

ABSTRACT

The inhibition of the dissolution of papermaking grade precipitated calcium carbonate filler with sodium oxalate and phosphoric acid at pH 7.5 increased with inhibitor concentration. The saturation points for sodium oxalate and phosphoric acid were 1.0×10^{-2} mol/L and 0.5×10^{-3} mol/L. Oxalate ions inhibited the calcium carbonate dissolution in the entire range of pH studied. The inhibition was greater at lower pH. At an inhibitor concentration of 0.0014 mol/L and pH 7.5, the most effective chemical was phosphoric acid. The solubility of calcium ion was 80% lower than that in a solution without inhibitor. The authors also studied the inhibition of calcium carbonate dissolution by phosphoric acid in a CTMP suspension. For each level of precipitated calcium carbonate loading, a saturation point occurred, and the amount of phosphoric acid required to achieve the saturation point increased with the filler loading.

Application:

Phosphoric acid is an efficient inhibitor for the dissolution of precipitated calcium carbonate in water. It has the potential for use in PCC solubility control in papermaking suspension.

CALCIUM CARBONATE FINDS extensive use as a mineral filler in the alkaline papermaking process (1, 2). The presence of calcium carbonate fillers improves the optical properties of paper (3–5). Calcium carbonate fillers also enhance the bulk, formation, printability, and durability of a paper sheet. An economic incentive to use calcium carbonate filler as a substitute for expensive wood fibers also exists. Calcium carbonate has a low manufacturing cost, and precipitated calcium carbonate (PCC) is often available at a site close to a paper mill (6, 7).

Inhibition of the dissolution of papermaking grade precipitated calcium carbonate filler

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Both ground calcium carbonate (GCC) and PCC find use in filling paper. Due to irregular particle shapes and low surface area, GCC filled papers often have less brightness, opacity, and bulk than papers filled with PCC. These papers have a higher sheet strength and better drainage.

PCC can have different crystalline structures depending on its production. The most common forms are scalenohedral calcite, rhombohedral calcite, and acicular aragonite (3). The scalenohedral form of calcite imparts the most opacity and bulk on a sheet of paper due to its high internal pore voids. The voluminous nature of these particles significantly detracts from the drainage of the paper web and subsequently decreases the production rate of a paper machine. Use of the rhombohedral form of calcite is an attempt to reduce the impact on sheet drainage (8).

The pH strongly influences the solubility of calcium carbonate. The change of pH from alkaline to acidic conditions causes a dramatic increase in the solubility by several orders of magnitude. At alkaline conditions where the solubility of calcium carbonate is small, darkening of pulp may occur. The pH conditions for using calcium carbonate in papermaking therefore impose limitations. The application of calcium carbonate in acidic condition may become feasible if discouraging the dissolution of calcium carbonate is possible.

The inhibition of calcium carbonate dissolution is also important in wastewater treatment technology and the natural environment. This has

prompted the interest of several researchers who identified several chemicals that may inhibit the dissolution of calcium carbonate. Certain ions such as magnesium (9–14), ions of 1,2-dicarboxylic acids (15), oxalate ions (16), and orthophosphate (17–20) are the inhibiting chemicals. The general mechanism of inhibition proposed is adsorption of these ions on the surface of the calcium carbonate. This causes blocking of the dissolution sites of the surface lattice of calcium carbonate.

Previous work used laboratory synthesized calcium carbonate to conduct experiments with a fixed concentration of inhibitor. The measurements focused on the kinetics of dissolution. The aim of the study was to elucidate the mechanisms of action of the inhibiting ions. With this fundamental information, we wanted to use the inhibiting substances with commercial calcium carbonate filler at papermaking conditions to obtain practical information to improve engineering practice at mills.

In our work, we used a PCC of papermaking grade to study the inhibition of calcium carbonate dissolution. We studied the inhibiting effect by measuring the concentration of dissolved calcium ions in a simple calcium carbonate with water open system. Our study had the following objectives:

- To compare the inhibiting effectiveness of ions on the dissolution of a commercial sample of PCC filler at pH conditions near neutral and alkaline papermaking

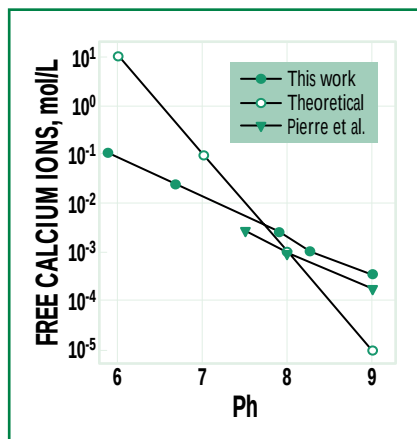
- To determine the minimum dosage of the most efficient inhibitor required to reach the maximum inhibition
- To study the effectiveness of inhibitors at different pH values
- To study the inhibition of PCC filler dissolution in a chemithermo-mechanical pulp (CTMP) suspension.

MATERIALS AND METHODS

CTMP came from a British Columbia mill. Calcium carbonate used in this experiment was a prismatic, paper-filling grade of PCC—Albafil M from Specialty Minerals Inc. (Bethlehem, PA) obtained as a 15.2% by weight suspension. The surface area and median particle size of this material reported by the manufacturer were 7 m²/g and 0.8 μm, respectively. The material contained approximately 3% impurities of which 2% and 0.06% were magnesium carbonate and iron oxide, respectively. The suspension was redispersed for two hours before its use by using a simple rotating apparatus in our laboratory. There was no additional purification. Disodium ethylenediaminetetraacetic acid (EDTA), phosphoric acid, succinic acid, maleic acid, sodium oxalate, and magnesium chloride were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI). Ethyleneglycol-bis(β-aminoethyl-ether)-N,N,N,N-tetraacetic acid (EGTA) was obtained from Sigma Chemical Co. (St. Louis, MO). All inorganic electrolytes of analytical grade were obtained from Fisher Scientific (Vancouver, BC). Hydroxy naphthol blue from Mallinckrodt Chemical Works (St. Louis, MO) was used as the calcium ion indicator. Distilled water used in all experiments was deionized and filtered through 0.05 μm filters in a commercial water purification apparatus supplied by Fisher Scientific (Vancouver, BC).

Inhibition of calcium carbonate dissolution

A desired amount of inhibitor was first

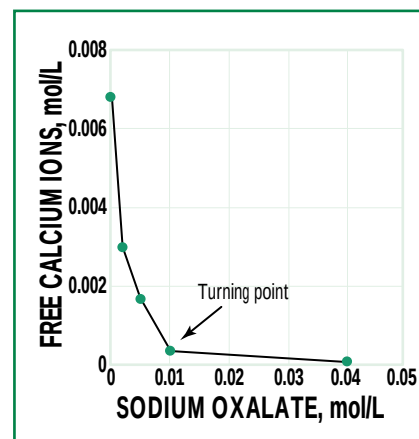


1. PCC solubility equilibrium

added to 100 mL of 1% mass calcium carbonate suspension. The suspension was agitated using a magnetic stirrer for 12 h, and the pH was periodically adjusted by aqueous solution of 0.1M NaOH or HCl. The suspension was then allowed to settle for 30 min. Aliquots of 10 mL were taken from the supernatant solution and filtered through a 0.2 μm membrane filter from Gelman Sciences (Ann Arbor, MI). Filtered samples were diluted to 50 mL by addition of deionized water. The calcium concentration was determined by photometric titration with EDTA solution using a Mettler Toledo DL25 Titrator with a DP550 Phototrode from Mettler-Toledo AG, Analytical (Schwerzenbach, Switzerland). When using magnesium ion as the inhibitor, photometric titration was conducted with EGTA solution instead.

Inhibition of calcium carbonate dissolution by phosphoric acid in the presence of CTMP

For one-day experiments, 20 g of oven dried pulp was suspended in 2 L of distilled water at 80°C and allowed to stand overnight. The suspension was disintegrated in the British Pulp Evaluation Apparatus from Mavis Engineering Ltd. (London, England) for 35 min. Desired amounts of calcium carbonate suspension and phosphoric acid were added to 500 ml of pulp suspension. The pH of the mixture was adjusted by aqueous solution of 0.1M NaOH or HCl for 6 h. The mixture was



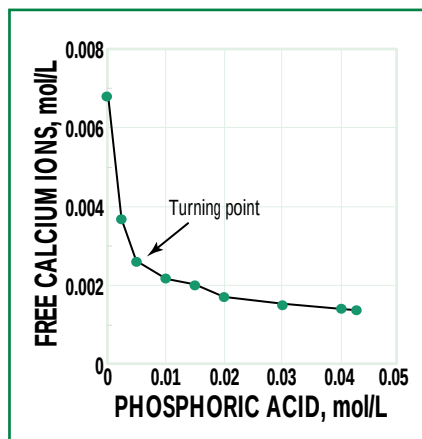
2. The effect of sodium oxalate on the solubility of PCC at pH 7.5

transferred into the Britt's Dynamic Drainage Jar (DDJ) with the 200-mesh screen from Paper Research Materials Inc. (Gig Harbor, WA) and stirred at 1200 rpm for 1 min. The drainage valve was then opened, and the first 40 mL of filtrate (equal to the dead volume of DDJ) was discarded. The following 100 mL of filtrate was collected. The filtrate was filtered through a 0.22 μm Millipore (Bedford, MN) membrane filter under pressure of nitrogen. The calcium concentration was then measured by photometric titration as described above. Each experiment was repeated three times, and the average value for the concentration of Ca⁺² was reported. The maximum standard error of the determined Ca⁺² concentration was less than 7% of the average value.

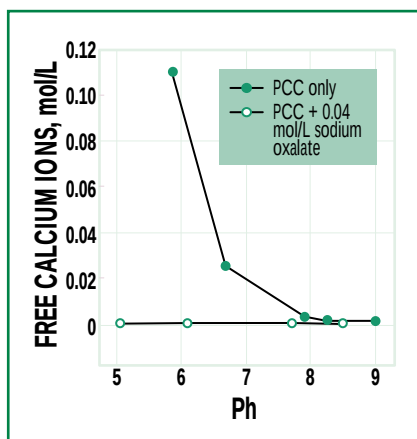
RESULTS AND DISCUSSION

It is important to measure the concentration of calcium ions at conditions when the solubility equilibrium is reached. For this reason, preliminary experiments were performed to determine the time required to reach the solubility equilibrium. The concentration of Ca⁺² ions in the calcium carbonate and water solution were monitored with time after the mixing. The system reached equilibrium after 6 h of agitation. The equilibrium pH of the suspension was 9.0.

Figure 1 shows the concentration of free Ca⁺² ions at equilibrium in PCC suspension at different pH values. The



3. The influence of phosphoric acid on the solubility of PCC at pH 7.5



4. The effect of sodium oxalate on the solubility of PCC as a function of pH

figure compares experimental data from this work with data from the literature and results based on theoretical calculations. The graph shows the increasing solubility toward the acidic conditions. The equilibrium concentrations of free Ca^{+2} ions at different pH compare well with literature data (21). The theoretical calculations used the thermodynamic data for the calcium carbonate water open system (22). The large discrepancy between the theoretical data and experimental results is probably due to the pretreatment of the surface of PCC with a dispersing agent and the presence of impurities.

Figure 2 shows the inhibition effect of oxalate ion, $\text{C}_2\text{O}_4^{2-}$ on the solubility of the PCC. The extent of inhibition is a strong function of the concentration of oxalate ions. The presence of 1.0×10^{-2} mol/L concentration of sodium oxalate dramatically inhibited the dissolution of the PCC. Further increase in the sodium oxalate concentration did not enhance the inhibition significantly. Under our experimental conditions, we estimate that the formation of calcium oxalate

hydrate crystals ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, whewellite) in the calcium carbonate water mixture with the addition of sodium oxalate was possible. Even with the lowest oxalate ions concentration studied, the solubility product, K_{sp} , of the whewellite (23), 2.34×10^{-9} , was exceeded. The calculations used the measured concentration of Ca^{+2} . It is therefore possible that the addition of oxalate ions into the calcium carbonate water system could cause the formation of calcium oxalate hydrate.

The solubility product of calcium carbonate (23), 4.96×10^{-9} , is higher than the K_{sp} of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. This means that in the system of two calcium minerals the solubility of the less soluble mineral will govern the concentration of free Ca^{+2} ions. The presence of PCC particles in the system would accelerate the formation of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ crystals, because the PCC particles could serve as "centers of crystallization" and host the newly formed solid phase on their surface. The inhibiting effect of oxalate ions therefore may be due to the precipitation of less soluble whewellite solid phase on the surface of the PCC. This in turn prevents the dissolution of the PCC. As Fig. 2 shows, the maximum inhibiting effect occurred after the addition of a small amount of sodium oxalate.

The "turning" point of the curve in Fig. 2 could correspond to the level of oxalate ions to form the required

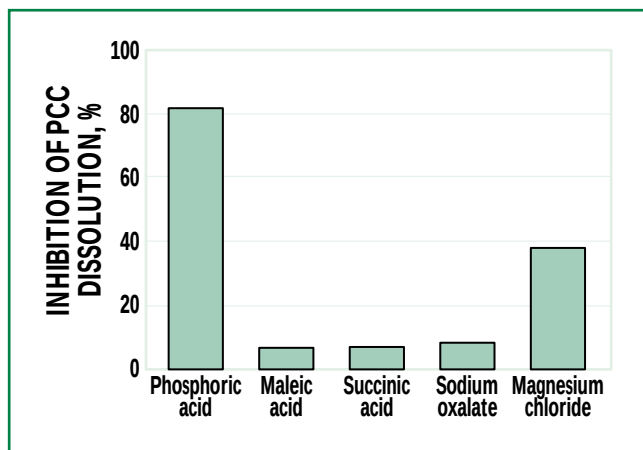
amount of calcium oxalate hydrate to cover completely the surface of PCC particles. At low concentrations of less than 10^{-3} mol/L of oxalate ions, note that the possibility of formation of whewellite in the calcium carbonate water system will not occur (16). At low oxalate concentrations, the absence of whewellite precipitation in the system could result in no inhibition of calcium carbonate dissolution as Fig. 2 shows. When the oxalate concentration increases, the whewellite could then precipitate and cover the surface of PCC particles.

Figure 3 shows that the free calcium ion concentration profile against the phosphoric acid concentration has a similar trend as the oxalate ions. Only 0.5×10^{-3} mol/L of phosphoric acid were necessary to achieve the saturation point. Further addition of phosphoric acid did not enhance the inhibition. Like the case with sodium oxalate, the formation of calcium phosphate solid was possible, since its solubility product (23) is 2.07×10^{-33} . At a concentration of phosphoric acid ions in the calcium carbonate water system less than 1×10^{-7} mol/L, the precipitation of any calcium phosphate solid phases was not possible, although the Gibbs free energy of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, formation was negative (20). At higher phosphoric acid concentrations, the rapid increase in growth of calcite crystals relates to the co-precipitation of hydroxyapatite and calcium phosphate (20). At the range of phosphoric acid concentrations studied, the inhibition of PCC dissolution could therefore be due to the formation of less soluble calcium phosphates. As Fig. 3 shows, the inhibition could start even at very low concentrations of phosphoric acid in the system because of the low K_{sp} values of calcium phosphate.

Figure 4 presents the inhibiting effect of oxalate ions at different pH. Oxalate ions inhibited the dissolution of PCC in the entire pH range studied.

KEYWORDS

Alkaline papers, alkalinity, calcium carbonate, chemithermomechanical pulps, dissolving, filters, inhibition, ions, oxalates, paper making, pH, phosphoric acid, precipitates.



5. Comparison of the effectiveness of different inhibitors with the inhibitor concentration at 0.0014 mol/L and the pH equal to 7.5 in all cases

The inhibition was greater at low pH. The adsorption mechanism plays an important role on the reduction of the rate of PCC dissolution. Besides the formation of insoluble solid phases with calcium, oxalate or phosphoric acid ions adsorb onto the surface of PCC and block the sites where the dissolution takes place. Many studies explained the inhibition by phosphate ions (17–20) and oxalate (16) by competitive adsorption of ions on the calcium carbonate surface. It is possible that the inhibiting ions adsorbed on the surface of calcium carbonate particles could play another role besides a simple formation of a barrier between calcium carbonate lattice and water phase.

Phosphate ions effectively control the hydrogen ion concentration in solution. For example, potassium phosphate is the element of standard buffer solutions. Obviously, phosphate ions adsorbed on the PCC surface would control the concentration of hydrogen ions on the PCC water interface. Most hydrogen ions reaching the surface of PCC particles must first react with the adsorbed phosphate ions. When the percentage of the surface of PCC covered with inhibiting ions increases, the number of available hydrogen ions to interact with the PCC lattice decreases. From their buffering ability, adsorbed phosphate or oxalate ions on the surface of PCC can prevent the reaction of hydrogen ions with PCC in

acidic media. This could explain the increased inhibition by oxalate ions at lower pH shown in Fig. 4.

Besides experiments with sodium oxalate and phosphoric acid, Fig. 5 shows the results of studies on the inhibition of the PCC dissolution by maleic acid, succinic acid, and magnesium chloride. All the experiments used pH 7.5 and 1.4×10^{-3} mol/L of inhibitor. Converting the results to percentage of inhibition used the following equation:

$$\text{Inhibition \%} = 1 - \frac{100[\text{Ca}^{+2}]_w}{[\text{Ca}^{+2}]_{w_0}} \quad (1)$$

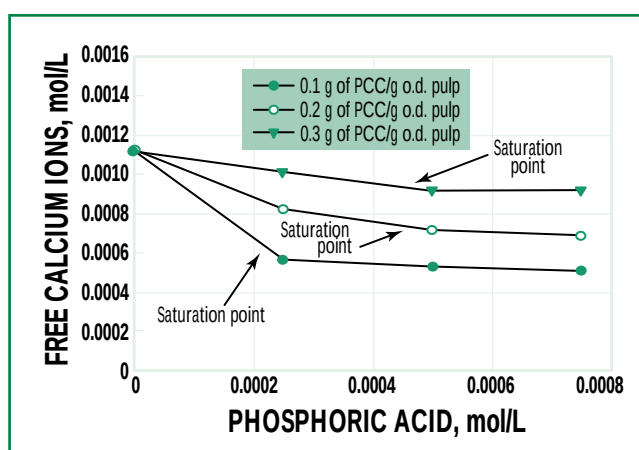
where

$[\text{Ca}^{+2}]_w$ = free calcium concentration in the presence of inhibitor

$[\text{Ca}^{+2}]_{w_0}$ = free calcium concentration in the absence of inhibitor.

Under these experimental conditions, phosphoric acid was the most effective inhibitor. The differences in adsorption affinity and buffering ability of the inhibitors on the surface of PCC may explain the differences in the inhibiting efficiency.

Dissolution experiments were also carried out in a DDJ in the presence of a CTMP pulp suspension using phosphoric acid, the strongest inhibitor. Figure 6 shows the results for three different loads of PCC. The inhibiting effect decreased with increasing PCC



6. The influence of phosphoric acid on the dissolution of PCC in the presence of CTMP at pH 8.25

loading. For each level of PCC loading, observation of the saturation behavior showed that the amount of phosphoric acid required to achieve the saturation point increased with the PCC loading. The increase in the number of PCC particles in the system increases the total surface to be inhibited. This results in shifting the saturation point toward higher concentrations of phosphoric acid.

CONCLUSIONS

We investigated the inhibiting capabilities of various chemicals on the dissolution of PCC fillers in water. Phosphoric acid was the most efficient inhibitor. The solubility of Ca^{+2} was reduced 80%. The extent of inhibition increased with inhibitor concentration until a point after which further addition of inhibitor did not enhance the inhibition. This effect could correspond to a level of inhibitor required to form the necessary amount of less soluble calcium containing solid phases to cover completely the surface of the PCC and prevent the dissolution of the PCC. We suggest that the higher inhibiting effect at lower pH was due to the buffering action of the absorbed inhibitors on the surface of PCC that prevented the reaction of hydrogen ions with PCC. Phosphoric acid also inhibited the dissolution of PCC in a CTMP suspension. The saturation point depended on the loading of PCC filler. TJ

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The authors appreciate the financial support provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). They also thank MacMillan Bloedel Research and PAPRICAN for pro-

viding equipment and materials for this research and Specialty Minerals for providing the PCC samples. Millie Leung and Tim Zhen deserve appreciation for their assistance with the laboratory measurements.

Received for review Aug 6, 1996.

Accepted May 5, 1997.

LITERATURE CITED

1. Britt, K. W., *Handbook of Pulp and Paper Technology*, 2nd edn., Van Nostrand Reinhold Co., New York, 1970, p. 627.

2. Gill, R., in *Applications of Wet-End Paper Chemistry* (C. O. Au and I. Thorn, Ed.), Blackie Academic & Professional, New York, 1995, p. 54.

3. Gill, R. and Scott, W., *Tappi J.* 70(1): 93(1987).

4. Gill, R., *TAPPI 1990 Neutral/Alkaline Papermaking Short Course Notes*, TAPPI PRESS, Atlanta, p. 91.

5. Gill, R., *Nordic Pulp and Paper Research J.* 4(2): 120(1989).

6. Fairchild, G. H., *TAPPI 1992 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p. 521.

7. Brown, A. J., *TAPPI 1996 Papermakers Conference Proceedings*, TAPPI PRESS, Atlanta, p.137.

8. Passaretti, J., Young, T., Herman, M., et al., *Tappi J.* 76(12): 135(1993).

9. Berner, R. A., *Am. J. Sci.* 265: 45(1967).

10. Berner, R. A., *Am. J. Sci.* 278: 1475(1978).

11. Reddy, M. M. and Wang, K. K., *J. Crystal Growth* 50: 470(1980).

12. Buhmann, D. and Dreybrodt, W., *Chemical Geology* 64: 89(1987).

13. Zuddas, P. and Mucci, A., *Geochimica et Cosmochimica Acta* 58(20): 4353(1994).

14. Compton, R. G. and Brown, C. A., *J. Colloid and Interface Sci.* 165: 445(1994).

15. Compton, R. G. and Brown, C. A., *J. Colloid and Interface Sci.* 170: 586(1995).

16. Giannimars, E. K. and Koutsoukos, P. G., *Langmuir* 4(4): 855(1988).

17. Morse, J. W., *Am. J. Sci.* 274: 638(1974).

18. Berner, R. A. and Morse, J. W., *Am. J. Sci.* 274: 108(1974).

19. Reddy, M. M., *J. Crystal Growth* 41: 287(1977).

20. Giannimars, E. K. and Koutsoukos, P. G., *J. Colloid and Interface Sci.* 116(2): 423(1987).

21. Pierre, A., Lamarche, J. M., Mercier, R., et al., *J. Dispersion Science and Technology* 11(6): 611(1990).

22. Stumm, W. and Morgan, J. J., *Aquatic Chemistry*, Wiley-Interscience, New York, 1970, pp. 150-163.

23. Anon., *Handbook of Chemistry and Physics*, 76th edn., CRC PRESS, New York, 1995, pp. 8-58.