Carbon dioxide in pulp/paper mill stocks: fix or fizz?

S. R. GRIST* and R. J. CANTY+
* Consultant Chemist,
+Business Development Manager
Covey Consulting Pty Ltd
1st Floor 660 High Street, East Kew, Victoria, Australia 3102

ABSTRACT
The use of carbon dioxide for neutralising pulp mill black liquor residuals and controlling paper machine stock pH has increased dramatically over the past decade. It is replacing, or supplementing, alum and sulfuric acid as the chemical of choice because it does not add any metal or sulfate ions to the water system; an important consideration with the trend to closed loop water systems in paper mills.

However, dissolved and entrained gases can create production problems and paper quality faults at the wet end of the paper machine. Pin holes (where there's a bubble of gas, there no fibre!), drainage loss and poor formation are some of the more noticeable impacts on paper quality, whilst sheet breaks and pump cavitation can create runability problems.

Entrained gases in stock systems have historically been due to mechanical inclusion of air in falling stock, leaky pump glands and poor piping design. Air has a limited solubility in water (~ 120 mg/L), whilst carbon dioxide has a solubility of 1450 mg/L in water at 25^{O}C and 1 atm. pressure. Thus carbon dioxide can create up to 12 times more dissolved gas than air, which will erupt out of solution when the stock pressure is reduced to one atmosphere as occurs at the flowbox slice. So while entrained air was a minor annoyance, entrained carbon dioxide can be a major problem.

Up until now, the method for measuring entrained gas yielded a total entrained gas result and did not distinguish between air and carbon dioxide. Recent developments have resulted in a new test procedure which allows the measurement of both total gases and CO_2. The method is simple, fast and reproducible as long as the carbon dioxide pressure-solubility ratio is borne in mind – i.e. correct sampling is a critical step in obtaining accurate results.

This paper discusses the development of the test method and the background chemistry of carbon dioxide addition to paper machine stock systems.

INTRODUCTION

The rise of carbon dioxide as a key chemical in the pulp and paper industry has been one of the most important steps in allowing mills to close-up their water systems. The acidic properties of carbon dioxide are being used to replace alum and sulfuric acid for neutralisation of pulp mill stocks and for adjustment of paper machine pH. The beauty of carbon dioxide in this role is that it leaves no residual sulfate or aluminium ions in the system, thus allowing the water to be used many more times before treatment is required. The other potential source of carbon dioxide in paper machine waters is the gas liberated when calcium carbonate filled papers are recycled under acidic conditions.

Carbon Dioxide Chemistry

The presence of CO_2 gas (i.e. bubbles) is governed by its equilibrium with dissolved CO_2 (carbonated water) as shown below.

$$CO_2(g) \Leftrightarrow CO_2(aq)$$

The equilibrium constant[(1)] for this reaction is:

$$K_{CO2} = \frac{[CO_2(aq)]}{P(CO_2)} = 2 \times 10^{-3} \text{ M/atm. at } 25^{O}C$$

The solubility of CO_2 also:

- decreases with increasing temperature
- increases under elevated pressure
- is independent of pH.

Once the CO_2 has dissolved, it then reacts with a water molecule to form carbonic acid, H_2CO_3, by the following reaction:

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3$$

The equilibrium in this reaction[(1)] is such that only a small fraction exists as H_2CO_3

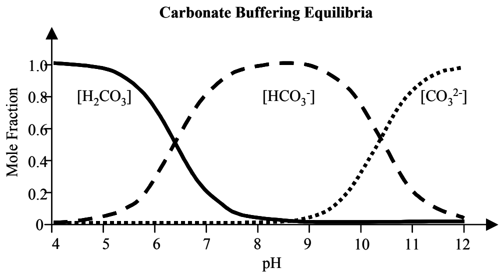
$$K_{H2CO3} = \frac{[H_2CO_3(aq)]}{[CO_2(aq)]} = 1.3 \times 10^{-3}$$

The carbonic acid then undergoes a series of acid-base reactions in which the products are dependant on pH: the Carbonate Buffering Equilibria.

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}$$

Carbonic Acid   Bicarbonate   Carbonate

This series of equilibria are kinetically favourable and the system will buffer itself rapidly. This three-component equilibrium is best represented in the following graph:



What this graph shows is that carbonic acid levels are significant only below pH ~8.5. If carbonic acid is present, then dissolved CO_2 will also be present as required to satisfy the $H_2CO_3/CO_2(aq)$ equilibrium equation. However, above pH ~8.5 any CO_2 present as entrained gas will be forced to dissolve and react with water to become carbonic acid but, as soon as this carbonic acid is formed it is rapidly drawn into the carbonate buffer equilibria, thus making room for more carbonic acid and hence more CO_2 to dissolve. Eventually there are only normal atmospheric levels of CO_2 are left in the entrained air. (This is the same mechanism that occurs in the oceans to buffer atmospheric CO_2; as atmospheric CO_2 levels have risen over the past decades, so ocean pH has begun to fall).

Thus, in theory at least, raising the pH of the stock to above pH ~8.5 should deplete the entrained air of any CO_2, leaving only the normal atmospheric level of 0.04% CO_2.

Our proposed method measures the presence of entrained CO_2 gas indirectly, by measuring the entrained air content on a stock sample at two different pHs; the difference being the CO_2.

RESULTS

Test Method Development

There are two main methods for measuring entrained gas in stock; mechanical compression and ultrasonics.

Various mechanical compression devices are discussed by Woodworth[(2)], including the Entrained Gas tester (EGT) which we chose because it is readily portable, allowing the same instrument to be used in the lab and mill. The operation of the EGT is described in greater detail in the manufacturer's brochure and manual[(3)].

Ultrasonic entrained gas instruments are mostly used for in-line applications and, as such, are of little value for a mill surveys where multiple sample points are involved.

The principle of the mechanical compression technique is based on Boyle's Law of gases (pressure-volume relationship). A sample of stock is placed in the apparatus, essentially a piston-cylinder device, at atmospheric pressure. The stock/gas mixture is then compressed to 2 atmospheres pressure by moving the calibrated piston, thus effectively halving the entrained gas volume. The volume reduction, as measured by the swept-volume of the piston, is due solely to the compression of the gas, as the liquid and solids phases are essentially incompressible. This principle works well for air with its negligible solubility in water. However, it ignores one important property of CO_2 – it is soluble in water, and as such does not follow the ideal gas laws.

When the stock is compressed from 1 to 2 atm. in the EGT apparatus, the solubility of CO_2 increases and some, or in many cases all, of the entrained CO_2 gas dissolves/re-dissolves in the stock. This results in a gas volume reduction of much more than the 50% predicted by Boyle's Law, thus leading to potentially erroneous results. In the case where all the CO_2 dissolves, the error using the Boyle's Law calculations is 100%.

Our dual-pH EGT method aims to eliminate this error by distinguishing between CO_2 the air in the entrained gases. The two essential points in this method are:

(i) the measurement of total entrained gas at two prescribed pH levels and

(ii) the mode of operation of the EGT instrument.

Dual pH Testing

The method involves performing the EGT test stock at it's original pH to measure the total entrained gas (CO_2 and air) in the original stock. The test is then repeated at pH10 by adding a 5 ml aliquot of 2M sodium hydroxide (NaOH) solution to the EGT device prior to addition of the stock. (It was noted that the NaOH had a detrimental effect on the O-ring in the EGT apparatus – we propose to use a more dilute NaOH solution in further work, or find a better O-ring) The NaOH consumes any CO_2 via the acid-base reactions described in the Introduction of this paper, thus allowing us to measure only the remaining entrained air. The results are calculated simply, as follows:

Ent. CO_2 = Total Ent. Gas (test at stock pH) - Ent. Air (test at pH 10)

Theoretically, raising the pH to just above 8.5 should deplete the stock of CO_2. In practice we found that elevating the pH to >10 ensured compete dissolution of the CO_2.

EGT Operation
The initial compression of the stock sample to 2 atm. must be done rapidly to avoid re-dissolution of the CO_2. Recommended time for sample compression is 5 seconds or less.

Investigations into the mode of operation revealed:

- After the initial rapid compression step, the stock pressure, as indicated in the sight tube, begins to gradually fall as the pressurised CO_2 micro-bubbles are forced to dissolve.
- Re-adjusting the device to 2 atm. must be done several times until steady state is reached. In practise we found that this takes between 10 and 60 sec, with re-adjustments required every 10-15 sec depending on the amount of CO_2 gas in the system.
- The final stepwise re-adjustment to 2 atm. should correspond to the amount CO_2 dissolved during the test. As such, this data was identified as a potential source of further information on the nature of CO_2 in the system. Unfortunately the results obtained for this recompression step were found to be highly variable and not very useful.

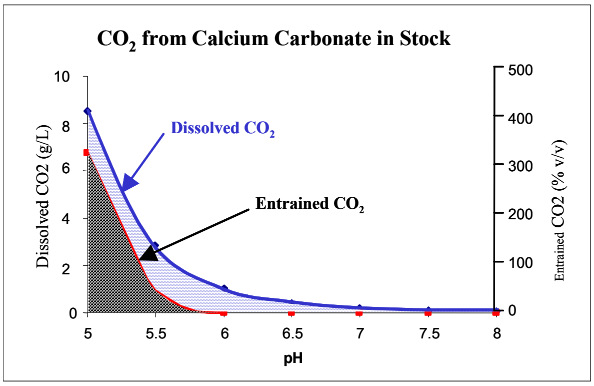
Interferences
Possible interferences could come from other acidic gases which may also be detected by this method. Sulfur dioxide is one the other most common acidic gas present in some mill systems. However, the relationship between SO_2 and pH is such that entrained SO_2 is only likely to appear below pH ~ 4 (mid point between $pKa_1 = 1.81$, $pKa_2 = 6.91$ for H_2SO_3)[1] which is well below any practical mill operating pH. Thus we conclude that SO_2 will not interfere with this proposed method.

Sampling
The effect of stock pH and temperature on the CO_2 content of the entrained gas is very significant. It thus becomes important to collect data on temperature and pH of the samples both when sampled and when analysed. Sampling and testing should be performed in-situ; delays resulting in a drop in temperature may compromise the results.

It is also important to recognise that the stock lines in most mills operate at around 2 atm. pressure and that releasing the stock into the EGT apparatus at 1 atm. will actually create the entrained gas in-situ. To avoid sampling errors the following steps should be taken.

1. Thick stocks are sampled by pouring directly into the open top of the apparatus. Stock should be allowed to fill and overflow the apparatus until a homogeneous sample is obtained.
2. Thin stocks can be sampled using the thin stock sampling head which allows the stock to flow through the apparatus. At least on full flush of the apparatus must be performed before a reliable sample is obtained.

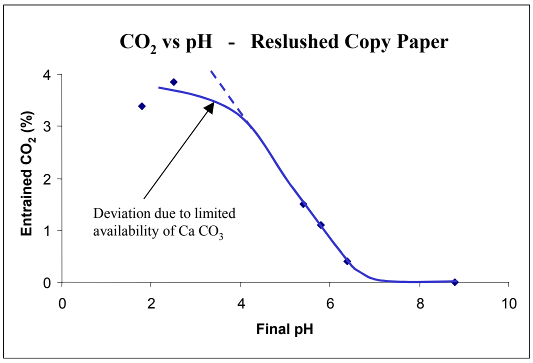
Calcium Carbonate Recycling Study
The presence of calcium carbonate in recycled fibre can lead to the generation of dissolved and entrained CO_2. Calculations based on the solubility of calcium carbonate suggest that CO_2 generation will increase with decreasing pH. The graph below shows the dissolved and gaseous CO_2 generated at various pH levels from a theoretical infinite source of calcium carbonate.



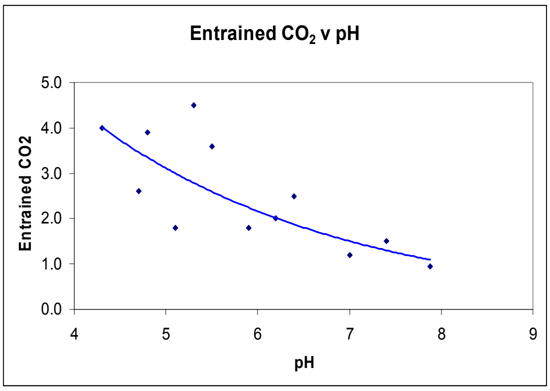
This shows that dissolved CO_2 decreases rapidly with increasing pH. At pH 7.0, the dissolved CO_2 levels would be 170 mg/L, which is equivalent to only 12 % saturation. However at pH 5.5, typical of acid-sizing systems, the CO_2 generation would exceed the saturation limit and form up to 40 % v/v entrained gas. This is only a theoretical figure based on an infinite supply of $CaCO_3$; in reality the amount of CO_2 actually released will depend on the amount of available $CaCO_3$.

Laboratory Study
A laboratory study of pH vs. entrained gas was undertaken in order to verify this theoretical CO_2 / pH relationships. In this study the source of CO_2 was from the laboratory re-slushing of Australian copy paper containing ~20 %

calcium carbonate filler. The paper was re-slushed in water (pH 7.0) and the pH of the stock was adjusted by addition of aliquots of 1.0M hydrochloric acid. The results show a similar trend to the theoretical results, but the maximum amount of CO_2 generated is limited by the finite amount of $CaCO_3$ in the batch of stock.

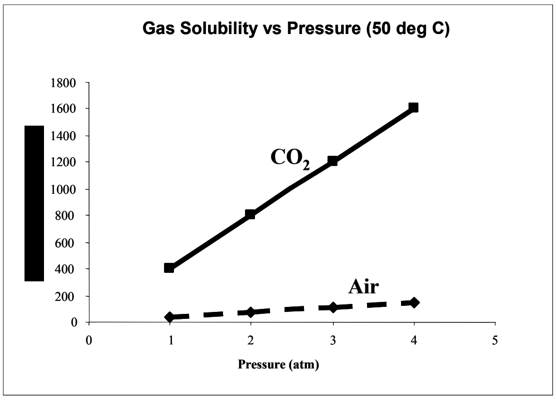


Mill Results
The "CO_2 vs pH" laboratory experiment was repeated at a mill using both CO_2 for pH control and $CaCO_3$-filled RCF. The mill thin stock was adjusted to various pHs and the entrained CO_2 measured. The results show a similar trend as the laboratory results, however they are more variable due to the inconsistent nature of the original CO_2 levels in the stock.



DISCUSSION
Entrained Gas Testing
In the EGT method, the standard procedure is to pressurize the sample to 2 atm., as observed by the 50 % volume reduction of the air in the tester instrument's sight tube. It is assumed that entrained air micro-bubbles of entrained gas respond to this doubling of pressure and are similarly reduced in volume by 50 %. Hence the volume of entrained gas (expressed at 1 atm.) can be calculated by multiplying the piston swept-volume by 2. This concept can correctly be applied to air because its solubility in water is negligible and does not change significantly with pressure.

However, CO_2 does not behave the same as the air in the sight tube. The sight tube air is effectively a reference gas, and must behave in the same manner as the entrained or dissolved gases under test for the results to be valid. The major difference between the sight tube reference gas and a CO_2-based sample gas is that the solubility of CO_2 is about twelve times higher than air, and it varies significantly with pressure. Figure 4 compares the solubility of CO_2 and air over a range of pressures.



Considering the case where the entrained gas is pure CO_2, operating the Tester to half-volume of sight tube (2 atm.) would cause the CO_2 micro-bubbles to not only reduce in size, but also partially dissolve before reaching a new equilibrium at the elevated sample pressure. The dissolution would further reduce the CO_2 bubble volume and consequently reduce the pressure in the EGT. The air in the sight tube would expand slightly to fill the void left by the dissolving CO_2 and settle in a position indicating somewhere between 1 and 2 atm. Thus the EGT screw would need to be further turned to resume the nominal 2 atm. final pressure, whereupon more compressed CO_2 bubbles would begin to dissolve. This step would be repeated several times until the sight tube level remains constant at 50 % of original volume, ie the tester has "flatlined" indicating that the gases and stock have reached equilibrium

This slow-piston procedure yields not only the Boyle's Law half-volume of the entrained gas, but also the volume of CO_2 which dissolved in response to the pressure increase from 1 to 2 atm. during the test. However, even this more rigorous test runs into complications when the line stock is saturated with dissolved CO_2 and is above the 2 atm. test pressure. In this case we would not be able to re-dissolve all the CO_2 originally dissolved in the high pressure stock.

If the piston compression is performed at a fast rate, ideally instantaneously, then entrained bubble compression will occur according to Boyle's Law, before any significant dissolution of the CO_2 occurs. Hence for a liquid containing an unknown ratio of air and CO_2, a fast compression rate will ensure that all the gases compress linearly without significant interference from the relatively slow dissolution processes.

The dual pH EGT was developed by Covey Consulting to enable measurement of entrained CO_2 and entrained air as well as to overcome these inconsistencies and errors in the standard test. The method relies on the fast compression technique to obtain a total entrained gas result and uses a high pH measurement to provide a measurement of the CO_2-free air; the difference being the CO_2 result.

Production and Quality problems with entrained air, CO_2

The literature[4,5,6] cites many cases of entrained gas but generally the gas is regarded as air mechanically entrained in the stock by either entrapment when free falling stock hits the surface of stock in a tank (rather than having the falling stock mix via a submerged discharge) or ingress through leaking glands and pump seals. Entrained air has also been reported to result from air trapped within dried fibres[4].

Matula and Kukkamaki[4] quote levels of entrained air in thick stock at 1-2 % v/v and dissolved gases at similar levels. Their analysis of air bubbles at the wet end of a paper machine indicated the minimum, average and maximum sizes were 10, 100 and 300 μm respectively. The 100 μm diameter bubble would be just visible to the eye. These bubbles are hydrophobic and tend to attach themselves to fibre surfaces or fines.

At pump discharges and other high pressure points, some entrained air will dissolve as the stock pressure is increased to 200-300 kPa (theoretically up to 300 mg/L dissolved air at 300 kPa and 50^{O}C). However, entrained CO_2 will dissolve at a much greater rate to a much higher level (up to 3600 mg/L dissolved CO_2 at 300 kPa and 50^{O}C) in this high pressure stock. Eventually this stock will discharge through the slice to atmospheric pressure, whereupon the air and CO_2 evolve as small bubbles, the latter gas in much greater volume because of its higher solubility at higher pressures. Thus as the stock is carried by the wire, with dewatering occurring by gravity and assisted by foils, the hydrophobic entrained gas bubbles remain with the fibres, leading to interrupted fibre-bonding, poor formation and, in severe cases, pin-holes .

Rauch and Burke[5] noted that typical production problems included the need for higher capacity pumps (for example, 3 % entrained gas means you have to pump 103 litres of fluid to get 100 litres of stock), deposits on forming wires, press felts and dryer screens, increased foaming, the accumulation of hydrophobic substances (the gas bubbles causing a flotation effect), web breaks from resinous and sticky substances and poor drainage on the wire. Paper quality losses could include poor formation, high porosity, poor print quality, pinholes/holes and strength losses.

Schulz and Scott[6] used the Manual Air Tester to determine levels of entrained air (EA) in a coated recycled boxboard mill. Inter alia, they found that the level of EA in successive process steps showed no correlation, nor did the level in the headbox with the amount of air introduced during stock preparation. As they were employing the standard method for the MAT, which assumes none of the gases dissolve substantially as the pressure increases, it is likely that the presence of a significant amount of entrained CO_2 would have lead to errors in EA due to that components solubility relationship with pressure.

One other phenomenon observed was cyclical variation in free-CO_2 levels resulting from pump cavitation. The free CO_2 levels were found to vary by a factor of up to three over a period of less than a minute. Pump cavitation occurs because the inlet pipe to the pump operates at reduced pressure, allowing some dissolved gasses to revert to free CO_2. As the gas builds up in the pump it reaches a point where coalescence of micro-bubbles can occur leading to pocket of gas in the pump housing. The pocket of gas grows until it reaches a size that allows it to swept from the pump, thus creating a slug of CO_2 which is swept along the outlet pipe. Re-dissolution of the gases from pump cavitation is difficult because the gas levels in the slug are by nature very high and are likely to exceed the solubility limits.

Calcium Carbonate Filled RCF

The growing use of calcium carbonate as a mineral filler for paper and as a coating pigment has also been identified by papermakers as a potential source of entrained carbon dioxide generated by reaction of the carbonate with acidic materials at the wet end. The acidic materials can include alum, PAC, wet strength agents and acid used for fine-tuning the pH control close to the machine.

Indeed the Calcium Carbonate Recycling study described in this paper confirms the evolution of CO_2 from the re-slushing of calcium carbonate filled RCF. Entrained CO_2 will begin to appear as the pH drops below approximately 6. At pH 7 the stock is 12 % saturated with CO_2, whilst at pH 8 the CO_2 saturation level is reduced to only 4 %. These results emphasise the importance of keeping the pH above 7 if using such stock. Even at pH 7, the CO_2 contribution from RCF should be taken into account when considering the overall management of CO_2 within the mill.

Standard de-aeration and antifoam strategies will not work with carbon dioxide while it is in the dissolved form, so that attempts to control defoamer addition by measured entrained air content could result in undersupply of the defoamer. This results in an inability to deal with the transient incidents of entrained CO_2 bubbles formed when the dissolved CO_2 encounters regions of lower stock pressure in its torturous path along the stock approach system.

Existing on-line equipment

Most on-line piston/cylinder EGT instruments operate at a relatively slow compression rate to allow the instrumentation to avoid errors due to pulsing and hysteresis. This is a correct strategy if the gas under test is only air but, as discussed above, this can lead to severe errors by falsely assigning the gradual dissolution of the CO_2 during the slow compression step as the Boyles Law half-volume of more entrained gas. Thus the results of a slow compression technique includes (i) the initial Boyle's Law half-volume of the entrained gas plus (ii) the falsely assigned half-volume due to dissolution of CO_2. This can result is severe over-estimation of results.

Various strategies may be possible for overcoming this error, but are yet to be fully investigated. Such possibilities include: modifying instruments to the fast compression method, continuing final compression until all gas is dissolved (> 2 atm.) and recalculating results algorithms.

CONCLUSIONS

- The dual pH entrained gas test developed in this study allows mills to distinguish between entrained air and entrained CO_2.
- The use of the simple Boyle's Law calculations for entrained gas testing gives erroneous results if CO_2 is present. This problem extends to some commercially available in-line entrained gas testers.
- The use of CO_2 in mills should be closely controlled to avoid evolution of entrained CO_2 in the stock approach system. Design of these control measures should take into account the buffering reactions of the CO_2/Carbonate system, the alkalinity of the stock to neutralised and the solubility of CO_2.
- Engineering design of the CO_2 addition system should take into account efficient gas dispersion, sufficient residence time for chemical reactions to occur and appropriate location of in-line pH sensors. However, most importantly, the engineering design must take into account the chemistry involved.

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