Inorganic scale control in today's pulp mills

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Pulp mills can experience considerable scale deposit problems. Forces that drive inorganic salts to precipitate from pulping and bleaching liquors include pH and temperature shocks, intense mechanical or hydrodynamic shear forces and super-saturation concentrations of scaling ions. Key steps proposed for the overall process of inorganic scale formation are shown in Figure 1. Troublesome and costly operational problems can be eliminated with the proper application of a chemical antiscalant.

DIGESTER SCALING

Calcium carbonate readily forms scale deposits under the high temperature, alkaline pH and high pressure conditions of a Kamyr continuous digester. Wood and white liquor are major contributors of calcium under kraft pulping conditions. Digester areas that are particularly prone to scaling are the chip chute, top separator, liquor heaters, and cooking and extraction screens. Scale deposits, especially in heaters and screens, severely impede cooking liquor flows. This results in lower pulp quality and reduced yield. While off-line acid washes are frequently used to de-scale the heaters, the opportunity to remove deposits inside the digester usually occurs just once or twice per year, during scheduled shutdowns. Many mills rely on continuous chemical antiscalant programs to keep their digesters operating scale-free for periods as long as a year or more.

Case Study—Digester Scale: A kraft hardwood mill experienced extremely severe calcium carbonate scaling of the lower extraction screens of a single vessel Kamyr digester, forcing the mill to shut down for an acid boilout every eight to nine weeks. Implementation of a continuous chemical antiscalant program doubled the digester's run-time to 19 weeks, with record production levels. The program is continuing with the goal of extending digester run-time even further.

EXTRACTION STAGE SCALING

Acid and alkaline bleaching and washing stages in a bleach plant create extreme pH swings that provide ideal conditions for scale formation. If an acid washing stage filtrate can be sewered, then many scaling ions are effectively purged from the pulp. Usually, however, the filtrate is reused and sent back to prior bleaching stages. This feeds scaling species back into the pulp. In alkaline washing/extraction stages, calcium carbonate or oxalate scales are typical. The acid-to-alkaline pH shock and a high concentration of calcium ions are strong driving forces for scale precipitation. Calcium oxalate and/or barium sulfate scales frequently form in chlorine dioxide bleach towers and washers.

Case Study—Bleach Plant Extraction Stage Scale: A kraft mill feeds a continuous antiscalant program to its Eo stage to prevent the accumulation of scale on the face wire, in the vat, drop leg and on doctor blades. Without the antiscalant program, pulp and process water flows and pulp washing are severely impeded due to calcium carbonate accumulation. The mill monitors scale deposition with coupons hanging in a side stream off the Eo vat and adjusts antiscalant dosage accordingly. Since the start of the program four years ago, the bleach plant has run continuously with no scale-related shutdowns.

BLEACH PLANT CHLORINE DIOXIDE STAGE SCALING

As a result of the Cluster Rule, many pulp mills have moved toward elemental chlorine free (ECF) bleaching, with 50 to 75% substituted chlorine/chlorine dioxide and 100% chlorine dioxide stages. Wood can be a significant contributor of barium ions in some parts of North America. When sulfuric acid is used for pH adjustment, it often results in the precipitation of barium sulfate, which forms a very hard, tenacious scale. These deposits are notoriously difficult to remove and require stringent boilout and/or severe hydroblasting conditions.

Case Study—C/D Scaling: A kraft hardwood and softwood mill experiencd severe barium sulfate deposits in its C/D_{75} bleaching state, on the washer wire and drum. To compound the problem, naturally occurring radon in the water co-deposited with the barium sulfate. The mill was unable to dispose of scrap metal that contained deposits of this "radioactive" scale. Implementation of an antiscalant program totally eliminated the deposits.

SCALING IN OTHER APPLICATIONS

There are many opportunities for nuisance scales to interfere with efficient operation of the recaus-ticizing and chemical recovery areas of pulp mills. Calcium carbonate and pirssonite scales can impede the flow of green liquor from the smelt dissolving tank to the classifier and the slaker. Calcium carbonate scale can build up on the surfaces of calciner scrubber fans and hot water accumulator spray condensers. Calcium carbonate and burkeite scales can adversely affect heat transfer efficiencies and liquor flows in kraft evaporator systems. Calcium sulfate is a troublesome scale that can form in sulfite mill evaporator systems. Chemical antiscalant prograsms specifically designed for the unique scaling conditions in each of these operations can successfully prevent these problems.

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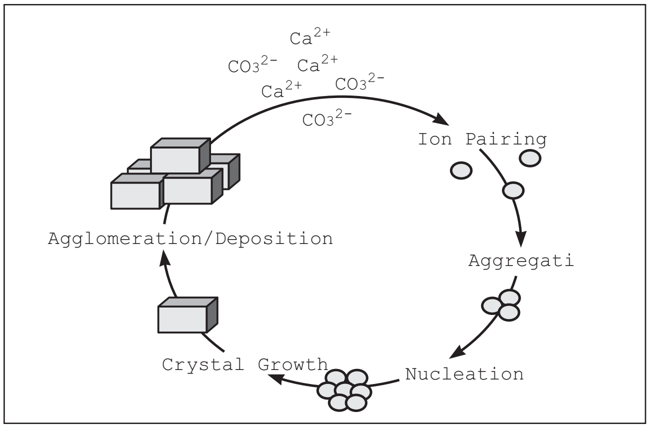

Figure 1 — *Key steps in the overall process of scale formation, shown for calcium carbonate*

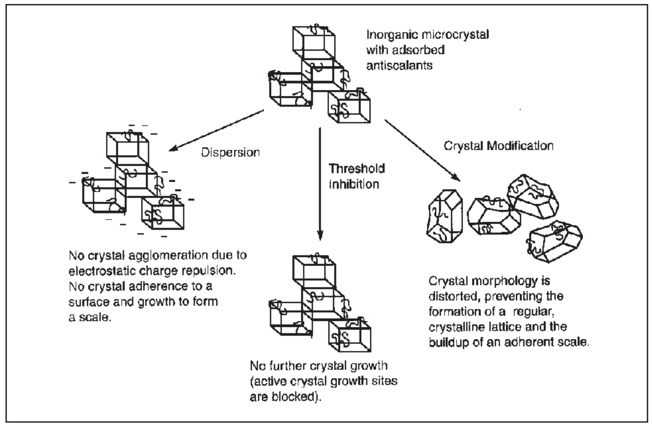

Figure 2 — *Primary chemical scale control mechanisms: dispersion, threshold inhibition and crystal modification*

Secondary fiber recycling mills that employ peroxide bleaching often encounter problems with calcium carbonate scale where peroxide and caustic are charged to the fiber. The alkaline pH and elevated temperature required for efficient peroxide bleaching causes even moderately hard waters to precipitate this scale.

Case Study—Peroxide Line Scale: A recycled fiber mill could not control the calcium carbonate scale in its peroxide chemical mix box, which was causing frequent shutdowns to remove the deposits. Doubling the dosage of the bleaching chelant had no effect on this problem. However, after implementing a continuous antiscalant program, the mill has been able to operate for several months with no scale related downtime.

HOW CHEMICAL ANTISCALANTS WORK

Specialty chemical antiscalants typically include components of polymers, phosphates and/or phosphonates. There are three major scale control mechanisms. These are described below and are shown schematically in Figure 2. Antiscalants typically act by more than one mechanism to control scale deposition.

Precipitated inorganic salts, such as calcium carbonate, initially form microcrystals that gradually increase in size to become macrocrystalline, adherent scales. Blocking or occupying the crystal growth sites with a chemical anti-scalant significantly impedes scale formation. These pre-cipitation threshold inhibitors "freeze" the growing micro-crystals just after nucleation (see Figure 1). They prevent crystal growth and the continuation of the scaling mechanism.

Anionic chemical dispersants also interrupt the scaling mechanism by impeding crystal growth and the agglomeration/deposition path to scale formation. Anionic antiscalants accomplish this by adsorbing onto the growing microcrystals and increasing their anionic surface charge, thereby increasing the electrostatic charge repulsion between the crystals.

Antiscalants can also alter or distort the geometry of a growing microcrystal. The antiscalant accomplishes this by adsorbing onto the crystal, thus modifying its surface properties. This interferes with the lock-and-key fit of precipitating scaling ions onto the crystal surface, making it difficult for the crystals to form hard, tenacious deposits. The modified crystal shape has less contact with surfaces, will take much longer to become incorporated into a scale deposit, and will much more likely be swept away from equipment surfaces by process flows.

BENEFITS OF ANTISCALANTS

Pulp mills are striving for higher production rates on equipment that is often pushed beyond original design capacities. Bleaching demands due to the Cluster Rule and increased effluent restrictions make the job of producing quality pulp ever more challenging. Typical pulp mill operations—which include pH and temperature shocks, significant levels of scaling ions, and water recycling—all contribute to increased deposit potential.

Many mills have successfully implemented chemical antiscalant programs that have proven to be highly cost effective. In addition to controlling troublesome deposits, chemical antiscalant programs provide benefits such as reduced equipment wear and corrosion associated with frequent acid cleanings and chemical boilouts; increased production resulting from the reduction or elimination of unscheduled downtimes; and cleaner, higher quality pulp due to more efficient washing on deposit-free face wires. Mills can readily determine a positive return on their investment if they weigh the negative effects of deposit problems against the benefits of effective scale control.

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