

The change in crystal morphology induced by chemical crystal modifiers reduces the rate of scaling by slowing the process of surface adsorption and agglomeration. The modified shape results in a crystal that 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 surfaces by process flows. Chemical anti-scalants, which act primarily as either threshold inhibitors or dispersants, can also function as crystal modifiers since they adsorb onto the crystal surface.

Chelation - Chelants are specialized antiscalant molecules which complex with soluble cationic scaling species to prevent their reaction with counterions to form aggregates and microcrystals. Chelants have the disadvantage of reacting on a stoichiometric level (i.e., one molecule of chelant reacts with, for example, one calcium ion); whereas, antiscalants which react by the other scale control mechanisms described above need only be added at sub-stoichiometric levels to be effective.

What analytical tests are available to identify scale deposits and scaling species in water and pulp samples?

Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy with Microscopy (FT-IR Microscopy), X-Ray Diffraction Spectroscopy (XRD), X-Ray Fluorescence Spectroscopy (XRF), Atomic Adsorption Spectroscopy (AA), and Inductively Coupled Argon Plasma Emission Spectroscopy (ICP) are all analytical measurement techniques which can be used to determine the components of scale deposits, and the type and amounts of scaling species in water and pulp samples.

How can scale be monitored in a pulp and paper mill?

A system survey can be conducted to determine the types and amounts of scaling species present at various points throughout the mill, before and after the implementation of scale control measures. Scale coupons are frequently used to monitor the effectiveness of a scale control program. Liquor and process water flows can also be monitored, as well as the frequency of acid washes to remove scale which has accumulated on system surfaces. Paper defects, which can form from the sloughing off of scale deposits in the pulp mill or bleach plant, can also be monitored.

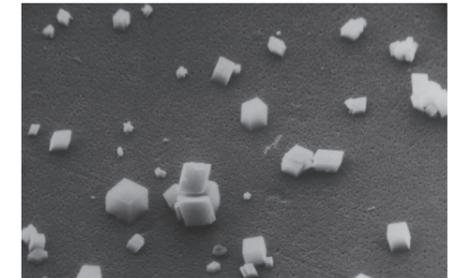
Questions and Answers

Scale Control Trends and Advances



What is scale?

Scale occurs when inorganic salts, such as calcium carbonate, calcium oxalate, calcium sulfate and barium sulfate, precipitate from pulp/paper making process waters to form a deposit on system surfaces.



What are the most common types of scale?

At alkaline pH, calcium carbonate (CaCO_3) is the most common type of scale formed. Calcium oxalate (CaC_2O_4) is frequently encountered in oxidative bleaching stages and in mills that use recycled fiber. At acid pH, barium sulfate (BaSO_4) is easily formed in systems that employ alum or sulfuric acid. Calcium sulfate (CaSO_4) scale forms in the evaporators of sulfite mills. A "soft" scale, burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), frequently forms in black liquor evaporators, along with calcium carbonate. Pirssonite scale ($\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3$) often occurs during green liquor clarification. Silicate scales (as various forms of sodium aluminum silicate) can form in black liquor evaporators and in mills that deink recycled fiber.

What causes scale to form?

Three conditions are necessary for the formation of scale:

Supersaturation occurs when dissolved ions such as Ca^{+2} , CO_3^{-2} , $\text{C}_2\text{O}_4^{-2}$, Na^{+1} , Ba^{+2} , and SO_4^{-2} increase in concentration to levels that exceed the normal solubility limits of the process water.

Accelerated Kinetics - Temperature shocks, intense mechanical and hydrodynamic shear forces, optimum pH conditions, and sudden changes in pressure can all accelerate the kinetics of scale formation.

Optimum Substrates - The non-uniform surfaces found on heat exchanger tubes, face wires, screen plates, etc. serve as optimum substrates to promote the adherence of inorganic microcrystals and the buildup of scale.

What is the effect of temperature on some scales?

The solubilities of calcium carbonate (CaCO_3) and calcium sulfate (CaSO_4) are inversely proportional to temperature. As temperature increases, so does the potential for the precipitation and formation of scale deposits from these inorganic salts.

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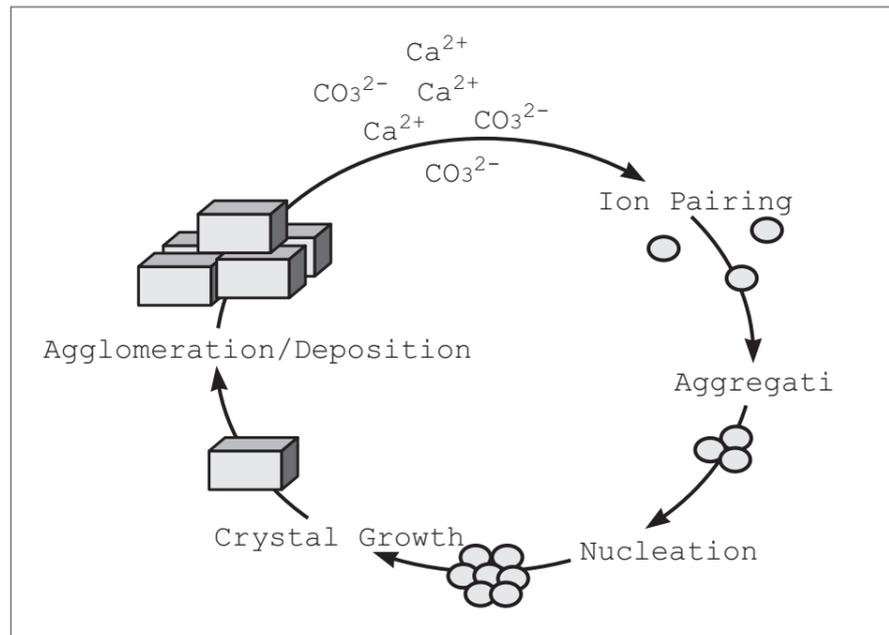


Figure 1 – A schematic representation of the most important steps in the overall process of scale formation.

How does scale form?

The overall process of scale formation can be described by a series of steps, as illustrated in Figure 1. First, cationic and anionic species, such as Ca^{2+} and CO_3^{2-} , collide to form ion pairs in solution. These pairs then go on to form microaggregates, and some of these aggregates go on to become nucleation centers for crystallization. Microcrystals are formed in solution, which agglomerate and/or adsorb to surfaces to grow into larger microcrystals which fuse to form adherent macrocrystals. These macrocrystals continue to grow through the adsorption of additional scaling ions from solution and eventually form the beginning of a scale film on a surface. The scale film builds and ultimately forms a deposit.

What are the main sources of scaling components?

Wood is a primary source of the calcium and barium ions that enter a pulp/paper making system. Kraft pulp mill white liquor can also be a significant source of calcium and carbonate ions. Carbonate ions also arise from the breakdown of cellulose and lignin during pulping and bleaching. Alum, sulfuric acid and sulfite-based cooking liquors are the primary sources of sulfate ions. Oxalic acid/oxalate ions come from wood and also are formed through oxidative bleaching of carbohydrate and lignin. Oxalic acid is also a metabolic by-product of fungi, typically found in unbleached secondary brown fiber. Silicates can enter a pulp/paper making system with the wood, lime makeup, and in the water. Water, of course, is a contributor of other scaling ions such as calcium, barium, and carbonate. In secondary fiber mills, sodium silicate is a frequently used pulper additive that often leads to silicate-based scale deposits.

What can be done to prevent scale deposits?

In most pulp/paper mills, it is impossible to eliminate all the conditions that promote the formation of inorganic scales. However, some mechanical and process changes can be implemented to minimize the potential for scale formation. For example, sudden and extreme pH and temperature changes should be avoided, if possible. In kraft mills, proper clarification of green and white liquors can minimize the carry-over of calcium and carbonate ions into the digester. Complete debarking can eliminate a significant source of calcium ions in the digester (calcium levels are 5-15 times higher in bark compared to wood). Efficient brown stock washing can minimize the carryover of cooking chemicals with the pulp into the bleach plant. In bleach plants, acidic washing stages make excellent purge points for metal cations such as Ca^{2+} , Fe^{3+} , Mn^{2+} , etc. Such purge points should be optimized for maximum washing efficiency to help prevent scaling in subsequent alkaline bleaching stages.

Specialty chemical antiscalants are often employed to inhibit or significantly reduce the formation of inorganic scales in problematic areas of a pulp/paper mill.

How do chemical antiscalants work?

Specialty chemical antiscalants may include components of polymers, phosphates or phosphonates and chelants. Such antiscalants typically work by one or more of the following mechanisms (as illustrated in Figure 2).

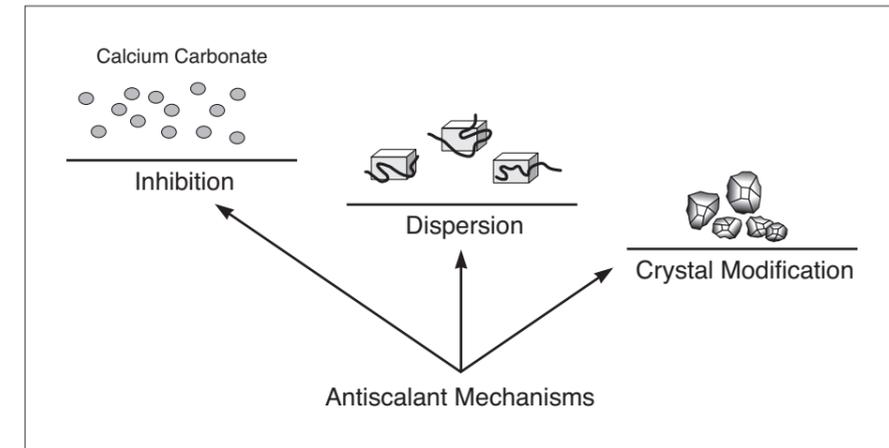


Figure 2 – The most effective antiscalant products are those that function via all three mechanisms: inhibition, dispersion and crystal modification.

Precipitation Threshold Inhibition

Microcrystals increase in size to become macrocrystalline scales through the diffusion of scaling ions (such as Ca^{2+} and CO_3^{2-}) to the crystal faces and the incorporation of these scaling ions at the relatively few active growth sites. It is possible to significantly impede the rate of scale formation by blocking or occupying these growth sites with an impurity, such as a chemical antiscalant. This is the key to precipitation threshold inhibition. Contrary to the popular description of precipitation threshold inhibitors as nucleation inhibitors, the actual function of these chemicals is to “freeze” the growing microcrystals just after nucleation. This prevents crystal growth and the continuation of the scaling mechanism. Precipitation threshold inhibition is most effectively carried out with chemical antiscalants that possess multiple attachment sites (e.g., organophosphates or polymeric antiscalants).

Dispersion

Anionic chemical dispersants interrupt the scaling mechanism by impeding microcrystal agglomeration and adsorption scaling pathways. Anionic dispersants accomplish this by adsorbing onto growing crystals, increasing the anionic charge of the growing crystals, and increasing the electrostatic charge repulsion between the crystals. A high anionic surface charge increases the activation energy barrier to crystal agglomeration, which in turn produces a more stable dispersion of the colloidal microcrystals. Thus, chemical dispersants effectively prevent scaling by retarding crystal agglomeration.

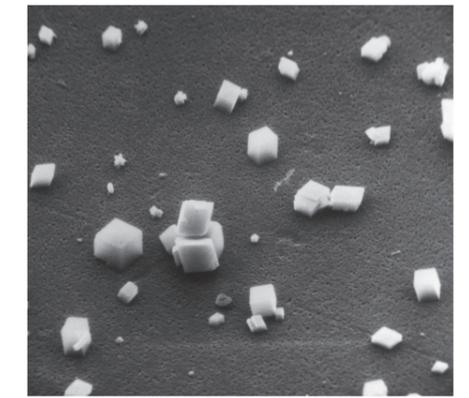


Figure 3 – CaCO_3 crystals, untreated (2000x, 4 microns)

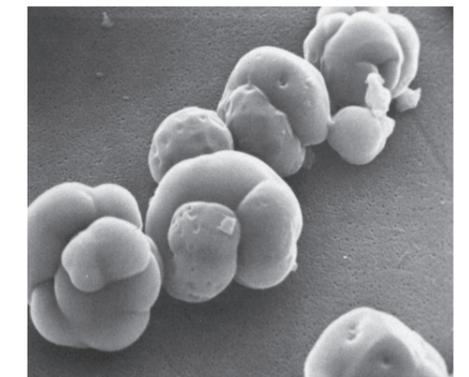


Figure 4 – CaCO_3 crystals modified through treatment with a chemical antiscalant (2000x, 15 microns)

Crystal Distortion/Modification

The shape of a growing crystal can be altered by the use of antiscalants that act as crystal modifiers. These chemicals selectively adsorb onto growing crystal faces, altering their surface properties. The lock-and-key fit of precipitating scaling species onto the crystal surface is thus lost. This not only slows the rate of crystal growth, but also makes it difficult for the crystals to form hard, tenacious deposits due to their modified crystal shape (see Figures 3 and 4).