

Trace Metals in Brownstock Washing

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THIS chapter will discuss the impact of trace metals in kraft cooking and brownstock washing. Although numerous trace metals are present, calcium tends to be the main concern because it is present at higher concentration and is the source of most scale problems encountered in mills. Calcium will also be the principal focus of this chapter. Other trace metals create management concerns in mills, but generally not within the brownstock washing system and cannot be effectively addressed within that system.

8.1. PRINCIPLES REGARDING CALCIUM IN KRAFT COOKING AND WASHING

There are several sound principles regarding calcium in kraft cooking and brownstock washing that if kept in mind, can help engineers and operators understand scale problems in this area of the mill and minimize scale buildup. Calcium carbonate scale is virtually guaranteed to occur in certain areas of the pulp mill, primarily on heating surfaces. Most mills have accepted this and have been designed to manage heat exchanger scale. However, ineffective management of problems that otherwise could have been avoided

The principles to remember are:

1. Every kraft digester and brownstock washing system is saturated in

calcium and carbonate and contains precipitated calcium carbonate suspended in the filtrates.

2. Because the entire system remains alkaline, lime deposits are due primarily to temperature changes rather than solubility changes due to pH.
3. Understanding calcium carbonate behavior will help minimize its negative effects in the mill.

In 2006, Hart and Rudie provided a case study on buildup of calcium carbonate (lime) scale in a white liquor strainer [1]. The strainer collected pin chips and fines that escaped through the holes in the top separator and prevented them from entering the high-pressure pump feeding liquor to the high-pressure feeder. The perforated screen was scaling over with calcium carbonate over a five-day interval. The strainer handles a mixture of white liquor and weak black liquor, which is typical of the top circulation of a continuous digester. Filtrate is used to convey the chips to the top of the digester, and the excess is removed by the top separator and returned to the high-pressure TC (top circulation) pump to repeat the cycle. Critical to understanding this process is the fact that no chemistry change occurs at the strainer. There are no chemicals added, no water dilution, and no opportunity for the pH to change significantly. However, the pins and fines that build up in the strainer must be removed, and this was accomplished by opening a steam valve and using steam flow to convey the wood back into the chip chute. Steam supplies heat, and unlike most salts that increase in solubility with temperature, calcium carbonate becomes less soluble in hotter liquor. Mill staff was asked to check for a steam leak, and although they had already done this once, a process engineer was sent to check again. The engineer found that steam was not leaking out of the strainer, confirming the earlier assessment of no visible leak. It was, however, radiating heat through an extremely small leak that was not detected under typical conditions. The automated steam valve was repaired, and the scale problem disappeared.

This case study is used to introduce this chapter because it demonstrates quite clearly two aspects of controlling scale in mills. First, it requires knowledge of the solubility behavior of the cation and anion forming the scale. Second, it requires knowledge of the process(es) occurring at the scale-forming site or just upstream. The three process changes typically involved in scale formation are:

1. An increase in concentration of either the cation (Ca^{2+}) or anion (CO_3^{2-}) from a stream added and mixed at the location in question.
2. A change in temperature.
3. A change in pH.

The other instructive feature of the white liquor strainer case study

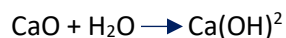
is that heat resulting from the small steam leak was the process change responsible for scale formation in the strainer and is the most common contributor to scale in the digester and brownstock washing process areas.

This chapter is organized as follows. First, the process chemistry of causticizing, kraft pulping, and brownstock washing will be summarized, with an emphasis on calcium and carbonate and how these processes affect calcium carbonate scale. The second part of the chapter goes into more detail on the chemistry of scale, or rather the chemistry of precipitation and solubility. All scale problems are fundamentally a precipitation event, and the chemistry of ion activity, ion pair solubility, and crystallization (precipitation) are the critical science involved.

8.2. CAUSTICIZING AND WHITE LIQUOR

The white liquor used in kraft pulping is made by reacting sodium carbonate from green liquor with calcium oxide from the lime kiln [2]. The calcium oxide first reacts with water to form calcium hydroxide [$\text{Ca}(\text{OH})_2$], which subsequently reacts with sodium carbonate, precipitating calcium carbonate and leaving the sodium and hydroxide ions in solution:

Slaking reaction:



Causticizing reaction:



The down arrow is used to identify the calcium carbonate as “insoluble” and forming a precipitate in the reaction. Calcium oxide reacts rapidly with water to produce the hydroxide used in the causticizing reaction. It should, however, be pointed out that calcium hydroxide ($K_{sp} = 5.5 \times 10^{-6}$) is not very soluble [3]. The cube root of the solubility

product is the approximate molar solubility, 0.02 M for calcium hydroxide. In comparison, calcium carbonate is three orders of magnitude less soluble, 4.5×10^{-9} , or 0.00006 M.

8.2.1. Causticizing

For causticizing, the reacting suspension is maintained in several stirred tanks to provide time for the reaction to progress, and then the calcium carbonate is separated by allowing it to settle in the white liquor clarifier. The result is a suspension of calcium carbonate (lime mud) that exits from the bottom of the clarifier, while the supernatant solution of fairly concentrated sodium hydroxide is removed from the top. The sodium sulfide in the green liquor is unchanged by the causticizing process and remains with the solution. This mixture of sodium hydroxide and sodium sulfide is the white liquor used in pulping.

Two balancing factors in the causticizing reaction impact calcium deposits in pulping and brownstock washing: one chemical in nature, the other economic. The causticizing reaction is an equilibrium-based phenomenon, meaning that it will never go to completion under industrial operating conditions. From a purely economic standpoint, the objective is to drive the causticizing reaction as far towards completion as possible, i.e., 100% sodium hydroxide and zero % residual sodium carbonate [4,5]. When the causticizing reaction does not go to completion, a significant concentration of sodium carbonate, known as dead load, remains in the liquor cycle. The dead-load component must be heated and pumped through the cooking, evaporation, and recovery processes, resulting in increased operating cost while adding little value to the process. The balance is to avoid over-liming, i.e., pushing the reaction to the point that unreacted lime, $\text{Ca(OH)}_2/\text{CaO}$, remains. This results in poor settling of lime mud (CaCO_3) in the white liquor clarifier, increasing the CaCO_3 component of the white liquor. The resulting white liquor contains ~30 gpl of sodium carbonate (~0.3 M). At this carbonate concentration, the maximum solubility of calcium in white liquor is about 10^{-8} mol/liter.

8.2.2. Clarification and Filtration

Clarifiers are not exceptionally good at removing precipitated calcium carbonate, and therefore the white liquor typically contains a small amount of suspended calcium carbonate. Even with pressurized disc

filtration of white liquor, the final liquor contains about 20 mg/L suspended solids, which is primarily calcium carbonate [5]. The suspended calcium carbonate is beneficial because it ensures that calcium carbonate particles are suspended everywhere in the digester pulping process, reducing the risk of a supersaturation condition. Supersaturation is an unstable condition in which the solution contains significantly more soluble calcium and carbonate than the chemical equilibrium allows. This situation can persist for quite some time, but only under conditions where no calcium carbonate particle surfaces are available to stimulate crystal growth. The second half of this chapter will discuss supersaturation further.

Carbon dioxide is formed from decomposition of lignin and carbohydrates during the kraft pulping process. Carbon dioxide in aqueous alkali rapidly forms carbonate, resulting in black liquor at the end of the cook that contains more sodium carbonate than the white liquor at the beginning of pulping—nearly half the inorganic content of the liquor [6,7]. The increasing carbonate concentration during pulping helps suppress calcium solubility further and ensure that any calcium carbonate buildup inside the digester will be slow.

8.2.3. White Liquor and Wood Chips

A final component in the calcium carbonate-containing processes in digesters and brownstock washing lines is the wood. Wood contains on average about 1 kg of calcium per dry ton [8,9]—often a little less for softwoods, sometimes substantially more for hardwoods. The form of the calcium in wood is less well understood. Wood has a native pH below 6, which is a pretty good indicator that the calcium does not exist as carbonate. The general opinion is that it is either associated with acid groups in the wood or precipitated as calcium oxalate [10]. In any case, the form is largely immaterial to what happens next. In a continuous digester, the chips are steamed before contact with white liquor. Usually this involves atmospheric steaming for 15–20 minutes in the chip bin, followed by low-pressure steaming for another nominal 10 minutes in the digester steaming vessel. After pre-steaming, the chips are dropped into the high-pressure feeder, where they mix with the white liquor. For well-steamed chips, some of the water in the chips has started to boil, and this displaces the air in the fiber lumens with steam. The steam in turn condenses on contact with colder white liquor, creating a partial vacuum that draws white liquor into the chips.

Pre-steaming and the associated liquor absorption is a critical operation in digesters. The chips become denser than the liquor, enabling the chip pile to settle inside the digester and encouraging chip column movement. It also provides a more uniform distribution of cooking chemicals and reduces the extent to which chip centers are undercooked. It also offers a huge calcium management benefit. The physical transport of white liquor into the chip draws in a considerable amount of sodium carbonate as well and initiates precipitation of calcium carbonate inside the chip. For practical purposes, by the end of the pulping process, most of the calcium is calcium carbonate and is contained inside the fiber lumens and fiber wall pores, with only about 20% extracted in the black liquor [9,11,12]. In a very careful mass balance, Barata and Carneias showed that just 1.3-1.7% of the calcium entering a digester was unaccounted for in pulp and Weak black liquor. This unaccounted-for calcium is the potential contribution to scale [13].

The presence of calcium carbonate and the carbonate concentration of the white and Weak black liquors ensure that calcium carbonate has every possible chance to precipitate, which limits soluble calcium to very low concentrations. Gu and Edwards reported the calcium concentration of digester extraction at 1×10^{-3} M (40 mg/kg) [12]. Lidén *et al.* showed values ranging from 22-66 mg/kg in the liquor at the end of commercial batch cooks, depending on the species mix in the digester [14].

Even though a digester is subjected to considerable calcium in normal operation, the conditions of the cook and the operation of the digester are such that calcium and carbonate are at their solubility limit. Because this condition provides very low solubility of calcium, scale formation is suppressed, and where it does deposit, it is generally restricted to a controlled and predictable accumulation. This also means that calcium carbonate scale is almost a certainty anywhere that heat is added to the digester, with the case study reported earlier being just one example. The main digester heaters are another obvious location for problems with lime scale.

HEAT IMPACTS

Because heat is the physiochemical change responsible for most scale problems in the digester, there is value in focusing on the impact that it has on calcium carbonate. For most salts, solubility increases when heated. As an example, the solubility of calcium oxalate increases

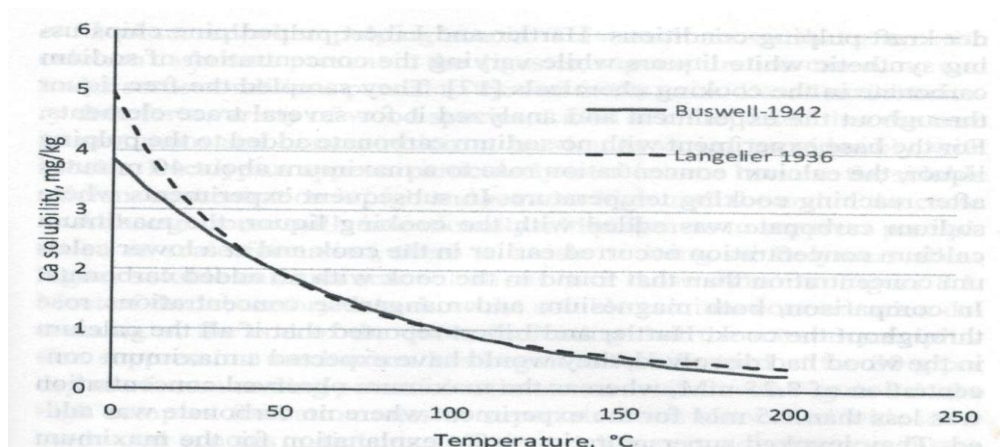


FIGURE 8.1. Solubility of calcium carbonate relative to temperature.

from 6 mg/L at 10°C to 14 mg/L at 40°C. $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ increases in solubility from 640 g/L at 20°C to 730 g/L at 50°C [15]. Calcium carbonate has the opposite behavior; as the temperature increases, its aqueous solubility decreases [16]. Figure 8.1 displays the solubility product using two different estimates, one from a paper by Larson and Buswell [16], and the other from a later critique by Langelier. The estimates are for alkaline conditions where the equilibrium between carbonate and bicarbonate is forced towards carbonate. Between room temperature and typical digester cooking temperature, solubility drops about threefold. In a continuous digester, this temperature change occurs at the surface of the tube and shell heaters, and some of the solubility difference ends up as scale on the tube surfaces. Of the nominal kg of calcium per dry ton of wood that enters the digester, about 0.015 g is soluble at 100°C, offering a maximum scaling rate of about 30 g per day for a 1000 tonne per day digester. Although chemical solubility theory cannot precisely predict full-scale operating practice, experience shows that deposition is generally slow and typically occurs in the digester heaters. There are also some examples of lime scale occurring on digester screens.

CALCIUM SOLUBILITY IN DIGESTERS

Several papers have experimentally evaluated calcium solubility un-

der kraft pulping conditions. Hartler and Libert pulped pine chips using synthetic white liquors while varying the concentration of sodium carbonate in the cooking chemicals [17]. They sampled the free liquor throughout the experiment and analyzed it for several trace elements. For the base experiment with no sodium carbonate added to the pulping liquor, the calcium concentration rose to a maximum about 40 minutes after reaching cooking temperature. In subsequent experiments where sodium carbonate was added with the cooking liquor, the maximum calcium concentration occurred earlier in the cook and at a lower calcium concentration than that found in the cook with no added carbonate. In comparison, both magnesium and manganese concentrations rose throughout the cook. Hartler and Libert reported that if all the calcium in the wood had dissolved, they would have expected a maximum concentration of 8.25 mM. Whereas the maximum observed concentration was less than 1.5 mM for the experiment where no carbonate was added. They invoked supersaturation as an explanation for the maximum and subsequent decrease in soluble calcium [17]. Similar results were reported in the control experiments conducted by Guo *et al.* [18].

Li *et al.* performed similar experiments on acacia and did not observe a maximum in calcium concentration when performing experiments without added sodium carbonate [19]. Instead, the calcium concentration continued to rise throughout the experiment. It did show a maximum at 120 minutes into the cook when 0.25 mM sodium carbonate was included in the pulping chemical charge. The authors argued that dissolved lignin complexes with calcium and increases solubility, at least temporarily. As carbonate concentration and temperature increase, they claimed, the solubility of calcium decreases sufficiently to overwhelm the complex formation and lower the observed soluble concentration.

However, there is one significant difference between a commercial kraft process and the laboratory experimental results in these papers. [17-19]. Commercially produced white liquor contains a small amount of insoluble calcium carbonate. Ideally, CaCO_3 suspended in the digester solution provides nucleation sites for crystallization, and can prevent supersaturation from occurring. Lidén *et al.* performed similar experiments to those reported above, but included data from three commercial batch kraft digesters [14]. Two of the three cases showed a maximum in the calcium concentration, but the third case, in a mill using a mixture of birch and eucalyptus chips, showed a near-stable calcium concentration throughout the last two-thirds of the cook, somewhat like what Li

et al. observed when pulping acacia. This result shows that even with calcium carbonate present in the digester, supersaturation can occur and under some conditions persist to the end of the cook. Based on laboratory data for a variety of wood species, Lidén et al. reported that the time at maximum and concentration at maximum varied considerably with species. Eucalyptus appears particularly troublesome because the soluble calcium concentration is high and remains high until the end of the cook.

Although some mills intentionally add polymers to suppress precipitation or scale formation, there is a risk in doing so. Polymers allow higher soluble calcium concentrations than those shown in Figure 8.1. Most of the laboratory data show the soluble calcium concentration decreasing at the end of the cook, indicating that the natural precipitation suppression mechanism has begun to fail. Instead of the 30 g per day maximum scaling potential estimate associated with Figure 8.1, the high complex formation rates or supersaturation associated with some hardwood species maintains sufficient calcium in solution to cause a scaling rate as high as 100 kg per day in a 1000 ton per day pulping line.

8.5 TECHNICAL ANALYSIS

Computational modelling of trace metal problems has been quite successful in creating a better understanding of scale and has helped prevent scale problems in bleach plants [20,21]. Application of these modeling methods to digester conditions is possible, but the prevailing digester conditions result in additional complications that are not present in the bleach plant. Calculating solubility and precipitation for the digester and brownstock washers is complicated by the following concerns:

- * The complex formation mechanism suggested by Li *et al.* [19] and Lidén *et al.* [14] can be included in equilibrium models, but suppression of precipitation is a non-equilibrium condition beyond the scope of this type of analysis.
- * High temperature requires extrapolation of ambient data for calcium carbonate solubility and complex equilibria to temperatures well beyond typical laboratory data. There is a risk that the values used for the solubility product of calcium carbonate and the formation constant of calcium with catechols are significantly in error at digester cooking temperatures.
- * At high ionic strengths, activity coefficients deviate significantly

from 1.0, and the extended Debye-Huckel calculation for ion activity is unreliable. Although the Pitzer method for estimating ion activity at high ionic strength is recommended for these conditions, an analysis of the estimated ionic activities calculated using this method does not reliably predict activities under kraft pulping conditions. As an example, calcium sulfate has similarities to calcium carbonate not only in the common cation (calcium), but also in the divalent anion. Similarly, sodium chloride, from an ion activity perspective, is similar to sodium hydroxide, at least at lower concentrations. Marshall *et al.* measured the solubility of calcium sulfate in sodium chloride solutions ranging from 40–200°C and ionic strengths up to about 6 molar. The standard extended Debye-Hückel estimate of activity was shown to be reasonably accurate and the addition of linear and quadratic terms of little to no value [22]. In comparison, an evaluation of the same data using several alternatives for estimating ion activity at high ionic strength, including the Pitzer method, was inaccurate [23]. Without experimental data under kraft pulping conditions, realistic ion activity values are more a guess than an estimate.

The solubility product was taken from the literature, but at digester temperatures is an extrapolation of data from lower temperatures [24]. The standard extended Debye-Hückel ion activity estimate was used because the Marshall and Slusher paper does provide some confidence that this method holds to higher ionic strength for calcium (and sulfate) [22]. Kraft cooking data published by Kerr list *EA* (effective alkali) and kappa throughout a kraft cook [25]. Maximum pulping temperature in the Kerr experiments was 175°C. Because this cooking temperature is unusually high, it was reduced to 170°C for this analysis, but *EA* and kappa were kept the same relative to cooking time. Soluble calcium in the presence of carbonate depends on temperature, and because that is the critical attribute being modeled, the lower temperature was thought to be more pertinent to the situation.

Cooking conditions are shown below and resulted in the initial chemical concentrations summarized in Table 8.1.

Kraft liquor parameters:

- * *AA*, 100 gpl, 18% on wood
- * *EA*, 85 gpl
- * Sulfidity, 23%
- * Causticity (80%) - $[\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{Na}_2\text{CO}_3)]$, with everything expressed as Na_2O

TABLE 8.1. Starting Conditions of the Kraft Cook. NaOH in Brackets Includes Hydrolysis of Sodium Sulfide to NaSH + NaOH.

	As Na ₂ O, g/L	As listed, g/L	M
NaOH	34.57	44.61	1.12 [1.29]
Na ₂ S	10.37	13.05	0.17
Na ₂ CO ₃	8.64	14.78	0.14

Literature results for the change in carbonate concentration during a cook are variable. Cooking pine, Hartler and Libert measured carbonate as rising from zero to 25 mM during the course of a kraft cook, but only when starting without any sodium carbonate in the white liquor [17]. Their measurements showed that the increase is suppressed by added carbonate: a 12 mM increase if the starting carbonate concentration is 100 mM, and no significant change if the starting concentration is 200 mM or higher. Chai *et al.*, starting without any carbonate in the cooking liquor, found that carbonate increased during the cook to about 3.4 g/L (32 mM) for both hardwoods and softwoods [26]. Li *et al.* also showed carbonate rising from zero to about 2 g/L when cooking acacia chips [19]. It is well known that kraft black liquor has a higher carbonate concentration than the starting cooking liquor, and therefore it was assumed that carbonate must be formed during pulping and that the Chai *et al.* outcome was more representative than the lack of an increase reported by Hartler and Libert. The regression equation obtained by Chai *et al.* for carbonate concentration when pulping loblolly pine was applied to the cooking data (Equation (8.1) from [26]):

$$[\text{CO}_3^{2-}] = [\text{CO}_{3i}] - 0.62 + 0.075(\Delta EA) \quad (8.1)$$

where CO_{3i} is the initial carbonate assumed from a causticized white liquor. One could assume a constant carbonate content as reported by Hartler, but it would have little impact on the results of the model. The starting calcium in a kraft process comes from a number of sources, but the major source is wood, with values ranging from 650-3000 ppm [11,13]. Typically, lower values are found in softwoods and higher values in hardwoods. The lower value of 650 ppm was chosen for this analysis. A higher value has one important effect on the estimate: reducing the starting carbonate concentration. The calcium concentration of 650 ppm, by precipitating in the Wood chips, reduces the starting carbonate concentration by only 3%. This is well within the

other errors of this analysis and can be ignored. However, a starting calcium concentration value three times higher (i.e., the 3000 ppm typically found in hardwoods) will reduce the carbonate concentration by about 15%. That is probably still within the error range of the analysis, but ignoring it in the estimate would likely increase the error or uncertainty of the model. In terms of modeling the calcium concentration, the hardwood case changes the soluble calcium concentration from a simple multiplication problem to a quadratic equation.

The difference in modeling the hardwood and softwood cases raises other concerns. Considerable data exist on organic fragments that are produced in pulping and that form complexes with calcium. For softwoods, this has virtually no impact on the free Ca^{2+} concentration because CaCO_3 will dissolve to make up the calcium and the increase in carbonate concentration is inconsequential. For hardwoods, this is not a safe assumption. For hardwoods, the resulting series of equations—solubility product for calcium carbonate, mass balance for carbonate, and formation equilibrium for calcium with the organic fragments in black liquor—requires simultaneous solution. This greatly complicates the analysis without adding to the discussion. In the softwood case, the equations can be solved sequentially and the errors safely ignored.

The solubility product for calcium carbonate is [27]:

$$K_{sp} = [\text{Ca}^{2+}] f_c [\text{CO}_3^{2-}] f_a \quad (8.2)$$

where f_c and f_a are the activity coefficients for the cation (calcium) and anion (carbonate) and are estimated from the ionic strength of the pulping liquor. Because $[\text{Ca}^{2+}] \ll [\text{CO}_3^{2-}]$, the solubility of calcium has little effect on the carbonate concentration or the activity coefficients, with the result that soluble calcium is constant for practical purposes and can be calculated as:

$$[\text{Ca}^{2+}] = (K_{sp} / f_c / f_a) / [\text{CO}_3^{2-}] \quad (8.3)$$

What this means is that insoluble calcium carbonate provides a buffer of calcium in the system and that sequestration by organic fragments may cause some calcium carbonate to dissolve, but that free calcium in solution remains essentially constant. This presupposes an outcome, but as long as some precipitated calcium carbonate remains after accounting for free soluble calcium and complexed calcium, the assumptions are acceptable.

During kraft pulping, all parts of the solubility product equation shown above are changing. K_{sp} changes due to temperature, and f_a , f_c , and $[\text{CO}_3^{2-}]$ are changing due to the decrease in hydroxide and increase in carbonate as the cook progresses. For the model calculation, the carbonate is estimated using Equation (8.1) and is dependent only on the starting carbonate concentration and the change in effective alkali during the cook. The two activity coefficients are determined by totaling up the ionic strength contributions of the cations and anions. As stated earlier, the ionic strength was used with the extended Debye-Hückel equation to estimate the activity coefficients [27].

The temperature dependence of the solubility product for calcium carbonate was determined using Equation (8.4) [16,24]:

$$pK_{sp} = 0.01183 T + 8.03 \quad (8.4)$$

where T is temperature in degrees Celsius.

Formation of complexes requires two estimates: the amount of reactive compound formed, and the formation constant of the complex with calcium. Westervelt *et al.* determined the equilibrium constant for calcium forming a complex with catechol at temperatures ranging from 5-80°C [28]. The value reported was 7250 L/mole and does not vary significantly over the temperature range evaluated. Niemela measured the concentration of catechol groups in pine black liquor during kraft pulping and reported values of 46 g/100 kg of wood at the end of the cook, and half that amount after the temperature rose to maximum cooking temperature [29]. His data were used to estimate the black liquor catechol concentration for the Kerr pulping data, using Equation (8.5);

$$R = R_f - R_f [\exp(-0.004 H)] \quad (8.5)$$

where R is the concentration of catechols dependent on the H -factor, R_f is the final concentration of catechol at the end of the cook in M/L (adjusting the 46 g/100 kg for the molecular weight of catechol and the liquor-to-wood ratio), H is Vroom's H -factor accumulated for the cook, and -0.004 is an adjustment factor to shift the resulting curve and provide approximately half the catechol at the 90-minute point of the cook. This results in the catechol concentration profile shown in Figure 8,2,

If the free calcium concentration is constant—i.e., if calcium carbonate will dissolve to make up for free calcium complexed by organic

fragments—the equilibrium equation for complex formation can be simplified to:

$$[CaR] = K [Ca][R_i]fcfa / (1+K[Ca]fcfa) \quad (8.6)$$

where K is the formation constant for the calcium-catechol complex, R_i is the starting concentration of catechols, and CaR is the concentration of the catechol complex with calcium.

Entering Equations (8.1)—(8.6) into a spreadsheet containing the Kerr effective alkali data provides an estimate of the catechol and total soluble calcium concentrations (free calcium plus calcium complexed to soluble lignin) shown in Figure 8.2.

The soluble calcium data show a decrease in solubility as temperature rises and the carbonate concnuation increases. Much of this reaction occurs inside the chips, with calcium carbonate depositing inside the lumens and the pore structure of the fiber Wall. The physical heating occurs at the tube walls of the digester heater(s), and the order-of-magnitude decrease in solubility often causes a lime scale deposit to form on the heat exchange surfaces. Note that there is no temporary maximum because supersaturation was not included in the model.

8.5.1. Catechol Influence

The impact of the catechol formed during pulping is not obvious because there is no observable increase in total soluble calcium with

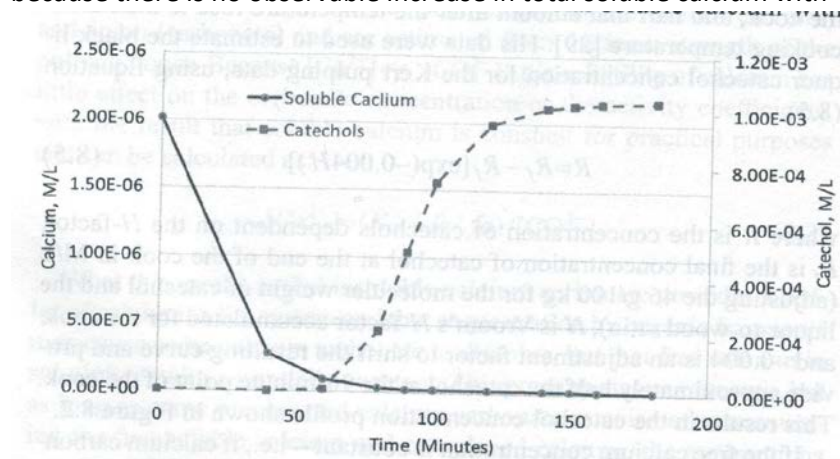


FIGURE 8.2. Total soluble calcium and catechol during kraft softwood pulping.

increasing catechol concentration. The impact is too small to be seen given the choice of axis for the graph, but the net increase, i.e., total soluble calcium, is about 25% higher than the free soluble calcium concentration at the end of the cook. The deposit potential, estimated as total soluble calcium at 88°C minus total soluble calcium at the end of the cook, is about 70 g per day. The estimated concentrations at the end of the kraft cook are 1.6×10^{-8} molar for free soluble calcium, 1.04 mM for catechol, and 4×10^{-9} M for the calcium-catecholate complex.

8.5.2. Pyrogallol Influence

Catechols are formed in pulp and black liquor when the methoxy group ortho to the phenol in guaiacyl lignin is replaced by an alcohol, creating adjacent alcohol groups on the ring. With hardwoods that also have syringyl monomers in the lignin, both ortho methoxy groups can be replaced, creating three adjacent hydroxyl groups. This is the gallol (pyrogallol or 1,2,3-trihydroxy benzene) group and has chemistry similar to catechol. In 1996, Lidén *et al.* presented evidence that lignin fragments with the gallol group were common in hardwood black liquor and participated in calcium complex formation similarly to catechol [14]. Reporting data for pine, spruce, and birch, they estimated the catechol concentration in the liquor as 1.0-1.6 mmole/kg, and nearly twice that amount for alder. The gallol group was also very species-dependent: as high as 4 mM for eucalyptus and oak, but just 0.3 mM for alder. The gallol group is not very stable under kraft pulping conditions, reaching a peak concentration 60-90 minutes into the cook and declining to less than half that amount 100 minutes into the cook. Because metals bond to only two of the OH groups in gallol-like organic fragments, it is assumed for this analysis that the formation constant with calcium is similar to that with catechol. Increasing the catechol concentration in the model from 1.04—4.0 mM evaluates the impact of the combined catechol plus gallol concentration available in hardwoods. This increase has a significant impact on the amount of soluble complexed calcium, approximately doubling the total soluble calcium in the process. Even with the higher assumed concentration of complex-forming organic fragments, the model significantly underestimates the amount of calcium remaining in solution as measured in the laboratory kraft pulping experiments (Table 8.2).

Table 8.2 provides a summary of the literature data of the end-of-cook apparent or as-measured soluble calcium concentration relative to

TABLE 8.2. Summary of End-of-cook Calcium Concentration. Hartler and Severtson Both Used Pine Chips for Their Experiments.

Hartler [17]		Severtson [18]		Lidén [14]		This Model	
Initial CO ₃ ²⁻ M/L	[Ca ²⁺] mM/L	Initial CO ₃ ²⁻ M/L	[Ca ²⁺] mM/L	Species	[Ca ²⁺] mM/L	Initial CO ₃ ²⁻ M/L	[Ca ²⁺] mM/L
0	0.42	0	0.44	Birch	0.2	0	0.0001
0.01	0.21	0.025	0.25	Pine	0.15	0.02	0.00009
0.1	0.053	0.13	0.06	Oak	0.35	0.13	0.00003
0.25	0.053	0.26		Alder	0.6	0.23	0.00001

the starting carbonate concentration for several wood species. For a typical causticity of 80%, the estimated starting carbonate concentration is about 0.13 M. The Hartler (Norway pine) and Severtson (red pine) data are nearly identical. The Lidén data (relative to species) show more variation. The equilibrium model predicts final calcium concentrations about three or four orders of magnitude lower than the experimental results. This could be due to insufficient data on complex formation, but a more likely explanation is the very slow approach to the equilibrium saturation state. The data at the end of the laboratory experiments routinely show decreasing calcium concentrations, which suggest that equilibrium has not been reached at the end of kraft cooks.

8.5.3. Chelation

Chelation, which is a complex formation process, is an equilibrium process and exhibits predictable behaviors. The resulting complexes increase the total soluble calcium concentration, but high concentration does not directly lead to additional scale. During the kraft pulping process, the increasing carbonate concentration causes a decrease in free soluble calcium in solution. The equilibrium model shows free calcium decreasing from 1.2×10^{-7} M when the process reaches 170°C to 1.6×10^{-8} M by the end of the cook. The decrease in calcium carbonate solubility with increasing temperature also decreases the free soluble calcium concentration. In the model, this decreases from 2×10^{-6} M to 2.2×10^{-8} M during the cook. The calcium complex with gallol + catechol initially rises as these functional groups form in lignin, but reaches a maximum shortly after the cooking temperature is attained. The rate of gallol/catechol formation slows, and continued formation of carbonate

suppresses soluble calcium, forcing the complexation reactions to reverse. Data for commercial processes implicate higher soluble calcium concentrations, but as long as the error is due to complex formation and equilibrium processes, the model should correctly predict behavior. A commercial process with complex formation should collect scale in the heaters, and the scaling rate should increase to the extent that complexes hold calcium in solution. Not all the calcium in solution will form scale. Because of the slow rate of calcium carbonate formation and the relatively brief time that the liquor spends in heaters, much of the calcium carbonate will come out of solution to remain in suspension in the digester. A significant portion of the calcium never diffuses out of the chips and precipitates within the fiber lumens.

8.5.4. Supersaturation

A key point of the equilibrium modeling approach is that it assumes equilibrium. Several papers have demonstrated that in addition to failing to reach equilibrium by the end of the cook, calcium and carbonate supersaturate in laboratory kraft experiments. The supersaturation results in peak calcium concentrations well above the concentration found at the end of the experiment [17—19]. Supersaturation, combined with the very slow rate of calcium carbonate precipitation that is obvious in many experiments, clearly show that end-stage calcium levels are not at equilibrium and, as shown in Table 8.2, are well above what the model predicts.

In addition to experimental data on species, Lidén *et al.* provide data from three commercial batch digesters. These data show that supersaturation also occurs in commercial systems where calcium carbonate should be suspended in the cooking liquor. This further complicates the situation over and above what has been described and modeled. Among other concerns, supersaturation in the presence of calcium carbonate cannot be explained without invoking precipitation inhibitors [30]. Precipitation inhibitors function by interfering with crystal growth, preserving or extending the supersaturated state. Although complex formation can increase the steady-state concentration of soluble forms of calcium, inhibiting precipitation extends the high concentrations found during supersaturation conditions. Lidén *et al.* showed that in commercial processing, birch behaves much like reported laboratory experiments on pine, but mixtures of birch with alder, and of birch with eucalyptus, extend the supersaturation state well into the cook [14]. Laboratory ex-

periments using similar chip mixtures confirm high levels of soluble calcium and extended times for the supersaturation state when cooking these species

Supersaturation is a non-equilibrium state [18]. Although calcium and carbonate can exist in clean solutions at concentrations several orders of magnitude higher than predicted by the solubility product, the presence of calcium carbonate in suspension normally provides the necessary surface for the ions to precipitate, eliminating the most critical condition necessary for supersaturation to persist. Pulping experiments with alder and eucalyptus suggest that lignin byproducts behaving as precipitate inhibitors must also be considered when assessing scaling potential in pulping. Considering the concentration peak of 2 mM for the supersaturated state when pulping birch [14], the potential scale formation rate has increased to 600 kg per day for a mill handling 2000 tons per day of wood. Fortunately, for the reasons mentioned earlier, only a small portion of that 600 kg is likely to end up in the heaters, but the potential has gone from minimal to huge.

8.5.5. Inhibition of Precipitate Growth

Supersaturation in the digester does not directly change the behavior or nature of the calcium problem. Inhibition of crystal growth presents yet another problem in that it can extend the supersaturated state to the final liquor extraction and the digester blow line. Black liquor with a supersaturated level of calcium has a significantly higher scaling potential in the evaporators. Because it is concentrated, it will eventually exceed the semi-stable supersaturation condition and begin to precipitate. When calcium carbonate precipitation occurs in the digester and controls soluble calcium to relatively low levels, the calcium carbonate contribution to scaling problem in the evaporators is more manageable. The problem with scale suppression is that it is impossible to predict when suppression will fail and in what part of the process scaling will occur. Effectively, inhibition of crystal growth moves the precipitation problem to somewhere else in the process, and success or failure depends on the sensitivity of the unit operation to scale problems. Although certain exceptions exist, for the most part, if suppression fails within the digester, most of the precipitate will still be contained within Wood chips or suspended in the liquor. The largest concern here is that because of the much higher amounts of soluble calcium, precipitate growth will likely be at a higher rate than digesters where the

sodium and calcium carbonate in white liquor prevent supersaturation. Although the normal reaction for a mill experiencing scale problems that are costly to manage is to add scale suppression chemicals, the outcome can be worse than the initial problem. In some mills, a better strategy might be selective injection of a small amount of lime mud. The sudden presence of fresh calcium carbonate surfaces will certainly break the supersaturation condition and will at least temporarily relieve inhibition of crystal growth. The question will be whether it does this effectively and in a way that can be managed. Unlike the case of scale suppressants, the outcome is more predictable. The precipitated CaCO_3 does not contribute directly to scale formation, only soluble calcium can do that. As an example of this approach, one of the two batch digesters evaluated by Lidén reported problems with heater scaling. That digester appeared to be highly supersaturated about 40 minutes into the cook. Injection of a small amount of lime mud in the heater circulation loop could drive precipitation and shift the process towards the equilibrium state. If this were started before the calcium concentration reached the maximum, the addition of fresh calcium carbonate surfaces could force precipitation and, by selecting the heater recirculation loop and the location of lime mud addition, control where the precipitation occurs. Obviously, there is a legitimate concern about intentionally forcing calcium carbonate precipitation, and this needs to be approached cautiously. However, lime injection after the heaters should force more of the precipitation to occur within the digester shell rather than in the heaters. Injection just before the heaters might cause more precipitate to form on suspended particles, reducing the amount forming on the heater tube surfaces.

8.6. DIGESTER SCALE

As stated several times, the most common location for scale in digesters is liquor heaters. The second most common location for scale in digesters is at the screens. Scale can form on any of the digester screens, including the top separator, heater circulation, and extraction screens [31,32]. Screen scale is more serious than heater scale because a digester shutdown is required to clean the internal screens.

Scale that forms on the digester shell and most other areas of the digester appears to be similar in composition to the lime scale that forms on heaters. However, extraction screen scale can be different, containing up to 70% organic material. According to Hartler and Libert, heater,

digester wall, and top circulation scale is typically 80-90% calcium carbonate, with very little organic matter [31].

The digester is supersaturated in calcium and carbonate. In most digesters, slow precipitation of calcium carbonate occurs after the cooking temperature has been reached. That precipitate is going to come out on surfaces: on the digester shell and on wood fiber. Anything inside the digester will experience a buildup at approximately the same rate as the scale forming on the shell. Scale forming in the top circulation and on the digester walls probably has the same source as other digester calcium carbonate scales. Slow-rate deposition is probably most responsible for buildup in many of these locations. A 3-4 mm layer of lime scale on the digester shell is generally not a cause for concern. A 3-4 mm deposit of lime on the extraction screens is a problem. Stopping or impeding that scaling means stopping or impeding all calcium carbonate formation in the digester. This might be accomplished with anti-scalant chemicals, but results in supersaturated weak black liquor being sent to the evaporator.

Screen plates seem to suffer from additional scaling concerns and, as reported by Hartler and Libert, different types of buildup [31]. No chemistry change that the mill can control occurs at these locations. Some heating at the face of the screens and cooling behind the screens may occur, with obvious turbulence going through the screens and an eddy region behind the screens. Flashing and cavitation are also possible contributing factors. Mills looking for process changes to reduce scale in these areas should consider the following list of possibilities. However, the evidence in the literature that any of these is an issue in the digester or impacts scaling rates is minimal.

- * Ensure that there is no possibility of flashing behind the screens [31].
- * Ensure that there is no permanent air pocket behind the screens. These should get flushed out shortly after startup.
- * Evaluate the possibility of cavitation (high flow through screen orifices and low pressure on the extraction side). Duggirala suggests that turbulence and changes in pressure can accelerate the kinetics of scale formation [32].
- * For black-colored (organic) deposits, evaluate residual alkali to ensure that it is high enough to prevent lignin precipitation.

8.7. SCALE IN BROWNSTOCK WASHING

In the digester portion of the brownstock system, the fundamental

chemistry generally suggests that the mill should be able to operate under standard conditions with the major scaling issues located at one specific unit operation, the heater. More extensive scale issues are usually the result of a non-equilibrium state: supersaturation, inhibition of precipitate growth, or the slow rate at which calcium carbonate approaches the precipitation equilibrium state. Brownstock washing experiences the opposite problem. The changes in chemical and physical state as the pulp proceeds through the brownstock washers encourage the highest soluble calcium level to occur at the final washer in the sequence. The countercurrent wash flow therefore is mixing filtrates with higher soluble calcium concentrations into conditions that are hotter and contain higher carbonate concentrations. This is an ideal situation for lime scale to form. Although mills certainly experience scale in brownstock Washing, its occurrence is not particularly common. The major reason for this is the “slow rate issue”—in this case, the rate at which calcium carbonate dissolves is sufficiently slow to prevent the increase in soluble calcium levels that would be needed to create a deleterious growth rate for scale on the earlier washers. Among other supporting issues:

- The first washer is normally operating at a temperature significantly below the temperature of the digester wash zone and, with the slow rate at which calcium carbonate dissolves, is not saturated in soluble calcium.
- Invariably, the pH of the brownstock washers remains alkaline.

Maintaining a pH high enough to minimize bicarbonate formation maintains a high enough carbonate concentration to help suppress the rate at which calcium dissolves. Figure 8.3 shows equilibrium calcium solubility and carbonate concentration relative to pH. At a pH of 9, there is still sufficient carbonate to suppress soluble calcium levels, and mills operating with the final wash stage at a residual pH of 9 or higher will generally have few problems. Even at pH 9, only about 15% of the total carbonate and bicarbonate is in the carbonate form. Calcium solubility is increased by a factor of 7 relative to a pH around 10. This is not obvious in Figure 8.3 because of the choice of axis scale. The scaling potential is, however, minimal. At pH 8.5, the solubility of calcium is about 50 mg per cubic meter of filtrate. This represents about 170 kg of calcium in a full year of operation for a 1000 tpd mill.

In cases where brownstock washwater has low buffering capacity, the pH of the wash line does not drop substantially. When wash water with a high buffering capacity is used, the calcium solubility can change

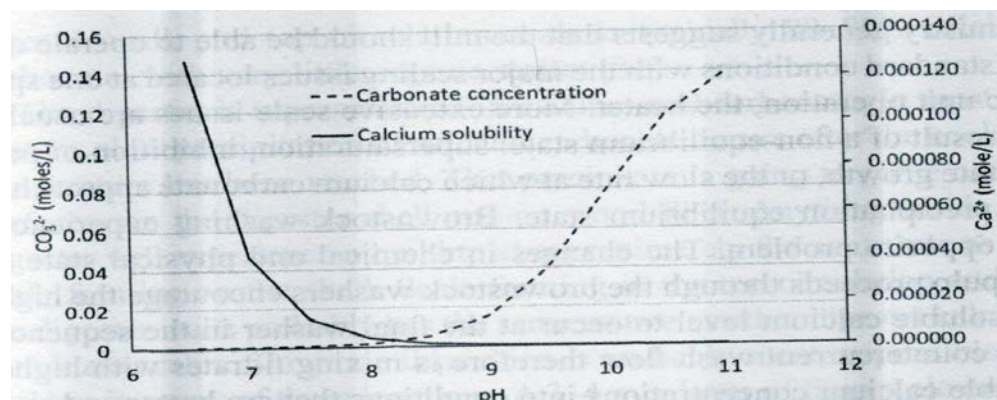


FIGURE 8.3. Effect of pH on carbonate concentration and calcium solubility. The total carbonate plus bicarbonate concentration assumed in the estimate is 0.15 M, K_a , and K_{sp} are for operation at 75°C.

markedly. Use of shower water with lower pH and buffering capacity at pH below neutral means mills need to pay attention to the pH throughout the brown stock washer line. In particular, paper machine white water can have considerable buffering capacity and can significantly reduce the pH on the brownstock washers. Of most concern are acid-sized wet end systems that can be buffered by alum to a pH near 5. Another problem can arise from the use of enzymes in the brownstock washing system to reduce xylans and benefit bleaching. The longer retention times, lower temperature, and neutralized pH requirement of enzymes [33] can aggravate scale issues if not managed effectively.

When mills experience calcium carbonate scaling problems in the brownstock washing system, they must consider raising the pH or increasing the wash-water temperature on the last washer. These changes will reduce the equilibrium driving force for calcium to dissolve, and because scale is caused by dissolved calcium, will reduce the amount of calcium available to form lime scale. Mill staff should also look at filtrate and pulp retention times and try to minimize them. The physics and chemistry of the system are designed to create scale; the slow rate at which calcium carbonate dissolves is what enables normal operation. Overly large filtrate tanks and unwashed brownstock storage are areas where calcium can dissolve and increase the risk of forming lime precipitates in earlier washers.

8.8. CONCLUSIONS

Kraft digesters are saturated in calcium and carbonate, and lime scale

is almost inevitable in digester heaters, but usually pretty rare in other parts of the kraft pulping process. Aspects of the process can encourage non-equilibrium states that cause more unpredictable behavior and are probably responsible for most of the significant scaling problems in the industry. It is suggested that mills investigate breaking supersaturation and precipitation inhibition conditions using small injections of lime mud. This might be a more controllable and reliable method to address scale problems than addition of specialty chemical precipitation inhibitors. Under normal conditions, wood containing higher than normal levels of calcium should not present a problem. The calcium should precipitate within the chips, and the soluble calcium should be controlled by the carbonate in the cooking liquor. The organic makeup of the wood can contribute to non-equilibrium conditions, including supersaturation and inhibiting precipitation. Where these conditions exist, scale problems can be present, even for species with low levels of calcium in the wood.

Significant lime scale formation in the brownstock washing system is also somewhat rare and generally controllable. Unlike the pulping process, where equilibrium conditions serve to minimize scale and non-equilibrium phenomenon increases scaling rates, the brownstock washing system relies on a non-equilibrium condition to minimize scale formation. The reaction rates for calcium and carbonate to precipitate and dissolve are very slow. As long as conditions are maintained that do not encourage faster rates, scale formation can be avoided. Specifically, maintaining a higher pH in the brownstock system, keeping wash-water temperature high, and reducing wash filtrate retention time can all assist in reducing scaling rates.

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Brownstock Washing

Fundamentals and Practices

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