Mineral Scale Management

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7.1. INTRODUCTION

Mineral scale problems are not new to pulp mills and bleach plants. The liquor recovery system ensures that white liquor is saturated in calcium carbonate, and this mineral will precipitate when heated to cooking temperatures in the digester [1,2]. The original single-vessel continuous digesters sold by Kamyr had an extra liquor heater as standard equipment to enable the mill to take one heater out of service for acid cleaning without impacting production [3]. Although lime scale in the digester is generally the most routine scaling problem in pulp mills, various other scales are common in the chemical recovery area [4,5], and several types of mineral scale can turn up in bleach plants or on the paper machines. Efforts to reduce wastewater discharge using countercurrent filtrate recycle schemes in the bleach plant [6,7] certainly increased problems with mineral scale, but except with direct countercurrent filtrate management [8], scale problems were usually not severe. Mechanical pulping operations can also have problems with scale, partially because these processes are less efficient at removing trace metals and partially because sodium silicate is typically used in peroxide bleaching of mechanical pulp. The zero-discharge bleached chemimechanical pulp mills in Canada had to plan for metal scale prob-

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lens, and at Meadow Lake, the mill carefully monitored calcium and magnesium in the process water and added magnesium as needed to ensure that deposits were soft and could be cleared with pressure washing [9]. Serious scale problems were also encountered by Great Lakes Paper Industries at their zero-effluent kraft mill in Thunder Bay, Ontario, and were among the several reasons that this mill was never able to operate as designed.

When the industry replaced elemental chlorine (Cl2) with chlorine dioxide (ClO2) in the first stage of the bleach plant (elemental-chlorine-free bleaching, or ECF), there was a corresponding switch to higher pH in this stage. Initially, many mills targeted a pH near 4, the natural pH of a D_o bleaching stage and near the traditional optimum pH for D_1- and D2-stage bleaching [10,11]. The higher pH was not as efficient at dissolving calcium and barium, and many mills began to encounter more serious scale problems, including both calcium -oxalate and barium sulfate in the D_o stage and calcium carbonate in the first extraction stage. Figure 7.1 shows a pipe that became scaled up with calcium oxalate shortly after the plant converted to ECF bleaching. In hindsight, the reasons for the increase in calcium oxalate scale are obvious. The natural chlorine dioxide pH close to 4 is low enough to dissolve calcium

FIGURE 7.1. Calcium oxalate scale constricting flow in a pipe.

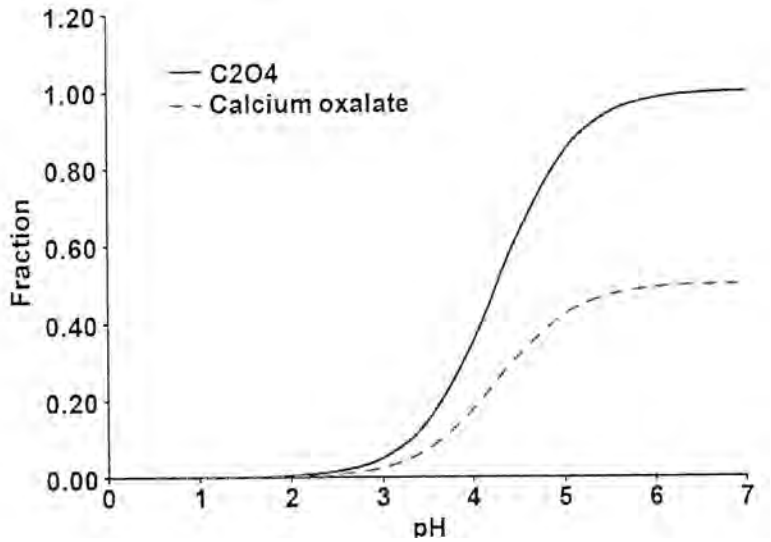

FIGURE 7.2. Concentrations of oxalate dianion and calcium oxalate as a precipitate relative to process pH.

carbonate, but not low enough to protonate the divalent oxalate ion, resulting in conditions under which calcium oxalate is likely to form (Figure 7.2) [12,13]. The traditional pH for chlorination, below 2 [10], is low enough to minimize the concentration of the divalent oxalate anion, which is necessary for calcium oxalate to form. Calcium oxalate was not only the source of scale in the D_0 stage, but it remains the major bleach-plant mineral scale problem, and precipitated calcium oxalate trapped in pulp fibers in D_0 stages contributes to formation of lime scale in extraction stages [14].

This increase in scale problems resulted in an increase in research on the behavior of calcium and barium in bleach plants and the development and marketing of numerous antiscaling chemical additives to reduce or eliminate mineral deposit problems [15,16]. Most of these initial efforts focused on understanding how trace metals were distributed within a mill, what the inputs and outputs were [17,18], and how the ion-exchange properties of wood pulp contributed to moving trace metals around a mill bleach plant [19-21]. Ultimately, two strategies evolved that address the majority of mineral scale problems in mills, but are not necessarily accepted as standard practice. For calcium scale, whether calcium oxalate in the D_0 stage, calcium carbonate in the extraction stage, or both, it is desirable to control the first bleaching stage to an end pH of 2.5-2.8. The insoluble for of calcium in this stage is

calcium oxalate, and the target pH of 2.5 is near the first pKa for oxalic acid, meaning that oxalic acid exists in the acid and mono-anion forms [13], not as the dianion, which complexes tenaciously with calcium and several other trace metals. This strategy maintains calcium as a soluble ion that can be removed with effective D_0-stage washing. This approach is supported by the realization that the target pH of 2.5 is still within the optimal pH range for use of chlorine dioxide in first-stage bleaching [22,23]. Mills that have followed this prescription diligently have generally been able to mitigate calcium oxalate and extraction-stage calcium carbonate scale problems. For mills suffering barium sulfate scale deposits, the only process-based control strategy is to eliminate sulfate [24,25]. Obviously, mills with calcium oxalate scale problems still want to maintain the end-stage pH of the D_0 stage close to 2.5, but within that constraint, there are several changes that mill personnel can make to minimize sulfate-ion concentration in the D_0 stage The rationale for this approach will be discussed in more detail later in this chapter. The practical aspects of the approach can be summarized fairly succinctly:

1. Eliminate use of spent acid (sodium sesquisulfate) for pH control in the D_0 stage
2. If this is not sufficient, work on improving brownstock washing.
3. Next, install oxygen delignification. The additional delignification and washing that occur in an oxygen delignification stage remove much of the residual carryover sulfate, sulfide, and lignin-bound sulfur from the pulp.

The key is to remove as much sulfate as possible while barium is still sequestered as barium carbonate. The first step is always to eliminate the use of spent acid for pH control because this adds four times the amount of sulfate anion to the D_0 stage as does sulfuric acid.

The good news about barium scale is that once barium sulfate forms, it is very stable in the bleach plant environment. This makes it much more amenable to treatment with antiscalants that function by suppressing crystal growth and keeping the small crystals dispersed in solution [26]. Scale-suppressant polymers offer an alternative approach to barium scale control if the mill is not willing to invest the capital to improve brownstock washing or to install oxygen delignification.

The remainder of this chapter summarizes pertinent research related to trace metal behavior in bleach plants and the fundamental behavior of both calcium and barium in pulp bleaching. It relates several case

studies in which inexpensive process changes have succeeded in eliminating scale problems and concludes with the more detailed chemical theory needed to understand scale problems in more depth. This chapter focuses on in-plant solutions to common bleach-plant mineral scale problems. It does not address bleach-plant closure and the additional problems with nonprocess elements in the bleach plant and chemical recovery systems that are encountered during these efforts. The chapter also does not discuss the trace-metal control issues encountered in peroxide bleaching, and to a lesser extent in ozone delignification, because these are covered in the chapters on these bleaching chemicals.

The intent of this book is to focus more on practical aspects of pulping and bleaching because there has been relatively little change in the fundamental understanding of bleaching processes since publication of the fourth edition of the TAPPI bleaching book in 1996 [27]. In the case of trace metals, the fundamental understanding has improved dramatically, and this edition is one of the first opportunities to present this material in a fairly comprehensive manner. As a nod to the practical intent of this book, the authors have chosen to present practical aspects of scale control in the beginning of the chapter and hold off on the more detailed inorganic chemistry until the end of the chapter, with the full understanding—even hope—that relatively few people will need to wade in that deeply.

7.1.1. Trace Metals in Wood and Pulping

All tree species contain some trace metals (Table 7.1) [28,29], and

TABLE 7.1. Trace Metals in Several Wood Species. Data from Koch, 1985 [28] and Young and Guinn, 1966 [29].

Species	Ca mg/kg	K mg/kg	Mg mg/kg	Na mg/kg	Mn mg/kg	Fe mg/kg	Al mg/kg
Green ash	1992	1560	467	238	23	70	25
Red maple	1937	974	290	198	82	75	22
Red oak	908	998	139	149	183	77	34
White birch	740	270	180	—	34	—	23
Aspen	1130	1230	270	—	29	—	—
Loblolly pine	1155-889	125-104	311-250	256-197	112-95	68-56	—
Red spruce	820	200	70	—	144	—	—
Balsam fir	830	770	270	—	127	—	—
Eastern hemlock	750	400	110	—	145	—	—

the majority of the problematic trace metals that enter the bleach plant originate with wood. Generally, hardwoods contain higher concentrations of trace metals than softwoods, often by a factor of two or more. Needless to say, mineral scale deposits are also more frequently found in hardwood bleach plants. The abundance of various trace metals in wood is partially dictated by their abundance in soil and groundwater. Mills in areas with many limestone deposits or with high concentrations of trace metals in groundwater will generally have more problems than mills in areas where surface waters are generally soft and free of calcium and other trace metals [30]. Barium is a less common problem, but follows the same general pattern of being more of a concern in areas where there is barium in the groundwater. An additional concern with barium is the possible presence of radium as well. Like barium, radium is an alkali earth metal and forms an insoluble sulfate that often coprecipitates with barite, making the scale deposit radioactive. Radium is a radioactive decay product of uranium and commonly shows up as a trace element in trees where uranium minerals are present. Radon gas is a radioactive decay product of radium, and the presence of this gas in basements is a warning that coprecipitation of radium and radioactive scale is more probable. Strontium is also among the alkali earth metals and has been anecdotally reported to coprecipitate in mill sulfate scales. Like radium, strontium has radioactive isotopes that can make scale radioactive and needs to be monitored in areas that have been subject to nuclear power-plant releases.

Obviously a mill needs wood and often does not have much flexibility in its source or species mix. In addition, most mills have probably not run a study to determine the regional variation in trace metals in their area. Short of trying to gain additional control over the trace-metal content of wood, the first thing a mill can do to reduce scaling is to ensure good debarking. Trace calcium concentrations are commonly ten times higher in bark than in stemwood [28].

A common feature of calcium and barium is that they are both highly insoluble under kraft cooking conditions. In addition to precipitating as calcium oxalate, calcium could precipitate as the hydroxide (K_{sp} = 5.5 x 10^{-6}), sulfate (K_{sp} = 6.8 x 10^{-8}), or carbonate (K_{sp} = 4.5 x 10^{-9}) [31]. The solubility products listed are all room-temperature values. Typically, solubility increases at higher temperature, as is the case for calcium hydroxide. Calcium carbonate is somewhat unusual in this respect because it becomes less soluble as temperature increases; this is one of the reasons that lime scale is prevalent on recirculation screens

and heaters in kraft digesters [3]. Calcium carbonate has been found in pitch deposits [32] and in brownstock pulp using X-ray spectroscopy [33]. It also is the scale predicted for kraft conditions and brownstock pulp by ion-equilibrium calculation software. Barium is also insoluble as the oxalate, sulfate, and carbonate. There is no direct evidence for the state of barium in kraft cooking and brownstock, but the equilibrium software predicts that its most common state will be as barium carbonate [25].

7.1.2 Generalized Behavior of Metals

The two most common scale problems are due to calcium and barium, and there are several reasons for this prevalence. Metals as a group are reducing materials willing to donate electrons to other molecules or atoms, and in the process picking up a positive charge referred to as a cation. In general, metals that prefer a single positive charge— monovalent metals—are routinely soluble and unlikely to cause mineral deposits. The most common monovalent metals found in wood are potassium and sodium, with potentially very small amounts of other Group Ia (alkali) metals. Other than alkali metals, very few elements are stable in the +1 state, and this routine solubility property, which is common in alkali metals, is uncommon among nearly all other elements. Metals with two positive charges—divalent cations—include the alkali earth metals (magnesium, calcium, strontium, barium, and radium) and several transition metals, such as manganese, cobalt, nickel, and copper. Calcium is usually found in wood at 1,000 mg/kg or higher concentrations. Manganese and barium are often present in the 20-60-mg/kg range. Divalent metals generally have low to very low solubility when mixed with divalent anions: carbonate, sulfate, and oxalate, among others. Of this group, magnesium and manganese are usually sufficiently soluble as carbonates and sulfates and occur in sufficiently low initial concentrations in wood that they do not contribute to scale problems. They may be found in minor amounts as coprecipitates in calcium or barium scale deposits. Cobalt, nickel, copper, strontium, and radium are less soluble with many divalent anions, but are not present in sufficient quantities to contribute to scale, other than as coprecipitates as mentioned earlier. Calcium and barium are sufficiently prevalent and sufficiently insoluble that mineral deposits containing these cations are more common.

Trivalent metals include the Group III metals (scandium group and

aluminum group) and many transition metals, including the most common oxidation states of iron and chromium. With relatively few exceptions, +3 cations are strong acids and readily react with water to form mixed aquo and hydroxyl ions:

$$M(OH_2)_6^{3-} + H_2O \rightleftharpoons M(OH_2)_5(OH)^{2-} + H_3O^-$$

One characteristic feature of a trivalent metal is the pH required to reverse the hydrolysis reaction, nominally pH 4 for aluminum(III) and chromium(III), pH 2 for gallium(III), and pH 1 for iron(III). At higher pH, even larger condensed structures form, leading to the flocculation chemistry observed in alum and ferric chlorides. Other than iron and to a lesser extent aluminum, there are no common trivalent metals in wood. However, aluminum, iron, and chromium can be prevalent in mill water systems. Both iron(III) and aluminum(III) stick fairly tenaciously to wood pulp. From the perspective of scale, this is a good property, but with iron in particular, it can cause problems with ozone or peroxide bleaching. Another feature of the trivalent metals plays a prominent role in their scale-related behavior: both aluminum(III) and iron(III) form oxy-anions at high pH. For aluminum, this pH ranges from approximately 8 to 12. Initially, the anions are condensed structures containing several aluminum ions and a net negative charge. At a pH of approximately 13, soluble $Al(OH)_4^-$ becomes the most prominent ion. Aluminum is largely soluble as the aluminate anion in alkaline pulping, and because of this, scale problems with aluminum usually occur in the evaporators rathefr than in the bleach plant. Iron(III) can also form oxy-anions at high pH, but more significant in pulping is that iron(III) is reduced by sulfide to iron(II), giving insoluble ferrous sulfide and elemental sulfur. This reaction dictates that more iron will stay with the pulp and less iron will dissolve in the black liquor or precipitate on surfaces.

There are several metals with even higher charges; these can have some utility in the paper industry, but are of little consequence in bleaching or in scale problems in the bleach plant.

7.1.3 Calcium

Calcium is the most common trace metal in bleach plants and the most frequent source of bleach-plant scale problems. It is not really a nonprocess element because it is used in recausticizing; however, with

good white liquor clarification, this source of calcium accounts for 20% or less of the total calcium in brownstock pulp [1,34]. Understanding scale problems requires an understanding of the state of the metals entering the process stage and the chemistry of the stage where the scale forms. The state of calcium in wood is not known with certainty and is subject to some debate. One assumption is that calcium in wood is associated with the carboxylic acid groups in hemicellulose. Many other scientists consider it to be precipitated calcium oxalate. Results of unpublished work carried out by the authors included a chemical analysis and equilibrium model of filtrate from a thermomechanical pulp (TMP) plug screw feeder. At approximately 1.5 mM, the calcium expressed from the wood chips is one-third of what is expected at pH 5.1, assuming that the calcium is associated only with ion-exchange sites in wood. This observation requires calcium to be in an insoluble state, with the most probable candidate being calcium oxalate. Oxalate is known to be present in wood [35], and the calcium and oxalate concentrations in this plug screw feeder experiment were high enough that calcium oxalate should have been present. The low solubility of calcium, however, suggests that oxalate is present at significantly higher concentrations than reported [35]. Efforts to validate the literature method demonstrated that the procedure could not effectively recover and analyze intentional spikes of oxalic acid on filter paper. The reported values are likely too low, by at least 50%. Although far from convincing, the evidence based on oxalate analysis, analytical work at the Forest Products Laboratory, and TMP equilibrium modeling suggest that much of the calcium in wood is present as insoluble calcium oxalate.

Trace metals that are soluble in the digester will be removed in brownstock washing, suggesting that the state of calcium in the digester must be as an insoluble salt. Options include calcium bound to ion-exchange groups in pulp, calcium oxalate, calcium carbonate, and calcium sulfate. Equilibrium modeling of digester conditions, analysis of lime scale deposits on digester heaters and screens [3], direct observation of calcite in brownstock pulps [32], and an extended X-ray absorption fine structure (EXAFS) study of calcium in brownstock pulp [33] all point to calcium carbonate as the dominant form of calcium in unbleached kraft pulp. That calcium exists as calcium carbonate in brownstock pulp is essential to its role as a scaling metal in the bleach plant because a prerequisite is that the calcium needs to dissolve under conditions found in the bleach plant. Calcium carbonate dissolves readily at pH below 7, whereas calcium oxalate requires a pH of approxi-

mately 3. If calcium in brownstock were in the form of calcium oxalate, it would remain stable under chlorine dioxide bleaching conditions (pH 4 target) and be unlikely to contribute to scale deposits. As a carbonate salt, calcium dissociates into a soluble state at pH 4 and is available to reprecipitate as the oxalate salt.

7.1.4. Oxalic Acid

Oxalic acid is found at trace levels in most plants, including wood. As stated earlier, calcium in wood is quite possibly already sequestered as insoluble calcium oxalate. This, however, is probably not significant to the scale-forming process in bleach plants. To the extent that any calcium oxalate dissolves and the calcium precipitates as the carbonate, the oxalate anion is left in solution and is extensively removed in brownstock washing. The oxalic acid found in the bleach plant is most likely formed by progressive oxidation of lignin or hemicellulose fragments by bleaching chemicals. Evidence is that most bleaching chemicals form oxalic acid at approximately the same rate relative to the molar oxidizing equivalents of the chemical—80 g of oxalate per ton of pulp, per unit of kappa number reduction [36].

7.1.5. Barium

As for calcium, the major source for barium in the bleach plant is the trace amounts found in wood. Barium, however, is truly a nonprocess element in that there are no mill operations, mill chemicals, or additives that intentionally use barium. The oxalate salt of barium is also insoluble, but is approximately one order of magnitude more soluble than calcium. This suggests that the state of barium in wood is more likely associated with ion-exchange sites and other possible coordinating organic fragments in lignin. The potential state of barium in the digester is also harder to predict with certainty. Barium sulfate is less soluble than barium carbonate (1.1×10^{-10} for sulfate compared with 5.1×10^{-9} for carbonate), and given the nominal 10% of total sulfur present as sulfate, the presence of barium sulfate is a realistic possibility. However, barium sulfate solubility increases by at least one order of magnitude as the temperature rises from room temperature to kraft cooking temperature, and barium sulfate becomes more soluble than the carbonate salt at approximately 160°C [25]. Equilibrium models indicate that carbonate is the favored salt under kraft conditions. Estimating chemical equilibria

at higher ionic strengths is fraught with uncertainties, but the presence of barium sulfate scale in bleach plants does suggest that the equilibrium calculations are correct. If the chemical state of barium exiting the digester were as barium sulfate, it would be stable in the bleach plant and unable to form significant scale deposits.

7.2. CHEMICAL FUNDAMENTALS

7.2.1. Acid and Base Equilibria

Fundamentally, mineral scale deposition is a chemical precipitation process. To gain a better understanding of mineral scale, it is necessary to introduce the acid—base behavior of the counterions and how this interacts with the stoichiometry of the precipitation process. Oxalic acid will be discussed in this introduction, but the chemistry is common to all precipitation processes involving divalent cations and divalent anions. An important aspect of the divalent precipitation processes which lead to scale in bleach plants is the acid-base chemistry of diprotic acids. For oxalic acid:

$$H_2C_2O_4 \rightleftarrows HC_2O_4^- + H^- \rightleftarrows C_2OH_4^{2-} + 2H^-$$

One mole of oxalic acid ($H_2C_2O_4$) first dissociates into one mole of acid and one mole of the monovalant anion ($HC_2O_4^-$). This equilibrium is referred to as Ka_1, which is. often written as the negative log of the equilibrium constant, plc_1. The acid equilibrium expression for this chemical reaction is:

$$\frac{[HC_2O_4^-][H^-]}{[H_2C_2O_4]} = K_{a1} \qquad (1)$$

Typical concentration units for equilibria of this type are molar, molal, or mole fraction. For purposes of this chapter, all concentration units are molar (moles/liter). For oxalic acid, pK_{a1} is approximately 2 (Table 7.2). Because pH is alpKain negative log units, pK,, indicates the pH at which half the oxalic acid is in the acid form and half is in the monovalent form (Figure 7.3). At higher pH, the second proton dissociates as well, giving the dianion $C_2O_4^{2-}$. This equilibrium K_{a2}, or in log form, pK_0 which for oxalic acid is approximately 4. At approximately

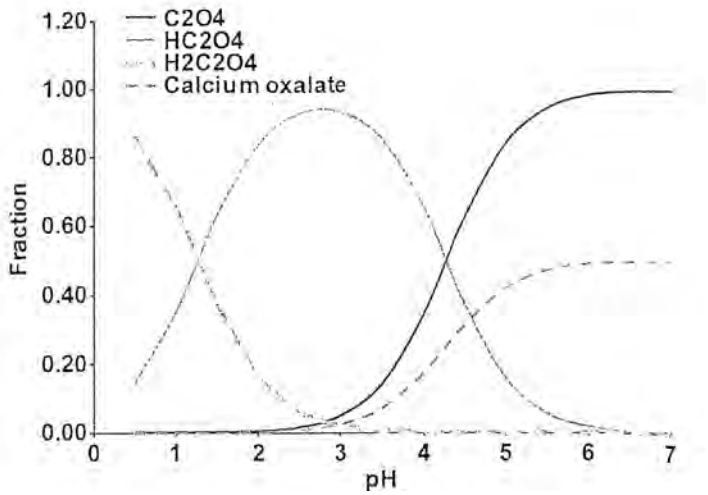

FIGURE 7.3. Concentrations of oxalic acid, the hydrogen oxalate anion, and oxalate dianion, relative to solution pH.

pH 4, 50% of the H2C2O4 acid is in the divalent form and 50% is in the hydrogen-oxalate or monoanion form:

$$\frac{[C_2O_4^{2-}][H^-]}{[HC_2O_4^-]} = K_{a2} \tag{2}$$

Similar graphs for sulfuric acid and carbonic acid are provided as Figures 7.4 and 7.5.

7.2.2. Precipitation Equilibria (solubility product)

The chemical equation for the precipitation equilibrium of oxalic acid with calcium is:

$$CaC_2O_4 \rightleftarrows C_2O_4^{2-} + Ca^{2-}$$

and the equilibrium expression is as follows:

$$\frac{[C_2O_4^{2-}][Ca^{2-}]}{[CaC_2O_4]} = K_{sp} \tag{3}$$

The concentration of the insoluble product (or the reactant as the equilibrium is shown) has no real meaning, and by convention this con-

TABLE 7.2. Room-Temperature Acid Dissociation Constants for Anions in Common Bleach Plant Scales. Data from Lang's Handbook [31].

	pK_{a1}	pK_{a2}
H_2CO_3	6.352	10.329
$H_2C_2O_4$	1.271	4.272
H_2SO_4	—	1.99

centration (or chemical activity) is assumed to be one. This simplifies the expression to the product of the reacting ions:

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

The equilibrium constant is often referred to as the *solubility product,* denoted as K_{sp} (Table 7.3). For calcium oxalate, Ks_p *is* approximately 10^{-9} at 25°C [31,37], which means that precipitation initiates when the product of the oxalate molar activity (concentration) and the calcium molar activity (concentration) is approximately 10^{-9}, or approximately 0.03 mM each. The key understanding is that only the divalent anion is active in the equilibrium and that precipitation of calcium oxalate becomes progressively more unlikely as the concentration of the divalent anion is reduced. Because the pH scale is a log scale, each unit change results in approximately one order of magnitude change in the equilibri-

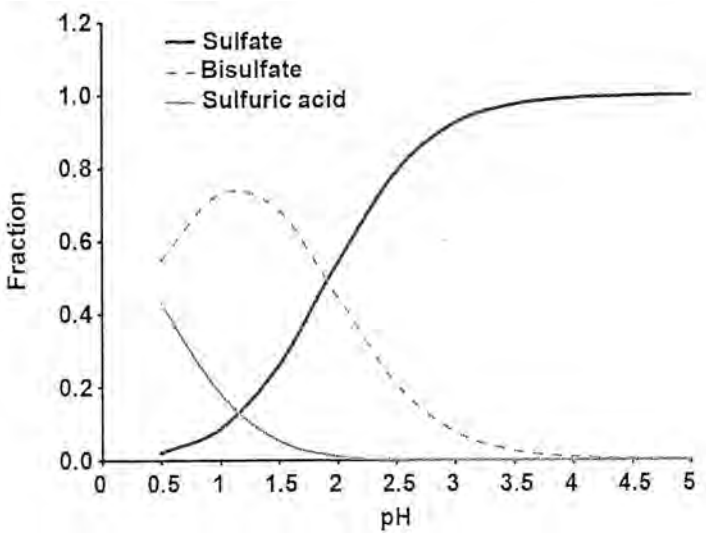

FIGURE 7.4. Concentrations of sulfuric acid, the bisulfate anion, and sulfate dianion relative to solution pH.

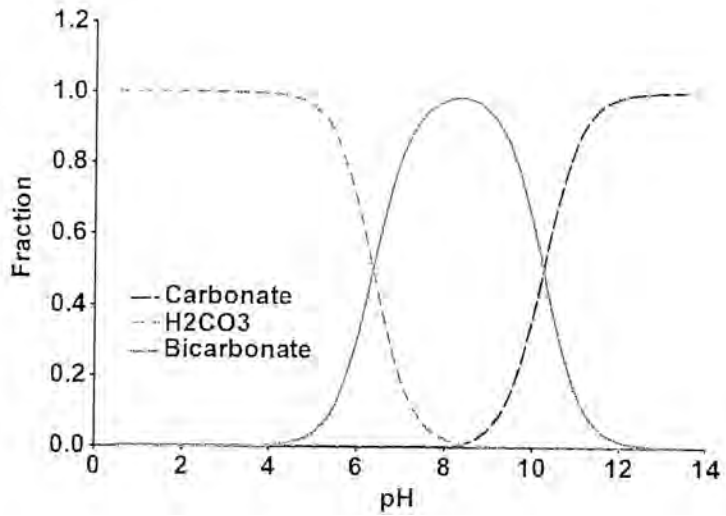

FIGURE 7.5. Concentrations of carbonic acid, bicarbonate anion, and the carbonate dianion relative to solution pH.

um: at a pH close to 3, approximately 10% of the oxalic acid in solution is still in the divalent form, and at a pH close to 2, approximately 1% is left in the divalent form (Figure 7.3). For this reason, simply lowering the pH reduces the critical form of oxalate in the precipitation reaction and reduces the fraction of calcium precipitated as oxalate scale (Figure 7.3).

Generally, in the mill bleach-plant environment, a reduction of 1-2 pH units is sufficient to eliminate scale formation. This crude estimate suggests a pH of approximately 2.5 to prevent calcium oxilate formation in D_0, pH 6 to prevent calcium carbonate formation in an extraction stage, or pH 0.5 to prevent barium sulfate formation in a D_0 stage. Although D0 stages can be operated near a final pH of 2.5 without seriously impacting pulp quality or bleach chemical efficiency, a pH of 0.5 is not realistic option to deal with barium sulfate scale, and a pH of 6

TABLE 7.3. Room-temperature Solubility Products for Common Bleach Plant Scales.

	K_{sp}	pK_{sp}
$CaCO_3$	4.5×10^{-9}	8.35
$CaC_2O_4 \cdot H_2O$	1.7×10^{-9}	8.77
$CaC_2O_4 \cdot 2H_2O$	4.6×10^{-9}	8.34
$BaSO_4$	1.1×10^{-10}	9.96

is not realistic for an extraction stage. For barium, the best strategy is to reduce the concentration of sulfate ion in the D_0 stage. The presence of lime scale in the first extraction stage generally means that calcium is not being removed effectively in the D_0 stage. The low-cost solution is the same as for oxalate scale in D_0: control the pH to approximately 2.5 to remove as much calcium in the D_0 stage as possible. Poor D_0-stage washing, use of calcium-containing papermachine white water as wash water in the bleach plant, and a poor filtrate recycle plan, such as direct countercurrent washing, are also possible causes of extraction-stage scale.

7.2.3. Ion Activity

Two more issues must be discussed to understand scale problems. The first is ion activity. At 0.01 mM (the solubility of $BaSO_4$ in water), the idealized acid-base and solubility-product equilibria are accurate. However, at realistic concentrations, ionic solutions do not behave as ideal solutions. As the concentration of ions increases in a solution, cations and anions take on a more ordered structure to minimize repulsion between ions of like charge. This impedes free diffusion, and the ions behave as if they were at a lower concentration. The correction can be made by multiplying the concentration by the ion-activity coefficient for the ionic strength and temperature of the process. There are several approaches to estimate activity coefficients, which differ largely by the ionic strength at which the prediction is no longer accurate. The extended form of the Debye-Hückel equation is accurate to ionic strengths of 0.01 M:

$$\ln(a_x) = \frac{Az_x^2\sqrt{I}}{1 + Ba_x\sqrt{I}} \tag{4}$$

where A and B are temperature-dependent constants; a is the hydrated size of the ion; and I is the ionic strength, miZi2d as $I = I/2\Sigma\, m_i Z_i^2$, where m_i is the molar concentration of ion i and Z_i is the charge of ion i. At 25°C, A = 0.5115 and B = 0.3291. At 65°C, they are 0.5558 and 0.3384, and at 80°C, they are 0.5767 and 0.3426 respectively. The value of a is 5 for Ba^{2+},6 for Ca^{2+}, 4 for $S0_4^{2-}$, and 4.5 for CO_3^{2-}.
Adjustments recommended by Robinson [38] and Davies [39] are used to extend accuracy to higher ionic strengths, but within the range typically observed in bleach plants (0.05-0.1 M [40,41]), the iBaxove-

ment over the extended Debye-Hückel approach is marginal, and the error introduced into bleach-plant solubility calculations is small relative to other errors and unknowns.

7.2.4. Supersaturation

The second issue that needs to be understood is the ability of insoluble salts to supersaturate—to form solutions that are several times more concentrated than the maximum indicated by the solubility product, and that moreover can be stable for an extended time [2,42]. Supersaturation can benefit a mill because even when conditions exceed the solubility limits of a salt, the mill can potentially operate scale-free. The problem is that once a scale forms, supersaturation conditions almost ensure that the scale will grow, and because it is not competing against suspended precipitates of the same salt, the scale deposit will grow faster than in a similar situation in which there is a competing surface area of suspended precipitate in solution.

7.3. CASE STUDIES

The following case studies describe incidences of and solutions for calcium oxalate, barium sulfate, and calcium carbonate mill scale problems [43]. Some of the cases are drawn from the authors' personal experience, and some are provided by other reliable sources. Because of the nature of the discussion, sources, mill names, and locations are not provided. With one exception in which a mill suffered from two case-study problems, each problem occurred in a different mill. The mills represent a wide variety of products and are geographically dispersed, including cases from outside the United States and Canada.

7.3.1. Digester (white liquor) Chip Strainer

In this case, the mill was experiencing regular problems with one of two inline strainers (wood particle strainers) on the softwood continuous digester. One of the two strainers was plugging on approximately a five-day cycle, and the deposit had been analyzed as calcium carbonate.

The inline strainer clears small wood debris from the filtrate which is returned from the digester top separator and then is used in the high pressure feeder to help convey chips to the top of the digester. Peri-

odically, a steam valve opens to clear the strainer by blowing the accumulated wood particles out, usually back to the chip chute leading to the high-pressure feeder. The liquid phase in this case is largely white liquor with some weak black liquor. Both are saturated in calcium carbonate. There is no intentional chemistry change in this operation—no change in pH, no chemicals added, and the temperature is at or below 100°C, which suggests that pulping reactions are slow. Only three things can initiate a scale problem—the process chemistry generates more free scaling anion or cation, a pH change increases the concentration of anion in the divalent state, or a change in temperature results in lower solubility. The lack of any significant chemistry in this case ruled out the first two reasons for scale, and the analysis therefore focused on temperature change—the problem had to be a steam leak in the strainer. Mill technical staff had already thought of this and had asked maintenance to check the strainer for a steam leak. It had been reported back that the strainer was fine. When a second review of the problem suggested that this was the only possible reason for the scale, the manager of technical services checked the strainer himself. Indeed, there was no obvious steam leaking from the strainer, but it was too hot to touch, whereas the second strainer was just warm to the touch. The manager requested that the steam valve be repaired, and the strainer returned to a normal maintenance schedule.

The principal issue in this case is a somewhat unusual aspect of calcium-carbonate solubility, which decreases with increasing temperature. This is why lime scale is prevalent on heated surfaces. The key piece of evidence was that there was no chemistry occurring in the unit operation, and therefore there was no other probable cause for the rapid scaling except a temperature change. Although steam leaks are a common controlling variable in lime scale, rapid cooling combined with some evaporation is probably a contributor to many washer scales.

7.3.2. Lime Scale on Extraction-stage Washer

The formation of mineral scale on washers, particularly on the wire, can be an especially difficult problem to diagnose because the pulp mat works as an ion-exchange column during the washing process [44-46]. This means that anions and cations can be released from the mat and can move at different rates relative to the wash-water front in the mat. This effect can be seen very nicely in research by Ivaska *et al.,* in which

Ca^{2-} and Ba^{2-} were the last two divalent cations eluted off a pulp column also containing Mg^{2-} and Sr^{2+}[46]. Concentrations can vary significantly by location on the mat and, because of the ion-exchange effect, are harder to predict. In addition, sudden cooling and evaporation can occur on the vacuum side of the mat in a traditional vacuum drum washer.

The mill in question encountered calcium carbonate scale on the wire of the first extraction-stage washer. The problem started after switching to a D_0-initiated bleach sequence which raised the initial-stage pH from the 2.1-2.3 typical of a chlorination stage to approximately 3.2, the target for the D_o stage. The mill had also initiated D_0-stage filtrate recycle to reduce wastewater volume. An additional source of calcium in this mill was the use of blowdown from the bleach-plant scrubber on the repulper of the D_0 washer entering the extraction stage. The higher end-stage pH meant that more calcium was retained by ion-exchange groups in the pulp, and the addition of D_0 filtrate recycle decreased washing effectiveness. Add the additional calcium from blowdown, and clearly there was considerably more calcium in the extraction stage after the bleach-plant modifications. Obvious recommendations in this case included improving calcium removal in the D_0 washer by dropping the pH to approximately 2.5, and either discontinuing the use of scrubber blowdown in the D_0-stage repulper or switching the source of caustic in the scrubber to eliminate the calcium. However, this mill stumbled upon another solution.

Before resolving the lime scale problem in the extraction stage, the mill completed modifications to insert an enzyme stage between brownstock washing and the brownstock decker. These changes reduced the pH to approximately 6.5 by adding sulfuric acid to the repulper of the last brownstock washer. After enzyme treatment, the pulp was washed one final time on a decker. At pH 6.5, some of the calcium carbonate lodged in the pores and lumens of the fibers will dissolve. At high pH, the ion-exchange process includes lignin phenolic groups, but at pH 6.5, nearly all these groups are in the acid form, releasing the metals associated with these functional groups as well. Furthermore, the enzymes function by depolymerizing xylans, which subsequently dissolve and wash out along with the associated glucuronic acids, releasing additional associated trace metals to be washed from the pulp. The net result of the enzyme treatment was a decrease in calcium entering the bleach plant, which was sufficient to eliminate the scale problem in the extraction stage.

7.3.3. Barite Scale in the D_0 Stage

The solution to this case is nearly identical to the previous case. The scale problem was barium sulfate on the washer wire following the D_0 stage in the bleach plant. This mill was also implementing an enzyme treatment after brownstock washing and had been using sulfuric acid for pH control. The solution was to switch to carbon dioxide as the acid source to lower the pH. Both barium and calcium appear to be precipitated as carbonates under kraft cooking conditions, and these precipitates are largely stable until the pH drops below 7. The use of carbon dioxide as an acid source means that there will be more carbonate in solution, which will suppress dissolution of barium and calcium. However, use of CO_2 also means there is less sulfate ion in solution. The reduced sulfate-ion carryover into the D_0 stage is the most likely reason for the elimination of this scale.

7.3.4. Oxalate Scale on the D_0 Washer

Calcium oxalate scale in the D_0 stage is probably the most common scale problem observed in bleach plants. As in many mills, this oxalate scale problem appeared shortly after switching the bleach plant to elemental-chlorine-free bleaching. The mill had been taking downtime approximately every eight weeks, but scale on the washers was reducing washing efficiency and thereby increasing bleaching costs between shutdowns. The scale was also extending the required downtime because it took longer than 6-8 hours to remove. The mill lowered the pH target for the C10-, stage to 2.5-2.8, and the scaling problem disappeared. At the initial pH target, 5% to 15% of the oxalic acid generated in this stage was in the active divalent form. At the lower pH, only 2% to 3% was in the active form. Four hardwood lines tested by the authors averaged approximately 150 mg/L dissolved calcium in D_0-stage filtrates (3.8 mM). Ulmgren reported approximately 0.5 mM oxalic acid in D_0-stage filtrates [41]. At 70°C, 3.8 mM calcium, and accounting for ion activities, the bleach stage can manage approximately 0.01 mM oxalate ion before exceeding the solubility product. Assuming 0.5 mM oxalic acid, the divalent oxalate-ion concentration does not drop to 0.01 mM until the pH is reduced to 2.5.

Another mill with oxalate scale in the D_0 stage was having problems with clogging in pipes, mixers, and the D_0 washer. Calcium oxalate scale in the D_0 stage was so severe that the concentration of calcium

carried into the first extraction stage was high enough to precipitate as lime scale in the E-stage washer as well. This bleach line was equipped with atmospheric diffusion washers, and scale was forming between the extraction plates on both washers. On occasions, the extraction screens became clogged to the point where they needed to be removed and cut open to provide sufficient access to clear the scale. Several problems contributed to the high rates of scale formation in this mill, but probably foremost among them was the use of a direct countercurrent wash scheme for bleach-plant filtrate recycle. The use of alkaline wash water was causing calcium oxalate to precipitate as the pulp was being washed, and the diffusion washer provided more than enough retention time for these reactions to take place. Between the precipitation process, which traps a lot of calcium in the fiber and carries it to the next stage, and the impact of the scale on washer efficiency, the problems in the D_0 stage were causing high organic carryover into the first extraction stage and the lime scaling problems in the E-stage diffuser. Mill personnel reduced the D_0 target pH to 2.5, but this simply kept the calcium in solution until it was mixed with the alkaline extraction filtrate used as the wash water in the washer. Although this eliminated the problems in the D_0 mixer and pipes, it increased the scale problems in the D_0 and E_l washers.

This mill was scheduled for replacement of the diffusion washers and had decided to install twin-roll presses instead of traditional washers. This also provided an opportunity to test the ability to predict the impact of process changes on the accumulation of nonprocess metals in this bleach plant and to design a strategy to eliminate scale. The project was a collaborative effort between the mill and the Institute of Paper Science and Technology, which involved linking an EXCEL-based (Microsoft Corp., Redmond WA) solution-equilibrium solver to the WinGEMS bleach plant mass and energy balance simulator (Metso, Norcross, Georgia) using the dynamic data-linking capability in both programs [14]. The modeling effort indicated that the mill would still have scale problems after the roll presses were installed and needed to reduce the D_0-stage pH to 2.5 to eliminate the problem. Having failed once with the low target pH, the mill ignored the advice and started up with a target D_0-stage pH above 3, only to find the rolls in the D_0 wash press scaling up after a couple of weeks. After the first hydroblast two months after startup, they started adding sulfuric acid to reduce the D_0-stage pH to the 2.5-3.0 target range. At the next scheduled shutdown eight weeks later, there was no evidence

of mineral scale on either the D_0 or E_1 roll presses or anywhere else in the bleach plant. This bleach plant was able to operate free of scale for several years until in an effort to reduce bleaching costs, they cut the sulfuric-acid addition to the D_0 stage—again. As a further note on the modeling effort, it predicted the trace-metal balance in the rebuilt bleach plant to better accuracy than the authors had bothered to tune up the base case model [14].

7.3.5. Oxalate Scale in an Extraction-stage Mixer

This mill was operating the D_0 stage at a pH target of 2.5 and did not have scale problems in the D_0-stage mixers, piping, or washer. However, calcium oxalate scale was occurring in the extraction-stage mixer and piping leading to the E-stage tower. The mill used D_1-stage filtrate and paper machine white water on the D_0 washer showers. The white water had a pH close to 5 and because the mill used a calcium carbonate coating, the white water had a high calcium concentration from recycled broke. Caustic for the E-stage was added at the suction of the extraction-stage MC pump. The mill realized that the high calcium concentration in the white water was reacting with the residual oxalic acid that had not been washed out in the D_0-stage washer. All that was needed for scale to occur was the higher pH in the extraction-stage mixer. Replacing the papermachine white water on the shower bars was not an acceptable option, even though it was known to be the biggest contributor to the problem. The mill decided to shift the caustic addition to a shower bar across the repulper of the D_0 washer. Mill personnel realized that this approach might simply shift the problem to the repulper, but this area was much easier to access and clean. The scaling problems disappeared entirely; surprisingly, even the repulper stayed clear of scale. More than anything else, this emphasizes a persistent problem in managing scale. The chemistry can predict that a precipitation process is likely to occur, but it does not necessarily result in a deposit on equipment surfaces, and supersaturation can cause the location to shift substantially from where it would be expected. In this case, a minor change in process treatment had a significant effect.

7:3.6. Barite Scale in the D_0 Stage

After conversion to ECF bleaching, the mill in question encountered a problem with calcium oxalate scale forming on the wire of the

D_0-stage washer. Using the standard remedy, the mill dropped the target D_0 end-stage pH to the 2.5 range, which successfully eliminated the calcium oxalate scale problem, only to find it replaced several months later by barium sulfate blinding of the same washer wire. The calcium oxalate deposits had been relatively easily removed with an acid wash, but this did not work on the barite deposits. Recovering use of the washer required a high-pressure wash (hydroblasting) using a solution of chelating agents and detergents. After initially returning to the original pH targets and re-experiencing the calcium oxalate scale problem, the mill was convinced to try again with an intermediate pH target. In its enthusiasm to eliminate the oxalate scale, the mill had set the target to pH 2.5 or below, operating at a pH between 2.0 and 2.5, with occasional excursions to as low as pH 1.9. A pH of 1.9 requires four times more sulfuric acid than a pH of 2.5. By targeting a slightly higher pH range, 2.5-2.8, and improving control, the mill was able to eliminate the oxalate scale without increasing sulfate ion to the point where barium sulfate scale became a problem.

Barium sulfate scale problems were encountered in three additional mills, but all had largely similar symptoms and solutions. The typical problem was a glassy scale plugging the face wire of the D_0-stage washer. Because of their location, these scales are always difficult to sample for analysis, but calcium oxalate scales that form in this location can typically be removed with either acid treatments or hydroblasting. Barium sulfate scales generally cannot be removed with normal acid treatments and are harder to remove with hydroblasting. In all three cases, the mill target end-stage pH was appropriate, and pH control appeared normal. However, all three were using chlorine dioxide generator spent acid for pH control. Spent acid is a buffer mixture of sodium sulfate and sodium bisulfate which is often referred to as sodium sesquisulfate. When used for pH control, it adds at least four times as much sulfate ion as commercial sulfuric acid. Once the mills replaced the spent acid with commercial acid for pH control, they were able to operate at a low enough pH to avoid oxalate scale and a low enough sulfate concentration to avoid barite scale.

One aspect of this problem is the location—a washer wire. In the case of a D_0 washer, the shower water is often D_1 filtrate with a pH of approximately 4. If the D_0 stage is operating at a pH near 2.5, the higher shower-water pH will increase the pH of the pulp, which causes some of the bisulfate ions to lose a proton, increasing the concentration of sulfate ions at the same time that soluble organics and salts are be-

ing displaced from the pulp. The sulfate-ion concentration is decreasing due to washing while increasing due to rising pH.

The pulp mat that forms on the wire is nominally at 10% solids. Assuming that it will naturally drain to approximately 15%, that means that for 1 tonne of pulp, 6.7 m^3 of water is physically associated with the pulp and 2.3 m^3 is free to be displaced. The point is that protons, barium, and sulfate ions must diffuse out of the physically associated water during the washing process. Among these three, the diffusion rates for protons are much higher, meaning that pH change occurs quickly relative to exchange of the other ions. This provides a mechanism by which the sulfate-ion concentration can rise more quickly (because of the pH change) than it is depleted by the washing process. If the process is near the saturation point for barite scale, this can initiate barium sulfate precipitation.

As stated earlier, it is hard to predict the location of scale deposition. Although most of the precipitation probably occurs within the fiber mat, the fraction occurring on the wire is sufficient to cause a significant problem. Even a saturated filtrate is not safe on a washer because the flashing and cooling when the filtrate escapes the mat and enters the partial vacuum behind the drum will drive precipitation, which can be observed as a scale buildup on the wire.

7.4. CALCULATING TRACE-METALS PARTITION IN A MILL ENVIRONMENT

There are three phases to the trace-metal partition in a pulp suspension. The phase of most concern is the precipitated or solid state. Although the presence of a precipitate does not guarantee scale, scale is a form of precipitation and cannot occur without it. The second phase is concentration of divalent metal Ca^{2}+ and Ba^{2}+ ions in solution. The final phase is the bound metal, the calcium and barium associated with ion-exchange sites on the pulp. In the Evadale mill project which coupled an ion-exchange equilibrium calculator to a WinGEMs model, the ion-exchange process was responsible for approximately 20% of the calcium that carried through the extraction stage to the D_1 stage [14]. Normal (solution) processes accounted for 75% of the calcium and precipitation for only 5%. In the equilibrium case presented in Section 7.4.5, ion exchange accounts for almost 85% of the calcium in the pulp suspension. With this understanding, characterizing the ion exchange of trace metals on pulp became a major research focus after 1995 [19-21].

7.4.1. Ion Exchange Using Solution State Equilibrium Theory

At least four different theoretical methods have been used to calculate or model the ion-exchange process in pulp. Bryant and Edwards used a solution equilibrium approach to model the ion-exchange process [19]. This approach has the huge advantage of working directly in existing equilibrium-modeling software. It also mimics the selectivity coefficient method of estimating ion-exchange equilibria (described later in this chapter), but has a serious deficiency for modeling ion exchange. Solution equilibria postulate a free solvated ionic state for both anions and cations in salts when they are dissolved. In an ion-exchange process, either the cation or anion is chemically bound to the insoluble substrate. No analytically measurable substance has been shown to have an imbalance in charges—cations must offset anions. The equation $HL \rightleftarrows H^+ + L^-$ needs to be written as $HL + Na^+ \rightleftarrows NaL + H^+$, where in this case, L represents a bound anion and Na+ and H+ are in the bulk solution. Several other issues arise from the understanding that cation and anion charges must balance in an ion-exchange medium. In an anion-exchange environment, a divalent cation like Ca^{2}+ balances charges on two ion-exchange sites. This may well be a case of LCa+ L^-, with the two anion sites well dispersed and one effectively overbalanced with a net positive charge and one technically free bound anion. However, the need to balance the charge of the ion-exchange particle masks any apparent free anion states from the solution, and for practical purposes, the state is CaL_2 and without effective charge. Although the Bryant and Edwards paper is notable as one of the first to recognize the critical importance of ion exchange in understanding trace-metal partitioning in pulp streams, the approach they took has limitations.

7.4.2. Donnan Theory

Towers and Scallan [20] used a second, more reliable method for estimating trace-metal partition in pulp suspensions--Donnan equilibrium theory. Donnan theory is still very limited, but accurate enough to be useful in estimates of trace-metal partitioning and more rigorous in its compliance with observed ion-exchange behavior. A simple ion-exchange chemical equation can be written as:

$$2(NaR) + [Ca^{2+}] \rightleftarrows (CaR_2) + 2[Na^+]$$

where *R* represents a pulp anion site (or the ion-exchange bound state). The equilibrium equation becomes:

$$\frac{(CaR_2)[Na^-]^2}{(NaR)^2[Ca^{2-}]} = K \tag{5}$$

In Equation (5), round brackets have been used to indicate concentrations in the ion-exchange particle internal solution and square brackets for the concentrations in the external solution. In ion exchange, it is often assumed that no physical bond forms between cations and anions, that the anion (or cation) is bound to the medium and the counterion is dissolved in the internal solution, nominally a free hydrated cation (or anion) associated with the ion-exchange particle only by the need to balance the charge. In practice, this is often not a bad assumption. As stated in Section 7.1.2 on the generalized behavior of metals in solution, monovalent metals such as sodium and potassium are almost always assumed to be free hydrated cations in aqueous solution, and the lack of any significant association or bonding to any type of anion is the reason that salts containing sodium or potassium as the cation are invariably soluble. As for divalent metals such as Mg^{2+}, Ca^{2+}, and Ba^{2+}, it was stated that they tend to have low to very low solubility with divalent anions, but this was not stated as a general trend with monovalent anions. Monovalent anions can generally be assumed to behave much like monovalent cations and to provide soluble salts. For barium and calcium, this is certainly true with chlorides, bromides, nitrates, and acetates. Any equilibrium constant between caldium or barium with organic monovalent anions such as a carboxylic acid or sulfonic acid is expected to be small; as an example, the equilibrium constant for formation of calcium acetate is about 4 at room temperature, and for barium it is 2.5. At a 0.01 M calcium concentration and 0.01 M acetate concentration, 96% of the calcium is free and just 4% is coordinated to acetate. This increases to 99% free calcium at 0.001 M calcium and acetate. The assumption that calcium is present within the ion-exchange medium to balance charge and not due to a direct bond-forming reaction with carboxylic acids is a good first-order simplification. Assuming that K is approximately one, Equation (5) can be rewritten as:

$$\frac{(CaR_2)}{[Ca^{2-}]} = \frac{(NaR)^2}{[Na^-]^2}$$

These ratios identify a relationship between internal and external concentrations which is dictated by the ion charges and the typical stoichiometry. The ratio itself is dictated by the total ion concentration because all ion-exchange sites need to have an associated counterion to balance the charge and the concentration of ions in external solution adjusts accordingly. The expressions are usually written as the square root, and the value of the ratio is often represented by the Greek letter lambda (X), which leads to the common form [20]:

$$\lambda = \frac{(MR)}{[M^-]} = \sqrt{\frac{(DR_2)}{[D^{2-}]}} \tag{6}$$

In Equation (6), M represents a generic mNa+ alent cation including Na+ and K+, and D represents a generic divalent cation including Ca^{2}+, Mg^{2+}, and Ba^{2+}. The considerable value of the Donnan equation is that it predicts that the ratio of internal to external concentrations for all monovalent cations will be a constant value, and that the square root of the ratio of internal to external concentrations for all divalent cations will be the same value.

Knowing simply the total ion-exchange capacity of the system, total cation concentration, and the valence of the cations, it becomes possible to determine X and hence the partition of all the cations in the process. Although this discussion has focused on wood-pulp ion exchange in which the fixed ions are anioniccarboxylic acid functional groups and the mobile ions are cations, the Donnan equation is equally valid for anion-exchange resins, in which the fixed groups are cations such as quaternary ammonium groups and the mobile ions are various anions such as Cl-, NO_3^-, and CO_3^{2-}. The advantage of the Donnan approach is that it provides a vastly simplified process for solving the trace-metal partition problem with reasonable accuracy and within the typical limitations of our knowledge of bleach-plant suspensions.

The disadvantages of this method are that λ is not really a constant; that the equation does not mimic typical chemical equilibria, making it harder to implement using traditional equilibrium-solving software; and that for those ions for which the theory is not accurate, the relationship fails, in some cases spectacularly. For pulp mill streams, that failure occurs with acid. As a monovalent cation, the proton should behave much like sodium and potassium, but as weak acids, the carboxylic acid functional groups present in pulp are largely in the protonated (acid) form at pH values be-

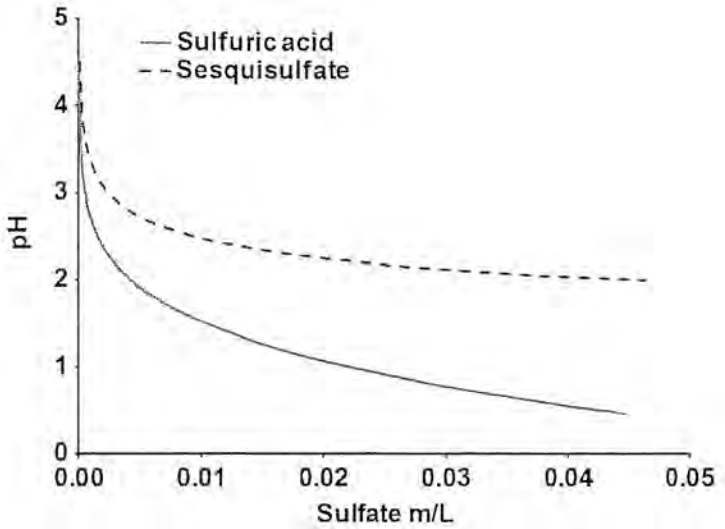

FIGURE 7.6. Amount of sulfate in solution when adjusting pH with sulfuric acid or sodium sesquisulfate.

low 4, and largely in the deprotonated (base) form at pH values above 4 (Figure 7.7). Effectively, the affinity for protons is 10,000 times stronger than the affinity for sodium ions. In their paper on the Donnan equilibrium method, Towers and Scallan add an acid-dissociation equilibrium term to the Donnan equation to address the pH sensitivity of carboxylic acid [20]. Duong *et al.* took this approach one step further and added an acid-dissociation equilibrium for phenols as well [47].

One issue in determining the Donnan equilibrium is worthy of additional discussion. The method used by Towers and Scallan [20] assumed an internal volume based on the fiber saturation point or water retention value: 1.4 g water per gram od pulp. The fiber saturation point as previously defined by Stone *et al.* is the volume of water that is not accessible to a dextran polymer of 2 x 10^6 molecular weight with an estimated spherical diameter of 56 nm [48]. This approach seems to be fairly common [49,50]. Using the Donnan approach, it is possible to determine the internal volume that is needed to make the divalent ratio and the monovalent ratio equal. Effectively, using metal content in moles per od kg and c_i as internal volume (L/kg), the numerator for the Donnan equation is $(NaR)/c_i$. Equation (6) can therefore be rewritten as:

$$\frac{(NaR)}{c_i[Na^-]} = \sqrt{\frac{(CaR_2)}{c_i[Ca^{2-}]}} \qquad (7)$$

Rearranging this equation one obtains:

$$c_i = \frac{(\mathrm{NaR})^2[\mathrm{Ca}^{2-}]}{(\mathrm{CaR}_2)[\mathrm{Na}^-]^2} \tag{8}$$

Using data from a previous project [54], this approach provides the graph shown in Figure 7.8:

Within the ionic strength range of the typical bleach plant (0.01 to 0.05 M), the amount of bound water needed to force the monovalent and divalent cations to the same distribution constant is approximately 0.15 L/kg, far less than the values used by Towers or Räsänen [20,49]. For the data in Figure 7.8, the solution concentration was estimated both with and without determining the ion activity for the cations in solution. A more rigorous approach would also determine the activity coefficients for the cations in the internal solution, but because the anions are not mobile, any estimate for their activity coefficient is suspect. This addition also complicates the calculation, and it can no longer be determined directly. Räsänen among others have also considered use of specific volumes more consistent with the electrical double layer [51,52] and have evaluated the impact of this parameter in fitting the Donnan model to metal-adsorption data [51].

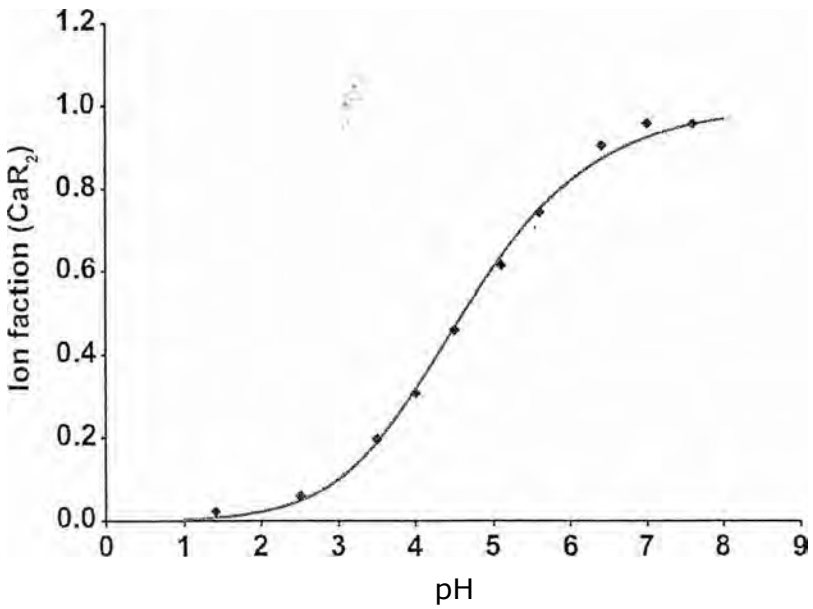

FIGURE 7.7. Fraction of pulp acid groups in the base form as a function of solution pH.

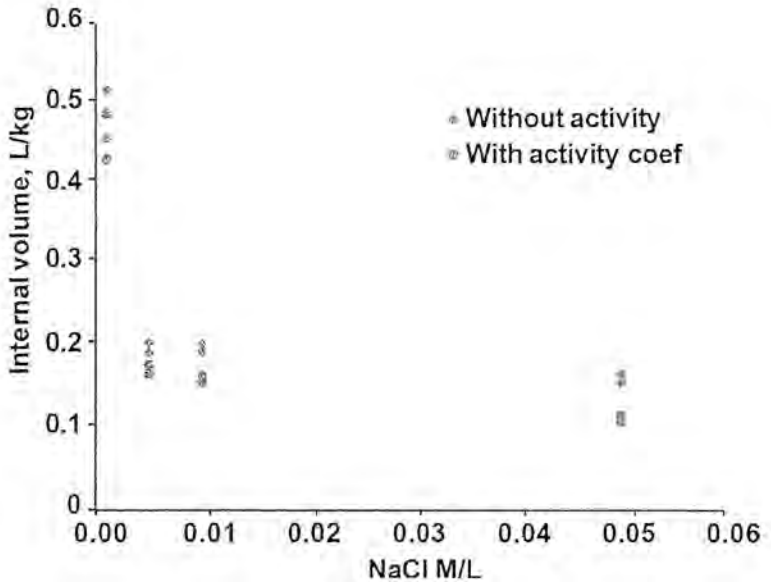

FIGURE 7.8. Internal volume determined by forcing the Donnan constant for monovalent and divalent cations to be equal.

7.4.3. Selectivity-Coefficient Approach

Returning to Equation (5), if one does not make the assumption that direct ion association with a fixed counterion site is minimal, this equation remains valid and provides a more accurate representation of ion partition in a suspension containing fixed anionic or cationic functional groups, and therefore of ion-exchange behavior. This approach is generally referred to as the *selectivity coefficient,* or in some cases as the *thermodynamic equilibrium constant.* The advantage of the selectivity coefficient is that it can handle ions with direct bond-like interactions using an equation which parallels standard solution equilibria, making it potentially easier to incorporate into equilibrium software. The major disadvantage is that now each ion pair needs to be calculated independently, a much more difficult mathematical task because these concentrations are interdependent. The value of the selectivity coefficient is a constant that obeys Arrhenius theory, and therefore the value of the selectivity coefficient can be determined at temperatures for which it has not been measured directly. It can also be converted into free-energy suitable for Gibbs free-energy minimization methods of determining the equilibrium. Because the equilibrium is specific for a pair of like-charge ions, it is written with a subscript and superscript, indicating the

internal ion concentration that appears in the numerator (superscript) and denominator (subscript) as:

$$\frac{(CaR_2)[Na^-]^2}{(NaR)^2[Ca^{2-}]} = K_{Na}^{Ca} \tag{9}$$

Disadvantages of the selectivity-coefficient approach are that the coefficient is not a dimensionless constant as is the case for solution equilibria and that the coefficient value depends on what is used to express both the internal and external solution concentrations. A fairly complete and consistent set of selectivity coefficients were published in 2002 [53] for H^+, K^+, Na+, Ca^{2+}, Mg^{2+}, and Sr^{2+} ion exchange in unbleached kraft hardwood pulp, using moles per kilogram as the concentration for the adsorbed state and moles per liter for the solution phase, and in 2006 for H^+, Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, and Ba^{2+} in unbleached kraft softwoods [54] using the ion-fraction for the adsorbed state and moles per liter for the solution state. All cation pairs evaluated by both research groups behaved nicely and provided the expected reaction stoichiometry, except for the proton. Karhu *et al.* [53] matched the proton data using a method first proposed by Laine *et al.* by assuming that there are two different types of acid groups With Ric, values of 3.6 and 5.6 [55,56]. Rudie *et al.* [54] matched the proton data with reasonable accuracy using a stoichiometry of one relative to magnesium and calcium, instead of the expected stoichiometry of two. This needs to be recognized as a compromise and is explained in detail in [54]. The softwood data used by Rudie *et al.* were also used for the ion-exchange modeling of the Evadale mill hardwood bleach plant and performed sufficiently well for the purposes of that study [14].

7.4.4. Fundamental Approaches

Several researchers have evaluated wood-pulp ion exchange using more fundamental approaches involving surface potentials and equilibrium constants [55–58]. These efforts have been responsible for several of the discoveries which are now commonly accepted in this area, including the presence of two different types of carboxylic-acid groups associated with the carbohydrate and lignin fractions of pulp. This approach is beyond the scope of this chapter, and the reader is directed to the referenced publications for more detail. A concern from the practical perspective of determining the probability of precipitation and po-

tential scale buildup is that all these methods require determination of the internal volume of the wood fibers, but there is little agreement on this value, and it is very likely subject to which cations have been adsorbed. Sodium counterions generally provide larger swollen volumes than calcium counterions, and calcium still larger swollen volumes than protons [59-61]. A number of methods and values for calculating internal volume have been proposed [51,54], but at this point, there does not appear to be much agreement on how this value should be determined. Delignification and hemicelluloses also impact swollen volume [62,63] and may similarly impact internal volume. Although there is considerable scientific value in these fundamental approaches, the amount of data required does not lend itself to efforts to predict or model trace metals in mill fiber lines.

7.4.5. Calculating Soluble Calcium

There are two typical engineering problems with regard to scale: determining the reason for and the best control parameters to mitigate an existing scale problem, and performing a mass and energy balance for a new or rebuilt fiber line that includes an evaluation of the potential for scale problems. The later needs to be included in many rebuild projects to avoid future scale problems. This approach requires coupling chemical partition and precipitation software with mass and energy balance software, which has been accomplished by several research groups [14,64,65]. The second problem is a significant software challenge because the precipitation and ion-exchange equilibria are co-dependent and need to be calculated simultaneously. The first problem is far easier because the solubility product can be ignored in the calculation. If the solubility product is exceeded, conditions are favorable for scale formation. Even though the precipitation process shifts the ion-exchange equilibrium, this is not critical to the evaluation because the shift does not start until the precipitation process has already begun. The problem is then simplified to that of determining how much of the calcium and barium are sequestered by the pulp and, by difference, how much remains in solution.

The Dorman model can be approximated with a few assumptions:

1. Assume that the hydrogen ion is minimally impacted by the other cations [58,66] and use data from one of many papers where the impact of solution pH on effective ion-exchange sites is determined.

Assume that the monovalent cation contribution to the sum of free and bound ions is small and can be ignored.

3. Use the ion-exchange capacity (bound acid content) to estimate the bound concentration of the divalent cations.

Using the basic Donnan model,

$$\lambda^2 = \frac{(DR_2)}{[D^{2-}]} = \frac{(MR)^2}{[M^-]^2} \tag{10}$$

Summing all divalent cations (D) and monovalent cations (M) (additive principle) and rearranging,

$$\lambda^2(\Sigma[D^{2-}] + \Sigma[M^-]^2) = \Sigma(DR_2) + \Sigma(MR)^2 \tag{11}$$

Dividing by the free metal sums,

$$\lambda^2 = \frac{\Sigma(DR_2) + \Sigma(MR)^2}{\Sigma[D^{2-}] + \Sigma[M^-]^2} \tag{12}$$

The value of Equation (12) is that the numerator can be estimated using assumption 3, and the concentration of free cations can then be determined using the analysis of total cations and subtracting the acid content.

Calcium oxalate scale in the D_0 stage is the most frequently encountered scale problem and will serve as a useful example. This case presents the added difficulty that the ion-exchange process is dependent on the acid-base response of the pulp, pK_a 3.6 and 5.6 [55,56], and the precipitation process is dependent on the di-anion of oxalic acid with a pK_a between these two values, at 4.27. Although increasing the pH will increase the fraction of metals sequestered by the pulp and decrease the solution concentrations, the rise in pH also converts more oxalate to the divalent form, increasing the anion contribution to the solubility product.

Results of a trace-metals analysis for a southern hardwood line are listed in Table 7.4. The first column contains total metal in milligrams relative to total flow (water plus pulp) in kilograms at 7.5% consistency. The mill was operating at an end-stage pH of 3.5 and suffering from scale formation on the wash press after the D_0 stage.

TABLE *7.4. Trace-metals and Oxalic-acid Analysis for a Southern Hardwood D_O-stage Pulp (as-received basis).*

Element	mg/kg Pulp + Water	Molar	[Monovalent]^2	[Divalent]
H^+	—	0.000316	—	—
Na^+	90.4	0.00393	1.54×10^{-5}	—
Mg^{2+}	3.0	0.000122	—	0.000122
Ca^{2+}	88.9	0.00222	—	0.00222
		0.2469		
Mn^{2+}	1.4	2.5×10^{-5}	—	2.5×10^{-5}
Ba^{2+}	1.6	1.2×10^{-5}	—	1.2×10^{-5}
Total cation	—		1.54×10^{-5}	0.00238
Oxalate	12.5	0.000142	—	—

Ignoring activity, the contribution of the monovalent cations to the Donnan equation is only 0.6%. At this ionic strength, the activity coefficient for the divalent cations is approximately 0.65 and for the monovalent cations approximately 0.9. Assuming these activities, the solution activity of sodium still contributes only 1% to the Donnan cation sum. Because this contribution is small, the monovalent cations can be ignored to simplify the estimate. A similar example using these data was provided previously, including the solution activities in the estimate [67]. For this case, the activities will be ignored in the ion exchange estimate, effectively incorporating the activity coefficients into the Donnan constant.

A bleachable-grade pulp has an acid content of approximately 50 meq/kg (Figure 7.9), and at pH 3.5 approximately 30% of the acid groups are in the base form (Figure 7.7). This provides 15 mEq/kg of active ion-exchange sites and requires 7.5 mM/kg of divalent metals to balance the charge. Note the switch from equivalents to moles of divalent cations. Assuming 150 ml (per kg) as the internal solution and ignoring the contribution from monovalent metals, the internal concentration is 0.0075/0.15, or 0.05 M. The total divalent-ion concentration from Table 7.3 is 0.00238 M. This needs to be adjusted by the fraction of divalent metals in the pulp, which is internal solution concentration times internal volume divided by total solution volume: 0,05M x 0.15 L/12 L:

$$\lambda^2 \approx \frac{0.05}{0.00238 - \dfrac{0.05(0.15)}{12.0}} = 28.49 \qquad (13)$$

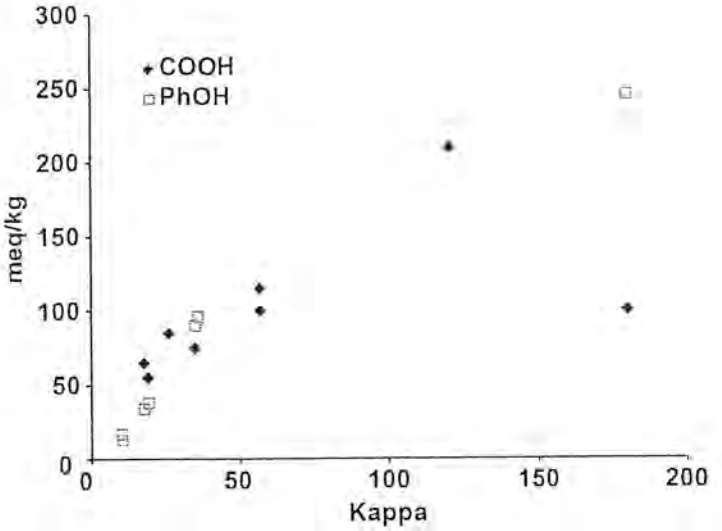

FIGURE 7.9. Acid group content of various pulps relative to kappa number.

Solving for calcium,

(14)

$$(CaR_2) = \lambda^2 \frac{Ca_T^{2-}}{\left(1+\lambda^2 \frac{0.15}{12.0}\right)}$$

where CaR2 is bound calcium as before and Ca_T^{2-} is total calcium. Total calcium is 0.00222, giving a value for bound calcium of 0.047 M. Free calcium is 0.00222 M — 0.047 M x (0.15 L)/12 L, or 0.00163 M. This

TABLE 7.5. Comparison of Trace-metal Concentrations Using the Donnan Approximation Compared with the Selectivity Coefficient Method as Used by Litvay et al. [14]. Total Bound Concentrations are Molar Concentration Times Charge (eq/L).

	Donnan Approximation		Selectivity Coefficient Model	
Cation	Free (molar)	Bound (molar)	Free (M)	Bound (M)
Na	0.0037	0.020	0.0038	0.0098
Mg	9.0×10^{-5}	0.0026	6.8×10^{-5}	0.0046
Ca	0.0016	0.047	0.0014	0.065
Mn	1.8×10^{-5}	0.00053	1.5×10^{-5}	0.00088
Ba	8.9×10^{-6}	0.00025	1.0×10^{-5}	0.00012
Total (M x charge)		0.12		0.15

compares to an estimate of 0.0014 M using the selectivity-coefficient-based spreadsheet [14].

Although the error in the estimated free calcium concentration is approximately 15%, the estimate is within typical process variations in the mill and close enough to evaluate precipitation or scale problems. Note also that pulp ion exchange decreased the estimated soluble calcium concentration by almost 30%. The most significant error in this estimate is in the bound sodium ion, which fortunately has little impact on the bound and free calcium concentrations.

The divalent oxalate concentration can be calculated from Equation (2) as follows:

$$[C_2O_2^{2-}] = \frac{5.35\times10^{-5}[HC_2O_4^-]a_1}{[H^-]a_2} \tag{15}$$

where a_1 and a_2 are the activity coefficients for the monoanion and dianion respectively and H+ is proton ion activity (pH). As stated earlier, the activity coefficients are approximately 0.9 and 0.65 respectively. Adding the mass balance for total oxalate and rearranging gives:

$$[C_2O_4^{2-}] = \frac{5.35\times10^{-5}[Ox_T]a_1}{a_1 5.35\times10^{-5} + [H^-]a_2} \tag{16}$$

Substituting 0.000142 M for Ox_T and 0.0003 for $[H^+]$ gives $C_2O_4^{2-}$ as 0.000028 M. The concentration proactivity coefficients$[C2O_4^{2-}]a_{Ox}$, where a_{Ca} and a_{Ox} are the activity coefficients for calcium and oxalate respectively. As stated above, the activity coefficients for divalent ions under these conditions are approximately 0.65, giving a value for the concentration product of 1.9×10^{-8}. Because the room-temperature solubility product for calcium oxalate is 1.7×10^{-9}, the concentration product exceeds the solubility product by an order of magnitude, and therefore this mill has a high probability of suffering from scale problems. The mill in question is one of the case-study mills, and itD0-stagee a serious calcium oxalate scale problem in the D_0-stage washer.

Determining whether the scale problem might be eliminated by reducing the target pH for the stage to 2.5 can be done using the same basic procedure. Again, one of the published equations or graphs can be used to determine the residual active ion-exchange capacity of the pulp. At pH 2.5, this is approximately 7% of the total ion-exchange sites,

3.5 mEq/kg of pulp, or 0.0117 M (for divalent counterions). Repeating the calculations in Equation 14 for the new conditions gives λ2 = 5.2. This gives bound calcium as 0.011 M and free calcium as 0.00222 — 0.011(0.15)/12 = 0.0021 M. Repeating the calculations in Equation 16 for pH 2.5 gives oxalate dianion at 3.24×10^{-6} and concentration product at $(0.0021)a_2(3.24 \times 10^{-6})a_2$, or 2.9×10^{-9}. This is still approximately twice the room-temperature solubility product for calcium oxalate. Factoring in some increase in solubility at process temperature and considering the complexation of calcium by organic fragments in the filtrate [40], precipitation is unlikely. This was also the mill's experience when they adjusted the target pH range to 2.5-2.8.

7.5. SUMMARY

The frequency of scale problems in bleach plants increased significantly with the adoption of elemental-chlorine-free bleaching as the most cost-effective method to reduce organic chlorine concentrations in effluent and in paper products. Chlorination stages that typically operated at a pH below 2 served as a very effective metals-removal process and enabled the rest of the bleach plant to operate with low concentrations of potential scale-forming cations and transition metals that can interfere with some bleaching reagents. The use of chlorine dioxide in the first bleach stage produces a higher pH, which makes this stage less effective at removing trace metals from ion-exchange sites in the pulp. Operation at a target ehd-stage pH of 4 has often resulted in calcium oxalate scale problems in the D_0 stage, and the increased carryover of calcium into the extraction stage can also result in calcium carbonate scale in the E_1 stage. Operation at a target end-stage pH below 3 normally reduces these risks and often eliminates scale problems. Barium sulfate scale also became more common after the conversion to ECF, and in this case a contributing factor is the need for sulfuric acid to adjust pH in the D_0 stage. Fortunately, barium is present as a very low-concentration trace metal and has not been a problem in most mills. Where there have been problems with barium sulfate scale, most of the time it could be traced to the use of chlorine dioxide generator spent acid for pH control in the D_0 stage. Some mills have also taken an overly aggressive approach to pH in the D_0 stage in an effort to eliminate oxalate scale and ended up adding enough sulfuric acid to generate barite scale. At a pH of 2.5, spent acid injects six times more sulfate into the D_0 stage than pH adjustment with sulfuric acid, and eliminating this

source is often sufficient to prevent barite scale formation in the bleach plant. The other big source of sulfur in D_0 is black liquor carryover from pulping. Removing this source of sulfate by improved brownstock washing or by oxygen delignifi cation and post-oxygen washing reduces this source of sulfate significantly.

This chapter has assumed that eliminating scale problems by manipulating process conditions is usually less expensive for a mill than using scale-suppressant polymers. These polymers can provide relief and in some situations may be a useful and cost-effective option. When they are used to suppress calcium scales (calcium oxalate and calcium carbonate), there is a risk the polymer will function effectively to prevent scale in the mixer or on the washer where the scale suppressant is applied. However, the calcium precipitates are not stable in the mill and can dissolve and precipitate again in a later bleach stage or on the paper machine. With countercurrent washing, these precipitates can also add soluble calcium into a filtrate used in the D_0 stage as wash water or dilution. The risk is that the scale suppressant will simply relocate the problem, and mills need to be cautioned against continuing to chase the scale with more polymer applied at more locations. For barium sulfate scale, there is little risk of a suppressed scale reappearing somewhere else because once the barium sulfate precipitate has formed in the bleach plant, it is stable under bleaching conditions and will not go back into solution. Ultimately, eliminating a scale problem requires an understanding of how trace metals behave in the bleach plant and how the mill target approach is supposed to function. Without this understanding, any solution will be temporary.

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Figure 7.1 Calcium oxalate scale constricting flow in a pipe. Print permissions granted by MWV.

The Bleaching of Pulp

5th Edition

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