

ANTI-SCALING AGENTS IN KRAFT PULPING

Fernando E. Felissia,¹ María C. Area,² Olga M. Barboza,¹ and Dora I. Bengoechea¹

Scale formation in the digester during kraft pulping represents a great problem in pulp mills. Scaling reduces pulping control and efficiency, increasing energy costs and leading to cleaning breakdowns, with subsequent losses in productivity. The kraft process promotes CaCO_3 scaling due to high calcium ion and carbonate concentrations, as well as high alkalinity and temperature levels, which increase the speed with which liquors reach a state of supersaturation. This work examines the action of diethylene triamine penta(methylene phosphonic acid) (DTPMPA), either alone or combined with commercial anti-scaling agents, as an inhibitor of calcium carbonate precipitation in the kraft pulping of *Pinus taeda*. The theoretical amount of calcium deposited in the digester was obtained by mass balance. Soluble calcium was stable throughout cooking when using the phosphonates alone or combined with anti-scaling agents. When adding only DTPMPA, calcium stays in the pulp, rather than forming deposits.

Keywords: Anti-scaling agents, *Pinus taeda*, Kraft cooking, Calcium - Phosphonates

Contact information: ¹ Investigators. ² Directora. Programa de Investigación de Celulosa y Papel - FCEQyN – Universidad Nacional de Misiones - Félix de Azara 1552, (3300) Posadas, Misiones, Argentina. Tel/Fax: 54-3752- 422198. Contact: m_c_area@fceqyn.unam.edu.ar

INTRODUCTION

Scale formation in the digester during kraft pulping reduces productivity, since it reduces the efficiency of pulping, increases energy costs, and increases the duration of downtime taken for cleaning of equipment (Guo and Severtson 2004). Dissolution of saline compounds in water forms solvated cations and anions. Generally, an increase in water temperature produces an increase in solubility in most salts. Important and noticeable exceptions are CaCO_3 , CaSO_4 , and $\text{Mg}(\text{OH})_2$, which turn less soluble when temperature increases (Kemmer and McCallion 1993). The main source of calcium is wood, followed by white liquor. The quantity of calcium released in cooking depends principally on the wood species and the quantity of bark entering the system. In the washing of brown pulp, only a 5% reduction of calcium in the pulp is obtained. Carbonate comes from various sources, from the decomposition of lignin-carbohydrate complexes, from the decarboxylation of hemicelluloses during pulping, from black and white alkaline liquors, from the incomplete clarification of liquor, from fresh water, and from the atmosphere (Barata and Candelas 1997). The kraft process, due to its operating conditions of high alkalinity, high temperatures, and high pressures, promotes CaCO_3 scaling. As the pH of a solution containing carbonate anion increases above 8, the predominant species in the solution is the carbonate ion (Manji, A., and Kaagiannis, J. 2005). Deposits are produced due to the fact that the saturation limit of CaCO_3 is

exceeded in the aqueous medium of the process, due to changes in temperature and pressure (Severtson et al. 1999).

Practically all of the materials present in the process (wood, water, limestone, others) contribute to the formation of deposits. Wood is a source of calcium, potassium, magnesium, silica, manganese, iron, aluminum, and sodium. Limestone possesses calcium, magnesium, strontium, etc. An analysis of the scaling in a white liquor preheater showed deposits containing 13 and 87% inorganic and organic materials, respectively. The inorganic portion included 41% of calcium and magnesium carbonates. Caustic deposits in the pipes contained more than 74% of inorganic materials (Stopka et al. 1987).

Scaling in the kraft pulping processes occurs as a result of the presence of organic ligands (Fader et al. 2005). Lignin fragments formed during pulping (especially those containing phenolic hydroxyls groups) have a high tendency to interact with the calcium, increasing its solubility in the black liquor. As long as the temperature increases, the pH tends to decrease, and the calcium ions are partially displaced from the lignin by the hydrogen ions. Thus, these react with the carbonate ions, resulting in calcium carbonate scaling.

In addition to lignin, different organic species are found that also complex the calcium in the black liquor (Fader et al. 2005). Together with the calcium and carbonate, black liquor normally contains other ions, such as sulfate, which can precipitate and form scale. Scale formation mechanisms of calcium carbonate include nucleation, crystal growth, and the addition of particles, which form the deposit.

For the treatment of pulping and bleaching process streams, the performances of additives in the presence of other dissolved organics are important because these liquors contain extracted wood polymers that can also interact with calcium and carbonate to affect nucleation and crystallization processes (Guo and Severtson 2004).

A study of the behavior of metallic ions in kraft pulping shows that the Mg and Mn concentrations increase continually in the liquors, while Ca concentrations increase to a maximum value and decrease rapidly, probably due to the precipitation of CaCO_3 in fibers and on metallic surfaces. Authors have suggested that as temperature increases, the concentration of Ca increases up to the supersaturation level necessary to initiate the precipitation, followed by a rapid fall in the Ca concentration up to its solubility limit. This shows that when the Na_2CO_3 concentration increases in white liquors, the calcium maximum concentration necessary for the precipitation decreases. Moreover, the CaCO_3 precipitation is produced even if initially there is no CaCO_3 in the white liquor. This is due to the carbonate generated by the uronic acids formed by the decarboxylation of hemicelluloses soluble in water (Guo and Severtson 2002).

Chemical treatments known as antiscalants impede mechanisms that result in the formation of crystalline deposits (Guo and Severtson 2004). Chelants or sequestering agents have been usually used to prevent the deposition, precipitation, and crystallization of calcium carbonate in water systems. Other types of reagents have been studied as threshold inhibition agents. These include water-soluble organic polymers, phosphonates, and polyphosphates. Organic polymer anti-scalants include products derived from acrylamide, maleic acid, vinyl acetate, vinyl alcohol, and acrylic acid. The list also

includes polyarilamines, with phosphonic, carboxylic, or sulfonic groups (Fader et al. 2005).

Guo and Severtson (2003) have described the influence of both molecular and polymeric carboxylic acid containing additives on the nucleation of CaCO_3 in solutions representative of process liquors found in the production of wood pulp. Studying aminocarboxylic acids as ethylenediaminetetraacetic acid (EDTA) and diethylene-triaminepentaacetic acid (DTPA), they found that parameters for the fit of nucleation data in the presence of these chelants were the same as those found when no additive was present.

In addition to the apparent requirement of regularly spaced acid groups, the efficacy of a polyacid in inhibiting nucleation and growth of crystalline phases appears strongly dependent on molecular weight (Loy et al 2004).

Polymeric anti-scalants work primarily by one or more of the following three mechanisms: threshold inhibition, crystal dispersion, and crystal modification (Duggirala 2005). Threshold inhibition occurs when an adsorbed anti-scalant blocks the active sites of crystal growth. Crystal dispersion is a mechanism by which agglomeration and growth of microcrystals is avoided by an increase in the surface anionic charge. Crystal modification is produced when the adsorbed anti-scalant alters the morphology of the microcrystal in the process of growing, resulting in crystals with irregular shape. These deformed crystals inhibit the growth of a regular crystalline lattice. In all cases, polymers avoid the formation of a layer of adherent scale.

The ability of aminophosphonates to inhibit CaCO_3 nucleation and crystal growth kinetics under high temperature and high pH conditions is based on adsorption, as these species are known to adsorb strongly to a wide variety of mineral surfaces including CaCO_3 (Guo and Severtson 2004).

This work studied the diethylene triamine penta(methylene phosphonic acid) (DTPMPA) chelant and commercial anti-scaling agents (alone or combined with the chelant), as inhibitors of CaCO_3 precipitation. The evolution of the content of total and soluble calcium in the black liquor during cooking was followed. The theoretical calcium deposited in the digester was obtained by mass balance.

MATERIALS AND METHODS

Raw Materials

Pinus taeda chips supplied by Alto Paraná S.A. were screened, accepting the fraction retained on a 5x5 mm screen and the fraction passing through a 25x25mm screen. The bark and the knots were manually discarded. White liquor was prepared using NaOH, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, and Na_2CO_3 (all of analytical grade) to control the quantity of Ca introduced to the system.

The anti-scalant polymers Dequest 9020 (modified polyacrylic acid, sodium salt), Dequest 9030 (sulphonated polyacrylic acid copolymer), and DTPMPA (sodium salt of diethylene triamine penta(methylene phosphonic acid)) in aqueous solution were supplied by Solutia Inc. (St. Louis, Missouri). All products assayed were commercial anti-scaling agents. They were cataloged as: A (Dequest 9020), B (Dequest 9030), C and D (both

sodium acrylate / maleic anhydride copolymer from different manufacturers). The concentration of DTPMPA (diethylene triamine penta(methylene phosphonic acid), Q) tested (2kg/t dry wood, or 0.2 %) is given in terms of active acid. The other products were added according to recommendations of the manufacturers.

Cooking

Kraft cooks were carried out in a 7L MK digester using a condenser for sample taking, with the system under pressure. Before cooking, the digester was washed with acid, circulating a solution of H₂SO₄ (10% v/v) during 10 minutes, and rinsing with deionized water. The cooking conditions were: liquor-wood relationship (5:1), active alkali: 24% OD wood (NaOH basis), sulfidity: 35 % (relative to active alkali), maximum temperature: 170°C, impregnation time: 60 min; H Factor: 2000, and Na₂CO₃: 10g/L.

The time 0 to 70°C was recorded, and a 20 ml sample was extracted from the digester, corresponding to the beginning of cooking. Every 20 minutes the temperature was recorded, and 20 ml liquor samples were taken in plastic flasks. A complete condenser relief was carried out after each sampling. Ten samples were extracted per cook. Pulpes were washed with deionized water.

Pulpes were screened by a 0.15 mm slit width screen and they were characterized by viscosity (Tappi T236 om-99) and kappa number (Tappi T230 om-99).

Calcium Monitoring

The method of calcium determination was adapted from the work of Guo and Severtson (2002). For the total calcium determinations, 2mL of samples were transferred to centrifugal tubes, adding 10 ml of an HCl 4% solution, stirring and centrifuging during 15 min at 2900 rpm. The supernatant (a solution of CaCl₂), was collected in a 10 ml test tube (acid washing, rinsing, and drying). For the determination of soluble calcium, 5 ml samples were filtered using a nylon mesh (0.45 µm pore), when calcium insoluble salts are retained (such as CaCO₃ and CaSO₄), passing the soluble Ca into alkali. Over the filtrate, the process was similar to that used for the determination of total calcium. Suspended calcium was obtained through the difference between total calcium and soluble calcium.

Metals in Pulp

For the determination of the Ca, Mg, Fe, Cu, and Mn contents in pulp, 4% HCl was added to a fraction of 5 grams pulp of 2% consistency, during one hour. Subsequently, the pulp was filtered with a Büchner funnel, and the filtrate was analyzed.

Calcium Balance

Calcium concentrations were determined in white liquor, wood, pulp, black liquor, pulp wash-water, and in the acid solution with which the digester was washed. All metals were determined by atomic absorption spectroscopy with a Perkin Elmer Analyst 200 model (Perkin Elmer web page).

Results

Cooking results are presented in Table 1.

Table 1: Results of Cooking With and Without Anti-Scaling Polymers

	Total yield	Screened yield	Rejects	kappa n°	Viscosity
	(%)	(%)	(%)		(cp)
Control*	46.8	46.1	0.68	23.6	32.4
A (0.05 %)	45.6	44.6	0.99	26.4	32.4
B (0.05 %)	45.1	44.9	0.18	24.9	32.2
C (0.012 %)	45.1	44.4	0.65	24.6	31.0
D (0.12 %)	46.3	45.7	0.68	25.6	32.1
D (0.012 %)	46.8	46.0	0.80	26.0	30.5
Q (0.2 %)	46.6	45.5	1.03	23.8	33.0
A (0.05 %) + Q 0.2	46.7	46.2	0.53	24.4	33.0
B (0.05 %) + Q 0.2	46.3	45.8	0.49	27.0	33.4

*Control = Cooking without anti-scaling nor chelant polymer aggregate

It can be appreciated that the presence of A, B and C polymers produced a slight yield loss. The chelant alone did not affect the characteristics of delignification and degradation of pulps, while polymers decreased delignification. C and D polymers produced a viscosity decrease. The main source of calcium entering the system was wood (750 ppm), followed by white liquor (6 ppm). The metal content in pulps is presented in Table 2.

It was observed that polymer D in the 0.012% dosage level did not modify the content of Ca in the pulp, when compared to cooking without additives. When the dose was increased to 0.12%, a reduction in the content of Ca of about 270 ppm was produced, comparable to the reduction produced by polymer C, but with a 0.012% charge (230 ppm). A similar reduction was obtained with polymers A and B (292 and 353 ppm respectively). A significant reduction was obtained when the chelant was added together with polymers A and B (722 and 928 ppm respectively). The polymers analyzed decreased the content of Mg, Fe, and Cu in pulps, as compared with those of the control pulp. On the other hand, Mn levels decreased solely in presence of the chelant. This can be of great importance if there are subsequent bleaching stages with oxygen and hydrogen peroxide.

Table 2: Metal Ion Content in Pulps (Cooking With and Without Anti-Scaling Polymers)

	Ca	Mg	Cu	Fe	Mn
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Control*	1322	329	4.75	20.2	38.4
A (0.05 %)	1030	216	3.53	10.2	45.0
B (0.05 %)	969	214	2.91	10.8	43.1
C (0.012 %)	1089	213	2.55	9.91	47.8
D (0.12 %)	1048	207	1.92	5.23	44.7
D (0.012 %)	1323	139	1.42	14.0	48.7
Q (0.2 %)	1043	426	2.35	5.29	17.0
A (0.05 %) + Q 0.2	600	243	3.58	8.52	14.1
B (0.05 %) + Q 0.2	394	160	n.d.	8.10	15.7

*Control = cooking with and without anti-scalant nor chelant polymers aggregate

Figures 1 and 2 show the evolution over time of total and soluble calcium in the cooking liquors.

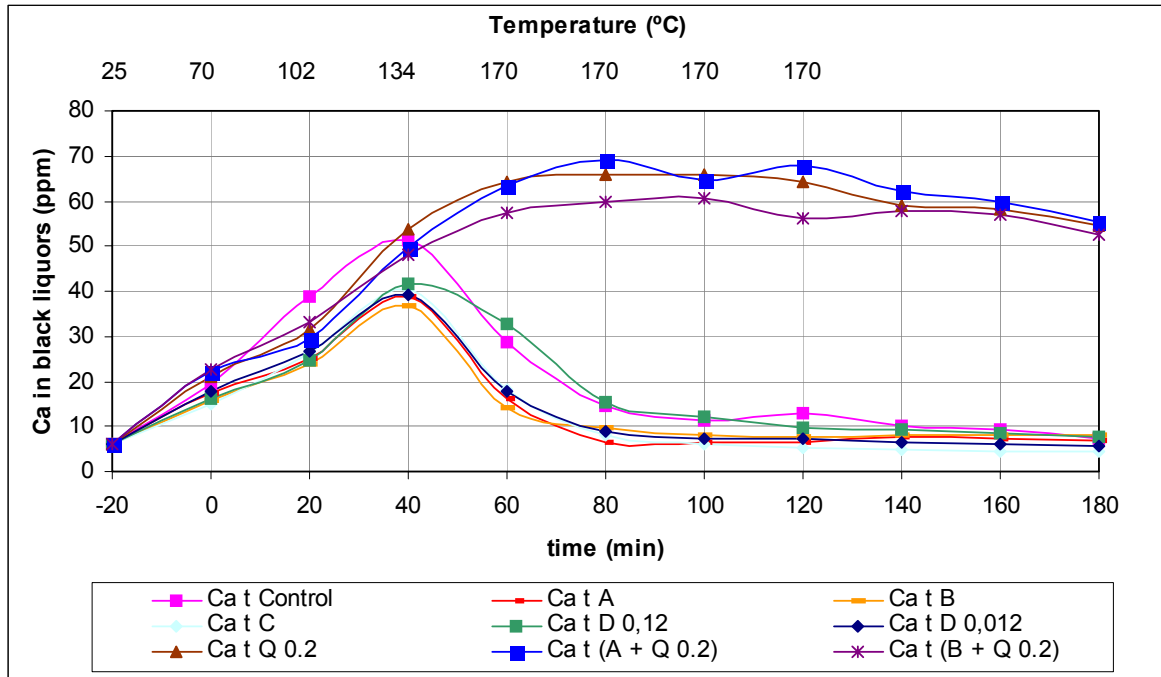


Figure 1: Total calcium content in the samples of black liquors obtained in cookings with DTPMPA and polymers

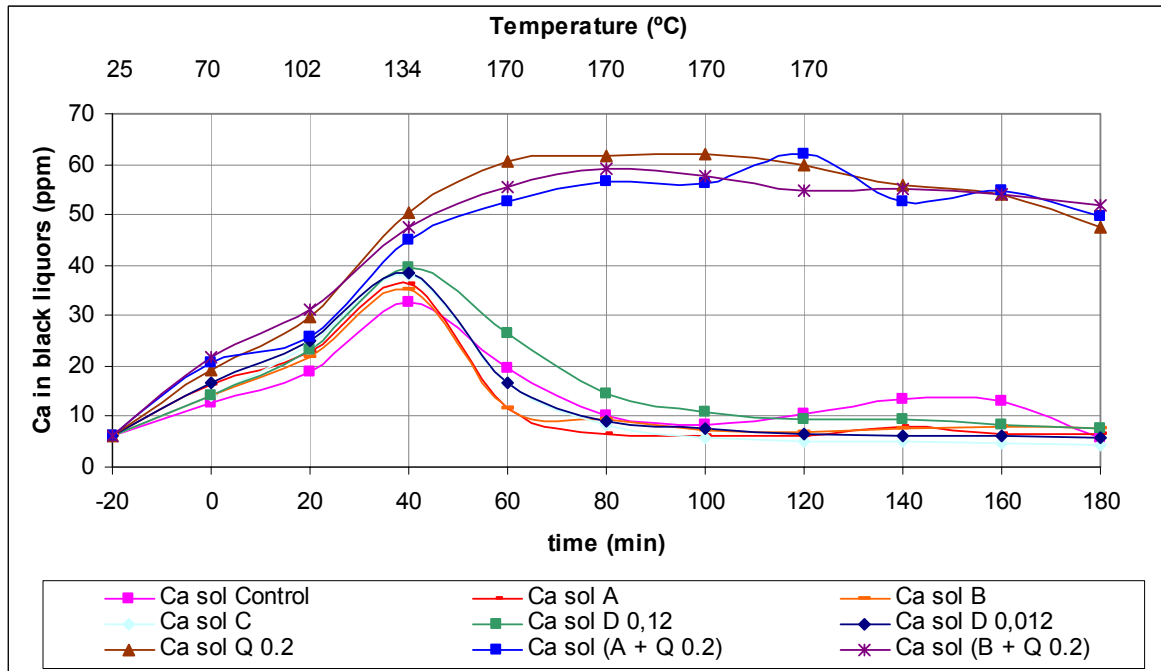


Figure 2: Soluble calcium content in the black liquor samples obtained from cookings with DTPMPA and polymers

Figure 1 shows two different behaviors of the evolution of total calcium in the liquor extracted during cooking. The first group included all the cooks incorporating DTPMPA. In this case, total calcium was observed to increase during the first 60 minutes, and then to remain practically constant, staying in the liquor during the entire process.

Soluble calcium showed similar behavior (Fig. 2), with a difference of approximately 5% in the total calcium (in most cases), which represents the suspended calcium. Curves appear similar to those reported by Severtson (1999) for similar products having comparable concentrations. The behavior of magnesium is presented in Fig. 3.

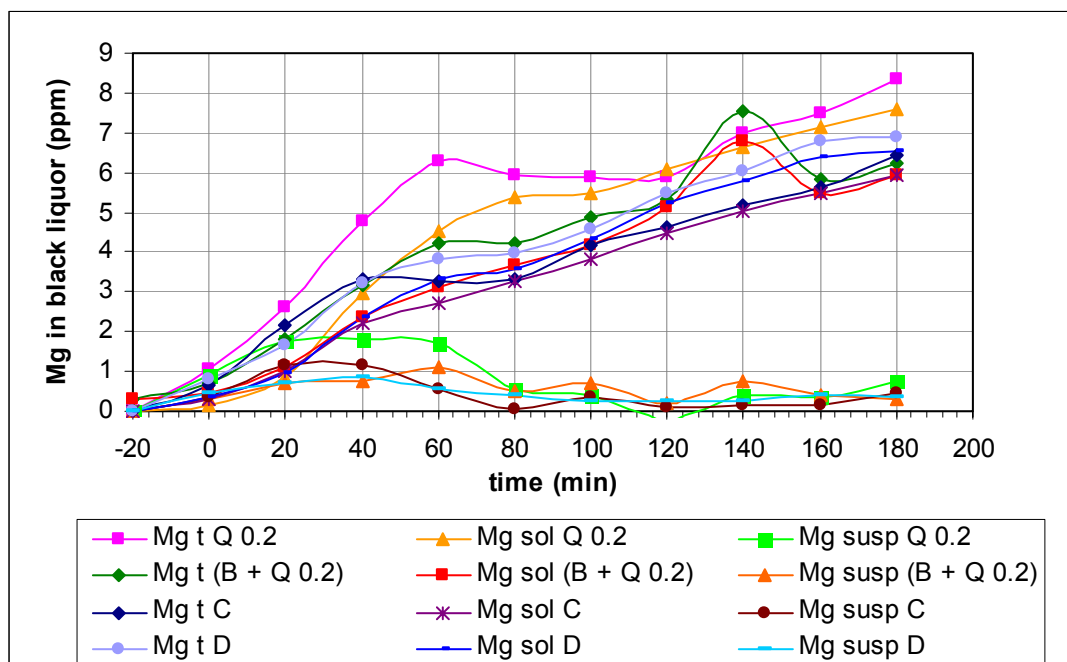


Figure 3: Total, soluble, and suspended magnesium in liquor samples (cookings with DTPMPA and polymers)

The second group comprised the control cooks (without additives) and cooks with the A, B, C, and D polymers. It was observed that total calcium increased, with a maximum after 40 minutes (135°C). After this point, it decreased until it almost disappeared from the liquor. This behavior can be explained through two hypotheses. Either the calcium re-precipitates onto the chips, or it is deposited onto the walls of the digester. In the latter case, it might be a hard deposit, or rather it might have a soft nature, not forming adherent scaling.

It can be observed that magnesium values were proportionally very low in the liquor samples, and suspended Mg, in a form susceptible of generating scaling, was minimal during the cooking. Figure 4 presents the final concentration of Ca (ppm) in pulps and final black liquors of all cooks.

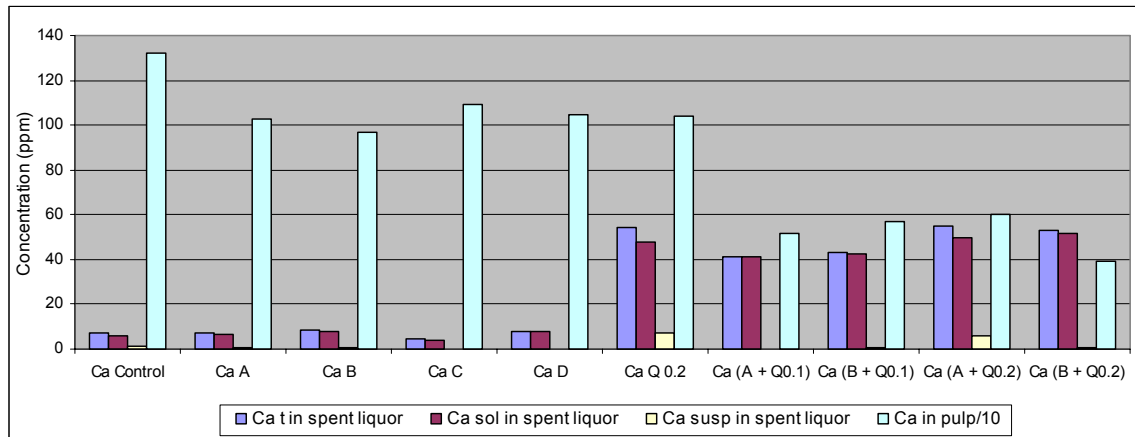


Figure 4: Concentration of Ca (ppm) in pulps and black liquors of all cooks

It can be seen that the chelant alone and the chelant combined with polymers A or B polymers increased the calcium concentration in the final black liquor. The quantity of suspended calcium reached a significant stage with the use of DTPMPA alone and of polymer A with 0.2% of DTPMPA.

Figure 5 shows the mass balance for the total calcium in all cooks. To perform this, the concentration of Ca in the liquor, within and outside of the chips after 180 minutes of cooking was assumed to be similar.

The calcium balance depended on whether the different products were applied alone or combined (Fig. 5). The calcium content of the pulps treated with DTPMPA alone and with all the polymers applied individually was approximately 22% less than the control (except for the case of polymer D at 0.012% concentration). On the other hand, the combination of anti-scaling products with DTPMPA extracted a great quantity of calcium from the pulps, transferring it to the liquor. This effect indicates an important interaction between the polymers and the chelant.

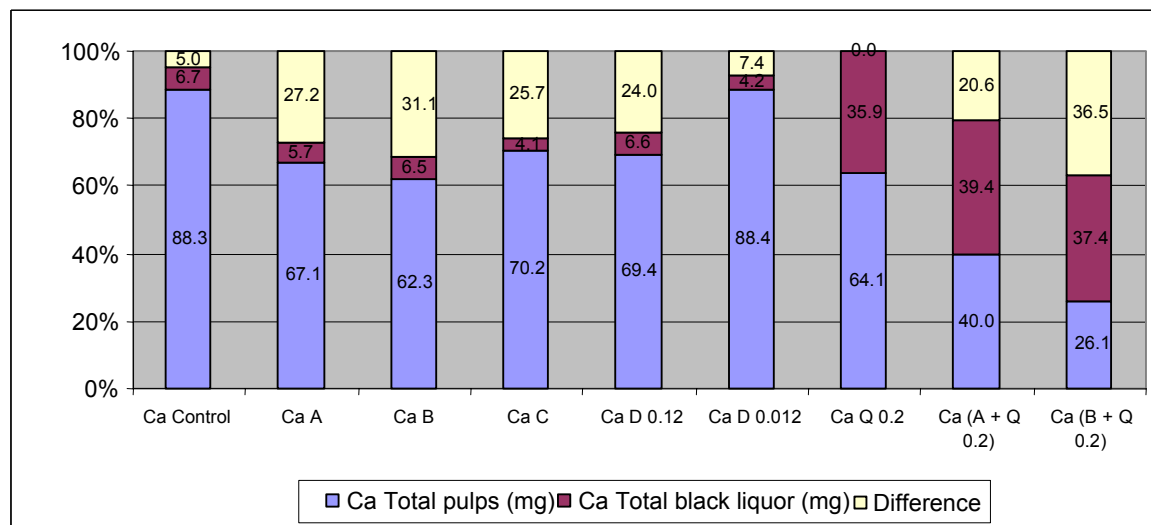


Figure 5: Mass balance for the total calcium in cooking with DTPMPA and anti-scaling polymers

This behavior can produce some practical implications. When DTPMPA is present, a great part of the calcium and also other metallic ions are extracted from the pulps. This is beneficial to the bleaching system, mainly the oxygen stage. Most of the calcium passes then to the recovery system. As the structure of the CaCO_3 -polymer complex is assumed to be stable, no problems are expected to occur in the evaporators. Theory indicates that phosphonates act as polymers, inhibiting the growth of the crystals through adsorption on the nuclei and the crystals under development (Guo and Severtson 2002). Hence, we can presume that the stability of the CaCO_3 -DTPMPA particles is similar to that of the CaCO_3 -polymer.

When DTPMPA alone was added, the non-detected calcium fraction was minimized (“difference” in the pulp or in the liquor). When polymers were combined with DTPMPA, the greatest extraction of calcium from the pulp occurred, indicating an important interaction between both types of additive.

Since a similar behavior was observed in the cases in which polymers were used alone, or were combined with DTPMPA, we tried to identify the destination of the non-detected calcium (difference). To verify the calcium losses in the laboratory washing system, after extracting black liquor, the cooked chips were disintegrated at 6% consistency, filtered, and rewashed twice, at 6 and 2% consistency. Table 3 and Fig. 6 present the mass balance of total calcium in the cooking carried out with 0.012% of anti-scalant polymer D. It should be made clear these results are valid only in our laboratory system. This is because, due to the absence of a blow-tank, the quantity of remaining liquor inside the chips is important.

Table 3: Calcium Balance in Cooking with Anti-Scaling Polymer D (0,012%)

Balance/ kg wood*	mg Ca
Black liquor	14,6
Pulp washing	140,3
Pulp	608,6
Acid washing digester	5,4
Difference	4,1

* Ca Entry = 773 mg (wood: 750 mg; liquor: 24mg)

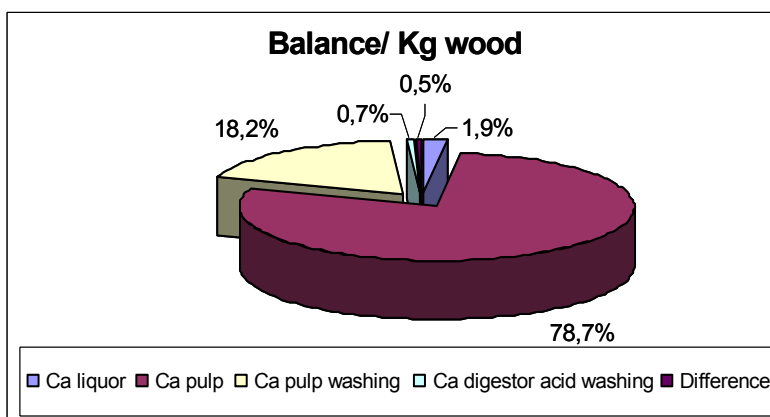


Figure 6. Pie chart of calcium balance in cooking with anti-scaling polymer D (0,012%)

It is clear that in the absence of chelant during the cooking, most of the calcium remains in the pulp. Going back to the hypothesis of disappearance of the liquor calcium (Figures 1 and 2), it is observed that 18% approximately is found on the pulp, and is easily extracted by water washing, whereas a 0.7% was deposited on the walls of the digester (probably, an adherent scaling), being susceptible to extraction solely by acid washing.

Another experiment simulated a system with high calcium content, without pulp. The system comprised black and white liquor and Ca until an initial concentration of 88 ppm. The concentrations of polymer D and chelant (24 and 200 mg/L respectively) were the same ones used in the previous experiences (calculated as if there had been pulp in the system). Samples were extracted every 20 minutes, to evaluate total, soluble and suspended calcium in the liquor. At the end of the experiment, the digester was washed with water and acid. The balance shows the quantification of the total calcium present in the liquor, water and acid (figure 8).

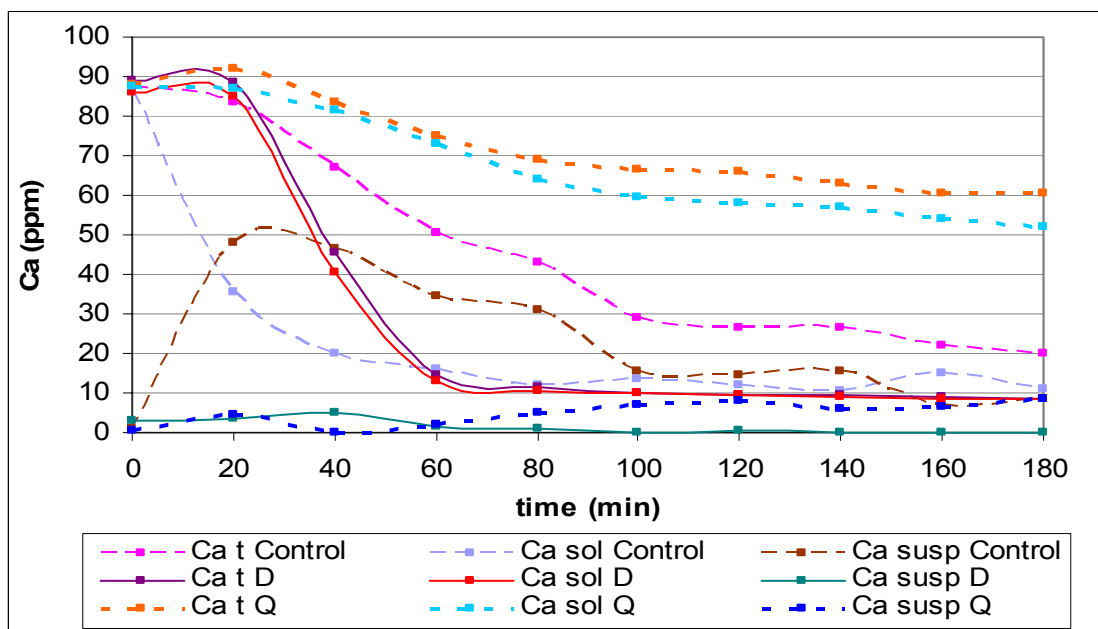


Figure 7. Total, soluble, and suspended calcium in liquor samples (cooking without pulp, with DTPMPA and D polymer)

Total and soluble calcium concentrations decreased in the period between 20 and 60 minutes (maximum temperature). The similarity of the two curves indicates that there was no suspended calcium in the system. A similar behavior, although less intense, was observed in the control experiment, but with an important amount of suspended Ca. In the treatment with chelant, total and soluble calcium decreased at the end of the treatment. The suspended Ca was similar to the control treatment.

Table 4 shows the Total calcium balance at the end of the experiences.

Table 4: Calcium Balance in the Simulated Experiment with Anti-Scaling Polymer D (24 mg/L) and chelant (200 mg/L)

Balance/ kg wood*	Control (% Ca)	Polymer (% Ca)	Chelant (% Ca)
Black liquor	52,7	15,9	73,3
Water washing	21,2	6,0	11,8
Acid washing digester	26,0	78,1	14,9

* Ca Entry = 88 mg/L

It is clear that chelant maintained calcium in the liquor phase, while polymer D resulted in deposition on the digester walls.

CONCLUSIONS

- Using laboratory techniques, the operation of anti-scaling products can be evaluated. However, other methodology is required to determine the nature of the suspended calcium and its participation in the cumulative process leading to the formation of a layer of adherent scale.
- Diethylene triamine penta(methylene phosphonic acid) (DTPMPA) acts also as anti-scaling agent in a way similar to that of polymers.
- Without additives (control), most of the calcium remained in the pulp, in a way similar to that in the presence of polymers or with DTPMPA alone, however at a lower proportion.
- In cooking without additives (control) and with polymers alone, it was observed that total calcium in the liquor increased up to a temperature of 135°C (where supersaturation occurs) and then decreased (due to the precipitation of CaCO₃), keeping at very low concentrations during the rest of the process. Soluble calcium showed a similar behavior, with an approximate difference of 5% in most of the cases (attributed to suspended calcium).
- When polymers were combined with DTPMPA, an important interaction was observed, increasing noticeably the quantity of calcium extracted from the pulps. Final pulps presented no differences in yield and viscosity with respect to the control.
- When using the phosphonate alone or combined with the anti-scaling agents studied, soluble calcium remained stable during the pulping. This could allow us to suppose that the highest Ca concentration in black liquor going to evaporation will not produce scaling in the system. On the other hand, the reduction of Ca content in the pulp could reduce the calcium oxalate deposits in subsequent stages of pulp bleaching.
- The quantity of calcium suspended in the liquor became significant only with the use of DTPMPA alone or polymer A with 0.2% DTPMPA.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Ind. Chemist Isabel C. Silva and Pablo Pezzano from Solutia Inc., as well as Dr. Alberto Venica and Alto Paraná S.A. The technical team was represented by Ing. Julieta Benítez. Chem Eng. Students included Mirta Morrone and Cristian Alfonso.

This article first appeared in the proceedings of the 4th Congreso Iberoamericano de Investigación en Celulosa y Papel, CIADICYP-2006, which was held in Santiago and Valdivia, Chile between October 23 and 27, 2006. By agreement with the organizers, selected articles from the conference were submitted to *BioResources*, subject to the usual peer-review process.

REFERENCES CITED

- Barata, P. A., and Candelas, C. F. (1997). "Calcium and magnesium balance in an unbleached fibre line: A mill case," *Appita J.* 50(6), 505-508.
- Duggirala, P. Y. (2005). "Formation of calcium carbonate scale and control strategies in continuous digesters", CD del II Coloquio Internacional sobre Celulosa de Eucalipto, Concepción, Chile, Mayo.
- Fader, M. K., Nguyen, D. T., Wang, X. H., Zhang, F., and Ling, T-F. (2002). "Methods of preventing scaling kraft involving inorganic compositions, and inorganic compositions therefore" *United States, HERCULES INCORPORATED 20020071783*, Url: <http://www.freepatentsonline.com/20020071783.html> (Consulted: 22/02/2005).
- Guo J., and Severtson S. J. (2002). "Influence of organic additives on calcium carbonate precipitation during kraft pulping," *Tappi J.* 1(8), 21-27.
- Guo J., and Severtson, S. J., (2003). "Application of classical nucleation theory to characterize the influence of carboxylate-containing additives on CaCO₃ nucleation at high temperature, pH, and ionic strength" *Ind. Eng. Chem. Res.* 42, 3480-3486.
- Guo J., and Severtson, S. J., (2004). "Inhibition of calcium carbonate nucleation with aminophosphonates at high temperature, pH and ionic strength," *Ind. Eng. Chem. Res.* 43, 5411-5417.
- Kemmer, F. N., and McCallion, J. (1992). *Manual del Agua. Su Naturaleza, Tratamiento y Aplicaciones*. Nalco Chemical Company. Tomo I. (ed.) McGraw-Hill. Capítulo 3, 4-5.
- Loy, J. E., Guo, J., and Severtson, S. J. (2004). "Role of adsorption fractionation in determining the CaCO₃ scale inhibition performance of polydisperse sodium polyacrylate" *Ing. Eng. Chem.* 43, 1882 – 1887.
- Manji, A., and Kaagiannis, J. (2005). "Inorganic scale buildup in a bleach plant-a mill study," *Tappi J.* 4(11), 29-32.
- Perkin Elmer, Inc., AAnalyst 200, Url: <http://las.perkinelmer.com/Catalog/FamilyPage.htm?CategoryID=AAnalyst+200+Spectrometer+Family>. (Consulted: 17/04/2007).

- Severtson, S. J., Duggirala, P. Y., Carter, P. W., and Reed, P.E. (1999). "Mechanism and chemical control of CaCO₃ scaling in the kraft process" *Tappi J.* 82(6), 167-174.
- Stopka, F., Kmet, L., and Gasparec, P. (1987). "Undesirable elements and deposits in a kraft pulp mill," *Papir Celuloza* 42(10), 241-244, 255.

Article submitted to journal: March 8, 2007; April 7, 2007; Revised version received: May 2, 2007; Accepted: May 2, 2007; Published May 4, 2007.