CALCIUM IN PULPING AND BLEACHING

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THE TENDENCY OF CALCIUM TO FORM MINERAL DEPOSITS ON HEATED SURFACES MAKES CALCIUM SCALES ALMOST UNAVOIDABLE IN DIGESTER HEATERS AND BLACK LIQUOR EVAPORATORS.

AMONG THE NONPROCESS ELEMENTS THAT HAVE TO BE handled in the pulping and bleaching process, calcium is probably the most pervasive and costly. The primary impact of calcium is in scale formation, but the tendency of calcium to form calcium carbonate (lime) mineral deposits on heated surfaces makes calcium scales almost unavoidable in digester heaters *(1)* and black liquor evaporators *(2)*. The scale problems in these areas are so pervasive that they have become part of normal operation. Consequently, these systems usually are constructed with the ability to remove one unit from operation without a general shutdown—primarily to remove calcium carbonate scale.

Calcium enters the process from three main sources: wood *(3, 4)*, white liquor, and water *(5)*. Wood typically contains 1000 ppm of calcium or more; in most mills, it accounts for the majority of calcium in the pulping and bleaching process *(5, 6)*. Depending on the efficiency of white liquor clarification, white liquor can account for as little as 5% or as much as 50% of the calcium present in the digester. Use of hard water is not a common problem in the industry, but this source of calcium can be important, primarily in the bleach plant and on the paper machines, where fresh water usage is high. The primary purge for calcium from the kraft process is unbleached pulp (~1000 ppm) and the primary purge from a bleach plant is the acid sewer. The calcium concentration in wood bark is also 5 to 10 times higher than its concentration in wood *(5)*; this also represents a significant but controllable source of nonprocess calcium in the digester.

Scale formation can occur either by continuous growth/crystallization on a surface or by aggregation of suspended crystals into a surface deposit—using either an organic or inorganic cementing agent. In either case, a necessary condition is that precipitation of the mineral must occur. For a precipitation process to occur, the cation and anion must be present in solution at concentrations that exceed the solubility product.

The solubility product for formation of calcite at room temperature abides by the expression

$$[Ca^{2+}][CO_3^{2-}] > 4.5 \times 10^{-9} \quad (1)$$

The calcium concentration of interest in this expression is the amount of free divalent cation (Ca^{2+}) present in solution. This is determined by the total calcium present less any already precipitated, bound to ion exchange sites in fibers or to competing ligands such as EDTA or dissolved lignin fragments.

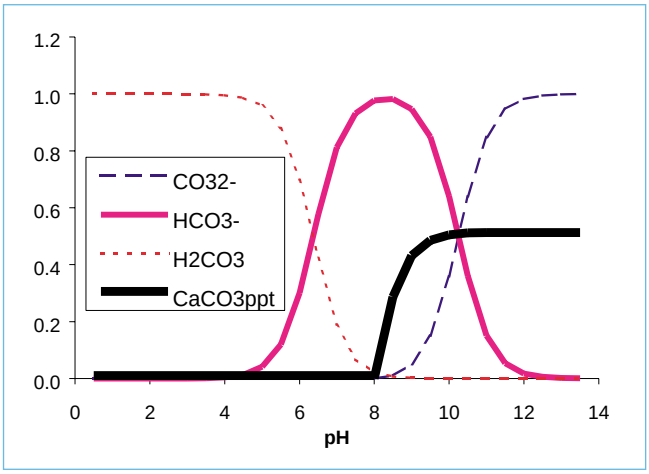
The anion concentration of interest is the free carbonate or CO_3^{2-} ion. As with calcium, this concentration is controlled by its total presence in solution less carbonate present as precipitates and competing reactions. By far, the most significant competing reaction for anions is the acid/conjugate base process, in this case formation of bicarbonate (HCO_3^-) and carbonic acid (H_2CO_3). The transition from carbonate to bicarbonate occurs at a pH around 10, as illustrated in **Fig. 1**. At a pH below about 8, the carbonate ion concentration falls below the minimum needed to support precipitation of calcium carbonate.

All these conditions are met in the kraft process, and the majority of the calcium present in unbleached pulp is found as calcite. So precipitation of calcium carbonate is a given; the only questions are to what extent it is attached to fiber, is suspended in solution, or deposits in the process. Of more concern, if calcite is present, the liquor is saturated in calcium and carbonate, and anything that increases either concentration or affects the solubility product will induce additional precipitation and potential scale formation.

A unique feature of calcium carbonate is that solubility decreases with increasing temperature. In a saturated system, additional calcite precipitates on heating, causing

routine mineral deposition on heat transfer surfaces such as digester heaters and black liquor evaporators. An additional concern rises in evaporators and smelt dissolving tanks. In the presence of high concentrations of sodium carbonate, pirsonite, a mixed salt of sodium and calcium carbonate, becomes the lowest solubility form of sodium carbonate.

With the conversion of many bleach plants to elemental chlorine free bleaching, mills have suffered an increase in problems with calcium oxalate scale. Oxalate is a much stronger acid than carbonate, and the critical pH between hydrogen oxalate and oxalate is around 4 *(7)*. In practice, mills experience calcium oxalate precipitation down to a pH of about 2. This is the most significant issue in the increased oxalate scaling problems. A chlorination stage typically operates at a pH around 1.5, below the point at which oxalate scales can form. The typical chlorine dioxide stage operates at a pH of 3 to 4, within the range where oxalate precipitates can form. The solubility product for calcium oxalate is about 4 x 10^{-9}, about the same as for calcite. In this case, solubility increases with temperature, so deposits are more likely to form where there is sudden cooling or a process change that will increase the concentration of calcium or oxalate. Examples are washer wires, where the filtrate transition to the low pressure drop leg results in cooling, or mixers where caustic is added for pH control. Using extraction stage filtrate on a chlorine dioxide stage washer also may induce calcium oxalate precipitation. TJ



1. Effect of pH on the formation of carbonate, bicarbonate, and carbonic acid, and precipitation of calcium carbonate in a solution that is 1 M in carbonate and 1 x 10^{-5} M in calcium chloride.

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LITERATURE CITED

1. Hartler, N., and Libert, J., *Svensk Papperstidning* 75(2): 65(1972).
2. Grace, T.M., *Southern Pulp and Paper Manufacture* 40(8): 16(1977).
3. Keitaanniemi, O., and Virkola, N.-E., *Paperi ja Puu,* (9): 507(1978)
4. Erickson, L.D., and Holman, K.L., "Non-process elements flows and control in a kraft pulp mill," AICHE (1986).
5. Magnusson, H., Mörk, K., and Warnqvist, B., *1979 Tappi Pulping Conference Proceedings,* TAPPI PRESS, Atlanta, p. 77.
6. Lindberg, H., Engdahl, H., and Puunmalinen, R., *1994 International Pulp Bleaching Conference Proceedings,* CPPA, Montreal, p. 293.
7. Ulmgren, P., *Nordic Pulp and Paper*, 12(1): 32(1997).