^+]_B^2 + [K^+]_B^2 + [Ca^{2+}]_B$$

$$\lambda^2 \left(\sum [M^+]_F^2 + \sum [D^{2+}]_F \right) = \sum [M^+]_B^2 + \sum [D^{2+}]_B$$

$$\lambda^2 = \frac{\sum [M^+]_B^2 + \sum [D^{2+}]_B}{\sum [M^+]_F^2 + \sum [D^{2+}]_F} \quad (6.a,b,c)$$

For practical purposes, the sum of the monovalent cations in this case is just sodium and potassium, and the sum of the divalent cations is magnesium, calcium, manganese, and barium. In Table I, the sum of the squared concentrations of monovalent cations is 1.5 E-5, where the sum of the divalent cations is 0.00238. The error in λ^2 from ignoring the monovalent contribution in this case is about 0.6%, presumably in both the numerator and denominator.

We do not know either the numerator or the denomi-

TABLE I. CONCENTRATION OF TRACE ELEMENTS AND TOTAL OXALATE IN D_0 TOWER DISCHARGE STREAM[A].

Element	Atomic weight	OD pulp (mg/kg)	Total (mg/kg)	M	M^2	D	$C \cdot z^2$
H^+	1			0.0316			0.0316
Na^+	23	1205	90.38	0.00393	1.5 E-5		0.00393
Mg^{2+}	24.3	39.5	2.96	0.000122		0.000122	0.000488
K^+	39	59.2	4.4	0.000114	1.3 E-8		0.000114
Ca^{2+}	40	1185	88.9	0.00222		0.00222	0.00888
Mn^{2+}	54.9	18.6	1.4	2.5 E-5		2.5 E-5	1 E-4
Ba^{2+}	137.3	21.5	1.61	1.2 E-5		1.2 E-5	4.8 E-5
Total	C_2O_4	88	12.5	0.000142	1.5 E-5	0.00238	0.0139

[a] M^2 is concentration of monovalent cations squared; D, concentration of divalent cations; Cz^2, molar concentration of all cations times charge squared.

nator in this equation or, for that matter, the contribution of the divalent cations to either. But if we assume that the divalent cations will dominate the bound state, the numerator has a mole fraction value close to 0.5. (The fibers can only absorb half as many moles of divalent cations as there are moles or equivalents of ion exchange sites. If this condition is exceeded, the fibers become positively charged and repel the cations.) To increase the accuracy of this estimate, it can be adjusted by the approximate divalent contribution to the ion exchange.

$$F_D = \frac{\sum [D^{2+}]_T}{\sum [M^+]_T^2 + \sum [D^{2+}]_T} \quad (7)$$

In Eq. (7); the subscript *T* denotes that this is total ion concentration.

The Donnan equilibrium, as expressed in Eq. (4), does not include the effect of ion activity. Technically, the concentrations of both the bound and free states are reduced by the respective ion activity coefficients in each. Because we do not really know the volume of the bound state, we cannot calculate an accurate activity coefficient. If we ignore it, the activity coefficient in the bound state gets incorporated into the value of the distribution coefficient. Unfortunately, this value is quite different for monovalent and divalent cations at high concentrations. Nothing can be done about this; it has to be accepted as part of the overall error.

Considering just the divalent cations and rewriting the Donnan equation with the solution activity coefficient (f_2) gives

$$\lambda^2 f_2 \sum [D^{2+}]_F = \sum [D^{2+}]_B \quad (8)$$

The sum of the bound and free states is the sum of the total divalent cation concentration that we know from the chemical analysis. The constant [Ie] is introduced to express the bound ion concentration as a total solution concentration, so that the bound and free states are on the same concentration basis and can be added and subtracted in the mass balance. For this case,

[IE]= 20(meq/kg)*(kg/1000g)*(eq/1000meq)*(7.4%/100%)*(1000g/L) = 0.0015 eq/L.

$$\sum [D^{2+}]_F = \sum [D^{2+}]_F + [Ie] \sum [D^{2+}]_B \quad (9)$$

Solving Eq. (9) for the free cations and inserting this into Eq. (8) gives

$$\lambda^2 f_2 \left(\sum [D^{2+}]_F - [Ie] \sum [D^{2+}]_B \right) = \sum [D^{2+}]_B$$
$$\lambda^2 f_2 \sum [D^{2+}]_F = \sum [D^{2+}]_B + \lambda^2 f_2 [Ie] \sum [D^{2+}]_B$$
$$\frac{\lambda^2}{1 + [Ie] f_2 \lambda^2} = \frac{\sum [D^{2+}]_B}{f_2 \sum [D^{2+}]_F} \quad (10)$$

On the right side of Eq (10), the numerator is approximately $0.5F_D$; the mole fraction of 100% divalent reduced by fraction as divalent from Eq. (7). The denominator is the activity coefficient for divalent cations times the sum of the concentration of all divalent cations. With these assumptions, it is possible to approximate A.

From Table I, $\Sigma[D^{2+}]_T = 0.00238$.

$F_D = 0.00238/(0.00238+1.5E\text{-}5) = 0.994$.

The fifth column in Table I is the cation concentration times z^2. Summing this, we get a cation contribution to ionic strength of 0.0139 M. Technically, $I = (\Sigma C_i z_i^2 + \Sigma A_j z_j^2)/2$. Using just the cation concentrations to estimate the ionic strength is a weak approximation, but we rarely analyze for all the anions, and the analysis we do have in this case is not close to balanced charge. For our purposes, we can assume 0.0139 M is the ionic strength and calculate an activity Coefficient for both monovalent (f_1) and divalent (f_2) ions using the extended Debye-Hückel [12] equation and an average value for the hydrated radius of 5Å:

$$f = \frac{Az^2\sqrt{I}}{1 + ba\sqrt{I}}$$

$$f_1 = 10^{\frac{-0.5115\sqrt{0.0139}}{1+(0.329)(5)\sqrt{0.0139}}} = 0.89$$

$$f_2 = 10^{\frac{-(0.5115)(4)\sqrt{0.0139}}{1+(0.329)(5)\sqrt{0.0139}}} = 0.63$$

Using this value of f_2, the denominator on the right side is $f_2 * \Sigma[D^2]_T$ = 0.63*0.00238 = 0.001499, and the right side comes to 0.497/0.00149 = 331.

Now, solving for λ,

$\lambda^2 = 331(1+f_2[Ie]\lambda^2) = 331 + 0.313\lambda^2$

$\lambda^2(1\text{-}0.313) = 313$

$\lambda = 21.3$

To determine the bound concentration for the divalents, multiply the total cation concentration by 331 (the value obtained from the right side of Eq [10]) and f_2. One can go through a similar derivation to show that the equivalent value for the monovalent cations is

$$\frac{\lambda}{(1 + [Ie] f_1 \lambda)} = \frac{\sum [M_B^+]}{\sum [M_T^+]} \quad (11)$$

For the current case, $\lambda/(1+[Ie]f_1\lambda)$ = 20.7.

Table II provides estimates of bound and free cations. The final cell of the bound fraction column is the sum of the monovalent fractions plus the twice the sum of the divalent frattions. This value should equal 1.0. The

TABLE II. ESTIMATE OF BOUND FRACTION AND REMAINING FREE CATION CONCENTRATION.

Element	Total (M)	Bound multiplier	Bound fraction	Free (M)
Na	0.00393	20.7	0.072	0.00382
K	0.000114	20.7	0.0021	0.00011
Mg	0.000122	313	0.024	0.000086
Ca	0.00222	313	0.43	0.00158
Mn	2.5 E-5	313	0.0049	1.8 E-5
Ba	1.5 E-5	313	0.0029	1.1E-5
Charge balance			1.07	

errors in the estimate are on the order of 7%, and the equivalent of assuming the initial ion exchange capacity of the pulp is 107 meq/kg rather than the original 100 meq/kg assumed. This is well within the accuracy of the original estimate of ion exchange capacity and is within the errors for the measurement of the solubility product of calcium oxalate. The free molarity is determined from total concentration minus the bound fraction times 0.0015 eq/L, where the 0.0015 eq/L is the solution concentration of ion exchange sites determined earlier. Note that there is an error in the estimate of the activity coefficients because these were determined from the total cation concentration. This too will be ignored.

The next step is to determine the concentration of $C_2O_4^{2-}$. The pH is the ion activity of the proton concentration, so the acid dissociation is

$$\frac{[H^+][C_2O_4^{2-}]f_2}{[HC_2O_4^-]f_1} = 6.5\times10^{-2} \quad (12)$$

The mass balance for total oxalate is

$$Ox = [HC_2O_4^-] + [C_2O_4^{2-}] \quad (13)$$

Where Ox represents the total oxalate analysis. In this pH range, the concentration of oxalic acid is small and can be ignored. Solving Eq. (13) for HC_2O_4 and substituting into Eq. (12) gives

$$\frac{[H^+]f_1[C_2O_4^{2-}]f_2}{[Ox-C_2O_4^{2-}]f_1} = 6.1\times10^{-5} \quad (14)$$

$$[H^+][C_2O_4^{2-}]f_2 = 6.1\times10^{-5}[Ox-C_2O_4^{2-}]$$

$$[C_2O_4^{2-}] = \frac{6.1\times10^{-5}[Ox]}{([H^+]f_2+6.1\times10^{-5})}$$

Enter 0.000142 M for total oxalate. The pH is the negative log of proton activity. Converting this to solution activity and dividing by the activity coefficient for monovalent ions puts this into the form needed for Eq. (14): $0.00316/f_1 = 0.000355$ M for H^+. With 0.89 for f_1 and 0.63 for f_2, $C_2O_4^{2-}$ can be calculated at 3.0 E-5 M.

The solubility product expression is

$[Ca^{2+}]f_2[C_2O_4^{2-}]f_2 = 2.3$ E-9

Substituting in the values obtained above, we get the product of the ion activities as

[0.00158](0.63)[3.0 E-5](0.63) = 1.9E-8

This is eight times the solubility product as listed. Consider the following extenuating issues:

•The values for the solubility product of calcium oxalate vary by at least a factor of 10, with the main experimental variation being the length of time provided for the precipitate to appear.

• Calcium oxalate solubility increases with temperature.

•The analysis ignores the effect of complex formation with calcium and dissolved organics. Although these tend to be weak complexes and have been ignored for this reason, they do reduce the available calcium slightly.

Considering these issues, this value for over-saturation is considered marginal, but with a probability of scale formation. When this mill encountered calcium oxalate scale under these conditions, it lowered the pH target of the DO stage to 2.5. Recalculating for this pH has the following pertinent points:

•The residual ion exchange sites are reduced to about 7% of the total. The solution concentration of ion exchange sites then becomes 0.00052 eq/L.

• λ changes to 19.25. The value of $\lambda^2/(1+[Ie]f_2\lambda^2)$ does not change and remains at 330.

•The value of $\lambda/(1+[Ie]f_1\lambda)$ goes to 19.1.

•The bound fraction of Ca stays at 0.464, but this is now 0.464*0.00052 eq/L or 0.00024 M, and the solution concentration is 0.00222 - 0.00024 = 0.00198 M.

•The lower pH favors HC_2O_4 over $C_2O_4^{2-}$, and the free oxalate drops to 4.2 E-6M.

•The product of the ion activities is $(4.2\text{ E-}6)(0.00198)(0.63)^2 = 3.3$ E-9.

This value is just slightly above the solubility product for calcium oxalate and suggests a greatly reduced risk of encountering this scale on the washer. Using the MS Excel-based partitioner spreadsheet [13], which uses selectivity coefficients for the ion exchange and an iterative approach to solving the interdependent equilibria, we determined the product of the ion activities at pH 3.5 to be 3.1 E-8, and at pH 2.5 was 2.9 E-9. The iterative solution indicates a slightly higher risk of scale at pH 3.5 and slightly lower risk of scale at pH 2.5.

In addition to the factors indicated earlier, precipitates are often carried into the succeeding stages of the bleach plant. This increases the concentration of these ions in the washer filtrates of these stages. They return to the D_0 stage in the shower water. Because of this recycle effect, the decreased amount of calcium oxalate precipitated in D_0 will result in a decrease in the recycle and further reduce the total calcium and oxalate in the D_0 stage. This means that even if calcium oxalate still scales the D_0 press after the pH is lowered, the reduced precipitate carryover will result in further reductions of these two ions in D_0 beyond what is calculated here.

CONCLUSIONS

This paper concludes a three-part series on managing mineral scale in pulp mills and bleach plants. There are two overriding conclusions from the series of papers:

1. Control to a pH of 2.5 in the first chlorine dioxide bleach stage to reduce or eliminate calcium oxalate scale and improve calcium removal in the first stage of the bleach plant. Do not go lower.
2. If there is any risk of barium sulfate scale, do not use chlorine dioxide generator spent acid for pH control. Sodium sesquisulfate increases the risk of barium sulfate scale.

The report presented here has supported the first of these two

conclusions at a level of detail beyond the interests and dedication of most mill technical staff. If a scale problem is not resolved by practicing recommendations 1 and 2, the cost-effective solution is to understand the problem using the methods presented in all the papers of this series. **TJ**

LITERATURE CITED

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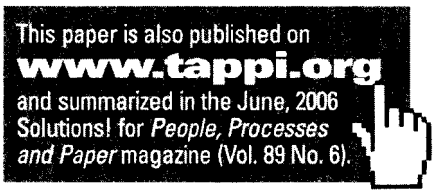

INSITES FROM THE AUTHORS

An unanticipated outcome of the switch from chlorine-intiated bleaching sequences to chlorine dioxide as the first stage bleaching agent was considerable increase in the number of mills experiencing mineral scale deposits. After five years of effort eliminating scale depsoit 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 the final paper in a three-part series addressing mineral scale problems. It 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 eqiulibrium 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 ClO2 generator spent acid with commercial sulfuric acid.

Application: This series of paper 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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