SCALE CONTROL

Mechanism and chemical control of $CaCO_3$ scaling in the kraft process

STEVEN J. SEVERTSON, PRASAD Y. DUGGIRALA, PHILLIP W. CARTER, AND PETER E. REED

ABSTRACT

Buildup of scale in the kraft digester and black-liquor evaporators is a major contributor to lost pulp mill productivity. Scale deposition occurs in areas such as the heaters and extraction screens of continuous digesters and the liquor side of heat-transfer surfaces in the evaporators. This reduces the efficiency and control of pulping and evaporation processes and eventually forces the costly cleaning of equipment. Since kraft pulping conditions require high temperatures and a high concentration of calcium and carbonate in alkaline liquors, the precipitation of $CaCO_3$ is inevitable. Traditionally, scaling tendencies have been managed using process control methods to reduce deposition rates. This paper examines the thermodynamic principals behind such process modifications while introducing the kinetic steps of the overall deposition pathway. Chemical additives that interfere with and retard the individual steps of the overall scaling mechanism can help to further reduce deposition rates.

Application:

Antiscalent chemistries can be used to impede the development of calcium carbonate scale deposits throughout a kraft mill.

CALCIUM CARBONATE SCALING of digesters and black-liquor evaporators is the most frequently identified inorganic deposit problem in the kraft cycle. Scale buildup on heat exchangers leads to increased steam usage in the digester and reduces production of strong black liquor at the evaporators. Digester scaling also reduces liquor flow rates, which generates fluctuating kappa numbers and increases carryover of pulping chemicals (the result of poor digester washing efficiencies). However, the greatest costs of scaling are associated with acid cleaning to remove scale. In addition to the cost of chemicals, personnel, and effluent disposal, acid cleaning wears and corrodes equipment and often requires unscheduled downtime, resulting in lost production.

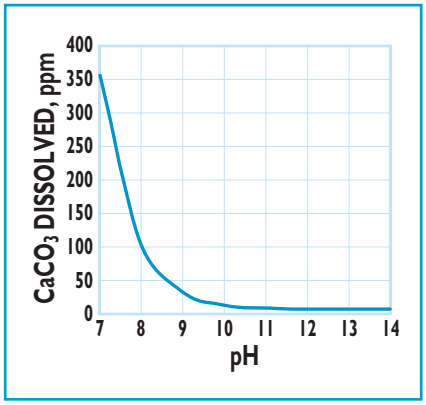
Unfortunately, the kraft cycle provides an ideal environment for the formation of $CaCO_3$ scale deposits. The calcium content of wood chips entering the digester and the high alkalinity and carbonate levels of the cooking liquor produce supersaturation conditions throughout the kraft process *(1)*. Moreover, the high temperatures necessary for delignification and evaporation produce a high driving force for $CaCO_3$ precipitation. Indeed, heavy scaling and frequent acid cleanings are typical in the digester because of the continuously supersaturated environment of the process water.

Strategies for handling scale problems have traditionally been divided into two categories: methods for prevention or methods for removal. Chemical treatment techniques have been widely accepted in removal processes such as acid cleaning treatments or calcium binding with ethylenediamine tetraacetic acid (EDTA) *(2, 3)*. Mechanical methods of cleaning such as steam shocks and hydroblasts have also been used effectively to remove mineral deposits *(4)*. Generally, these removal methods create additional costs and interrupt normal digester operation. In contrast, scale prevention strategies are attractive because they minimize the costs associated with downtime.

Chemical treatments for scale prevention were reported thirty years ago *(5)*. Despite this early success, process control is generally the favored means for scale prevention *(6)*. Control of temperature, soap separation efficiency *(7)*, and process flows has been shown to minimize scaling tendencies. Thermal deactivation is another process used to prevent deposits from forming on the critical surfaces of a heat exchanger *(8)*. Filtration of calcium salts has also been reported as a method of scale prevention *(9)*. In all these cases, however, the term "prevention" really refers to a reduction in scaling rates rather than a complete elimination of scale-forming pathways.

Clearly, any method that reduces shutdowns/acid cleanings can be a cost-effective option for running a continuous digester. Moreover, the use of process-control prevention techniques does not preclude the use of chemical treatment strategies. Indeed, combining chemical and process control strategies should provide the best overall protection from scale deposits.

Antiscalent chemistries are well known to impede scale formation in a wide variety of industrial applications *(10)*. Pulp mill liquors represent a unique set of harsh solution conditions, including elevated temperatures, pressures, and solids concentrations. Therefore, an effective chemical treatment program must provide antiscalent activity while



1. Solubility of $CaCO_3$ in pure water as a function of pH

maintaining sufficient stability and chemical compatibility in these environments. Clearly, an efficient chemical treatment strategy must couple the correct additive with its appropriate application (i.e., feed point, dosage, etc.)

This paper examines the mechanisms responsible for pulp mill scaling and explores the effects of chemical additives on the various scaling pathways. There are many types of scale deposits that can occur in the pulp mill *(11)*. However, the following discussion focuses on the mechanisms important for disrupting the growth and deposition of calcium carbonate solids. Mechanisms such as:

- Precipitation threshold inhibition
- Dispersion
- Crystal habit modification

provide a rational basis for understanding how chemical treatments can slow the overall scaling rate. Typically, the appropriate application of antiscalents leads to a decrease in the frequency of acid cleanings.

The traditional thermodynamic view of the critical factors influencing scale formation is presented. This is followed by a discussion of the kinetics of scale formation. The thermodynamic perspective is useful for both chemical and nonchemical process modifications, while the kinetic perspective is useful in identifying scale prevention strategies.

SCALING THERMODYNAMICS

One simple explanation for scaling in the kraft process is that changes in conditions of process liquors—temperature, pH, and chemical composition—push $CaCO_3$ past its solubility limit (i.e., the liquors become supersaturated), resulting in precipitation and scaling. This explanation alone is insufficient, since the process liquors of the kraft cycle tend to contain calcium carbonate at concentrations above its solubility limit throughout the entire kraft cycle, while scaling only occurs at certain locations. Clearly, a more detailed description of crystallization from solution is required to understand why deposition occurs at some sites within the digester and not at others.

What is often lost in discussions of scaling is the importance of kinetic variables. A sparingly soluble salt like $CaCO_3$ can remain in an aqueous solution to levels well above its solubility limit in a metastable state. Previous work has clearly demonstrated regions of metastability for calcium carbonate solutions in kraft liquors *(12)*. This means that scale prevention strategies must include the factors that control the rate of precipitation rather than those that solely control its equilibrium solubility. This is not to say that solubility is unimportant. Knowledge of when the system is supersaturated indicates where the potential for scaling exists, and the level of this supersaturation plays a role in determining the rate of scaling. Thus, a comparative discussion of thermodynamic solubility principals and kinetic models is appropriate for a more accurate understanding of scaling phenomena in the kraft process.

$CaCO_3$ solubility

The solubility of calcium carbonate is described, in part, by its solubility product K_{sp}, which is simply the product of the equilibrium Ca^{2+} and CO_3^{2-} activities, i.e.,

$$K_{sp} = \gamma_{Ca}[Ca^{2+}]\ \gamma_{CO_3}[CO_3^{2-}] \qquad (1)$$

The activities of the ions are given as their equilibrium concentration multiplied by an aqueous ionic activity coefficient γ. For dilute solutions, these activity coefficients are close to unity, and K_{sp} is approximated as the product of equilibrium ion concentrations. The K_{sp} for $CaCO_3$ in pure water at 77°F is $4.8 \times 10^{-9} M^2$ which means that about 6.9 mg of $CaCO_3$ will dissolve in 1 L of pure water *(13)*. Solubility products are strongly dependent on temperature *(14)*, and for $CaCO_3$ there is an inverse relationship between temperature and solubility (i.e., solubility decreases with increasing temperature). One reported relationship for this temperature dependency, empirically determined between 32°F and 180°F, is given as:

$$\log \frac{K_{sp,f}}{K_{sp,i}} = 6.57 \times 10^{-3}(T_i - T_f) \qquad (2)$$

where $K_{sp,i}$ and $K_{sp,f}$ are the solubility products at the two temperatures, T_i and T_f. So, at 180°F, the estimated solubility of $CaCO_3$ drops to about 3 mg for 1 L of pure water (a K_{sp} of $1.0 \times 10^{-9} M^2$). What is missing from this calculation is the dependency of solubility on pH. Although pH has no direct impact on K_{sp}, it does affect solubility by controlling the level of CO_3^{2-} present. This can be seen by studying the chemical equations for the system (Eqs. 3–5).

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (3)$$

$$CO_3^{2-} + H_3O^+ \leftrightarrow HCO_3^- \text{(bicarbonate)} + H_2O \qquad (4)$$

$$HCO_3^- + H_3O^+ \leftrightarrow H_2CO_3 \text{(carbonic acid)} + H_2O \qquad (5)$$

Because both the carbonate and bicarbonate ions are conjugate bases of weak acids, they are involved in

equilibrium with the hydronium ion (H_3O^+), and their concentrations will be fixed by pH. The effect of this dependency is shown in **Fig. 1** *(15)*. Over the full pH range, this dependency is dramatic. Although less dramatic between pH 7 and 14, there is still a drop of about two orders of magnitude in solubility. This solubility decrease essentially ends above a pH of 10.5, where most of the added CO_3^{2-} remains as CO_3^{2-} because of the high alkalinity of the solution.

Another important example of how the composition of an aqueous solution will affect the solubility of $CaCO_3$ is the common-ion effect. Adding a soluble salt, Na_2CO_3, to a simple solution ($CaCO_3$ in deionized water) sets up the equilibria depicted by Eqs. 3–5, as well as Eq. 6 for the dissociation of Na_2CO_3:

$$Na_2CO_3 \leftrightarrow 2Na^+ + CO_3^{2-} \qquad (6)$$

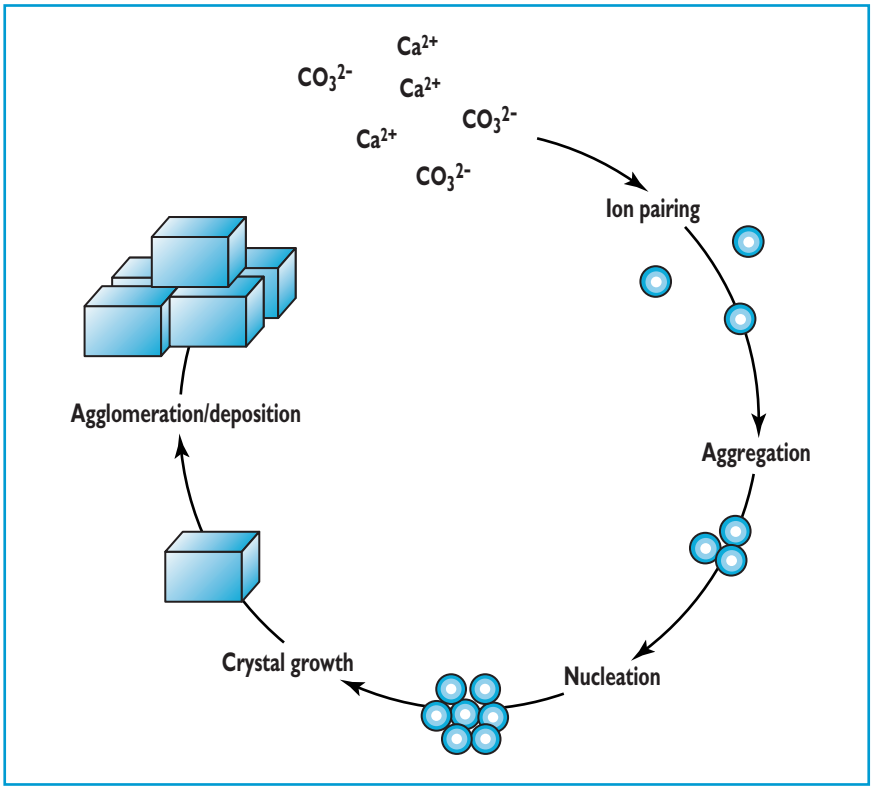
At pH 11, the effect of the hydronium ion (Eqs. 4 and 5) can be neglected, and the amount of $CaCO_3$ that dissolves can be expressed by rewriting Eq. 1 as:

$$K_{sp} = [Ca^{2+}]\left([CO_3^{2-}]_{CaCO_3} + [CO_3^{2-}]_{Na_2CO_3}\right) \qquad (7)$$

where the subscripts indicate the introduction of the carbonate ion from either $CaCO_3$ or Na_2CO_3. Because $[Na_2CO_3] > [CaCO_3]$, the following expression applies:

$$[Ca^{2+}] = \frac{K_{sp}}{[Na_2CO_3]} \qquad (8)$$

Equation 8 means that the amount of $CaCO_3$ that will dissolve in an aqueous solution is strongly dependent on the amount of Na_2CO_3 present. For example, the solubility of $CaCO_3$ at 77°F in a 10 g/L (0.094*M*) solution of Na_2CO_3 is less than 0.1% of its solubility in pure water! In other words, the addition of Na_2CO_3 to a system dramatically decreases the solubility of $CaCO_3$, and it should be noted that any other source of carbonate would have the same common-ion effect on solubility. The decarboxylation of uronic acid groups of hemicelluloses during the cook is another potential source of carbonate to consider *(12)*. Furthermore, any additional sources of calcium would have the analogous reduction in $CaCO_3$ solubility based on the same common-ion principal.



2. Schematic representation of the most important steps in the pathway from soluble ions to a macroscopic calcium carbonate scale deposit. Ion pairing, aggregation, nucleation, crystal growth, adsorption, and agglomeration contribute to the overall kinetics of scale formation.

These examples demonstrate how the constituents of an aqueous solution can strongly affect the equilibrium solubility of a salt. Quantifying the solubility limits for the simple, pure water system is not easily extended to more complex solutions such as kraft process liquors. White and black liquors have a high ionic strength (high ion concentration) produced from an array of different ions. Under these conditions, activity coefficients for calcium and carbonate will decrease in an unpredictable manner from unity. All of the ions in solution are affected by the interplay of temperature, pH, common-ion effects, and ion–ion interactions such as ion pairing and complexation *(16)*. In the absence of all the standard-state equilibria involved in kraft liquors, the thermodynamic $CaCO_3$ solubility limits in kraft liquors remains undetermined. However, we can outline some generalizations that will help explain some of the thermodynamic effects on scaling in the kraft cycle:

- $CaCO_3$ solubility decreases with increasing temperature (Eq. 2) *(2, 3)*.
- At pH < 6, increasing pH strongly reduces $CaCO_3$ solubility.
- At pH > 10.5, there is little change in $CaCO_3$ solubility with increasing pH.
- The presence of additional calcium or carbonate sources reduces $CaCO_3$ solubility.

- Increasing ionic strength reduces the activity coefficients for the calcium and carbonate ions, which increases $CaCO_3$ solubility (Eq. 1).
- The complexity of the solution species present in a kraft liquor precludes the quantitative determination of the equilibrium $CaCO_3$ solubility limits.

A thermodynamic viewpoint is instructive for demonstrating the strong driving forces for precipitating calcium carbonate in the kraft process, but it offers little to predict desirable prevention strategies. Thermodynamic considerations ignore differences in collisional frequencies dictated by process flow conditions and preexisting particle concentrations. A kinetic approach to scaling is a separate, equally valid viewpoint that has some useful predictions for exploring solutions to scale deposition problems.

SCALING KINETICS

The overall process of forming $CaCO_3$ crystals and crystalline deposits can be described by a series of steps, as seen in **Fig. 2**, with each step possessing its own rate constant *(17)*. In the first, calcium and carbonate ions collide to form ion pairs. These pairs then coalesce to form aggregates, and some of these aggregates grow further to nucleate calcium carbonate particulates. In scaling, the calcium carbonate particulates formed in solution can adsorb to surfaces, agglomerate, and eventually fuse to form a deposit. Thus, in addition to the rate of crystal nucleation and growth in solution, scaling rates must take into account the rate of adsorption and surface agglomeration. Because the models describing these processes are beyond the scope of this discussion, no attempt will be made at a comprehensive review of $CaCO_3$ crystallization literature. Instead, this section will provide a descriptive background of known scaling mechanisms and focus on those factors that initiate and accelerate the process. The processes reviewed include nucleation, crystal growth, agglomeration, adsorption, and phase transitions.

Nucleation/crystal growth

It is often reported that the loss of calcium to precipitation does not occur readily until the concentration of $CaCO_3$ is pushed well beyond its solubility limit. This is a result of extremely slow kinetics, even above saturation levels. Nucleation, which is the initial step of scaling, is a strong function of supersaturation and temperature *(18)*. Nucleation can be described as the development of a new phase within an existing supersaturated homogeneous phase. It is a consequence of rapid, local fluctuations in a supersaturated solution to form aggregates. Some of these aggregates can grow and develop into a crystal while others simply redissolve. The number of new crystals formed per unit volume per unit time in solution is defined as the nucleation rate.

Aggregate formation and growth is governed by the balance of surface and volume free-energy terms *(19)*. The growth of an aggregate particle is hindered by the unfavorable surface free-energy term associated with a particle's increasing surface area. This increase in free energy is countered by the free-energy decrease achieved by the precipitation of a new phase from a supersaturated solution, or the volume free energy. At low supersaturation levels, this volume free-energy gain is insufficient to offset the instability introduced by the formation of new aggregate surface area. Therefore, most formed aggregates spontaneously redissolve, and the nucleation rate is low. However, as supersaturation increases, the volume free-energy term provides enough stabilization energy to promote particle growth. This classic competition between surface free-energy and volume free-energy terms produces a critical aggregate size above which continued growth is favored. As the supersaturation is increased, the critical size required decreases, resulting in an increase in the rate of nucleation. Raising the temperature also accelerates the nucleation rate by raising the level of supersaturation (for species with an inverse solubility relationship) and increasing aggregate collisional energies and frequencies. The onset of particle formation in the absence of foreign material is termed primary nucleation and is a homogeneous process.

Homogeneous nucleation almost never occurs because of the presence of solid surfaces, including the walls of the containment vessel and suspended foreign substances. In fact for the kraft process, it is far more likely that primary nucleation occurs via a heterogeneous mechanism in which the other species present in the system promote the nucleation process. These materials are believed to catalyze nucleation by lowering the surface free energy associated with the developing aggregates. One classic example of heterogeneous nucleation is silver iodide seeding of clouds to facilitate water vapor condensation. Thus it could be said that primary nucleation rates are affected by supersaturation levels, temperature, the presence of foreign matter, and the walls of a containment vessel.

In addition to primary nucleation, growing crystals can be created from existing crystals in what is known as secondary nucleation *(20)*. Secondary nucleation mechanisms are commonly classified as either fluid-shear nucleation or contact nucleation. Fluid-shear nucleation can occur when a saturated solution moves past the face of growing crystals at a substantial velocity. Under these conditions, shear forces

can sweep away embryos or nuclei that would otherwise be incorporated into the growing crystal. Contact nucleation is the dislodging of particles from a crystal surface through collisions with other crystals, the walls of the container, or other solid objects. Although the ability of materials dislodged from an existing phase to grow into new crystals is dependent on supersaturation levels and temperature, the rate-determining step in secondary nucleation tends to be the removal of particles. This means that the rate is controlled by the hydrodynamic forces on the crystal as well as the frequency and energy of the crystal–surface collisions, both of which are a function of fluid shear.

The primary and secondary nucleation rates control the amount of particle centers introduced into a liquor, but the subsequent steps of scaling (crystal growth, agglomeration, and adsorption) influence deposition rates. The first of these to consider is crystal growth *(21)*, which is a result of mass transfer and chemical kinetics. Calcium and carbonate solute molecules must both diffuse through the solution to encounter a growing crystal, and upon reaching a crystal face, these molecules must then be accepted and organized into its lattice. The mechanisms of crystal growth can be quite complex, but they generally rely on a small percentage of surface sites that readily incorporate the solute molecules. The growth depends upon mass transfer and surface diffusion, followed by lattice incorporation. The incorporation step most often involves an "active" site on the crystal surface that readily "locks in" the solute ions to the growing crystal. Active sites are usually identified by their topology on a crystal surface with step sites, kink sites, and screw dislocations being the most common. If an active site becomes "blocked" by an adsorbed impurity, then crystal growth must occur via an alternative route, usually with slower incorporation rates (e.g., two-dimensional islanding). Thus, blocking active sites with tailored impurities form the basis for developing most crystal growth inhibitors.

Phase transitions

In addition to surface topology, the crystal surface composition and the spatial arrangement of surface molecules are also critically important. A crystal phase describes the unique stoichiometry and spatial arrangement of lattice molecules. Therefore, the crystal phase also plays a critical role in growth kinetics, as previously reported for aluminosilicate scaling in the kraft process *(22)*. Phases possessing the same unit cell stoichiometry with different spatial arrangements are termed polymorphs. The three principal polymorphs of calcium carbonate—ordered from least-to-most stable at temperatures >70°C—are vaterite, calcite, and aragonite *(10)*. Hydrated, amorphous phases containing organic contaminants are also commonplace, especially at the early stages of precipitation. These organic- and water-rich phases usually undergo phase transitions to more stable, dehydrated phases. Layered deposit structures containing phases rich in calcium, magnesium, or manganese have been observed in Kamyr continuous kraft digesters *(23)*. The diversity of phases that may be present simultaneously in a process liquor offers many crystallization pathways for continued growth.

In general, the most important process parameters governing the mechanisms of nucleation, crystal growth, and phase transitions are supersaturation, temperature, and the liquor constituents. Although crystal growth has many diversified kinetic pathways, it represents only one subset of the ways in which calcium carbonate particles grow. Another route for particle growth is adherent interparticle collisions or particle agglomeration.

Agglomeration/adsorption

Agglomeration and containment-vessel-surface adsorption *(24)* are processes dependent mainly on crystal concentration and fluid shear. Actually, particle number, shape, and size are important because these factors influence the frequency of crystal–crystal and crystal–surface collisions. The particle collisions provide the opportunity for growing crystals to coagulate or fuse in solution and on surfaces. The rate of these collisions is greatly enhanced by the presence of fluid shear forces. Units such as heat exchangers found in digesters and evaporators are designed to create high turbulence in the heated fluid. Although high fluid shear increases the surface collision frequency, it provides enough translational forces to prevent particle adherence to a surface, thus preventing deposition. In areas of lower flow or where eddy currents exist, the translation forces may be insufficient and deposition can occur.

CHEMICAL CONTROL STRATEGIES

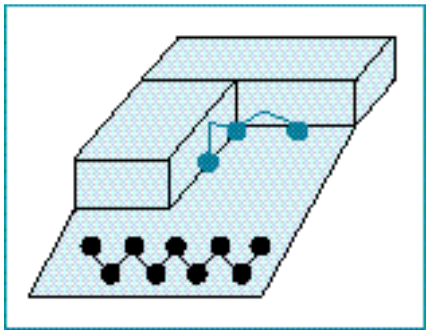
The use of chemical additives can dramatically reduce scaling tendencies at problematic points in the kraft process. Antiscalents usually function through the mechanisms of:

- Precipitation threshold inhibition
- Dispersion
- Crystal distortion mechanisms.

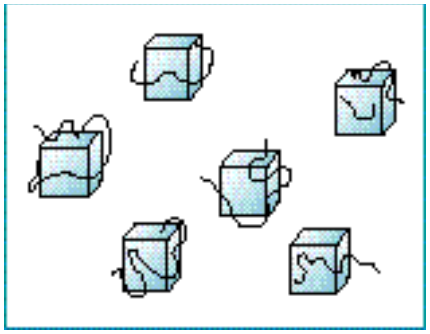
Antiscalents may include components such as polyphosphates, phosphate esters, phosphonates, lignin derivatives, carboxylate polymers, and others.

Precipitation threshold inhibition

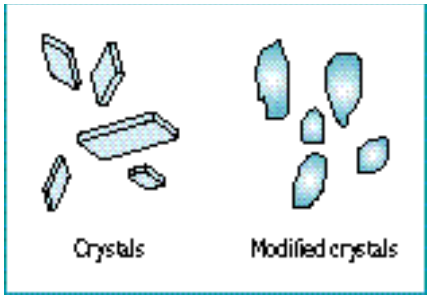
Crystal growth progresses through the diffusion of solute to crystal faces and its incorporation at active growth sites. Because crystals grow through relatively few sites, it is pos-



3. Precipitation threshold inhibitors block growth sites on crystal faces, shutting down crystal growth; or growth sites advance to be "blocked" by an adsorbed polymer



4. Dispersants slow agglomeration and deposition of solid calcium carbonate through electrostatics and steric repulsion



5. Addition of a modifier alters crystal habit, which prevents formation of hard, dense deposits

sible to slow this rate, and thus the rate of scaling, by blocking or occupying these sites with an impurity. This is how precipitation threshold inhibitors work. Contrary to the common description of precipitation threshold inhibitors as nucleation inhibitors, the actual function of this treatment is to "freeze" the growing crystals just after nucleation, which prevents the continuation of the scaling mechanism. A threshold inhibitor essentially interferes with or eliminates rapid growth mechanisms by adsorbing at rapid growth sites, as seen in Fig. 3. The submicron particles are then carried with the process flow and may be difficult to detect by conventional analytical techniques. Precipitation threshold inhibition is most effectively carried out with specialized impurity solutes that possess multiple attachment sites.

Precipitation threshold inhibitors typically contain anionic functional groups that can replace lattice anion sites because of their electronic charge and geometric match with the surface. Inorganic phosphates such as sodium hexametaphosphate were initially used in small quantities to inhibit the growth of calcium carbonate *(25)*. The adsorption of hexametaphosphate was promoted by its geometrical match to the surface ions of a growing calcium carbonate crystal. Sodium salts of other phosphates—including orthophosphate, pyrophosphate, tetrametaphosphate, polyphosphates, and trimetaphosphate—have also been used as precipitation threshold inhibitors for calcium carbonate. However, these inhibitors are limited by their instability to hydrolysis and revert to orthophosphate, losing some of their scale inhibition efficiency for calcium carbonate.

Organophosphonates are used most regularly as threshold inhibitors for calcium carbonate *(26)*. Aminotrimethylenephosphonate (ATMP), aminomethylenephosphonates (AMP), 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP), and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) are the most commonly used organophosphonate threshold inhibitors. The organophosphonates probably act by adsorption to an active calcium carbonate crystal site, as shown in Fig. 3. Organophosphonates are typically limited by their calcium salt solubility (calcium tolerance), hydrolytic stability under caustic conditions, and thermal stability.

Aminopolycarboxylic acids and hydroxycarboxylic acids have also been applied in scale control with reduced inhibition effectiveness. The activity of such carboxylate chemistries is attributed to chelation effects rather than a substoichiometric phenomenon indicative of threshold inhibition. Poly(acrylic acid) and poly(maleic acid) also have crystal growth inhibition properties, but these are more often associated with dispersancy or crystal modification, as discussed in the following section.

Dispersion

In Fig. 2, a simple schematic of the mechanism involved in scaling was introduced. Again, the steps include ion pairing and aggregation, nucleation and crystal growth, and finally, adsorption and agglomeration to form scale. Anionic dispersants interrupt the scaling mechanism by slowing the particle adsorption and agglomeration scaling pathways. They accomplish this by adsorbing to growing crystals, increasing the growing crystal's anionic character, and creating interparticle charge repulsions, as seen in Fig. 4. A higher average anionic surface charge increases the activation energy barrier to agglomeration, which in turn produces a more stable colloidal dispersion. It is interesting to note that even without the addition of dispersants, a dispersion mechanism may be playing a role in the location of scale in the kraft cycle. This is due to the presence of lignin derivatives that can act as anionic dispersants. This may help explain why scaling is reduced in areas of the digester where delignification occurs. Nevertheless, more specialized dispersants often reduce scaling rates in other areas by retarding agglomeration.

The most efficient dispersants for calcium carbonate particulates are synthetic anionic polymers in the molecular weight range of about 1,000–100,000. The anionic charges originate predominantly from pendant carboxylate functional groups derived from monomers such as acrylic acid, methacrylic acid, and

maleic acid. Polyacrylic acid, polymethacrylic acid, and partially hydrolyzed polyacrylamides are the most commonly used polymers for dispersing calcium carbonate. Each has sufficient anionic character to adsorb to the calcium sites on a growing surface while imparting a more negative zeta potential and steric barrier, which reduces agglomeration rates.

A wide variety of polyacrylate-based scale inhibitors are utilized in scale control, depending on the specific process application. These polymers contain acrylic acid as the predominant "mer" unit, along with lesser amounts of units containing sulfonate, phosphonate, amide, ester, or ether. Synthetic polyelectrolytes are usually more efficient dispersants than naturally occurring anionic biopolymers such as the lignin example mentioned previously. Synthetic polymers have tailored properties such as charge density, charge type, molecular weight, branching, and end groups to maximize dispersancy in the environment of interest.

Crystal distortion/modification

The crystal habit refers to the geometrical shape of a crystal as it grows. This is determined by the relative growth rates of the crystal's various faces. Significant differences in the relative growth rates of orthogonal faces can produce an irregularly shaped crystal such as a needle, while a nucleus that possesses several fast-growing planes in orthonormal axes can produce more isotropic shapes. The shape of a crystal can be modified by changing the relative growth rates of the principal faces of the crystal. This can be achieved by the addition of habit or crystal modifiers. These chemicals selectively adsorb onto certain crystal faces or a series of faces, thus altering their surface properties. The lock-and-key fit of precipitating molecules to the crystal surface is lost, which slows down or eliminates its growth. The adsorption is selective because of the chemical functionalities and periodicity differences among the different crystal faces.

The change in crystal habit induced by modifiers is illustrated in **Fig. 5**. The change in habit reduces the rate of scaling by slowing the surface adsorption and agglomeration step of the mechanism and by making it difficult for growing crystals to form hard, tenacious deposits. That is, the modified shape results in a crystal that will have less contact with surfaces, take much longer to become incorporated into a deposit, and be more likely to be swept away from surfaces by process flows.

The threshold inhibitors and dispersants listed earlier also have the potential to be crystal modifiers, since they adsorb to the calcium carbonate surface. Previous work has demonstrated some of the morphological influences of acrylate- and phosphonate-based additives *(27)*. Other additives as well as ions have been shown or predicted to have similar morphology-altering effects. Nevertheless, controlling the shape of the crystal is generally a secondary consideration when preventing scale deposits, despite its important impact on adsorption and agglomeration kinetics.

Mill application

The success of a chemical treatment program is measured by the efficiency of digester, evaporator, or heater operations. Scaling rates can be monitored with process variables such as liquor flows, temperatures, and heat-transfer coefficients, all of which are reduced as a result of inorganic deposition. In the absence of such data, the frequency of acid cleanings or acid usage provides measures of antiscalent performance.

At mills where antiscalent chemistries have never been used, treatment typically results in a two- to fourfold reduction in acid cleanings for locations such as the digester shell, extraction screens, chip screens, and liquor heaters. Although the discussion here focused on individual scale control mechanisms, a treatment chemical is generally designed to function via several mechanisms (e.g., chelation, dispersion, and crystal modification for the polymer used in this mill example). A comprehensive chemical treatment program for the prevention of calcium carbonate deposition should retard crystal growth, agglomeration, and surface adsorption. Additive chemistries need to be tailored for the application of interest, taking into account the impact of process conditions and solution constituents on inhibitor activities.

CONCLUSIONS

The kraft process provides an environment that strongly promotes the formation of calcium carbonate scale deposits. High concentrations of calcium and carbonate ions and elevated temperatures raise the $CaCO_3$ supersaturation ratio in the process liquors. Contact between the supersaturated liquors and other surfaces (heat exchangers, screens, and impurities) promotes rapid precipitation kinetics. Although process improvements—higher causticizing efficiencies, better lime mud clarification, and operation of equipment at designed production capacities—can help to reduce the $CaCO_3$ scaling rate, further reductions in scaling rates require the use of antiscalent chemistries.

Chemical control of particle growth, agglomeration, and morphology significantly impedes the formation of thick, tenacious scale deposits in the digester and evaporators. Treatment chemicals function by adsorbing to growing $CaCO_3$ particles, resulting in slower particle growth, reduced agglomeration rates, and altered particle shape. There are a wide variety of industrial antiscalent

additives based primarily on phosphate, phosphonate, and carboxylate chemistries that function by one or more of the previously described mechanisms. An effective antiscalent chemical treatment program combines the proper additive(s) with an application strategy tailored for the process environment. **TJ**

Severtson is an assistant professor in the Dept. of Wood and Paper Science at the University of Minnesota, Kaufert Laboratory, 2004 Folwell Ave., St. Paul, MN 55108. Duggirala, group leader, pulp mill; Carter, senior research chemist; and Reed, group leader, polymer science, work for Nalco Chemical Co., One Nalco Center, Naperville, IL 60563.

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