# *Influence of organic additives on calcium carbonate precipitation during kraft pulping*

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**ABSTRACT:** In this study we monitored calcium during laboratory batch cooks to evaluate the influence of various organic additives on the precipitation of $CaCO_3$ during kraft pulping. Included in the study were antiscalant chemicals thought to be capable of withstanding the harsh environment of kraft pulping and recovery operations. Results indicate significant differences in the way the tested chemicals inhibit calcium precipitation and their efficacy. For EDTA—an aminocarboxylic acid used to examine the effect of sequestrants—results were consistent with a reduction in dissolved calcium levels to slow nucleation and growth kinetics. EDTA used in molar excess of the released calcium prevented precipitation of $CaCO_3$ during a kraft cook. For the carboxylic acid containing polymers tested, inhibition of calcium precipitation required concentrations similar to that used with sequestrants, in contrast to the high efficiencies demonstrated by these same polymers at lower temperatures. Even at concentrations well above that required for sequestering mechanisms, tested polymers could not completely prevent the precipitation of calcium at temperatures commonly used in kraft pulping reactions. In contrast, many of the organophosphonic acids tested demonstrated a significant inhibitory efficiency. Tests indicate a threshold effect with concentrations well below a stoichiometric match with dissolved calcium providing significant inhibition of calcium precipitation. This study identifies antiscalants that are effective under kraft pulping conditions. Future work will examine how best to apply this technology to control scale problems.

***Application:*** This study identifies antiscalant chemicals that are effective for controlling calcium carbonate scale problems in kraft process liquors.

Formation of inorganic deposits or scale continues to be a significant problem in the kraft process [1-4]. Scale deposition on heat exchanger surfaces increases steam requirements and diminishes capacity producing variable delignification at the digester, reduced strong black liquor production at the evaporators, and increased energy consumption by both operations. Also affected by scaling are screens, pumps, and any conduit carrying process liquors. Scale formation on these devices disrupts operations and requires downtime and, often, lost production for removal. Unfortunately, the kraft process provides an environment that promotes the formation of several types of inorganic scale, with the most common being calcium carbonate. The high concentration of calcium from wood and carbonate carryover, combined with high temperatures and liquor alkalinity, produce significant supersaturation and a strong tendency to form crystalline $CaCO_3$ deposits. The location and severity of crystalline deposits are governed primarily by factors such as supersaturation, temperature, colloidal stability of the developing phase, and fluid shear [5-7]. In addition, chemical species present in process streams that slow precipitation kinetics can influence scaling [6, 8]. These chemicals can be additives introduced to control deposit problems or species released into process liquors by delignification reactions. This paper examines the influence of various types of chemical additives on the formation of $CaCO_3$ under kraft pulping conditions.

The mechanism by which crystalline phases form is complex [9,10]. The onset of $CaCO_3$ precipitation is usually not observable until the system is well beyond its solubility limit. The existence of a metastable region where the system can exist under supersaturated conditions without precipitating and an upper limit to this region beyond which these processes rapidly occur is often used to explain the dynamics of calcium concentrations in studies of digester scaling [11]. In laboratory studies, Hartler and Libert drew liquor samples from a laboratory batch digester during kraft cooks to monitor total calcium, magnesium, and manganese concentrations [11]. They found that magnesium and manganese rise continuously throughout the kraft cook, while the calcium concentration climbed to a maximum value and then decreased rapidly presumably due to precipitation of $CaCO_3$ onto fiber and metal surfaces. The authors suggest that experiments involve a climb in temperature and calcium concentration to supersaturation levels necessary to initiate precipitation followed by a rapid drop in calcium to its (low) solubility limit. They show that increasing the $Na_2CO_3$ concentration in the cooking liquor decreases the maximum calcium concentration at precipitation. They also demonstrate that even when no $Na_2CO_3$ is initially present in the white liquor, calcium carbonate precipitation occurs, which they argue is driven by carbonate produced in the decarboxylation of uronic acids groups from solubalized hemicelluloses.

Using a similar procedure, we collected data for this paper using laboratory kraft cooks. The experiments examine how the presence of antiscalants influences the dynamics of liquor calcium concentrations. Antiscalant chemicals impede scale formation by slowing processes that lead to deposits. The mechanisms by which they work are poorly understood but are thought to fall under two broad categories based on whether they involve an interaction with scaling species in solution or at the interface of the developing crystalline phase. Treatment chemicals that function prima-

rily in solution to form soluble complexes with dissolved ions are known as sequestrants [5]. By complexing dissolved calcium, sequestrants reduce supersaturation, slowing the nucleation and growth of $CaCO_3$ deposits. To prevent the precipitation of $CaCO_3$, a minimum of a molar match with the calcium species is usually required, which is why sequesterants are referred to as stoichiometric treatments. Treatment chemicals that impede scale formation primarily through a direct interaction with developing crystalline phases are broken down into several subcategories depending on how this interaction manifests itself [5,6]. The reported influence of adsorbed species includes impeded nucleation, slowed growth, altered morphology and dispersion of formed crystals, all of which can inhibit the formation of scale deposits. These types of influences typically occur at antiscalant concentrations well below that required of sequestrants; thus, antiscalants demonstrating these interactions tend to be more efficient treatments for controlling scale. The ability of a treatment chemical to prevent the precipitation of a salt at concentrations well below a molar match with the metal of the precipitating species (i.e., at substoichiometric levels) is often referred to as the threshold effect or mechanism [12]. When a treatment chemical demonstrates substoichiometric influence it is likely that their primary interaction is interfacial. However, the absence of the threshold effect does not exclude interfacial interactions and for many additives it is possible to influence precipitation processes through both solution and interfacial mechanisms.

To a certain extent, the influence of antiscalants can be described in terms of models for nucleation and crystal growth. The formation of a scale deposit requires first the nucleation of a new phase followed by its growth from a supersaturated solution. According to the classical nucleation theory [13], the steady-state rate of nucleation can be expressed as,

$$J = J_{max} \exp\left[ -\frac{\beta\, V_m^{\,2}\, \gamma^{\,3}\, N_A\, f(\theta)}{(RT)^3\, (\ln S)^2} \right] \qquad (1)$$

where J is the number of nuclei formed per unit volume and unit time, $J_{max}$ is the frequency factor, $\beta$ is shape factor for the developing nuclei, $V_m$ is the molar volume of the new phase, $\gamma$ is its interfacial energy with the solution, $N_A$ is Avogadro's number, $f(\theta)$ corrects for heterogeneous nucleation where $\theta$ is the contact angle the growing phase makes with solid surfaces, R is the gas constant, T is absolute temperature, and S is the supersaturation or supersaturation ratio, which for $CaCO_3$ is defined as,

$$S = \frac{a_{Ca^{2+}}\, a_{CO_3^{2-}}}{K_{sp}} = \frac{\gamma_{Ca^{2+}}\, C_{Ca^{2+}}\, \gamma_{CO_3^{2-}}\, C_{CO_3^{2-}}}{K_{sp}} \qquad (2)$$

In Eq. 2 the numerator contains the activities for the calcium and carbonate ions, which can be broken down into their aqueous activity coefficients and concentrations, and the denominator contains the solubility product for the phase of $CaCO_3$ formed, $K_{sp}$. With a sparingly soluble salt such as $CaCO_3$, the rate of nucleation tends to be negligible with increasing variables such as temperature and supersaturation until critical values are approached, whereupon the rate rises nearly asymptotically. Once a deposit has nucleated, it continues to grow in a supersaturated solution. It has been reported that the rate of crystal growth for calcium salts in seeded solutions can be described by a second order rate law, which for $CaCO_3$ takes the form,

$$-\frac{dC_{Ca^{2+}}}{dt} = kA(C_{Ca^{2+}} - C^{\infty}_{Ca^{2+}})^2 \qquad (3)$$

where k is the rate constant, A is the effective surface area of growing crystals and $C^{\infty}_{Ca^{2+}}$ is the equilibrium concentration of the dissolved calcium [14, 15]. Equations 1-3 do not provide a comprehensive mechanistic description of the scale formation, but do provide insight on processes that likely contribute to the formation of most deposits.

## MATERIALS AND METHODS

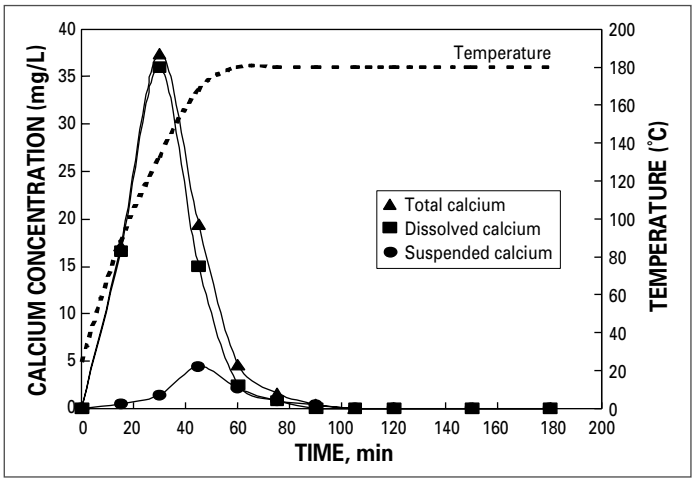
### *Chemicals, materials, and solutions*

The $Na_2CO_3$ (anhydride), NaOH (50% w/w aqueous solution) and $Na_2S{\bullet}9H_2O$ were purchased from Fisher Scientific (Pittsburgh, Pennsylvania, USA). Ethylenediaminetetraacetic acid (EDTA) was purchased from Avocado Inc. (Ward Hill, Massachusetts). Sodium polyacrylate, 40% w/w aqueous solution with $M_w$ ~ 10,000, and poly(maleic acid), 50% w/w aqueous solution with $M_w$~1000, were purchased from Polysciences Inc. (Warrington, Pennsylvania). We obtained the commercial carboxylic acid containing polymer from a supplier in the form of an aqueous solution. The organophosphonates were obtained from Solutia Inc. (St. Louis, Missouri) as aqueous solutions. The organophosphonates tested included 1-hydroxyethylene-1, 1-diphosphonic acid tetra sodium salt (sodium HEDP), ethylene diamine tetra(methylene phosphonic acid), pentasodium salt (sodium EDTMPA), diethylenetriamine penta (methylenephosphonic acid), pentasodium salt (sodium DTPMPA), hexamethylenediamine tetra(methylene phosphonic acid), potassium salt (potassium HDTMP), and amino tri(methylene-phosphonic acid), and pentasodium salt (sodium ATMP).

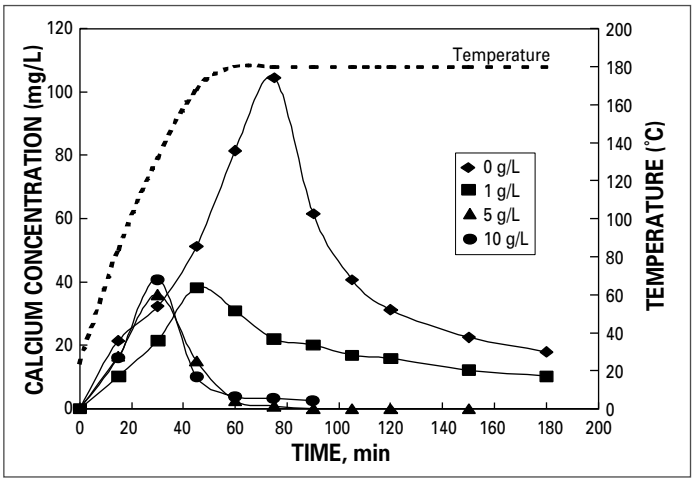
Chemicals tested in this project came in both free acid and neutralized salt forms. Whenever possible concentrations are reported in terms of active acids (mass concentration of the acid form of the active species) to provide for direct comparisons in performance. Potlatch Corporation (Cloquet, Minnesota) provided wood chips (red pine) used in laboratory pulping. Before use, the chips were passed through a slotted screen to isolate those with a thickness between 2 and 7 mm, hand sorted to remove materials such as bark, and dried. The white liquor used in pulping reactions combined 296 g of 50% NaOH, 163.8 g $Na_2S{\bullet}9H_2O$, a known amount of anhydrous $Na_2CO_3$, and an inhibitor in a 4-L volumetric flask.

### *Kraft cooks and calcium monitoring*

Kraft cooks were carried out in an MK Systems (Danvers, Massachusetts) 6 L digester on which an extractor port and condenser were added to allow samples to be pulled while the system was under pressure. Conditions used in the kraft cook included liquor to wood ratio of 5:1, 18.5% effective alkali, 25% sulfidity and variable levels of $Na_2CO_3$, with 5 g/L being the most frequently tested concentration. Prior to each kraft cook, a 10% (v/v) aqueous solution of $H_2SO_4$ was circulated in the digester for 10 minutes to remove any existing deposits. This acid solution was drained and the digester was rinsed several times with deionized water. Four liters of white liquor (described above) were added to the digester and the initial temperature was




*1. Typical kraft cook calcium concentration curves showing the total, dissolved, and suspended calcium levels as a function of cooking time.*




*2. The influence of $Na_2CO_3$ concentrations on the dissolved calcium concentration curves.*

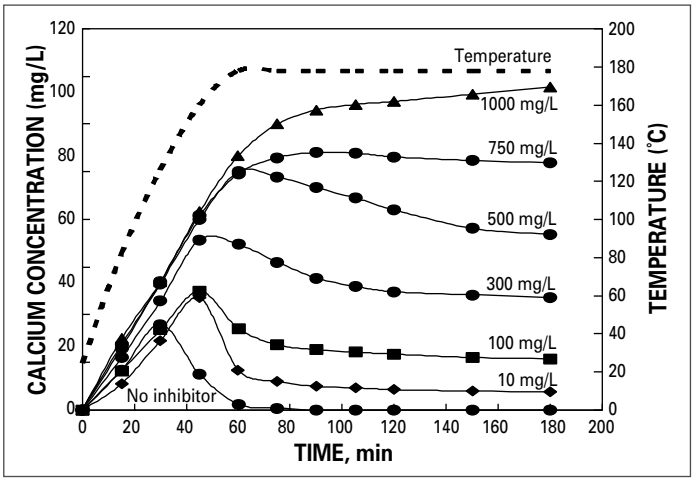
recorded. Eight-hundred grams of the oven dried pine wood chips were then placed in the digesters chip basket and submerged into the liquor. When the basket was in place, the stopwatch was started, a sample (≈5 mL) was drawn from the digester and the reaction heating sequence was initiated. A liquor sample was drawn every 15 minutes using the water-cooled condenser, which had a total volume of less than 10 mL. The condenser was completely purged prior to each sampling. One milliliter of the drawn sample was quantitatively transferred to a 15-mL centrifuge tube with 5 mL of 4% HCl solution. Approximately 3-mL of the remaining sample were drawn into a 10-mL disposable syringe and passed through a syringe filter (0.45-µm pore size membrane). One milliliter of the filtrate was quantitatively transferred to another 15-mL centrifuge tube containing 5 mL of 4% HCl solution. The acid in test tubes precipitated the black liquor lignin. Centrifugation of the test tubes then produced a clear supernatant. A PerkinElmer (Shelton, Connecticut) 100 AAnalyst Atomic Absorption spectrometer was used to determine calcium concentrations.

## RESULTS AND DISCUSSION

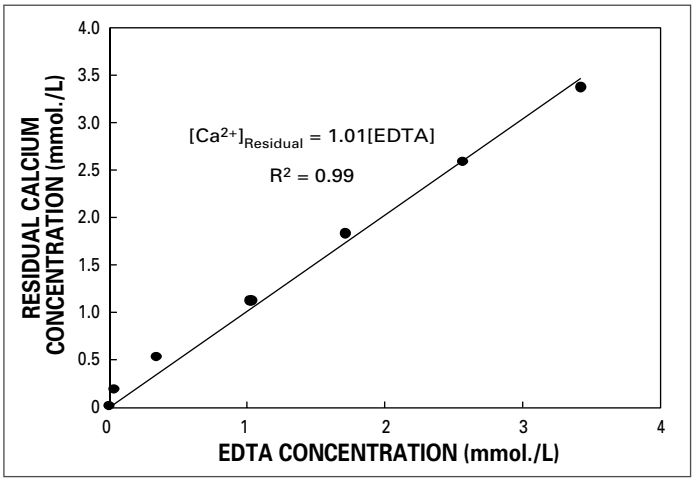
### *Calcium carbonate precipitation in untreated liquor*

**Figure 1** shows the concentration of the various forms of calcium in the cooking liquor as a function of reaction time for white liquor containing 5 g/L $Na_2CO_3$. Here dissolved calcium refers to calcium not removed by a 0.45 µm pore-size membrane, and suspended calcium is the difference between the total calcium concentration in the cooking liquor and the dissolved concentration. Note that the dissolved fraction of calcium may contain nuclei and small crystals too small to be separated, but these contributions are assumed to be small. As pulping reactions proceed, calcium is being leached from the chip mass into the cooking liquor, increasing the dissolved calcium concentration and supersaturation. The water solubility of $CaCO_3$ is inversely related to temperature; so the increasing temperature reduces its solubility product, $K_{sp}$, further increasing supersaturation in addition to accelerating nucleation and growth kinetics. Eventually, the liquor reaches a combination of temperature and dissolved calcium levels at which dissolved calcium is rapidly depleted from the liquor. This is consistent with a climb to conditions that initiate detectable nucleation and crystal growth [11]. At this carbonate concentration, nearly all of the calcium is removed from the liquor due to its apparent precipitation of $CaCO_3$. The increase in suspended calcium concentration indicates the growth of calcium-containing particles in the cooking liquor. The concentration of calcium in this form never achieves significant levels. To determine the distribution of the dissolved calcium during pulping reactions, the heater, shell (along with the empty chip basket), and the chip mass were all leached separately with acid. The average values for three runs were 8.9%, 13.3%, and 77.8% for the distribution of calcium between the heat exchanger, shell, and chip mass respectively. The high concentration of calcium associated with the wood is likely due to its dominance of surface area in the digester and possibly its ability to produce a localized enhancement of supersaturation. Precipitated solids collected from the spent cooking liquor and analyzed consisted primarily of $CaCO_3$ in its calcite phase.

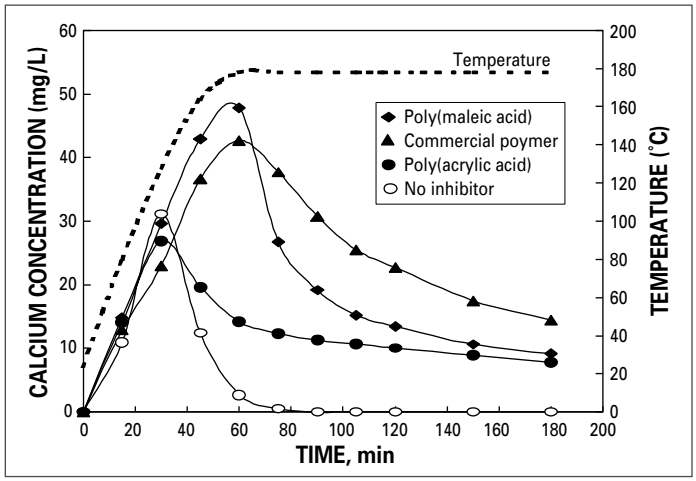
**Figure 2** shows the effect of $Na_2CO_3$ concentration on the calcium concentration curves for laboratory kraft cooks. Here, only the dissolved calcium concentrations are shown, which appears to provide the best gauge of how scaling reactions are progressing. The amount of $Na_2CO_3$ carryover from chemical recovery in the kraft process has a significant influence on supersaturation and thus the temperature and calcium concentration necessary to induce the dissolved calcium drop. For an initial concentration of 0 g/L $Na_2CO_3$ in white liquor, the concentration of dissolved calcium climbs to its highest level. Because carbonate is required to initiate the precipitation, it must eventually be generated during pulping, possibly from decarboxylation reactions of acid groups from solubilized wood polymers [11]. For the kraft cooks with 0 and 1 g/L of $Na_2CO_3$ in the white liquors, residual dissolved calcium is found in the spent cooking liquors. This is likely a result of the slow growth kinetics at the lower supersaturation and possibly a non-negligible calcium concentration at its solubility limit. With increasing levels of carbonate, the combination of calcium concentration and temperature necessary to induce precipitation decrease. However, this decrease is tempered at the higher carbonate concentrations as would be predicted from Eq. 2 as well as from the influence of the higher $Na_2CO_3$ concentrations on activity coefficients and possibly complexation.




*3. Kraft cooks carried out in the presence of no inhibitor and ethylenediaminetetraacetic acid (EDTA) at various initial concentrations in the white liquors.*




*4. The residual calcium molar concentrations in the digester liquors as a function of initial EDTA molar concentrations.*



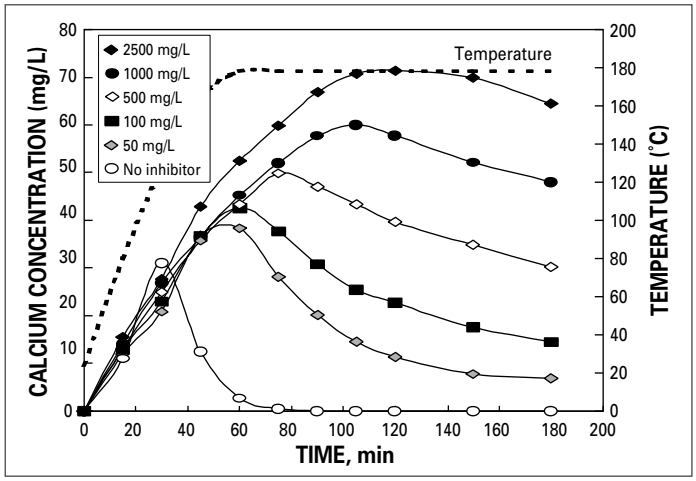

*5. Kraft cooks carried out in the presence of no inhibitor, poly(maleic acid), sodium polyacrylate, and a commercial polymer. Additives had initial concentrations of 50 mg/L in the white liquors on an active acid basis for poly(maleic acid) and sodium polyacrylate and a solids basis for the commercial polymer.*

### *Influence of sequesterants on calcium carbonate precipitation*

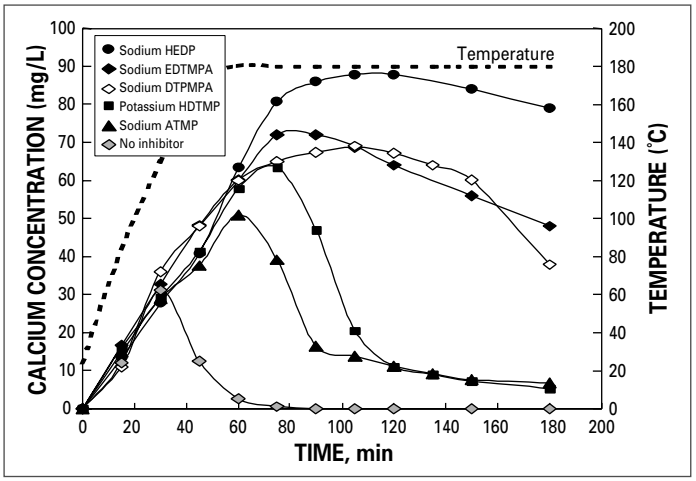
A number of chemicals provide sequestration of metal species [5]. Ethylenediaminetetraacetic acid (EDTA) is a commonly used additive for this purpose. We used it to demonstrate the influence of sequestrants on $CaCO_3$ precipitation during kraft cooks. The influence of EDTA can be predicted using Eqs. 1 and 2. Assuming that the concentration of the calcium-EDTA complex formed is approximately equal to the concentration of added EDTA [16], the calcium free to participate in scaling reactions that helps supersaturate the liquor (Eq.2) is given by the difference between the calcium released from wood (measured as dissolved) and the EDTA present, i.e.,

$$C_{ca^{2+}} \approx [(C_{ca^{2+}})_{dissolved} - C_{EDTA}] \quad (4)$$

where $(C_{Ca^{2+}})_{dissolved}$ and $C_{EDTA}$ are the molar concentrations of dissolved calcium and EDTA in the liquor, respectively. It is difficult to quantitatively apply the equations discussed to this system due to the complexity of the liquor and conditions in kraft pulping reactions, including the potential binding of calcium by other species and the variable nature of the calcium release from wood chips. However, we can make several semi-quantitative predictions through the combination of Eqs. 1-4. First, the presence of EDTA should increase the dissolved calcium and temperature combination necessary to initiate nucleation (Eqs. 1 and 4). **Figure 3** shows the effect of EDTA on the calcium concentration curves (dissolved calcium) for laboratory kraft cooks at various initial concentrations in the white liquors. The curves are consistent with this prediction. Second, according to Eqs. 2 and 4, the supersaturation should become negligible, preventing the onset of precipitation when the EDTA concentration is above the concentration of dissolved calcium. If the maximum concentration that can be released by the chip mass is taken as 125 mg/L or 3.13 mmol/L, an EDTA concentration of 914 mg/L or greater would be expected to significantly inhibit precipitation. As can be seen from Fig. 3, a concentration of 1000 mg/L did prevent the onset of precipitation while a concentration of 750 mg/L was only able to slow its onset. Third, the residual calcium and EDTA molar concentrations should be approximately equal. The high carbonate concentrations present in these studies make calcium virtually insoluble in kraft pulping liquors. Therefore, nearly all of the calcium that is free to participate in scaling reactions will be consumed during pulping reactions. The calcium remaining and quantified as dissolved will be in the form of water-soluble complexes primarily with EDTA due to its high formation constant for complexation with the calcium ion. **Figure 4** is a plot of the residual calcium molar concentrations in the liquors subsequent to laboratory kraft cooks as a function of the added EDTA molar concentrations. As predicted, there is a linear relationship between these quantities with a slope near unity. One final prediction that can be made is that the presence of EDTA, which reduces free calcium levels, should reduce not only the rate of nucleation, but also crystal growth. This is qualitatively consistent with the calcium concentration curves shown in Fig. 3, which appear to show a




*6. Kraft cooks carried out in the presence of the commercial polymer at various initial concentrations on a product basis in the white liquors.*




*7. The influence of sodium HEDP, sodium EDTMPA, sodium DTPMPA, potassium HDTMP, and sodium ATMP on kraft cooks at initial active acid concentrations of 50 mg/L in the white liquors.*

decreasing slope following the onset of precipitation with increasing EDTA concentrations.

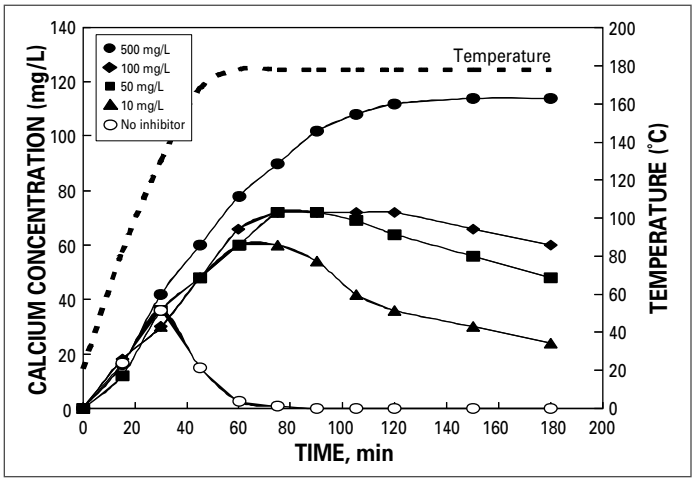
### *Influence of carboxylic acid containing polymers on calcium carbonate precipitation*

It is well established that certain polyacids can inhibit the nucleation of crystalline phases, slow their growth and alter their morphologies. This phenomenon is apparent from the widespread use of carboxylic acid containing polymers to inhibit scale formation in industrial processes [5]. The influence of polymeric additives is believed to result primarily from their adsorption on developing nuclei and crystal faces to act as an immobile impurity significantly inhibiting continued growth, although some sequestration interactions are likely also present [17,18]. Polymeric treatments commonly used as antiscalants include poly(acrylic acids), poly(maleic acids) and heteropolymers containing acrylic and maleic acid monomers. In addition to the apparent requirement of regularly spaced acid groups, efficacy of a polyacid in inhibiting development of crystalline phases appears strongly dependent on molecular weight. For carboxylic acid containing polymers, it is reported that precipitation inhibition is greatest for molecular weights of less than about 20,000, with the optimal molecular weight being dependent on the particular polyelectrolyte and salt being formed [19,20].

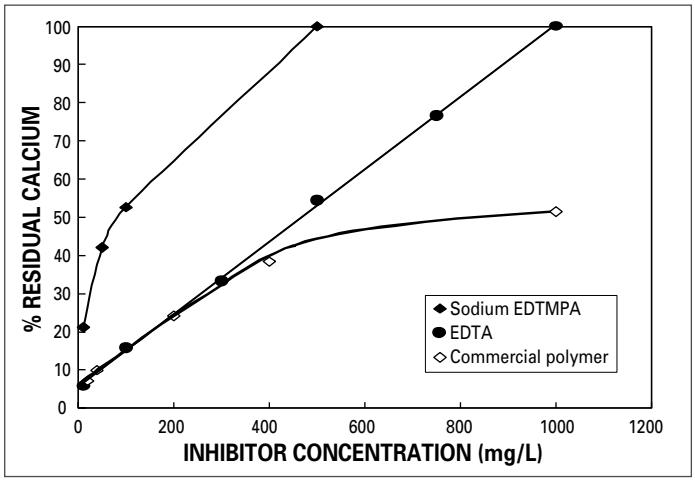
As part of this study, the influence of 3 carboxylic acid containing polymers on laboratory kraft cooks was examined. The polymers included a sodium poly(acrylate), a poly(maleic acid), and a commercial product commonly used for digester scale problems, which is believed to be a heteropolymer composed primarily of acrylic and maleic acid monomers. The sodium poly(acrylate) and poly(maleic acid) used here were at or near their optimal molecular weights for inhibiting $CaCO_3$ precipitation (based on prior studies). **Figure 5** shows the influence of these polymers on the dissolved calcium concentrations in kraft cooks. The curves were measured at polymer concentrations of 50 mg/L in white liquor (on an active acid basis for the two homopolymers and a solids basis for the commercial polymer). From the figure it appears that this dosage of additives has only a small effect on the conditions (i.e., temperature and calcium concentration) necessary to induce precipitation and on the rate at which the calcium is depleted from the liquor. The modest influence of the carboxylic acid containing polymers shown here is in contrast to the strong inhibition effect commonly reported under milder temperature conditions [5]. We found that the ability of carboxylic acid containing polymericantiscalants to inhibit precipitation is mostly lost as temperatures near those found in kraft pulping. The cause of this temperature dependency is unclear. **Figure 6** shows the influence of the commercial product for a range of dosages on a product basis. As the concentration is increased, so is the influence of the additive; however, it appears that prevention of calcium precipitation is not possible with this polymer. Although polyacids are believed to function in part via mechanisms characteristic of threshold treatments, the results here indicate that concentrations similar to that required for the sequestration mechanism are necessary to influence precipitation.

### *Influence of organophosphonic acids on calcium carbonate precipitation*

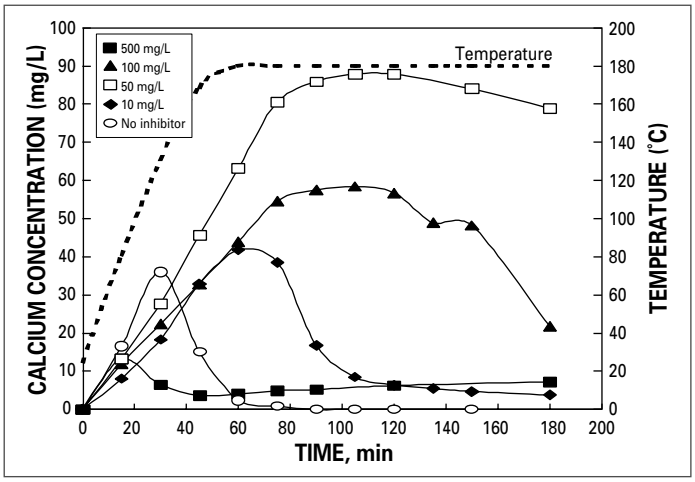
**Figure 7** shows the influence of several organophosphonic acids on kraft cooks at active acid concentrations of 50 mg/L in the white liquors. The curves demonstrate the high level of $CaCO_3$ precipitation inhibition that is achievable with certain organophosphonates at relatively low concentrations. Organophosphonic acids used in industrial applications to control scale can be described as organic molecules that usually possess two or more phosphonic acid groups. Organophosphonic acids are stable at high pH and temperature, which may explain their effectiveness under digester conditions. In general, these species provided the best inhibition efficiency under kraft pulping conditions of additives tested for this study. This is exemplified in **Fig. 8**, which shows the influence of sodium EDTMPA on the dissolved calcium curves in kraft cooks for a range of additive concentrations. A concentration as low as 10 mg/L in white liquor produces a significant increase in the temperature and dissolved calcium concentration required for the onset of precipitation and a slowing of dissolved calcium depletion from the liquor once precipitation has begun. **Figure 9** shows the percentage of dissolved calcium concentration remaining in the cooking liquors subsequent to 180




*8. Kraft cooks carried out in the presence of no inhibitor and sodium EDTMPA at various initial concentrations in the white liquors.*




*9. Residual calcium concentrations in the digester liquors as a function of additive concentrations for EDTA, sodium EDTMPA, and the commercial polymer (on an active acid basis for EDTA and sodium EDTMPA and a solids basis for the commercial polymer).*




*10. Kraft cooks carried out in the presence of no inhibitor and sodium HEDP at various initial concentrations in the white liquors.*

min kraft cooks as a function of additive concentrations for EDTA, sodium EDTMPA and the commercial carboxylic acid containing polymer. The concentrations of EDTA and sodium EDTMPA are in terms of active acids, while the polymer concentration is provided on a solids basis due to a lack of information on the specific formulation. The figure demonstrates the greater efficiency provided by the organophosphonic acid.

Organophosphonic acids are believed to function through adsorption onto developing nuclei and crystals to inhibit further growth [15]. Although it is not clear whether the classical nucleation theory remains applicable when a threshold treatment is present, studies have interpreted the influence of organophosphonic acids on the nucleation of inorganic salts in terms of Eq. 1. It has been suggested that their influence is to increase the argument of the exponential (i.e., the free energy of nucleus formation) slowing the nucleation rate [21]. Adaptations of growth models for interpreting the influence of threshold treatment on seeded growth of calcium carbonate suggest that additives adsorb at active growth sites on crystal surfaces blocking them and decreasing the rate constant for growth [15]. Although the mechanism of their influence is not entirely clear, it is apparent from the data that organophosphonates provide significant inhibition of $CaCO_3$ formation under digester conditions. One potential problem with the use of organophosphonates is their solubility in the presence of calcium. As seen in **Fig. 10**, the influence of sodium HEDP on the precipitation of calcium decreases at higher concentrations. This is believed to be a result of its precipitation with calcium. In practice, formation of an insoluble complex with calcium is only a problem if the precipitate produces or contributes to deposits. However, even if this is not the case, the formation of the complex means the chemistry is not providing the sought after threshold effect. Care must be taken to select an additive and dosage that is stable under the conditions of the application.

## SUMMARY AND CONCLUSIONS

In this study, we examined the influence of various organic additives on the tendency of calcium carbonate to precipitate during kraft pulping reactions. These included an aminocarboxylic acid, several carboxylic acid containing polymers and several organophosphonic acids. Aminocarboxylic acids are well known sequesterants and their influence on the nucleation and growth is easily understood in terms of classical nucleation theory and growth models as a reduction in the calcium that is available to drive such processes. Species such as EDTA are effective at controlling CaCO3 scaling processes, but the required concentrations under typical kraft pulping conditions likely make this treatment prohibitively expensive. The threshold effect of carboxylic acid containing polymers such as poly(acrylic acids) and poly(maleic acids) in controlling CaCO3 precipitation is well documented. However, at kraft process temperatures much of the influence of these treatments appears lost. Their effects increase with increasing dosages, but the concentration required to significantly inhibit calcium precipitation are similar to those used for the sequestrant treatments. Many of the organophosphonic acids tested for this project demonstrated significant efficiencies. These were the only additives tested that demonstrated the threshold effect in laboratory kraft cooks with relatively low concentrations providing a significant delay in the onset and slowing the rate of precipitation. These results

indicate that organophosphonic acids may provide a tool for controlling calcium carbonate scaling under kraft process conditions. **TJ**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## *2002 Van den Akker Prize awarded for study on stress-strain measurement*

TAPPI and the Institute of Paper Science and Technology (IPST) have awarded the 2002 Van den Akker Prize for Paper Physics to Niclas Stenberg, Christer Fellers, and Sören Östlund from the Swedish Pulp and Paper Research Institute (STFI) and KTH, Sweden's Royal Institute of Technology. An international panel of judges selected their paper, "Measuring stress-strain properties of paperboard in the thickness direction," from the June 2001 *Journal of Pulp and Paper Science*, as the most significant contribution to the field of paper physics this year.

The authors described a modified Arcan device for measuring stress-strain properties in the thickness direction of paperboard. The device is used for out-of-plane tensile compression and shear loading. This is one of the few investigations to describe the out-of-plane, or Z-direction, normal, and shear properties, and combinations of these loadings. The modified device enables further knowledge of paper deformation. It is a significant step forward compared to other test methods.

The key modification of the original Arcan device was to the fixture, which restricted the movement by omitting all rotations, and allowing movement in only two of the principal directions in order to measure stress and strain accurately. A method for determining the penetration of the glue used to attach paperboard to the device was developed in order to find the true strain in the material.

Stenberg is an associate in paper physics at STFI. His thesis studies concerned mechanical properties in the thickness direction of paper and paperboard.

Fellers has devoted his scientific career to providing the paper industry with relevant and well-defined methods for testing the mechanical properties of paper and corrugated board, including the STFI Short-span Compression Test-SCT, or simply "STFI." He is currently research leader and professor at KTH Paper Technology, which is associated with STFI.

Östlund is a professor in packaging technology in the Department of Solid Mechanics at KTH. He received a Ph.D. in solid mechanics from KTH in 1989. He worked as a scientist at the Swedish Institute of Composites and then returned to KTH in 1991 as a senior lecturer.

The Johannes A. Van den Akker Prize for Advances in Paper Physics was established in 1999 by IPST, with an endowment from the generous donations of the family, friends, and students of Van den Akker, a former senior research associate and chairman of the Department of Physics and Mathematics at the Institute of Paper Chemistry (IPC). The prize recognizes the best contribution made to the field of paper physics and to the paper industry. It is awarded annually through TAPPI's Paper Physics Committee, of which Van den Akker was a member for many years. Van den Akker was known for his brilliant mind, demand for excellence, and leadership in the field of paper physics for over 40 years. His paper, "General discussion of the measurement of adhesion and cohesion," *Tappi* 35(4):155A-162A (1952), was used as a reference in the winning paper. **TJ**