Identification of acid-insoluble filter-plugging compounds and optimal acid-washing procedures for tubular backpulse pressure filters

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ABSTRACT: Over time, performance of tubular backpulse pressure filters in kraft mills deteriorates, even with regular acid washing. Unscheduled filter replacement due to filter plugging results in significant costs and may result in mill downtime. We identified acid-insoluble filter-plugging materials by scanning electron microscope/energy-dispersion X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD) analysis in both polypropylene and Gore-Tex™ membrane filter socks. The major filter-plugging components were calcium sulfate (gypsum), calcium phosphate (hydroxylapatite), aluminosilicate clays, metal sulfides, and carbon. We carried out detailed sample analysis of both the standard acid-washing procedure and a modified procedure. Filter plugging by gypsum and metal sulfides appeared to occur because of the acid-washing procedure. Gypsum formation on the filter resulted from significant hydrolysis of sulfamic acid solution at temperatures greater than 130°F. Modification of the acid-washing procedure greatly reduced the amount of gypsum and addition of a surfactant to the acid reduced wash time and mobilized some of the carbon from the filter. With surfactant, acid washing was 95% complete after 40 min.

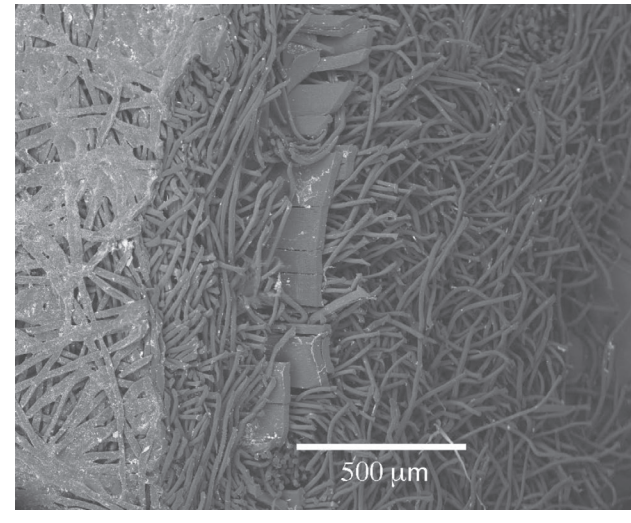
Application: By modifying acid-washing procedures, process engineers can reduce costs of pressure filter operation by increasing the time between acid washes and reducing unscheduled filter replacement due to plugging.

Tubular backpulse pressure filters consist of a large filter housing containing several hundred perforated stainless steel tubes with filter socks on each tube. Each filter sock is roughly 7 cm (2.75 in.) in diameter by 120–180 cm (48–70 in.) in length. This system provides excellent filtration efficiency at high flow rates with high solids content. This filtration system is commonly used with lime mud slurry to produce clarified white liquor and for filtration of weak wash.

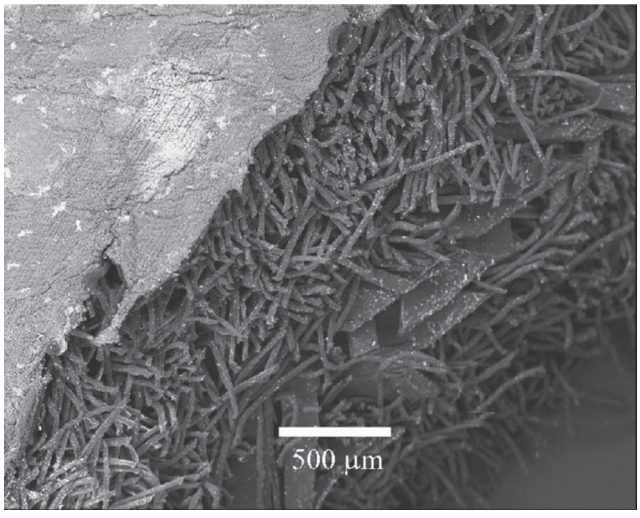
The filter socks are available in two types—polypropylene and Gore-Tex™—consisting of a woven polypropylene-fiber filter fabric. In the polypropylene filter, the woven surface is calendered to flatten the surface fibers. Fiber diameter is about 25 μm, pore size is typically 10–150 μm, and sizes are irregular. **Figure 1** shows a scanning electron microscope (SEM) image of a used polypropylene white liquor pressure filter (WLPF); the filter surface is on the left and shows the flattened polypropylene fibers. The filter body consists of polypropylene fibers and thicker reinforcing fibers.

A typical Gore-Tex filter consists of a woven polypropylene-fabric base filter with a very thin membrane of Gore-Tex fabric bonded to the filter surface. **Figure 2** shows an SEM image of a used Gore-Tex WLPF; the surface is on the left, and the pore size is too small to see at the magnification used.

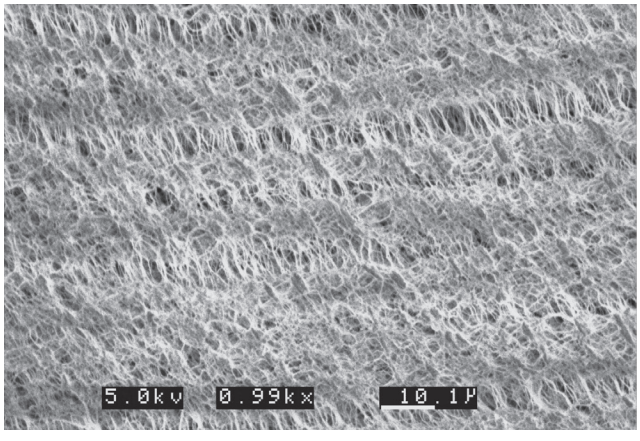
Trademarked Gore-Tex filter membranes are expanded film polytetrafluoroethylene (PTFE) polymers. A highly oriented film is stretched at right angles to the original orientation of the polymer crystallites to produce voids in the membrane surface [1]. The size of these voids, or pores, will vary depending on the manufacturing conditions and intended use. Pore sizes of Gore-Tex filter membranes are much smaller (0.5–3 μm) and more uniform than those of the polypropylene filter material shown in Fig. 1. **Figure 3** shows a



1. Scanning electron microscope (SEM) image of used white liquor pressure filter (WLPF) polypropylene filter cross section (sample T1). Filter surface is at left.



2. SEM image of used WLPF Gore-Tex™ filter cross section (sample T3). Filter surface is at left.



3. SEM image of Gore-Tex membrane. (Image supplied by McFarlen Engineering, North Vancouver, BC, Canada.)

typical Gore-Tex filter membrane at much higher magnification than in Fig. 2.

Since the introduction of backpulse pressure filters in the pulp and paper industry, very little information has been published on filter-plugging mechanisms. Taylor and McGuffie [2] showed an SEM image of a used pressure filter that contained high concentrations of nonprocess elements, as well as gypsum crystals.

During use, the pressure drop across the filters increases with time. Filters are typically cleaned using 10 wt% sulfamic acid (H_3NSO_3) solution. A mill in Kamloops, BC, Canada, has used 10 wt% hydrogen chloride (HCl) with a corrosion inhibitor [3]. Filter performance deteriorates over time and regular acid washing only partially restores it. Ideally, filters should remain effective between major shutdowns. In practice, emergency filter replacements are often required when acid washing is not effective.

In our study, we sought to fully characterize material that remains in used pressure filters after standard acid-washing procedures; investigate and understand the chemistry of standard acid-washing procedures; and identify and implement improved acid-washing procedures for backpulse pressure filters.

METHODS AND MATERIALS

For scanning electron microscope/energy-dispersion X-ray analysis (SEM/EDS), samples were coated with evaporated carbon and examined on a Philips XL30 SEM equipped with a Princeton Gamma-Tech EDS system (Princeton Gamma-Tech Instruments, Princeton, NJ, USA). Some samples were examined without carbon coating.

Step-scan X-ray powder-diffraction data (XRD) using the quantitative Rietveld method were collected on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer (Siemens, Munich, Germany) at the University of British Columbia Earth and Ocean Sciences department.

Metal concentrations were determined by Econotech Services (Delta, BC) using inductively coupled plasma (ICP) spectroscopy.

RESULTS AND DISCUSSION

We collected WLPF Gore-Tex filter socks (sample T3) on September 29, 2006, from the Tembec Skookumchuck mill in British Columbia, Canada. The socks were collected after a standard acid washing with 10 wt% sulfamic acid at an initial acid temperature of 65°C (149°F). At that time, polypropylene weak-wash pressure filter (WWPF) socks were also collected (samples T1 and T2) after an acid washing.

Detailed sampling of a standard acid-wash treatment was conducted on January 15, 2007. Filter socks were not changed at that time.

After a modified acid-wash treatment, WLPF Gore-Tex filter socks (sample T8) were collected on June 13, 2007. Modifications included a reduction in initial acid temperature to 54°C (130°F), the addition of a surfactant to the acid, and minor changes to procedure.

We found that the WLPF filter socks (sample T3) were plugged primarily on the surface membrane by carbon; calcium sulfate (gypsum), $CaSO_4$; and sulfides of zinc, cobalt, nickel, and manganese.

The WWPF filter socks (samples T1 and T2) contained primarily calcium sulfate along with zinc sulfide (ZnS) and calcium phosphate (hydroxylapatite), $Ca_5(PO_4)_3(OH)$. Deposits were on the surface and within the filter. These were the primary materials plugging the filters, and minor amounts of manganese and titanium compounds (sulfides and oxides), as well as aluminum and silicon compounds, were present. Carbon deposits contributed to surface plugging.

The WLPF filter socks (sample T8) contained very little gypsum after the modified acid-wash treatment. The filter surface showed some blockage by carbon, but was primarily covered with a fine-grained mixture of magnesium hydroxide (brucite), $Mg(OH)_2$; hydroxylapatite; and kaolinite, $Al_2Si_2O_5(OH)_4$. This mixture had low solubility in 10 wt% sulfamic acid. The interior of the filter contained primarily hydroxylapatite.

Phase, wt%	Ideal Formula	T3 (9/29/2006)	T8 (6/13/2007)
Calcite	$CaCO_3$	43.4	16.2
Hydroxylapatite	$Ca_5(PO_4)_3(OH)$	35.0	33.6
Brucite	$Mg(OH)_2$	-	36.7
Graphite	C	16.7	-
Kaolinite	$Al_2Si_2O_5(OH)_4$	-	8.6
Gypsum	$CaSO_4 \cdot 2H_2O$	4.3	-
Hydrotalcite	$(Mg0.88Al_{0.12}(OH)_2)_2$ $((CO_3)_{0.12}(H_2O)_{0.64})$	-	3.0
Quartz	SiO_2	0.7	0.7
Sphalerite (tentative)	(Zn,Fe)S	-	1.3

I. Composition of WLPF surface solids determined by XRD.

XRD results

Solids were present on the surfaces of the WLPF socks after the acid washing. Components of the surface solids were analyzed by Rietveld XRD and the results are shown in **Table I**. The Rietveld XRD method can identify microscopic crystalline materials in samples. Although the method can't identify amorphous materials, it is able to give an idea of the different chemical species present. The method can measure concentrations but is not as accurate as ICP or atomic absorption (AA) measurements.

Surface solids from WLPF sample T3 were black in color, with calcite as the major component (43 wt%). The acid washing reduced the calcite content in comparison with the calcite present in lime mud (96 wt%). Calcite concentration was lower in surface solids on filter sample T8, suggesting that the modified procedure produced better contact between the acid and the filter solids.

Hydroxylapatite was present at a concentration of 35 wt% in filter sample T3 surface solids and about 34 wt% in sample T8 solids. Hydroxylapatite is the most common form of phosphorus in lime mud [2,4] but is normally found at concentrations of less than 10 wt% and is slightly soluble in sulfamic acid solutions. Phosphorus is an important dead load component in the lime kiln because 1 wt% phosphorus in lime mud is equivalent to 5.4 wt% hydroxylapatite [2].

Sample T3 filter solids contained a significant amount of carbon in the form of graphite (16.7 wt%), which is normally present in dregs but is not normally a component of lime mud. In contrast, the filter solids we examined after the modified acid washing (sample T8) were very light in color and did not contain appreciable amounts of graphite by XRD analysis.

Sample T3 filter solids contained a significant amount of gypsum, which is not normally present in lime mud but was reported previously on a lime-mud pressure filter by Taylor and McGuffie [2]. Gypsum would be expected to be slightly soluble in sulfamic acid solutions and likely formed as a result of standard acid-washing procedures. Thermal hydrolysis of sulfamic acid produces sulfate anions that combine with dissolved calcium ions to form gypsum. By modifying the acid-washing procedure, sulfamic acid hydrolysis was greatly reduced and no gypsum was observed in the filter solids of sample T8.

Table I shows the presence of high-surface-area clay, kaolinite, in sample T8 filter solids. Kaolinite, which was previously reported in lime mud by Taylor and Bossuns [5], is a concern because its high surface area and small particle size can easily lead to filter plugging. The likely source of this kaolinite was an impurity in purchased lime.

The major components of the white surface solids in sample T8 were brucite at 37 wt% and hydroxylapatite at 34 wt%. Kaolinite was present at 9 wt%. Brucite would be expected to dissolve in sulfamic acid and was not seen in other filter solid samples. The source was likely high magnesium concentrations in purchased lime. We discuss the reason for the slow dissolution of magnesium hydroxide in the next section.

Hydrotalcite was observed in sample T8 solids at a concentration of 3 wt% and was previously reported as a component of lime mud by Ulmgren [6]. This compound is thought to form from the reaction of solid magnesium hydroxide with aluminum ions in green liquor.

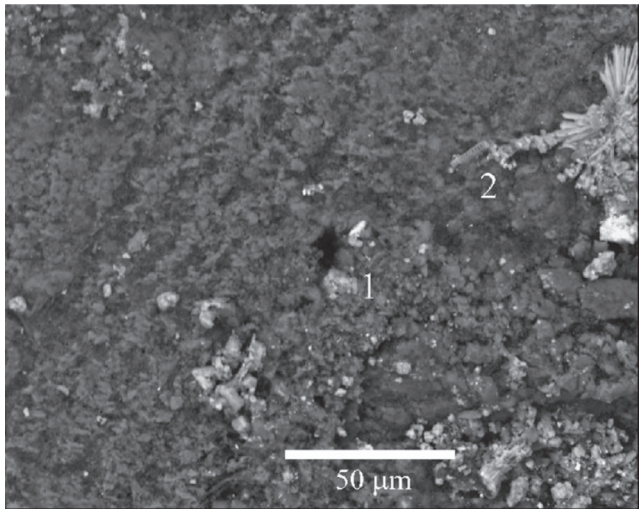
Table I also shows that the zinc sulfide compound sphalerite was tentatively identified by XRD. This metal sulfide compound has been identified as an important filter-plugging compound at other mills. Sphalerite normally contains 95 mole% zinc and 5 mole% iron. Other metals such as nickel, manganese, cobalt, copper, cadmium, lead, and tin may be incorporated into the ZnS crystal structure at low levels in naturally formed sphalerite [7]. The compound was likely formed during the acid washing as dissolved metals in the recirculating acid solution came in contact with residual lime mud on the pressure filter surface. Lime mud can contain iron sulfides [2] that will form hydrogen sulfide on reaction with sulfamic acid solution. The dissolved metals and sulfide ions can precipitate on the filter surface as sphalerite, which has low solubility in sulfamic acid solution [8].

SEM/EDS results

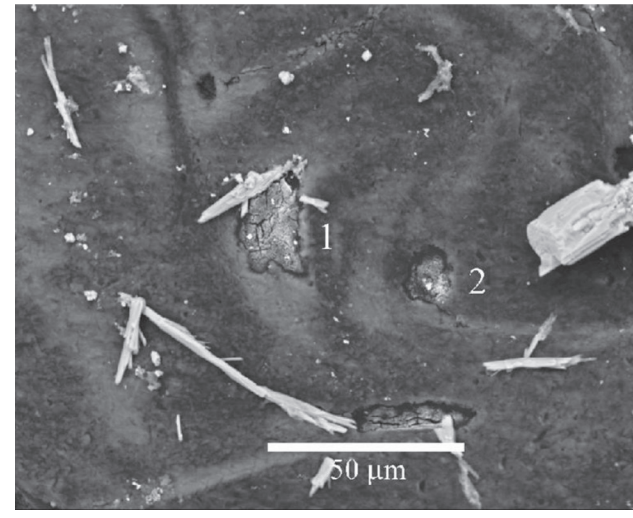
Figure 2 shows a cross section of a used WLPF (sample T3); the filter surface is on the far left. EDS measurement identified most of the lighter-colored material on the surface of sample T3 as calcium sulfate. Significant amounts of cobalt, nickel, and zinc were also present, likely as sulfides in the compound sphalerite. The interior of the filter was relatively uncontaminated with metal compounds but contained a significant amount of carbon, most likely as graphite, which was confirmed by SEM images collected without carbon coating the sample. Results suggested that carbon particles easily passed through the filter's PTFE surface film. The size of carbon soot particles in the white liquor would be expected to be much smaller than the pore size of the Gore-Tex surface membrane [9].

Figure 4 shows a higher-magnification SEM image of the filter surface shown in Fig. 2. The image is of an uncoated sample and is of similar magnification to a new Gore-Tex membrane image shown in Fig. 3. The dark patches observed diagonally from the bottom left corner of Fig. 4 represent pores plugged with carbon (graphite). A significant amount of carbon was present on the surface. By EDS measurement, the surface was primarily carbon but elements from the filter surface were seen, such as F from the PTFE membrane. Sulfur, sodium, calcium, and potassium were present. Calcium sulfate was the major inorganic component of the filter surface. EDS measurement of the partially blocked pore 1 in Fig. 4 showed calcium and sulfur as major components with silicon, aluminium, and iron as minor components. The crystal near pore 2 in Fig. 4 contained primarily calcium and sulfur and was likely calcium sulfate in the form of gypsum.

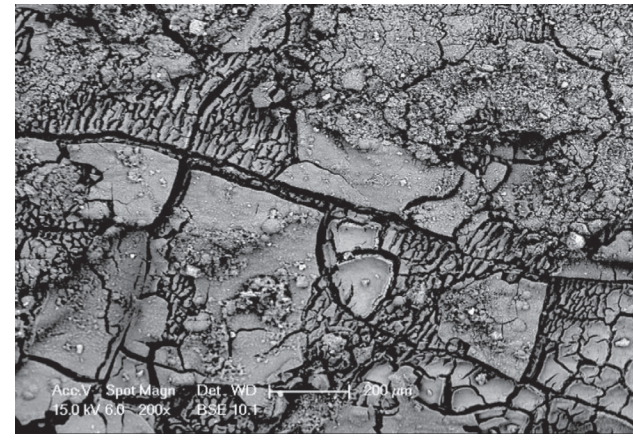
We also examined a used polypropylene filter (sample T2) from a weak wash pressure filter. **Figure 5** shows a magnified SEM image of the surface of sample T2. The white crystals on the surface contained only calcium and sulfur by EDS measurement and were identified as calcium sulfate. EDS measurement of pore 1 showed the presence of sulfur (major component) and zinc, aluminium, silicon, phosphorous, calcium, and manganese. The material in pore 2 was similar in composition with a higher proportion of zinc and phosphorous. Figure 5 also shows pore blockage by lighter-colored deposited carbon (graphite).



4. SEM image of used WLPF Gore-Tex filter surface (sample T3).



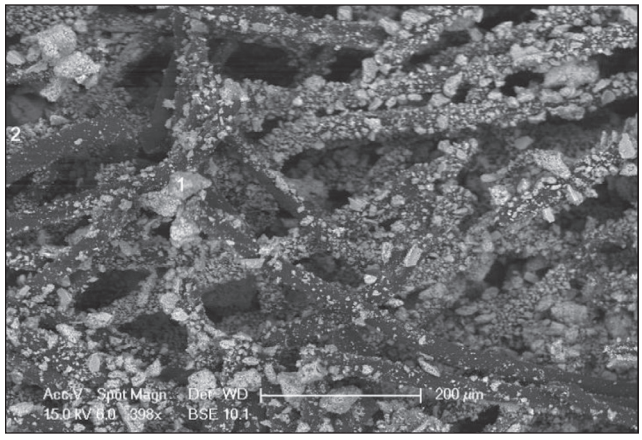
5. SEM image of used weak wash pressure filter (WWPF) polypropylene filter surface (sample T2).



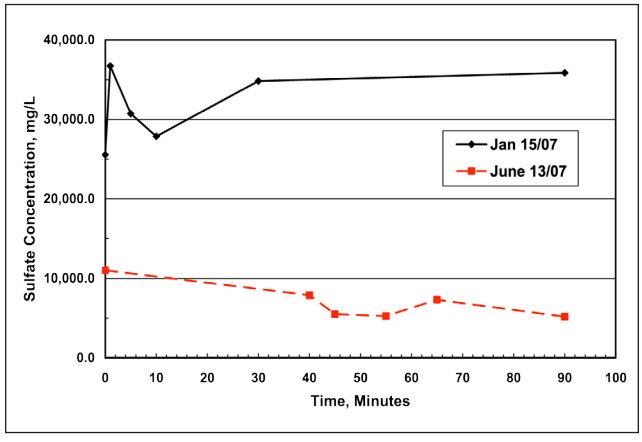
6. SEM image of used WLPF Gore-Tex filter surface, June 13, 2007, acid-wash treatment (sample T8).

Solids deeply invaded the interior of the WWPF filter (sample T2). EDS measurement was consistent with the presence of gypsum and hydroxylapatite, and zinc sulfide crystals were also observed.

After a modified acid-wash treatment on June 13, 2007, we obtained a Gore-TexWLPF sample (sample T8). The white surface deposits present on the filter were examined by SEM/EDS and are shown in **Fig. 6**. Results were consistent with XRD results of the surface solids shown in Table I. These solids were a fine-grained mixture of magnesium hydroxide, hydroxylapatite, and kaolinite. The magnesium hydroxide did not dissolve in the acid-washing procedure due to mixing with insoluble kaolinite and hydroxylapatite. The presence of kaolinite likely contributed significantly to the formation of the surface solids. The source of the kaolinite was likely from



7. SEM image of WLPF Gore-Tex filter cross section, June 13, 2007, acid-wash treatment (sample T8).



8. Sulfate concentrations of January 15, 2007, and June 13, 2007, acid-wash samples.

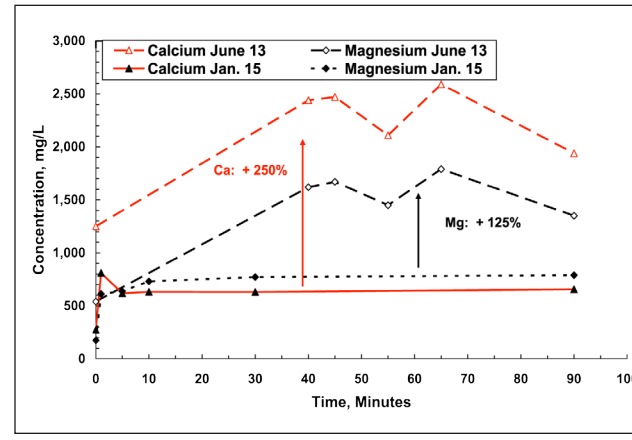
impurities in purchased lime. Very little gypsum was detected in this filter sample.

The filter body of sample T8 contained primarily hydroxylapatite in significant quantities (**Fig. 7**). Very little gypsum was observed. This hydroxylapatite may have formed in place but was most likely present from lime mud contamination during backflush of the pressure filters. When a filter is acid washed, most of the calcium carbonate dissolves, leaving the hydroxylapatite in the filter body. This hydroxylapatite can serve as a nucleation point for further crystal growth in the filter, if the white liquor becomes supersaturated with it.

Acid-wash treatments

Samples were collected during the standard acid washing carried out on January 15, 2007, and the modified acid washing done on June 13, 2007.

The pH values at the end of the treatment were in the 1.3–1.6 range. However, there was significant variability in the measured pH values. Standard laboratory pH electrodes used for water and effluent are generally not accurate at pH < 2 and high ionic strength. The pH of 10 wt% sulfamic acid is expected to be 0.4 at 25°C (77°F) [10].



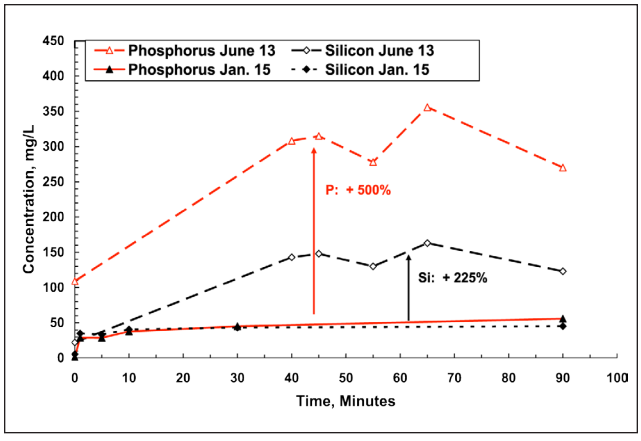
9. Comparison of calcium and magnesium in January 15, 2007, and June 13, 2007, acid-wash samples.

It is important that the acid not be completely consumed during the acid washing, as this would lead to re-precipitation of dissolved compounds. In particular, the metal sulfides are more soluble in acid solution and will precipitate from solution as the pH increases. It is recommended that the acid wash be terminated before the pH increases above approximately 2 [11].

Figure 8 shows acid-wash sulfate concentrations. In the graph, time zero shows the initial concentration in the acid in the mixing tank. Sulfate concentrations in the modified treatment were much lower (5000–8000 mg/L) than those observed in the January acid-wash treatment (25000–35000 mg/L). The decrease in sulfate concentration was due to lower acid temperature, better mixing of the acid solution, and less time spent at high temperature. Calculations showed that hydrolysis of sulfamic acid decreased from 30% (January) to less than 10% (June). High sulfate concentrations are likely to increase gypsum formation, as we describe later. With good operating procedures, sulfate concentrations below 1000 mg/L have been obtained in the mixed sulfamic acid before start of the acid treatment.

Figure 9 compares the calcium and magnesium concentrations of the January and June acid-wash samples. In the June samples, calcium and magnesium concentrations were approximately 250% and 125% higher, respectively. This is important because the maximum solubility of calcium-containing compounds in the sulfamic acid solution increased at that time. In previous treatments, calcium concentration reached a plateau at 600–700 mg/L. The higher calcium concentrations in the modified acid wash were likely a result of the decreased sulfate concentration. The solubility of gypsum in the acid-wash samples was expected to increase with decreasing sulfate concentration as a result of the common ion effect. Magnesium concentration increased due to the presence of more magnesium oxide in the June filter solids.

Figure 10 compares the phosphorus and silicon concentrations of the January and June samples. The phosphorus concentration increased by approximately 500% due to in-



10. Comparison of phosphorus and silicon in January 15, 2007, and June 13, 2007, acid-wash samples.

creased solubility of hydroxylapatite. Solubility of silicon compounds increased by 225%, and the solubility of aluminum ion (not shown) increased by 100%.

Figures 9 and 10 show that maximum concentrations of calcium, magnesium, phosphorous, and silicon were reached within 40 min (within measurement experimental error). In addition, Fig. 8 shows that sulfate concentration gradually decreased throughout the treatment, which likely meant that sulfate compounds were precipitating from solution. Also, the amount of acid reacted at 40 min was approximately 90% of the 90-min value. These factors suggested that an acid-washing time of 40–60 min was optimal for the modified procedure.

Solids produced with the collected acid-wash samples were isolated and analyzed. The acid-wash solids from January appeared to contain mostly calcium sulfate. In contrast, calcium in the solids from June appeared to be present as hydroxylapatite. June solids (average of 45- and 55-min samples) contained calcium (24600 mg/kg); phosphorous (8545 mg/kg); magnesium (14200 mg/kg); silicon (6675 mg/kg); and titanium (7955 mg/kg) as major components. Magnesium compounds (as dolomite), silicon compounds (in clays), and titanium compounds (in clays) were known impurities in the purchased lime used at the mill site.

Minor components of the June acid-wash solids included aluminum (1360 mg/kg); barium (2070 mg/kg); iron (1475 mg/kg); lead (1980 mg/kg); sodium (2405 mg/kg); and zinc (650 mg/kg).

Results from the June acid-wash treatment suggested that the modified procedure improved acid washing and greatly reduced filter plugging by gypsum formation. A significant cause of WLPF plugging was due to impurities in purchased lime. The use of the modified acid-washing procedure remains in place, while a project was initiated to improve the quality of purchased lime.

Removal of acid-insoluble filter-plugging compounds

During cleaning procedures, acid-insoluble compounds can be removed from pressure filters in three primary ways. Methods depend primarily on the nature of the acid-insoluble material.

Some acid-insoluble material can be removed as particu-

ABOUT THE AUTHORS

This study built on previous work on the chemistry of non-process elements (NPE) in kraft pulping. During a study of the NPE mass balance of the Elk Falls Mill in Campbell River, BC, Canada, in 2006, a used white liquor pressure filter was being examined using SEM/EDS. The surface appeared to be covered with crystals of calcium sulfate and other NPE compounds, and a literature search showed that no work had been reported on the identification or source of the compounds that form on these pressure filters. Thus, our aim was to characterize the acid-insoluble materials that are present in used backpulse pressure filters.

It was surprising to find that much of the long-term damage to backpulse pressure filters occurs during acid washing. The first interesting result was that hydrolysis of the sulfamic acid cleaning solution leads to the formation of gypsum on the filters. From a chemistry standpoint, it was puzzling how sulfides of zinc, nickel, and cobalt could build up on the filter surface. At one mill, nickel and cobalt sulfides were the primary filter-plugging compounds. This work was satisfying in that it led to an understanding of the formation mechanism.

Mills can see direct financial benefits through simple modifications to their acid-washing procedures. The modifications can increase the useful lifetime of white liquor and weak wash pressure filters, increase the time required between acid washes, and greatly reduce the number of expensive unscheduled filter changes.

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The next step is to help mill implement these modified procedures. Future areas of interest are the carbon deposition of soot particles that occur on white-liquor pressure filters, as well as ways to reduce suspended solids content in clarified green liquor and reduce NPE carryover into the recaust area. This type of analytical approach can also be applied to other filters in mills.

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lates suspended in the acid-wash solution. This mechanism can be promoted by the addition of a suitable surfactant (or wetting agent) to the acid wash. This improves the contact between the acid and the filter solids, which is especially important when hydrophobic carbon deposits are present on the filter. By dissolving most of the acid-soluble material, particulates can become suspended in the acid solution and removed. A suitable surfactant can also mobilize deposited carbon from the filter surface and remove it as a suspended solid. Minor process improvement and addition of a surfactant provide a low-cost method to improve filter acid-wash treatments.

Some solids, particularly hydroxylapatite and metal sulfides, can be dissolved with chelating agents similar to EDTA. This treatment requires an efficient acid washing before use to minimize the amount of chelating agent required.

Silicate and aluminosilicate materials can be dissolved using solutions containing buffered fluoride ion. The required fluoride concentrations, in the 1–5 wt% range, are available in forms that are much safer to handle than hydrofluoric acid. This treatment method is the most aggressive. Taylor [12] provides more details on these methods.

CONCLUSIONS

Our work identified several compounds that cause long-term plugging of backpulse pressure filters used for clarification of white liquor and weak wash. These compounds are relatively insoluble in sulfamic acid solution and are not removed during standard acid washing.

Filter-plugging compounds such as gypsum and metal sulfides appear to be formed during the acid-washing process itself, and simple changes to the water-washing and acid-washing procedures can greatly reduce their formation and improve long-term filter performance.

A very effective water wash of the filters is critical to good acid washing performance. Residual lime mud in the filters contains acid-insoluble impurities such as hydroxylapatite that become trapped in the filter fabric during acid recirculation. Residual lime mud on the filter surface appears to promote the formation of insoluble metal sulfides on the filter surface during the acid washing.

Clay impurities from purchased lime were identified as a major filter-plugging component. Improved quality control of purchased lime can greatly increase pressure filter life. In addition, carbon deposition on filter surfaces by suspended soot particles was identified as an important filter-plugging mechanism.

Specific recommendations

An effective water wash of the filters is critical to a good acid-washing procedure. As much lime mud as possible must be removed from the filter socks and from the floor and sides of the pressure filter unit because even small amounts of lime mud that dissolve in the acid reduce acid-washing efficiency.

The temperature of sulfamic acid solution must not exceed 130°F. Above this temperature, sulfamic acid hydrolyzes to ammonium sulphate, which is then available to react with dissolved calcium ion to form gypsum on the filter surface.

Addition of a surfactant to the sulfamic acid solution improves acid-lime mud contact and mobilizes additional fines and soot particles. During the acid washing, socks should be kept filled with acid at all times. Finally, mills should implement quality control of purchased lime to reduce long-term filter plugging. **TJ**

ACKNOWLEDGEMENTS

The authors thank Tembec Enterprises for permission to publish this paper and Jonn McFarlen of McFarlen Engineering for useful discussions.

LITERATURE CITED

1. Gore, R.W., U.S. pat. 4,187,390 (Feb. 5, 1980).
2. Taylor, K. and McGuffie, B., *Pulp Pap. Can.* 108(2): 27(2007).
3. Bruce, P., Dennis, B., and Henzler, B., *Pulp Pap. Can.* 89(5): T155(1988).
4. Ulmgren, P. and Rådeström, R., *Nord. Pulp Pap. Res. J.* 12(3): 167(1997).
5. Taylor, K. and Bossuns, D., *Pulp Pap. Can.* 107(3): 37(2006).
6. Ulmgren, P., *Nord. Pulp Pap. Res. J.* 12(1): 32(1997).
7. Stanton, M.R., Taylor, C.D., Gemery-Hill, P. A., et al., *ICARD 2006, Proc. Int. Conf. Acid Rock Drain., 7th*, American Society of Mining and Reclamation, Lexington, KY.
8. Acero, P., Cama, J., and Ayora, C., *Appl. Geochem.* 22(9): 1872(2007).
9. Dannenberg, E.M. and Paguin, L., in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York, 2000.
10. Yoshikubo, K. and Suzuki M., in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York, 2007.
11. Taylor, K. and Nasr-El-Din, H., *Prog. in Oilfield Chem.* 7: 143(2007).
12. Taylor, K., U.S. pat. app. 11/923,527 (Oct. 24, 2007); Canadian pat. app. 2,608,790 (Oct. 24, 2007).