

NEUTRAL GROUNDWOOD PAPERS: PRACTICAL AND CHEMICAL ASPECTS

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ABSTRACT

More and more producers of groundwood (woodcontaining) publication papers, from newsprint to supercalendered (SC) to lightweight coated (LWC), are converting to neutral papermaking using calcium carbonate fillers. The challenges and benefits of these conversions depend on paper grade, furnish, paper mill configuration, and method of pH control. The weak acid/chelant (WAC) pH control system has been successfully used in many groundwood paper mills and has been the subject of several recent technical publications. This paper examines the operative wet end chemistry of WAC systems on commercial machines. Other published chemical mechanisms, based on laboratory data, are shown to be less predictive of "real life" behavior. Finally, detailed knowledge of WAC chemistry is shown to be critical for deriving the maximum value of carbonate fillers such as precipitated calcium carbonate (PCC) in these applications.

INTRODUCTION

PCC and other carbonate fillers have been widely used in freesheet paper grades since the 1980's because of their good optical properties. In freesheet, the alkaline nature of calcium carbonate is an additional benefit because it creates a stable buffered system and provides some paper strength improvement. However, the alkalinity of carbonate fillers has limited their use in groundwood publication papers due to the negative effects of alkalinity on groundwood pulps, primarily alkaline darkening [1].

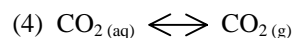
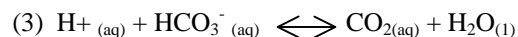
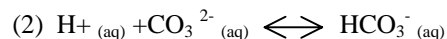
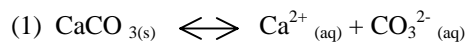
A number of papermaking processes have been developed to enable the use of calcium carbonate in groundwood papers. The early methods were developed to allow use of calcium carbonate coating pigments and broke in coated groundwood grades. Very early on, Dinius [2] developed and patented a process where the calcium carbonate in coated broke is completely dissolved with acid and then reprecipitated as an acid stable phosphate. However this method is both time-consuming and expensive, and found limited commercial use. "Pseudo-neutral" papermaking was later developed primarily for use of ground calcium carbonate (GCC) in LWC grades [3,4]. This method uses alum to control pH to around 7.1-7.5 and to aid in scavenging wet end anionic trash. Although successful for LWC, pseudo-neutral systems have not been widely used for more highly filled grades or groundwood grades containing high virgin mechanical fiber content.

The first process that has been widely used to incorporate calcium carbonate in grades having a high virgin groundwood fiber content is the weak acid-chelant (WAC) system developed by SMI [5,6]. The WAC system has seen growing commercial acceptance over the last 3-4 years and has been the subject of a number of technical papers [7-13]. This paper examines the chemical mechanisms of the WAC pH control

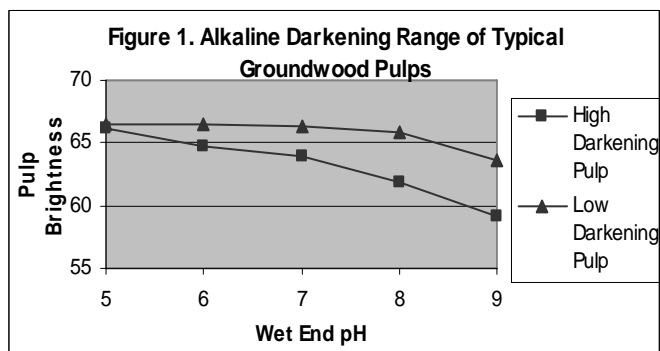
system and how they apply in real-life groundwood paper applications with calcium carbonate pigments.

CHEMISTRY OF CaCO₃ in GROUNDWOOD PULPS

CaCO₃ in water is in equilibrium with carbon dioxide, carbonate ion and bicarbonate ion to form a highly buffered system as described in Equations 1- 4 below:



The equilibrium pH of calcium carbonate in paper making systems is typically about 7.7-8.3. The high pH and buffering characteristics of the aqueous CaCO₃ system is an advantage in the production of freesheet paper grades produced from chemical pulps. However, groundwood pulps are prone to alkaline darkening as illustrated in Figure 1.



This alkaline darkening effect has historically limited the use of calcium carbonate fillers in groundwood paper production. Early carbonate filler usage was limited to grades made from furnishes with relatively low alkaline darkening as represented by the upper curve in Figure 1. Relatively low darkening furnishes are used in LWC which has a relatively high chemical pulp content, and in recycled grades (deinked pulps tend to have less darkening).

However, virgin mechanical pulps typically have higher alkaline darkening as illustrated by the lower curve in Figure 1. Brightness losses of greater than 10 points between pH 5 and 8 have been seen in some mills. Thus newsprint, directory, groundwood specialty and SC grades made with high virgin groundwood content have traditionally been made on the acid side using clay fillers to avoid darkening problems.

WAC SYSTEM FOR pH CONTROL

The WAC pH control system was developed after it was recognized that even for high darkening pulps, most of the alkaline darkening could be avoided if wet end pH was controlled to 6.8-7.2 (see Figure 1). The WAC system was developed in the early 1990's [5,6], and is now widely used commercially, mostly in grades with high virgin pulp content.

The WAC system is run by adding a weak acid continuously to the wet end of a paper machine containing CaCO₃ and an appropriate chelant/sequencestrant. The acid demand

depends on a number of factors including targeted pH, machine closure, carbonate filler type and first pass ash retention. Typically, a pH of around 6.8-7.2 is readily and cost-effectively achievable.

While most weak acids function in the WAC, system, a number of criteria determine which acids are most preferred. The criteria are listed in Table 1.

TABLE 1: Weak Acid Criteria

1. Water Soluble
2. Multi-protic
3. Significant difference in pK_a of acid groups
4. Limited calcium salt solubility
5. Cost effectiveness

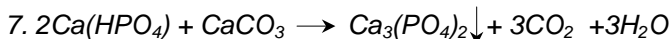
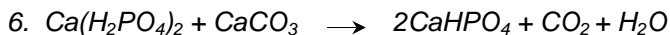
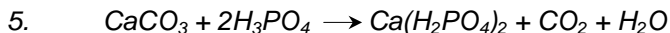
Three preferred weak acids for the WAC system have been identified through many years of trials and lab experiments: phosphoric acid (H_3PO_4), sulfurous acid (H_2SO_3), and carbonic acid (H_2CO_3). Phosphoric acid has seen the most commercial success, but SO_2 and CO_2 have been run where effluent phosphate limits are a factor.

As discussed in detail later, a number of chelant types can be used in WAC systems, but phosphate-based chelants have been most used commercially.

WAC pH CONTROL MECHANISMS

As discussed above, the mechanism of wet end pH control with calcium carbonate by weak acids has been the subject of a number of recent studies [7-13]. The common theme through most of these studies is that enhanced stability of $CaCO_3$ at lower pH is obtained by surface absorption of species at the $CaCO_3$ /aqueous phase interface. The concept proposed is that the adsorption reduces $CaCO_3$ dissolution by a surface "blocking" mechanism. The published results were largely obtained in the lab, sometimes under conditions significantly different than found in real papermaking systems. This paper proposes a different mechanism that has been supported by extensive commercial paper machine experience.

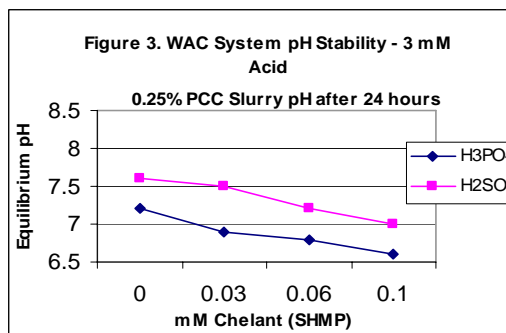
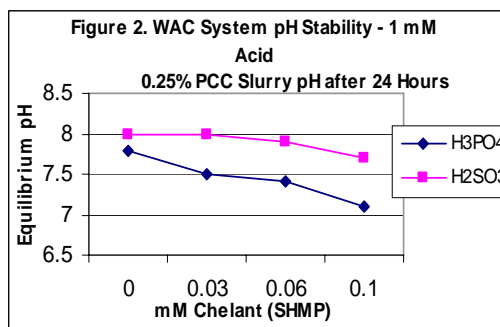
When phosphoric acid is added to an aqueous suspension of $CaCO_3$, the following reactions occur:



Equations 5 and 6 show the formation of calcium di-hydrogen phosphate and calcium hydrogen phosphate, respectively. These species are key to WAC pH control with phosphoric acid; they are soluble, are weak acids, and form an effective wet end buffer system. Equation 7 shows the formation of relatively insoluble calcium phosphate (hydroxyapatite). This is a "bad" reaction for pH control as it removes buffering species from solution. This causes pH to rise, increases acid demand, and forms scale on exposed papermaking surfaces.

The prevention of hydroxyapatite formation is the primary reason for the addition of chelant in the phosphoric acid WAC papermaking system. We have found that chelant addition stabilizes the soluble species in Equations 5 and 6 and minimizes the precipitate formation in Equation 7.

The stabilizing effect of chelant on both phosphoric acid and SO_2 systems is illustrated in Figures 2 and 3. These plots show pH stability results for dilute PCC suspensions treated with 1mM and 3mM acid. The slurry pH after 24 hours is indicated for a range of chelant addition from 0 to 0.1mM. The chelant used in this case was sodium hexametaphosphate (SHMP). Figures 2 and 3 show the significant impact of SHMP on pH stability after 24 hours for both acids. The plots show that slurry pH is reduced significantly at higher acid and higher chelant addition levels. With phosphoric acid, a pH close to 6.5 can be maintained at higher chelant levels (0.1 mM).



This experience has been duplicated on commercial paper machines where pH as low as 6.5 has readily been maintained with PCC in groundwood systems. However, most commercial machines operating the WAC system today run at pH 6.8-7.2. This range has proven to be most cost-effective for minimizing brightness loss from alkaline darkening.

The beaker experiments illustrated in Figures 2 and 3 also can be used to qualitatively show the negative impact of Equation 7 on the WAC system. At high acid levels with low chelant addition, a small amount of insoluble calcium phosphate can be seen to form at the air/water interface in the slurry. This corresponds to relatively poor pH stability (i.e. high pH). This behavior has also been observed on commercial paper machines. In cases where adequate chelant levels have not been added to the system, very high acid demands and/or precipitative scaling problems have been encountered. When chelant additions are adjusted back to proper levels, scaling is eliminated and acid demand returns to normal.

Thus, the mechanism by which the WAC system enables reduced pH in calcium carbonate systems is not based strictly on reducing the solubility of calcium carbonate as proposed in other studies. Rather it is based on the formation of buffering species from the reaction of calcium carbonate with the weak acid. The presence of these species actually increases the soluble calcium

ion present in the wet end. Typically, we have found that calcium levels increase by 50-100 ppm (as CaCO₃) above the levels observed when a “natural” pH around 8 is run on the paper machine. These reaction products are the active source of acidity that buffers the wet end at near neutral pH in the WAC system. The role of the chelant is to stabilize this buffered system through a combination of ion sequestration and scaling inhibition. The critical role of the chelant is further examined in the next section as different chelant systems are compared.

CHELANT EFFECTS IN THE WAC SYSTEM

A significant research effort has been applied toward optimizing chelant type for the WAC system. In general, almost all classes of chelants have been shown to provide some stabilization effect with PCC (reduced acid demand and stability against scaling). However, effectiveness can vary greatly among commercial chelants.

Initial lab work and commercial trials were done with phosphates such as SHMP and sodium tripolyphosphate (STP). These products were found to be chemically active and cost-effective. However, after extensive commercial usage we found that the poor stability against hydrolysis exhibited by polyphosphates could be a problem in some applications. Therefore a number of other chelants have been evaluated and used.

Interestingly, the common aminocarboxylates like DTPA and EDTA were found to be only marginally effective in the WAC system. Sodium polyacrylates, commonly used as dispersants, have been found to be quite effective, as have some organophosphonates. The sequestration properties of several commercial chelants including organophosphonates diethylenetriaminepenta methylenephosphonic acid (DTPMP) and 1-hydroxyethylidene-1, 1-diphosphonic acid (HEDP) are compared in Table 2.

**Table 2. Sequestration Properties
Of Various Chelating Agents***

Agent	mgs CaCO ₃ /gm Sequestrant	
	pH9	pH 10
<i>Organophosphonates</i>		
HEDP ¹	815	840
DTPMP ¹	700	800
<i>Aminocarboxylates</i>		
NTA	350	350
EDTA	300	300
DTPA	250	250
HEEDTA	325	325
Sodium tripolyphosphate ¹	325	335
Sodium polyacrylate ¹	150	150

¹ Threshold Inhibitor
(works in sub-stoichiometric amounts)

* From Callaway Chemical Company brochure “Mayoquest®
High Purity Organophosphates,” 1997.

It appears that the ability to perform effectively in the WAC system may be related more to whether the chelant is a threshold inhibitor (works below stoichiometric dosages) than to its total chelation capacity. This is consistent with the WAC mechanism

proposed above where the chelant’s role is to stabilize the soluble species formed by the reactions between the weak acid and the calcium carbonate. This stabilization probably occurs through a combination of aqueous sequestration and surface crystal growth inhibition. Other researchers have reported the positive effect of polyphosphates on CaCO₃ systems using CO₂ and SO₂ for pH control [8,12].

Threshold inhibitors are known from commercial water treatment experiences to be able to keep large amounts of scalants in solution. Also, blends of different chelants are sometimes found to work synergistically for scale inhibition. Since most groundwood paper mills already add active chelants for scale control, bleaching, pitch and pigment dispersing, etc., sometimes little or no extra chelant is required for running the WAC system, particularly for systems with low filler levels like newsprint and LWC. However, for highly filled systems like SC papers, extra chelant should almost always be added either with the filler or directly to the paper furnish.

DISCUSSION

As discussed above, a number of papers have been published recently on the mechanism of pH control in neutral CaCO₃ systems. These tend to support a theory that the operative mechanism for reduced pH is a reduction in carbonate solubility through the surface blocking action of different additives. These theories will now be reviewed in light of the WAC theory proposed here.

The concept of “surface blocking” to reduce reactivity of CaCO₃ has been around for quite some time. A number of surface treatments have been proposed and studied in the literature: phosphates/silicates or formaldehyde resins [14], sodium stearate [15], zinc silicate [16,17,18], and a variety of acids and ions, most notably phosphoric acid [7,9,10].

The use of precipitation to form a physical barrier on the carbonate surface (e.g. with silicates or stearates) has not found commercial application not only because it is relatively expensive but also because it has a performance flaw. Surface barriers (encapsulates) in both organic and inorganic systems suffer from the limitation that usually only the kinetics of reactions of the base compound are altered, not the equilibrium chemistry. For instance, the acid resistance of silicate treated CaCO₃ was increased as measured by titration with alum solutions [16,17,18]. However, this gives an indication of only the rate of the reaction with alum. Our experience on pilot paper machines with precipitate-covered PCC’s is that the equilibrium pH or reactivity does not change since a given portion of added fillers goes around the system many times (can have many hours contact time in real mill situations). The moderate reduction in acid reaction rate is not worth the effort and cost of surface treatment and does not significantly affect the overall system pH stability.

The concept of phosphoric acid as a calcium carbonate solubility reducer is more interesting and is worth further discussion. PANG et al. [7,9,10] have proposed that phosphoric acid acts a dissolution inhibitor for CaCO₃ via the presence of Ca-P phases that precipitate on the carbonate surface. Besides the problem with ineffective “encapsulation” discussed above, the conclusions from this work are biased due to the experimental procedures used.

The solubility of CaCO₃ as a function of pH was determined in these experiments by adding inhibitor candidates to dilute carbonate slurries and then measuring soluble calcium after a

period of time. Slurry pH was periodically adjusted with NaOH or HCl to maintain pH at the chosen level. In essence this procedure is not indicating that phosphoric acid is a solubility inhibitor for calcium carbonate, but is showing that a CaCO₃ slurry adjusted down in pH with HCl has a higher soluble calcium level than a similar slurry adjusted with phosphoric acid or a phosphoric acid/HCl blend. This is not surprising since the buffered system represented by Equations 4-6 will give lower calcium levels than HCl or other strong acids which will simply dissolve the calcium carbonate on a stoichiometric basis. Thus, the acid intermediate/stabilization mechanism of pH control better describes the WAC system than simple solubility reduction.

This is further supported by another machine trial experience. PANG et al. [9] propose that the surface blocking effect of phosphoric acid on calcium carbonate can be used to the point where dissolution eventually "terminates". They further propose that it is possible to effectively control wet end pH by pretreating CaCO₃ filler with phosphoric acid prior to addition to the paper machine. Initial WAC trials were run commercially in the late 1980's using PCC pre-treated with phosphoric acid and chelant combinations. The wet end pH rose to above 7.5 (target was 7.0) and could not be controlled down further without direct addition of phosphoric acid to the paper machine furnish. This concept doesn't work because the phosphoric acid is mostly converted to insoluble calcium phosphate when added as a pretreatment. There are then no soluble buffering species left to react with bases and lower the wet end pH on the paper machine.

SUMMARY AND FINAL REMARKS

The results reported here are based on some 15 years of research and commercial trial activity involving PCC fillers in neutral groundwood paper systems. About 35 machines are now using the WAC system for pH control, some having converted in the mid-1990's. Every major groundwood publication grade is now being produced with PCC fillers using the WAC system.

The ability to minimize alkaline darkening allows the paper maker to better take advantage of the superior brightness and light scattering properties of PCC. This can be used as a key strategic advantage as the publication paper market struggles to compete in the "electronic" world in the years ahead.

However, the performance advantages of PCC-filled groundwood papers mean little if the paper machines cannot be run efficiently and cost-effectively at neutral pH. The WAC system and the mechanistic explanations for its application presented here are based on close scientific scrutiny of many real paper mill experiences. WAC system stability has been found to be the result of the development of a stable wet end buffer system, not on the simple reduction of CaCO₃ solubility.

When PCC, weak acid, and chelants are added to the papermaking furnish, the resulting reaction products form a highly buffered system. As long as the addition rates of the three components are kept in balance, paper machine runnability is found to be excellent. The buffering effect can actually be a benefit throughout the mill compared to acid systems. Also, the scavenging ability of PCC can actually help with wet end pitch problems, an early industry concern with neutral groundwood conversions.

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