

needs to be established. Most of the remaining unconverted SC mills referred to in Table 1 are based primarily on virgin mechanical pulps.

In addition to the effect on pulps and wet end chemistry, PCC alkalinity also affects other operations throughout the pulp and paper mill. The high pH, alkalinity, and calcium ion content from white water on an alkaline SC machine can impact the pulping, bleaching and paper machine operations throughout an entire mill. These need be evaluated to determine the overall PCC/neutral impact.

The third area of impact of PCC is on the operation of the paper machine. PCC (and alkaline/neutral pH) can affect retention, drainage, draws, water removal, rewinding and the supercalendering of SC paper. Proper pretrial testing and preparation must be done to eliminate any potential problems in the machine or calendering systems.

Finally, PCC impacts the finished SC paper properties significantly. In addition to optical properties, PCC affects the porosity, coefficient of friction (COF), bulk, smoothness, and absorptivity properties of SC paper. These changes, in turn, affect the offset and rotogravure printability of PCC-filled SC paper. Filler, papermaking, and/or printing pressroom modifications may be necessary to get optimum overall paper performance.

In summary, PCC affects SC production in four primary ways:

- higher wet end pH
- pH, calcium and alkalinity changes around the mill
- machine and supercalender operation
- paper properties and printability

These four areas will be examined individually, thereby describing a “holistic” approach to neutral conversion and a blueprint for the most successful use of PCC for production of SC grades.

1. PCC, pH, and Control of Alkaline Darkening

As discussed above, virgin mechanical pulps tend to exhibit higher alkaline darkening than recycled pulps. This is illustrated in Figure 4 for a deinked pulp and two virgin pulps. The deinked pulps, due to their extensive processing, generally lose a point or less of brightness from pH 5 to 8, while virgin mechanical pulps can lose from 3-8 points of brightness. To date we have evaluated the pulp brightness characteristics of more than 100 groundwood mill systems and have found there is no sure way to predict the extent of alkaline darkening. It must be measured experimentally and then dealt with appropriately.

Obviously the presence of severe or even moderate alkaline darkening can impede the performance of PCC in SC paper. The loss of 3-8 points of paper brightness can be the difference between a great conversion and a total conversion failure. For this reason, the weak-acid-chelant (WAC) pH control system was developed⁽²⁻⁷⁾. This system allows for both the successful reduction of alkaline darkening as well as for stable operation of the wet end of the SC paper machine.

The WAC system is run by adding a weak acid to the wet end of the paper machine containing both CaCO_3 and an appropriate chelant/sequestrant. Typically, a pH of around 6.8-7.2 is readily and cost-effectively achievable. At this pH, alkaline darkening can usually be controlled to a level where the brightness benefit of PCC over standard filler clays can be realized to a high degree. This is illustrated in Figure 4 that shows the alkaline darkening reduction possible with WAC pH control. The exceptional brightness of the WAC system is due to a combination of pH control (reduced alkaline darkening) and soluble ion reduction (calcium and other species). The WAC system almost always enables the cost-effective use of PCC to produce both SCA and SCA+ grades.

Two weak acids have been shown to be most cost-effective in the WAC system for pH control in SC machines; phosphoric acid (H_3PO_4) and carbon dioxide (CO_2). Phosphoric acid is generally preferred for ease of use and maximum brightness gain, but its use is more difficult in areas where strict effluent phosphate limits exist. In these situations, effluent phosphate removal steps are required or the use of CO_2 is warranted. Phosphate can be removed from paper mill effluent in many cases through the use of well-known precipitation chemistry with

iron or aluminum salts. Data for the treatment of paper mill effluent with polyaluminum chloride (PAC) is shown in Figure 5. Cost-effective removal of P with PAC is achievable in many paper mill systems. However, in areas with extremely low P limits, it may be necessary to partially or completely replace the phosphoric acid with CO₂. The choice between phosphoric and CO₂ is usually based on overall cost optimization and the alkaline darkening characteristics of the pulps involved. In general, the phosphoric acid system is preferred for maximum brightness.

2. Mill Impact of PCC and Alkalinity

Whether the WAC system is used to control pH or it is a standard “alkaline” conversion at around pH 8, the addition of virgin PCC filler to a SC machine can have a significant impact around the paper mill. The first area of potential concern is in multi-machine mills where cross-over between machines can occur through white water, broke, or process water systems that can allow particulate calcium carbonate or soluble alkalinity to be shared among different paper machines. Even in mills where machines are considered “isolated”, our experience is that almost always the presence of carbonate on one machine will affect other machines. Therefore, trials in multi-machine “acid” mills must be run on all machines simultaneously or specific steps must be taken to limit cross-contamination. These steps can include running trials when non-trial machines are down for maintenance, temporarily sewerage excess white water on trial machines, and/or the complete segregation of trial broke. If cross-machine contamination occurs, the most common result is a rise in pH on the non-trial machine leading to alkaline darkening and difficulty in meeting brightness targets.

The second area of concern in SC PCC trials is the effect of PCC-containing white water being used for dilution in the mechanical pulping and bleaching operations. Often cloudy (or even raw) white water is used for dilution throughout the mill. This can raise the pH, alkalinity and hardness levels of process streams going back in the system. This can lead to non-optimal bleaching efficiency and/or the initiation of scaling problems as calcium hardness levels get too high. Of particular concern is when raw white water with significant particulate calcium carbonate is blended with a pulp stream that is later treated with strong acid (e.g. the quenching of peroxide bleached pulp). This can lead to very high soluble calcium levels and can cause scale and other related problems. Another area of concern is the potential formation of gypsum deposits on TMP refiner plates caused by high dithionite and calcium levels in the system.

Several steps need to be taken to avoid these potential problems with white water contamination in the mill. First, the extent of possible contamination needs to be determined prior to any trial activity. This can be done by a detailed machine audit where white water and other process flows throughout the mill are charted. Often this process includes the use of a mill lithium trace, a procedure developed by SMI to facilitate SC PCC conversions.

Lithium Trace Procedure

The lithium trace was originally developed to determine paper machine closure and to estimate the amount of acid required for WAC pH control. In the lithium trace procedure, paper machine closure is calculated by measuring the buildup of Li⁺ ions in a white water system while a solution of LiCl is accurately pumped into the wet end of the paper machine using a small peristaltic pump. The equilibrium concentration of Li⁺ is determined by taking white water samples periodically over, typically, a 24-36 hour period. These samples are then analyzed for Li⁺ by an inductively coupled plasma (ICP) procedure⁽⁸⁾. The Li⁺ concentration is then plotted versus time and the equilibrium plateau lithium concentration is taken from the graph. This value is used to calculate the Enrichment Factor (EF) and machine closure from the equations below:

$$\text{Enrichment Factor} = \text{EF} = \frac{\text{equilibrium concentration of wet end additive}}{\text{added concentration of a wet end additive}}$$

$$\text{EF} = 1/(1-r) \quad \text{where } r = \% \text{ closure}/100$$

A lithium trace plot for a commercial SC machine is shown in Figure 6. In this analysis, about 0.3 liters/minute of a 3.6% lithium chloride solution (as Li^+) was added to the white water tray. The measured lithium content in the white water increased from zero to about 1.5 ppm after about 10 hours. Calculations based on headbox flow rate (95,000 liters/minute) showed that the enrichment factor was 12.6 and the closure was 92.1% for this machine. These calculations can be used to accurately predict weak acid demand for the WAC system.

A secondary benefit of the lithium trace is that it allows the analysis of the flow of white water throughout the mill. If process water samples around the mill are collected while the machine lithium trace is ongoing, the extent of cross-contamination from any machine can be accurately determined. This information can be used to plan any changes required to run the trial or conversion more effectively.

In addition to the lithium trace, there are some SC conversion 'rules of thumb' to minimize the impact of PCC on other mill operations:

- Maintain good first pass PCC retention (minimum 20%, 30% or higher preferred)
- Minimize raw or cloudy white water use in pulping and bleaching operations
- Maintain good saveall efficiency; consider use of polymers for higher solids removal
- Never use raw white water where post-quenching with strong acids is employed
- Discuss scale control options with your water treatment chemical supplier if some carbonate – containing water use is inevitable in some areas of the pulp and bleach plants

3. PCC Effects on Machine and Supercalender Operation

PCC and alkaline pH affect all aspects of the paper machine and calendering operations to some degree. As discussed above, the most obvious and immediate effect is an increase in wet end pH to about 8 for a completely alkaline conversions and to about 7 when using the WAC system for pH control. Both of these options have the advantage that they are highly buffered. That is, they lead to a very stable pH and resist any sudden pH change. This is preferred for long-term wet end stability and good machine productivity. As mentioned above, the WAC system gives an optimal blend of stability, low pH for brightness optimization, and low calcium levels for good runnability and machine cleanliness.

Below is a checklist of expected changes associated with PCC in SC manufacture and recommendations for steps to optimize.

Retention

The retention system may need to be adjusted because PCC is usually delivered as an undispersed slurry as compared to clay which is usually dispersed. This typically requires some optimization of chemical dosages, not a complete change in the retention system. The lack of dispersant with PCC often reduces the demand for the cationic donor portion of the retention system. Appropriate optimization is required to avoid overfloculation, poor formation and/or a non-optimum wet end charge balance. This can be effectively done with pre-trial lab work by the retention aid supplier followed by appropriate final adjustments during initial trial periods.

Entrained Air / Foam

There is sometimes an increase of entrained air or foam during alkaline or neutral SC conversions. It seems that at higher pH, pulp foams can be more stable. An appropriate alkaline defoamer or deaerator should be available on standby to prevent potential problems. Often it is preferred to add the defoamer to the white water tray before the silo.

Wire / Felt / Felt Wash:

Paper machine wire life with PCC is usually equal or better than wire life with clay (much better if calcined clay was used). Although some ceramic surfaces of flat boxes or uhle boxes can retain

PCC and cause excessive fabric wear, this is only the case with older equipment and is almost never a problem today.

We have seen increased felt wear in several conversions (not an issue during short trials). It can be related to the felt wash or the use of fabrics that are not suited to neutral/alkaline pH. PCC washes out of the felt easily, so if good pressure showers and uhle box vacuums are in place, there should not be any problems. It is recommended to use a felt with high porosity, and monofilament felts are usually preferred to multi-filament types.

The choice of felt wash is very important. There are a number of considerations relating to type (batch or continuous) and chemistry (acid or alkaline). Felt wash options should be discussed with the felt supplier.

Machine Draws:

Alkaline paper webs tend to be more elastic (softer) than acid webs. It is very important to minimize draws with an alkaline SC sheet (approach 90° sheet-take-off angle to minimize web tension). The draws may appear slacker than they are on the acid side. Over-stretching the alkaline sheet can hurt a number of paper properties.

Wet End Chemicals

Additives such as biocides, dyes, and defoamers may have to be changed to reflect the pH and chemistry changes associated with PCC use. In general, biocide costs can increase compared to acid systems, but other costs should not change much. Biological counts in PCC storage tanks should also be monitored. Regular acid boil-outs are also recommended.

Wet end starch is almost always used for SC paper filled with PCC, especially for offset grades. Our experience is that addition of starch does not hurt SC rotogravure printability with PCC but may do so with clay.

Pitch control additives can usually be eliminated or reduced when PCC is used. This is because PCC acts as a scavenger of dissolved and colloidal materials in the wet end ⁽⁹⁾.

Ash and Moisture Measurement

Ash and moisture gauge suppliers should be contacted to determine the specific capabilities of equipment in place. In particular, analysis of clay/PCC blends can be problematic. It may be necessary to do some pre-trial calibration with paper containing PCC/clay blends with some installed systems.

During trials, using a combination of quick ash and EDTA titration measurements can be used for fast and accurate clay and calcium carbonate analysis in the sheet. This procedure gives both PCC and total filler values in about 10 minutes.

Sheet Feel and coefficient of friction (COF)

The alkaline SC sheet may feel softer and limper to the touch. Also, the sheet will have higher COF, both uncalendered and calendered. This may necessitate slight adjustments in rewinder operations.

Supercalendering

The PCC sheet will be bulkier, softer, and slightly more porous than the acid sheet. Often optimization will require slight changes in supercalender operations. Uncalendered bulk can be significantly higher with PCC and may require changes in roll handling from the reel to the

supercalender. Supercalender pressure and moisture will need optimization to get the best gloss. Because of the micro-porosity of the PCC sheet, it can carry more moisture without problem and is often more resistant to calender blackening.

Calender deposition is an issue in some mills. It is related to moisture in the sheet from steam showers/boxes. Steam shower use, position, and operating variables should be monitored.

4. Paper Properties and Printability

PCC Effect on Paper Properties

As discussed above, the primary benefit and driver for PCC use is optical (sheet brightness and opacity) improvement. However, many other SC properties are affected. Table 2 summarizes some key paper tests from a pilot SC trial run at the KCL pilot machine in Espoo, Finland. This table gives SC paper test data for a 56 gsm sheet at 30% filler made from a 75/25 PGW/kraft pulp blend. The data is for water washed filler clay compared to a clustered aragonitic filler PCC. These results are quite typical of our experiences in commercial SC trials and conversions.

Since virgin PGW was the dominant pulp used in this study, the WAC system was used to control pH to about 7.0. This enabled the PCC system to give about 5 points of brightness and 1 point of opacity over the acid (pH 5) clay system, a very typical response for SCA paper.

Table 2 shows that gloss is quite similar for clay and PCC. In our commercial experience, sometimes PCC gives slightly less gloss than clay but calendering conditions can usually be adjusted to make gloss a non-factor during conversions. The lower density (higher bulk) shown in Figure 2 is typical of both calendered and uncalendered paper with PCC. This combined with higher moisture-carrying capacity of the PCC paper often makes it more resistant to calender blackening, thereby giving the papermaker more flexibility in calender operation.

The higher Parker Porosity (more open sheet) for PCC in Table 2 is also typical. The same particle structural effects that give PCC such good optical properties tend to open up the SC sheet. This is further reflected in the PDA absorptivity results in Table 2 that show the PCC sheet gives faster absorption (lower PDA values = faster absorption). The PDA measures adsorption at short contact times and has been shown to give useful information for predicting offset piling in SC paper with PCC^(10,11).

Although the difference in porosity between PCC and clay can be minimized via changes in PCC morphology, pulp refining, and papermaking conditions, the general nature of the pore structure in PCC-filled SC paper is fundamentally different as indicated in Figure 7. This figure shows the pore structure of the KCL papers as measured by mercury porosimetry. Generally PCC generates a structure with more pores and smaller pores (shifts porosimetry curve down and to the right). This pore structure difference has implications in printability as discussed below.

The smoothness improvement shown in Figure 2 (reduced PPS-10) is also typical. PCC, by virtue of its bulking effect, usually produces a smoother sheet than clay after supercalendering. This may be due to a real reduction in surface imperfections or an apparent reduction based on increased sheet compressibility.

The PCC effect on COF higher and tensile (lower) seen at the bottom of Table 2 is also well supported by our commercial experience. The tensile effect is related to the slight debonding/bulking impact of PCC and the COF of PCC paper has been found to always be higher than clay in publication papers from newsprint to SC. The higher COF should be considered in rewinding, calendering and printing operations as it can impact all aspects of roll handling. In general this is not a problem, just a factor that must be dealt with in the learning curve.

PCC Effect on SC Rotogravure and Offset Printability

The net effect of the paper property changes with PCC is that there are some differences in how SC paper performs in the pressroom and in the final printed product – the ultimate test of success for any publication paper grade. These differences can be compensated for, thereby allowing printers to take advantage of the benefits that PCC gives these papers.

The brightness, whiteness, and opacity advantage of PCC is often evident in the overall appearance of the printed SC sheet. The opacity benefit also gives a significant print-through advantage for PCC paper. Usually print-through, strike-through and show-through are all improved (reduced) compared to clay. However, this is counterintuitive considering the higher absorptivity of the PCC sheet. This is further illustrated in Figure 8, which shows print-through results from a survey of commercial PCC and clay SC papers we recently completed. It shows that PCC is generally better than clay for PT – it usually gives lower PT values. We consistently see reduced print-, strike-, and show-through with PCC in all commercial SC and groundwood production grades. We believe this is due to a combination of higher paper opacity and a higher paper “oil absorption” when using PCC.

The other major rotogravure influences with PCC are on missing dots, ink demand and print mottle. Because of good paper smoothness and compressibility, PCC tends to reduce missing dots as measured by the helio-test and other tests⁽¹²⁾. However, the higher paper absorptivity with PCC can increase ink demand and print mottle. This effect can be minimized with papermaking optimization and use of new PCC morphologies that reduce porosity as discussed below in offset optimization.

SC Offset Printability

The major challenge in early SC conversions to PCC was offset printability^(13, 14). This has been the subject of considerable study at SMI. A schematic of a 4-color offset press is shown in Figure 9 along with the location, by color station, of common offset issues that can occur with SC papers. These will be briefly reviewed relative to optimizing alkaline/PCC effects.

Piling or linting can occur in the first (black) unit, typically on the top (forward) roll. This has not been generally a problem with SC conversions or trials and is readily controlled by ensuring good first pass filler retention and adequate sheet bonding. Bonding is best developed by good fiber refining and with appropriate use of wet end starch, often 15 to 20 lb/paper ton.

The second area of concern on the heatset offset press is with plate scumming, abrading, or piling. These problems can occur at any point along the offset press train, and generally occur due to fountain solution (fount) chemistry problems. When printing an alkaline sheet, the fount must be in the proper pH range and have adequate buffering and sequestering capacity to handle the calcium ion that comes with the PCC system. We recommend that you make sure the pressroom has experience printing alkaline sheets; if not, then a discussion with the pressroom technical group and/or fount supplier is recommended.

The final and most significant area of concern is downstream piling which typically occurs on the 3rd or 4th units of the offset press^(10,11,13). Downstream piling occurs as ink laid down in the first (black) unit gets redeposited on the blanket from the paper in the “downstream” units. This effect is directly related to pore structure, porosity and higher absorptivity of the sheet.

Several approaches have been taken to overcome the downstream piling problem. First, the impacts of pressroom operating conditions have been examined, including ink and fount properties. Most notably, it has been found that fountain solution efficiency (FSE), as defined by Bassemir and Krishnan⁽¹⁴⁾, is critical for optimal printing of alkaline SC paper. Decreasing the dynamic surface tension and increasing the dynamic viscosity of the fount optimizes the FSE. Regulating (lowering) fount temperature and/or use of fount additives can do this effectively. This concept has been successfully applied in a number of pressrooms.

Ink properties have also been found to affect alkaline SC piling. Significantly, the water-holding capacity of ink has been found to be a major factor⁽¹¹⁾. Inks with high water pick-up tend to pile less. This is

consistent with the finding above that the FSE is an important factor in piling and that the ink/fount interaction is critical.

The final approach for improved piling has been in the development of PCC morphologies that give reduced SC sheet porosity and absorptivity. New PCC morphologies are available that approach the porosity of clay paper while maintaining a significant advantage in optics. This is illustrated in Figure 10 that shows data from a pilot offset print trial at ICGQ in Montreal. SC porosity for clay and PCC sheets is plotted against downstream piling as ranked visually after printing of 20,000 impressions. A new clustered aragonite PCC gives sheet porosity and clay values that are very close to the acid clay control sheet. The porosity reduction has been verified in several commercial trials and a commercial SC conversion.

Summary and Conclusions

More and more SC producers are taking a serious look at converting to PCC fillers. The driver is the significant improvement in paper optics that can be used to save money and/or differentiate the sheet in both the SCA and SCA+ markets. The more difficult remaining conversions are those mills using primarily virgin mechanical pulps. However, advances in wet end technology, alkaline papermaking experience and alkaline paper printability make PCC use possible for everyone. Taking a holistic approach limits or eliminates problems with trials and conversions. This approach considers that all aspects of the SC production process are affected, from pulping, bleaching, and wet end/paper machine operation to supercalendering and printing. When these changes are properly planned and accounted for, the performance and economic advantages of PCC can be more quickly and effectively leveraged to bring maximum benefit to the mill's bottom-line.

References

1. EVANS, D.B., DRUMMOND, D.K. AND KOPPELMAN, M.H., "PCC Fillers for Groundwood Papers", Proceedings 1991 Papermakers Conference, TAPPI Press, 321-330 (1991).
2. EVANS, D.B. AND SLOZER, M., "Neutral Groundwood Papers: Practical and Chemical Effects", Proceedings 2003 International Paper and Coating Symposium, Montreal, QC:43-46 (August 2003)
3. EVANS, D.B., HASKINS, W.J. A and Laakso, A-P., "Adapting Wet End Chemistry and PCC for Enhanced Brightness, Smoothness and Printability of SC paper Made of Virgin Fibre", Proceedings 2004 PTS Symposium, Chemical Technology of Papermaking, Munich, Germany, Chapter 15, (September 2004)
4. AIN, R. and LALEG, M., "Mill Experiences with AT® PCC in Papers Containing Mechanical Pulp", Pulp and Paper Canada 98(12): 172 (July 1997).
5. PASSARETTI, J., U.S. Patent 5,043,017, August 27, 1991.
6. PASSARETTI, J., U.S. Patent 5,156,719, October 20, 1992.
7. DRUMMOND, D., U.S. Patent 6,228,161, May 8, 2001
8. THOMAS, R., "A Beginner's Guide to ICP-MS", Spectroscopy 16(4):38 (April 2001).
9. MIYANISHI, T, and YASUYUKI, K., HIROSHI, O., "Adsorption of Anionic Dissolved and Colloidal Substances Onto Calcium Carbonate Fillers", TAPPI Journal, 83(7): 1 (July 2000).
10. AIN, R. and STEVENS, S., "Offset Printing With Wood-Containing, Filled, Alkaline Supercalendered Paper", Pulp and Paper Canada 104(12):88, December 2003.
11. AIN, R. and WAKEMAN, G., "Impacts of Ink Properties in Downstream Piling", International Printing and Graphic Arts Conference (2004).
12. AIN, R. Zellcheming Paper
13. AIN, R. and CATINO, J., FAN, J., STEVENS, S., WRIGHT, R., "Effects of Filler Pigment Type on the Offset Printability of Supercalendered Paper" Pulp and paper Canada 103(3): T79 (March 2002).
14. BASSEMIR, R. AND KRISHNAN, R., "A Study of Lithographic Performance, Mechanical vs. Thermodynamic Considerations", Proc., TAGA, City, 339 (1988).