DISSOLUTION BEHAVIOUR OF CALCIUM CARBONATE IN MILDLY ACIDIC CONDITIONS

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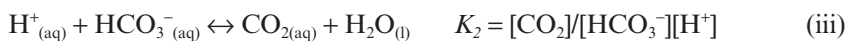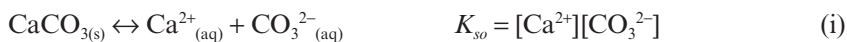John Keay House, St. Austell, Cornwall, PL25 4DJ, UK

INTRODUCTION

Calcium carbonate pigments have been used in wood-containing papers for many years, either as added fillers or as components of coated broke or recycled paper. These papers are normally made at a wet-end pH of between 6.5 and 7.5. This was originally called 'pseudo-neutral' papermaking, in which papermakers alum was used as an additive [1]. Whilst the use of alum in this type of papermaking is now less common, the pulp systems used continue to be acidic, so that the wet-end pH is determined by the partial dissolution of the calcium carbonate pigments in the acid pulp water. More recently, precipitated calcium carbonate (PCC) fillers have been introduced to wood-containing papers which can create pH control problems and which sometimes require chemical treatments to inhibit their dissolution [2].

   The dissolution behaviour of calcium carbonate has been widely studied and reviewed [3,4], as it is of interest to geologists and to many industries. The majority of authors have been interested in the specific processes occurring at the surface of calcite during dissolution, and have studied clean surfaces and aimed to keep external factors such as pH, calcium and carbon dioxide concentrations constant. Under papermaking conditions these factors are not independent of the carbonate dissolution process, and indeed are likely to be entirely governed by it. Recent studies of the inhibition of dissolution of paper filler grade calcium carbonate have been reported [5], but these too have not considered the effect of the products of dissolution, in particular carbon dioxide, on the process itself.

In this paper, the dissolution kinetics of calcium carbonate under conditions similar to those found in papermaking are examined. The effects of dissolved calcium and carbon dioxide on pH and dissolution are shown to be critical, and the effect of some insoluble calcium salts on the inhibition of dissolution is discussed.

EQUILIBRIA BETWEEN CaCO₃ AND CO₂ IN WATER

When calcium carbonate dissolves in acid, the following sequence of reactions take place:

$$CaCO_{3(s)} \leftrightarrow Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \qquad K_{so} = [Ca^{2+}][CO_3^{2-}] \qquad (i)$$

$$H^+_{(aq)} + CO_3^{2-}_{(aq)} \leftrightarrow HCO_3^-_{(aq)} \qquad K_I = [HCO_3^-]/[CO_3^{2-}][H^+] \qquad (ii)$$

$$H^+_{(aq)} + HCO_3^-_{(aq)} \leftrightarrow CO_{2(aq)} + H_2O_{(l)} \qquad K_2 = [CO_2]/[HCO_3^-][H^+] \qquad (iii)$$

$$CO_{2(aq)} \leftrightarrow CO_{2(g)} \qquad K_H = P(CO_2)/[CO_2] \qquad (iv)$$
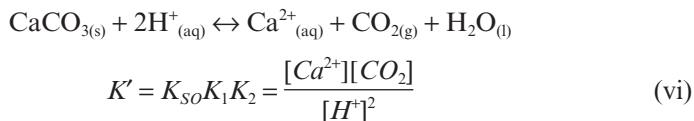
Equilibrium constants for these reactions are represented by the K values to the right of the equations, molar concentrations in water are represented by square brackets [], and $P(CO_2)$ denotes the partial pressure of CO_2 in the atmosphere in contact with the suspension. Suspensions are considered to be dilute so that $[H_2O]$ is constant. To a first approximation, variations in activity coefficients at different ionic strengths can be incorporated into the values of the equilibrium constants [6]. Of these reactions, only (i) *has* to take place at the particle surface, although in practice all of the first three reactions may occur there more-or-less simultaneously. Reaction (iv) takes place at the air/liquid interface. In a well-stirred system, the liquid phase reactions (ii) and (iii) will be very fast, so the rate at which the system reaches equilibrium with the atmosphere is likely to be dependent on the rates of steps (i) and (iv). If (i) is very fast compared with (iv), then equilibrium between solid and solution will be established quickly, and the observed dissolution rate will be dependent only on step (iv).

For a pure calcium carbonate dispersed in pure water, the equilibrium pH can be derived from these constants by applying the relevant mass balance equations:

$$[H^+] = \left(\frac{1}{2k_1^2 K_2 K_H^2 P(CO_2)^2 K_{SO}} \right)^{\frac{1}{3}} \qquad (v)$$

This gives a 'natural' pH of around 8.3 for a carbonate slurry in contact with air. More generally, for any suspension of carbonate where equilibrium between solid and solution has been established, all of the above reactions can be summarised and understood in terms of the overall equilibrium:

$$CaCO_{3(s)} + 2H^+_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

$$K' = K_{SO}K_1K_2 = \frac{[Ca^{2+}][CO_2]}{[H^+]^2} \tag{vi}$$

Loss of a highly-soluble gas such as CO_2 from solution is a relatively slow process, which is significantly affected by agitation (witness the fact that fizzy drinks lose their sparkle much more rapidly if shaken or stirred vigorously). Hence it is likely that, in an environment such as a papermachine, equilibrium between the solid carbonate and the solution will be established. Thus the observed dissolution rate will be dependent on the rate of loss of CO_2 from the process water, and the pH at any point will be determined by the local concentrations of dissolved calcium and CO_2 and independent of the amount of carbonate in the system.

Table 1 shows the estimated pH (calculated from the equilibrium constants described above [6]) of a calcium carbonate slurry as a function of the concentrations of dissolved CO_2 and calcium. At a calcium concentration of 200ppm, which is typical for a neutral papermachine using carbonate and mechanical pulp, about 50ppm of CO_2 are required to maintain the machine pH below 7.0.

Table 1 Effect of concentrations of dissolved Calcium and Carbon Dioxide on pH in equilibrated Calcium Carbonate suspension at 25°C and 0.01M ionic strength.

pH values	CO_2/ppm			
Ca/ppm	1	10	50	200
20	8.27	7.77	7.42	7.12
100	7.92	7.42	7.07	6.77
200	7.77	7.27	6.92	6.62
500	7.57	7.07	6.72	6.42
2000	7.27	6.77	6.42	6.12

EXPERIMENTAL

The dissolution rate of calcium carbonate was studied by means of a pHstat measurement. In this simple experiment, a suspension of calcium carbonate particles is maintained at a constant pH over a fixed period by addition of a solution of acid. The rate of acid addition is monitored and recorded. By considering the stoichiometry of the dissolution process, the dissolution rate can be directly calculated from the rate of acid addition.

The pHstat experiments were carried out in the apparatus illustrated in Figure 1. The apparatus consists of a cylindrical glass vessel which has a sintered glass disc at the bottom through which a constant flow of air can be passed. This air creates air/liquid interface (bubbles) within the slurry and transports evolved CO_2 away from the sample. The rate of removal of CO_2 from the slurry is thus controlled both by the rate of stirring and the airflow rate. The vessel has a thermostatted outer jacket and a variable speed stirrer. The vessel holds a calcium carbonate slurry sample of approximately 100mls, into which a pH electrode is immersed. The electrode is connected to an autotitrator which controls and records the acid addition rate. The dissolution of filler calcium carbonate suspensions of between 0.5 and 2% solids in various different acids was examined as a function of solids and airflow, under fairly vigorous stirring conditions of 500rpm.
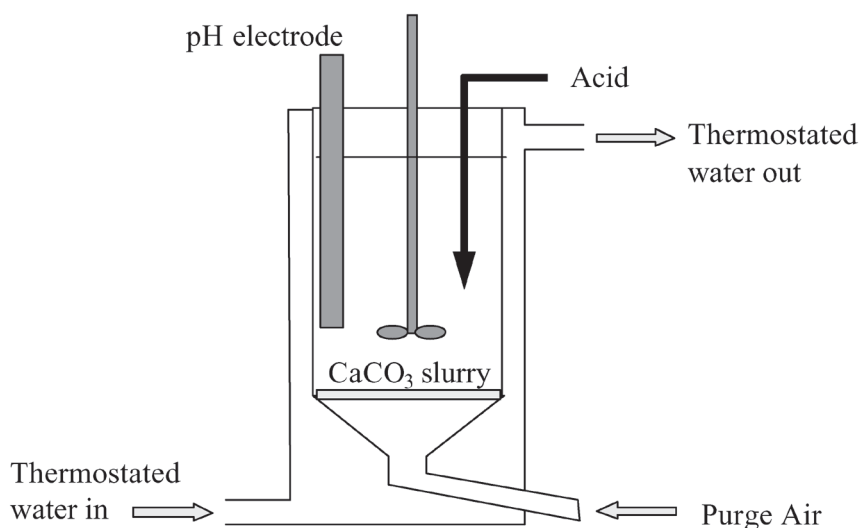

Figure 1   Apparatus used for pHstat experiment.

RESULTS AND DISCUSSION

1   Dissolution behaviour of calcium carbonate in hydrochloric acid

The dissolution rate of a 2% solids slurry of a 90% below 2 micron, dispersant-free ground calcium carbonate (GCC) filler in hydrochloric acid at pH6.5 is illustrated in Figure 2.
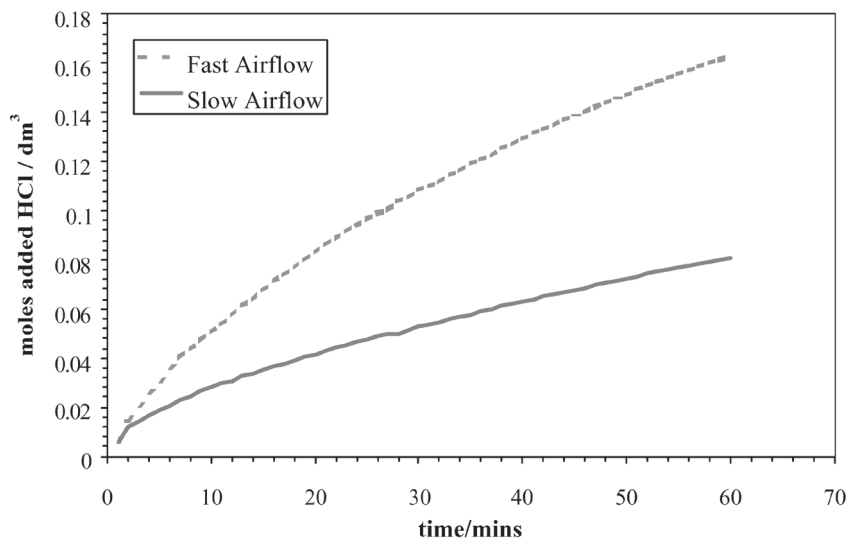

Figure 2   Dissolution of 2% solids GCC filler in hydrochloric acid at 25°C and pH6.5.

Hydrochloric acid was chosen for the initial studies because it produces a freely soluble calcium salt whose formation should not interfere with the dissolution process beyond the expected effects of raising the solution calcium concentration. As can be seen, the dissolution rate is highly dependent on the airflow rate through the apparatus. Further experiments show that it is independent of the solids concentration (and hence the surface area) of the carbonate. It thus appears that under these conditions the rate-determining step of the dissolution process is not the reaction at the particle surface, but rather the loss of carbon dioxide from the water.

To test this hypothesis further, a simple mathematical model was derived in which equilibrium between solid and solution was assumed so that the dissolution rate was proportional to the rate of CO_2 evolution only. It was
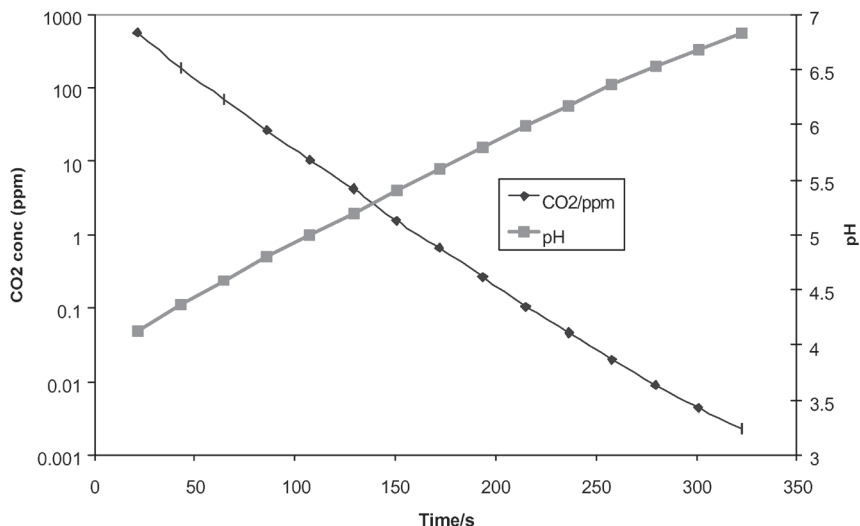
Figure 3 Rate of evolution of CO_2 from water in the pHstat apparatus at 25°C.

also assumed that the rate of CO_2 evolution is a first order process, the rate constant of which is dependent on the rate of stirring and airflow. This latter assumption was tested by placing a sample of deionised water that had been carbonated in a domestic drinks maker in the apparatus and monitoring its pH as a function of time under typical conditions of stirring rate and airflow (Figure 3). The linear increase in pH with time confirms that the process has first order kinetics; carbon dioxide concentration was calculated from pH using equation (iii).

From the stoichiometry of the dissolution of calcium carbonate in acid, the rate of production of CO_2 is equal to the rate of production of dissolved calcium and hence the rate of acid addition, and thus:

$$\frac{d}{dt}[CO_2] = \frac{d}{dt}[Ca^{2+}] - k_{loss}[CO_2] \qquad \text{(vii)}$$

where k_{loss} is the rate constant for CO_2 evolution, and is dependent on the airflow and stirring conditions. From equation (vi),

$$[CO_2] = \frac{[H^+]^2 K'}{[Ca^{2+}]} = \frac{K''}{[Ca^{2+}]} \qquad \text{(viii)}$$

and so by combining equations (vii) and (viii) an expression can be obtained which relates concentration of calcium (henceforth abbreviated to *Ca*) to the time elapsed since the start of pHstat experiment:

$$\int_0^t dt = \frac{1}{K'' k_{loss}} \int_{Ca(0)}^{Ca(t)} \left(Ca + \frac{K''}{Ca} \right) dCa \qquad \text{(ix)}$$

which solves to

$$t = \frac{1}{k_{loss} K''} \left[\frac{Ca(t)^2 - Ca(0)^2}{2} + K'' \ln \frac{Ca(t)}{Ca(0)} \right] \qquad \text{(x)}$$

where *Ca(t)* is the concentration of dissolved calcium at time *t*. This equation was fitted to the data shown in Figure 2 by adjusting the parameters *Ca(0)* and k_{loss}, and produced satisfactory fits, shown in Figure 4. The fitted values
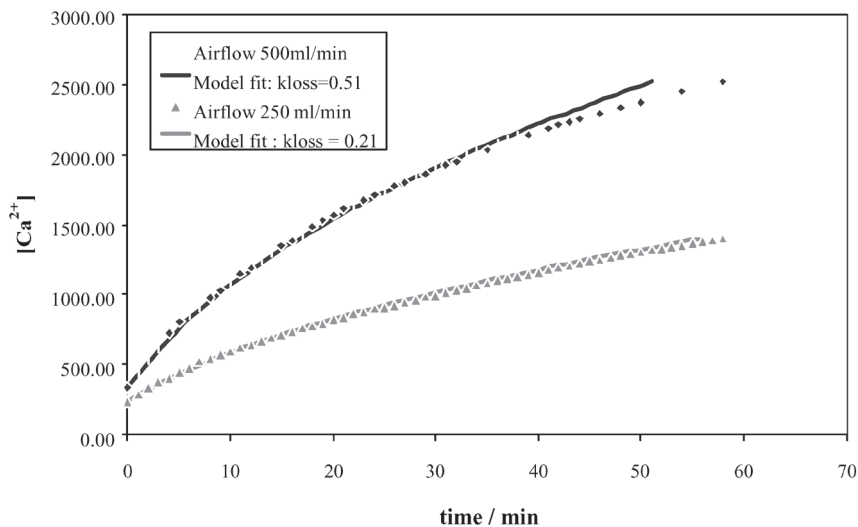

Figure 4 Fit of kinetic model to pHstat data for dissolution of GCC at pH6.5 and 25°C.

of $Ca(0)$ are around 300ppm: this represents the calcium produced in the initial phase of the experiment before the pH has been brought down to its constant level.

As expected, the dissolution rate increases with increased airflow, and this is reflected by a larger value of k_{loss}. The curvature of the graphs is caused by the increase in calcium concentration with time; at constant pH an increase in calcium decreases the amount of dissolved CO_2 required for equilibrium with the carbonate, and since the rate of CO_2 loss (and hence dissolution) is proportional to the CO_2 concentration the rate decreases with time. Likewise the concentration of dissolved CO_2 calculated from the equilibrium expression also decreases with time (Figure 5). Even under the conditions of fast stirring and airflow, the CO_2 concentration remains above 50ppm throughout the experiment. On a papermachine with a background calcium concentration of 200ppm, this would be sufficient to keep the pH below 7 (Table 1). The assumption that equilibrium between carbonate and solution is achieved on a typical machine would thus appear reasonable.

At higher temperatures the solubility of carbon dioxide in water is decreased, and the rate of loss of carbon dioxide would thus be expected to increase. However, increased temperature also decreases the solubility product of $CaCO_3$ and changes the other equilibrium constants for the process, so
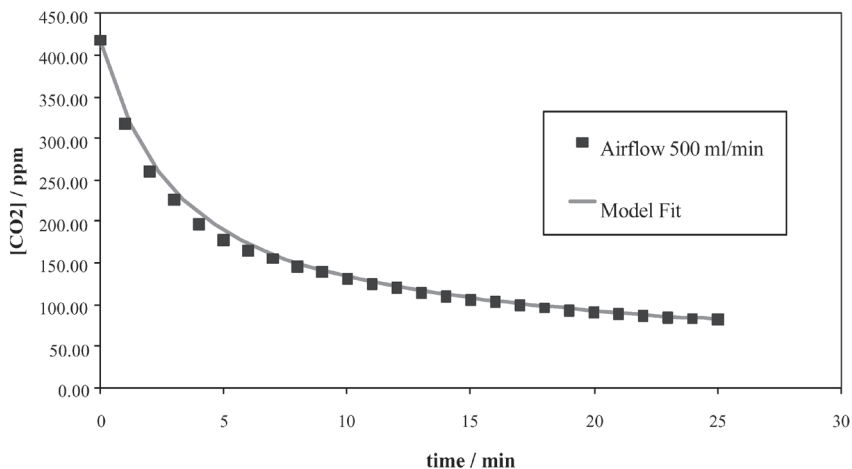

Figure 5 Calculated concentration of carbon dioxide during pHstat experiments shown in Figure 2.
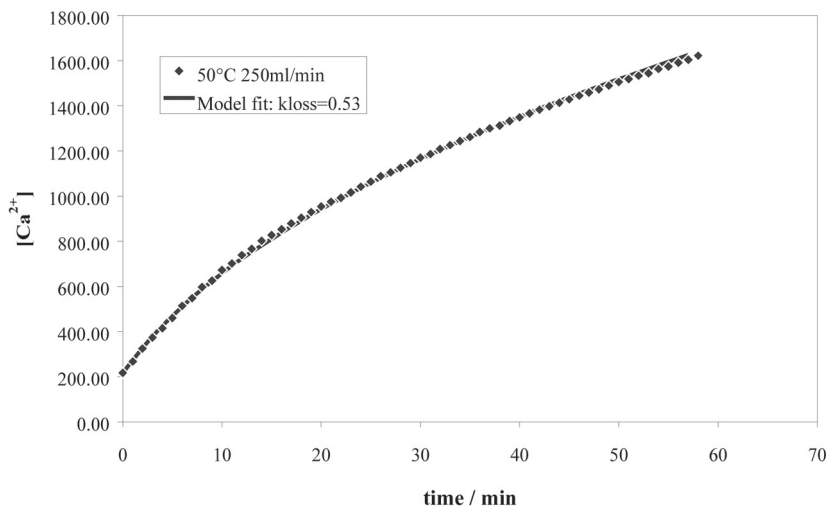
Figure 6 Fit of kinetic model to pHstat data for dissolution of GCC at pH6.5 and 50°C.

that the observed dissolution rate at 50°C (a common temperature for a papermachine) is similar to that at 25°C. However, application of the model to these data using the equilibrium constants for the higher temperature does give an increased value for k_{loss} as expected (Figure 6).

2 Dissolution of calcium carbonate in other acids

It is still quite common for papermakers to use alum as an acid source in wood-containing papers. The use of phosphoric acid in order to control both pH and dissolved calcium concentration was first proposed many years ago [7] and continues to be practised. Both of these compounds will produce insoluble salts on reaction with calcium carbonate. In principle alum will make aluminium hydroxide (hydrated alumina), although the species actually produced may be polymeric and much more complex than this simple salt. At high concentrations, the solubility limit of calcium sulphate may also be exceeded. Phosphoric acid will produce either brushite [$CaHPO_4$], whitlockite [$Ca_3(PO_4)_2$] or hydroxyapatite $Ca_5(PO_4)_3OH$, depending on the conditions. All of these compounds could potentially precipitate on the particle surfaces and thus inhibit dissolution.
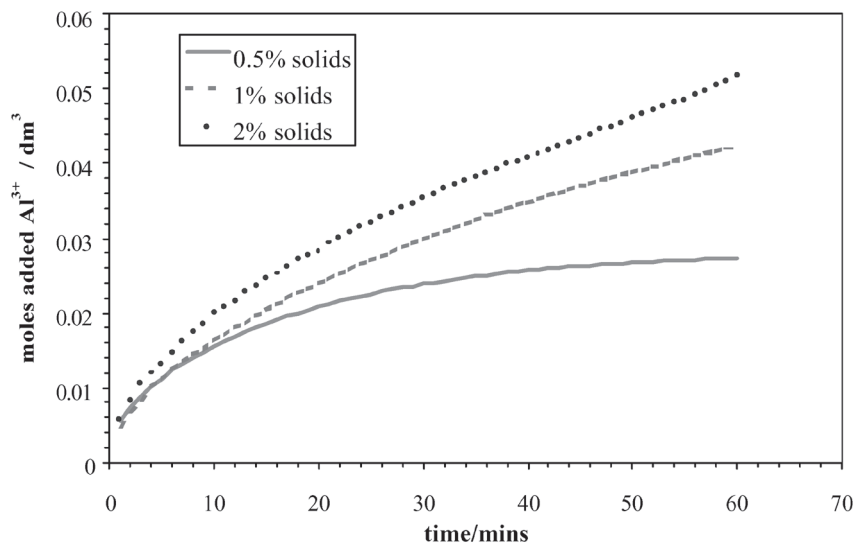
Figure 7 Dissolution curves of GCC in aluminium sulphate solution at pH6.5

The effect of these acids on dissolution rate was examined by using them as the titrant acids in the pHstat experiment. The dissolution rate of a GCC in alum at pH6.5 is shown in Figure 7. Assuming one H^+ ion is produced for every aluminium ion added, the dissolution rate is much lower than that seen with HCl as the titrant acid. Also, in contrast with dissolution in HCl, there is now a dependence of the dissolution rate on the solids concentration of the carbonate. This suggests that the rate of dissolution at the surface is inhibited sufficiently to be comparable to the rate of CO_2 loss from solution. However, it should be noted that the pH of papermachines using alum is generally not dependent on the amount of GCC being used, and so in such cases the inhibition effect is probably negligible.

Figure 8 shows dissolution curves for GCC in phosphoric acid at pH6.5. The initial dissolution slows rapidly and almost completely stops over a period of ten minutes, but then accelerates again. In this second phase the dissolution rate is approximately proportional to the solids concentration of the carbonate, but independent of the airflow rate. If we assume that at this pH there are two available H^+ ions associated with each phosphoric acid molecule, then for the higher solids sample the dissolution rate in the second phase approaches that found in hydrochloric acid. However, with phosphoric
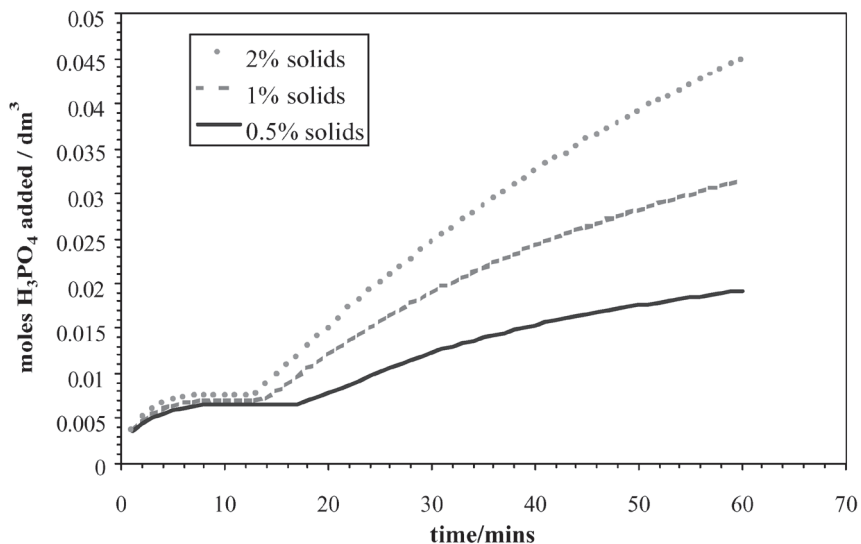
Figure 8   Dissolution curves of GCC in phosphoric acid solution at pH6.5.

acid, equilibrium with the solution is less likely to be established, because the concentration of dissolved calcium is suppressed to a very low level by the precipitation of calcium phosphates. Therefore the observed dependence on solids and not on airflow is not surprising even if in this second phase the inhibition effect of adsorbed phosphate is minimal.

The behaviour of the dissolution rate in the initial phase is harder to explain. Its independence on solids level suggests that the rate determining step does not occur at the particle surfaces, and yet its dramatic decline to near zero suggests that effective inhibition exists. The sudden acceleration at the beginning of the second phase may be some kind of nucleation event; for example, it is possible that at this point calcium phosphate crystals nucleate homogeneously in solution and become the preferred sites for crystal growth, thereby stripping the carbonate of its protective calcium phosphate layer. Whatever the mechanism, these data indicate that the use of phosphoric acid alone does not provide a very reliable barrier to dissolution.

3 Effect of a simple surface treatment on the dissolution of calcium carbonate

Ever since calcium carbonates were first introduced as fillers, chemical treatments have been proposed to inhibit the dissolution of the particles and thus enable them to be used in acid or pseudo-neutral papermaking. Several authors have proposed the use of polyphosphates in order to precipitate an insoluble layer on the carbonate particles which will protect them from acid attack [8,9]. Figure 9 shows the dissolution behaviour in HCl of a GCC which has been treated with 2 wt% of sodium hexametaphosphate. Compared with the untreated carbonate, the dissolution rate is slowed substantially, and, in contrast with the untreated sample, it is dependent on the solids concentration of the carbonate. It thus appears that this simple treatment inhibits the dissolution at the surface sufficiently to prevent equilibrium from being established with the solution, and thus may be an effective method of lowering the pH of a pseudo-neutral papermachine.
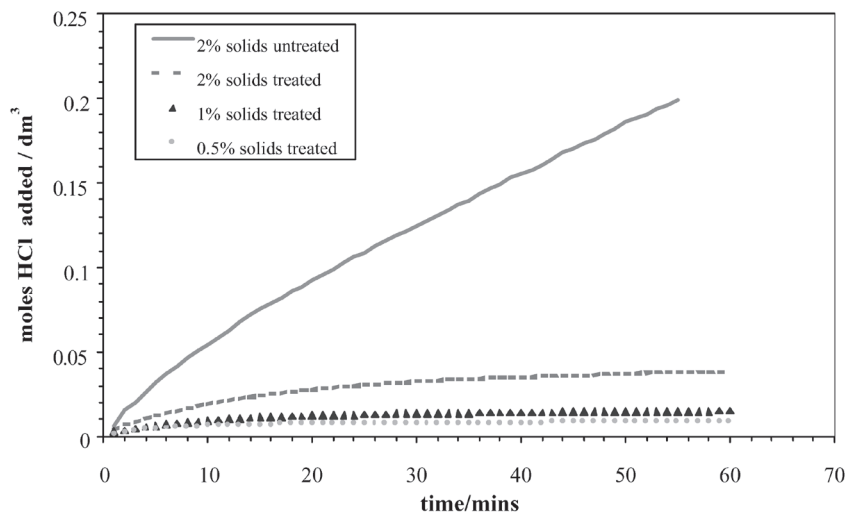

Figure 9   Effect of 2% sodium hexametaphosphate addition on dissolution of GCC.

SUMMARY

Measurements of the dissolution rate of calcium carbonates at pH6.5 show that under the type of conditions likely to be found on a papermachine a pseudo-equilibrium between solid and solution is established, such that the rate of dissolution of the carbonate is dependent only on the rate of loss of carbon dioxide from the water. This implies that the pH of a machine will be dependent primarily on the relative rates of acid addition and removal of CO_2 and dissolved calcium from the system. This is in broad agreement with experience, which shows that a stable pH can be obtained irrespective of the addition rate of calcium carbonate to the machine. The use of alum or phosphoric acid to control pH may complicate this by precipitating insoluble salts which inhibit dissolution. The use of a polyphosphate pre-treatment appears to be an effective method for protecting calcium carbonates from dissolution.

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Transcription of Discussion

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I have intimately experienced this at a mill in another part of the world, which was essentially trying to run a rosin-alum sizing system, whilst increasing the amount of calcium carbonate because they were using increasing levels of recycled fibre and the machines were absolutely coated with calcium sulphate or aluminum hydroxide deposits, and they were asking me why this was.

Jonathan Phipps

The calcium sulphate question is interesting. The first mills to convert to 'pseudo-neutral' using alum expected calcium sulphate to be a problem and they were quite surprised that it wasn't. The solubility of calcium sulphate is actually reasonably high – you have to reach about 600 ppm of calcium before you expect to see it precipitate. What they saw instead was re-precipitated calcium carbonate, because at locations where dissolved CO_2 was removed the equilibrium shifted towards precipitation. At these points they found deposits of very large particles of calcium carbonate. This was quite well documented in a series of papers on the conversion of Haindl Walsum in the 1980s *(reference no. 1 in our paper)*.

Kari Ebeling   UPM-Kymmene Corporation

We have the patent together with AGA for using CO_2 gas to control the pH – it seems to be working very well with de-inked stock with plenty of calcium – its slow enough – the other control principles for pH are too fast.