

INVESTIGATION OF NON-PROCESS ELEMENT CHEMISTRY AT ELK FALLS MILL – GREEN LIQUOR CLARIFIER AND LIME CYCLE

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ABSTRACT

As a result of low solids content and the dark green colour of Elk Falls lime mud, an investigation of non-process element (NPE) chemistry at the mill was initiated in April/05. Extensive sampling and analysis of green liquor clarifier deposits, dregs, grits, lime mud, lime and lime kiln deposits was carried out. In addition to elemental analysis, NPE chemical compounds were identified using the quantitative Rietveld method of X-ray diffraction (XRD) analysis. The Rietveld method was able to identify and quantify a number of previously unreported inorganic compounds in mill process streams. Aluminum and silicon were lost from the green liquor clarifier primarily as the magnesium silicate diopside, $\text{CaMgSi}_2\text{O}_6$, as well as the aluminosilicates pargasite, $\text{NaCa}_2\text{Mg}_3\text{Fe}^{2+}\text{Si}_6\text{Al}_3\text{O}_{22}(\text{OH})_2$, and vermiculite, $\text{Mg}_{1.8}\text{Fe}^{2+}_{0.9}\text{Al}_{4.3}\text{SiO}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$. At Elk Falls mill, magnesium ion was completely depleted in clarified green liquor and resulted in low removal efficiency of aluminum and silicon in the Elk Falls green liquor clarifier. The compound hydrotalcite, frequently mentioned in the literature, was not found in any of the mill samples. A new dead load component identified by XRD in Elk Falls lime was $\text{Ca}_4\text{Na}_2(\text{PO}_4)_2(\text{SiO}_4)$. This compound ties up nearly 8 times the mass of phosphorus present in lime, making phosphorus the most significant contributor to dead load in the Elk Falls lime kiln. Application of these results to mill process improvement is discussed.

INTRODUCTION

The Elk Falls mill was experiencing high dregs concentration in clarified green liquor and low solids content in lime mud from the rotary filter. In addition, lime mud pressure filters required frequent cleaning and the lime mud was dark green in colour. The incremental fuel cost resulting from low solids content of the lime mud to the lime kiln was estimated at more than \$200,000/year, while kiln dead load incremental cost was more than \$150,000/year.

Located near Campbell River on the east coast of Vancouver Island, Elk Falls began operation in 1952 as a single-line newsprint mill. The paper machine was joined with a kraft pulp mill on the same site in 1956 and two other paper machines followed in 1957 and 1982. A kraft paper machine was installed in 1966. Sawdust pulp, a product pioneered at Elk Falls, was first manufactured in 1964 and capacity

expanded in 1983. The Kraft mill was simplified in 2004, and is now a single-line operation. Elk falls currently produces about 830 t/d of Kraft and 1600 t/d of TMP.

A research project was initiated in April, 2005, to investigate the contribution of non-process elements (NPEs) to operational problems in the recaust area of the mill. Recent work by Taylor and Bossons suggested that aluminosilicate compounds in lime mud could lead to reduced filtration efficiency [1]. The effects of non-process elements on kraft mill operation have been extensively reviewed [2-11] and include increased scaling, increased lime kiln fuel use, reduced lime mud settling and reduced filtration efficiency. Dregs carryover to lime mud is known to significantly reduce lime mud solids content [12]. Most of these studies have focused on the concentration of individual non-process elements, their source and purge points, with little information on the NPE compounds themselves. Identification of the compounds formed by NPEs would allow a better understanding of their behaviour in the mill process and how to reduce their concentration in critical areas.

For instance, Magnusson et al. [6] provide a list of potential dissolved and solid phase forms of NPEs in green liquor and white liquor. This paper has often been cited, but these species were not directly observed. They were proposed based on simple equilibrium chemistry.

Formation of hydrotalcite in lime mud, $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}$, was first observed by Bennett et al. [5] in their studies of wet air-oxidation (WAO) soda recovery. Magnesium from dolomite was intentionally added to make-up limestone to reduce aluminum concentration in the white liquor. Ulmgren [13] suggested that hydrotalcite was formed in the green liquor clarifier. He reported a successful mill trial where aluminum concentration in green liquor was reduced by the addition of magnesium sulfate to the dissolving tank.

The Skoghall mill in Sweden has added aluminum ion to the dissolving tank to reduce excess magnesium ion in green liquor [14]. It was assumed that hydrotalcite was formed, but this was not confirmed by any measurements.

Aluminosilicate scales in black liquor evaporators are well known [8,9,11]. Kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot (\text{OH})_4$, and gehlinitite, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, were reported in Harmac lime by Taylor and Bossons [1].

Experimental equilibrium solubility data for hydrotalcite and several aluminosilicates in black, green and white liquor streams were reported by Wannemacher et al. [8].

Hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, has been identified by XRD as the primary phosphorus-containing component of lime mud [15]. Phosphorus is an important dead load component in the lime kiln, since 1 wt% phosphorus in lime mud is equivalent to 5.4 wt% hydroxylapatite.

This paper describes NPE compounds and chemistry occurring in the green liquor clarifier and lime cycle of the Elk Falls mill. This information allowed the design of a successful NPE mass balance mill trial that is reported in a separate paper [16].

METHODS AND MATERIALS

Step-scan X-ray powder-diffraction data (XRD) using the quantitative Rietveld method were collected on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer. For SEM/EDS measurements, samples were coated with

evaporated carbon and examined on a Philips SL30 SEM equipped with a Princeton Gamma-Tech EDS system. These measurements were performed at the UBC Department of Earth and Ocean Sciences by M. Raudsepp and E. Pani.

Visible light diffuse reflectance measurements were made with a Carey 1 UV/VIS/NIR spectrometer at the University of Victoria Chemistry Department.

Metal concentrations were measured by Econotech Services Ltd., Delta, BC. Samples were digested with aqua regia at 100°C for 2 hours. Some samples required alkali fusion with sodium carbonate and boric acid at 1000°C. After digestion, samples were analyzed by inductively coupled plasma (ICP) spectroscopy. Total metals content was measured in liquid samples.

Soluble elements in clarified green liquor were measured after filtering a freshly collected sample through a Whatman 542 filter.

RESULTS

1. Elk Falls NPE Levels Compared with Other Mills

The concentrations of non-process elements in lime muds from seven different Canadian kraft mills were reported by Richardson et al. [2] (**Figure 1**). Phosphorus concentration was obtained from the average values of ten Canadian kraft mills [4], estimating the concentration in lime mud by dividing the lime values by 1.78. Average Elk Falls values were taken from four samples collected from November/04 to August/05. Error bars represent the average value plus or minus one unit of standard deviation.

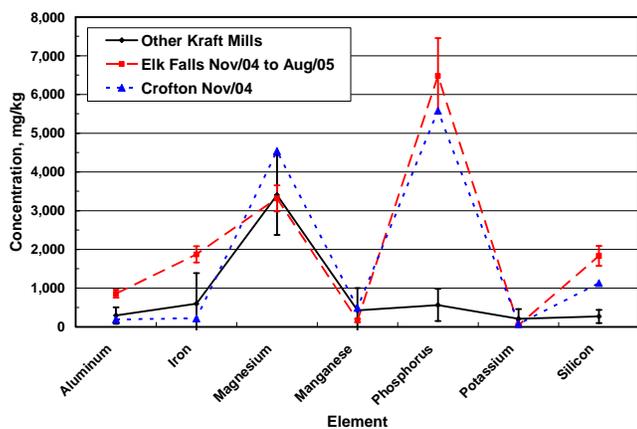


Figure 1. Comparison of NPE Levels in Lime Mud

Figure 1 shows that aluminum, iron, phosphorus and silicon concentrations in Elk Falls lime mud are all significantly higher than reported values at other mills. Magnesium, potassium and manganese concentrations are within the range of values reported at other mills by Richardson et al. [2]. Sodium concentration is not shown, but is within the range of values seen at other mills.

Results for the Crofton mill are also shown in **Figure 1**. Crofton has much lighter coloured lime mud and normal solids content. At Crofton, only the phosphorus and silicon concentrations are significantly higher than values reported at other mills. The major differences between the Elk Falls and Crofton lime muds are the higher concentrations of aluminum, iron and silicon at Elk Falls. High phosphorus concentration does not appear to result in green lime mud or low solids

content at the Crofton mill.

Current values of NPEs in Elk Falls lime mud were compared with historical values. The trends in phosphorus and zinc concentrations since 2000 are shown in **Figure 2**. The amount of these elements has increased significantly, from 185% for phosphorus up to nearly 1600% for zinc. **Figure 3** shows trends for magnesium, silicon, iron, and aluminum. From 2000 to May/05, these elements increased in concentration from 83% for magnesium up to 700% for silicon. Non-process elements in **Figure 3** appeared to decrease after May/05, due to several factors that are discussed in more detail by McGuffie and Taylor [16]. These include a change in the lime rock source, increased precipitator catch to sewer, and improved operation of the green liquor clarifier. Phosphorus and zinc both continued to increase in concentration and the reasons for this are discussed in detail [16].

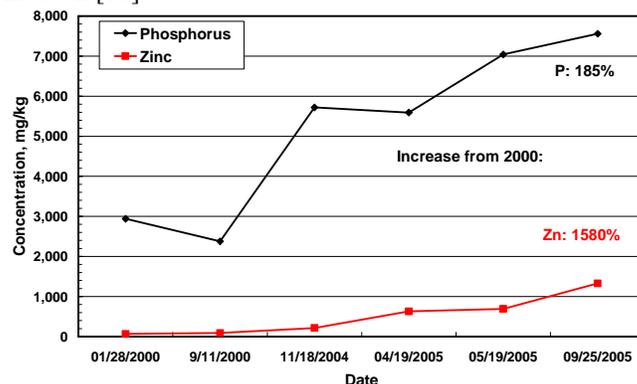


Figure 2. Trends in P and Zn in Elk Falls Lime Mud

Figure 3 also shows that aluminum, iron and silicon concentrations in Elk Falls lime mud were much lower in 2000 and were consistent with average values of other mills shown in **Figure 1**. NPE increases since 2000 may be due to increased system closure or increased input of NPEs into the mill. These results are a further indication that increasing NPE concentrations may be a factor in low solids content of filtered lime mud at Elk Falls.

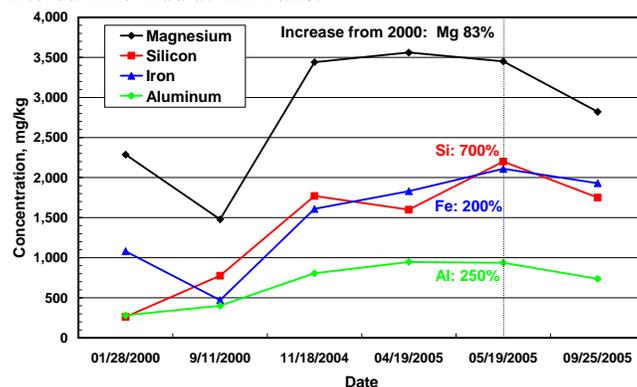


Figure 3. Trends in Mg, Si, Fe and Al in Elk Falls Lime Mud

The reflected light spectrum of Elk Falls lime mud was compared to spectra of Harmac lime mud and kaolin/synthetic green liquor results published by Taylor and Bossons [1] in **Figure 4**. The green kaolin produced from mixing synthetic green liquor with kaolin clay showed light absorption maxima at 425, 530 and 640 nm. The Harmac lime mud sample

showed less intense absorption maxima at the same wavelengths. Elk Falls lime mud showed the same maximum values but was much more intense. The green colour of the lime mud is composed primarily of a blue colour (absorption at 640 nm) and a yellow colour (absorption at 425 nm). It is likely that the green colour of Elk Falls lime mud is caused by the interaction of sulfides with aluminosilicate compounds that are known to occur in the lime cycle such as kaolinite [1], $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot (\text{OH})_4$, or hydroxysodalite, $\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ [9,11]. A detailed discussion of this sulfide/aluminosilicate interaction is given by Taylor and Bossons [1]. Aluminosilicates like kaolinite are known to have very high surface area that could lead to low solids content in lime mud.

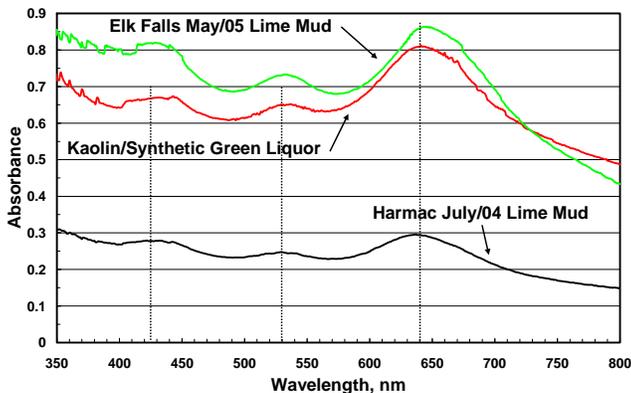


Figure 4. Reflected Light Spectrum, Elk Falls Lime Mud

Green liquor NPE levels were also investigated. **Figure 5** shows that the aluminum concentration in the clarified green liquor is significantly higher than average values for other mills. In addition, the magnesium concentration is much lower and is almost zero. This is significant because the concentrations of these two elements are often related [1]. For instance, it has been reported that aluminum and magnesium ions may sometimes form insoluble hydrotalcite that is separated from green liquor in the dregs [5,7]. In addition, removal efficiency of both aluminum and silicon in the green liquor clarifier was much lower than values for other mills reported by Richardson et al. [2]. XRD results in the following section will show how magnesium is depleted from the clarified green liquor in the clarifier.

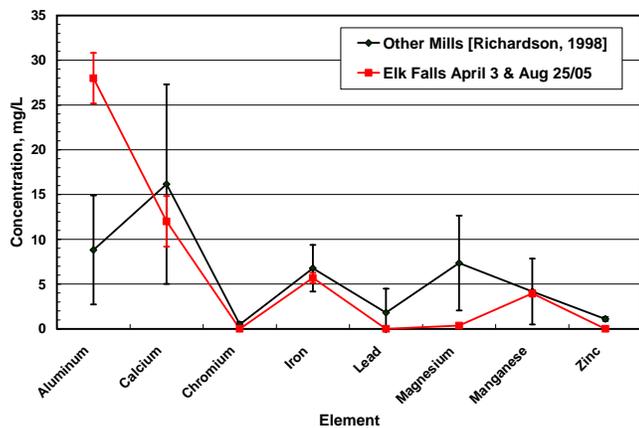


Figure 5. NPEs in Elk Falls Clarified Green Liquor

In general, it was found that aluminum and silicon concentrations in the Elk Falls liquor cycle were up to 5 times

higher than published values for other mills, while magnesium concentrations were much lower. Aluminum and silicon removal efficiency in the green liquor clarifier was much lower than values reported by other mills. In the lime cycle, aluminum, silicon, phosphorus, iron and zinc concentrations were higher than published values for other mills and showed an increasing trend since 2000.

2. NPE Components in Dissolving Tank, Green Liquor Clarifier and Dregs

Deposits were collected on May 24/05 from the bottom of the dissolving tank and also from the raw green liquor line going into the top of the green liquor clarifier. XRD results for these two samples are shown in **Table 1**. It is important to mention that XRD only identifies crystalline compounds, and that additional amorphous materials are likely to form in the green liquor clarifier. Elemental analyses of the deposits listed in **Table 1** were consistent with the XRD results, suggesting that most of the material in the deposits was present in the crystalline phase.

The dissolving tank deposit was primarily pirssonite, $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$. It also contained nearly 7 wt% thermonatrite, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. This indicates that both pirssonite and thermonatrite must occasionally exceed their maximum solubility in the dissolving tank. Small amounts of calcite, quartz, and erdite (an iron sulfide compound) were present. An excellent discussion of pirssonite deposition in green liquor processing is given by Frederick et al. [17]. The total titratable alkali (TTA) in the dissolving tank must be high enough at times to cause pirssonite deposition. As a result, the maximum TTA that can be achieved in the green liquor will be limited by pirssonite formation at the Elk Falls mill.

Phase	Ideal Formula	Dissolving Tank, wt%	GL Clarifier Line, wt%
Pirssonite	$\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$	91.6	11.4
Calcite	CaCO_3	0.6	85.1
Thermonatrite	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	6.5	-
Quartz	SiO_2	0.7	-
Graphite	C	-	1.0
Erdite	$\text{NaFe}^{2+}\text{S}_2 \cdot 2\text{H}_2\text{O}$	0.7	0.5
Sulfur, elemental	S	-	2.0

The scale deposit in the green liquor line at the top of the clarifier was also examined. **Table 1** shows that this material was mostly calcite (85 wt%) but also contained a significant amount of pirssonite (11 wt%). Graphite was present from carbon in the smelt. Elemental sulfur was present, which suggests that oxidation of sulfide ion has occurred. This is possibly due to a temporary period of air injection into the dissolving tank before May 24/05.

Additional samples from the wall and the floor of the green liquor clarifier were collected during a shutdown on May 24/05. A dregs sample from April 14/05 was also examined. XRD results are shown in **Table 2**. Two additional dregs samples were collected on August 25/05,

from before and after the rotary filter. The filtered sample may have been contaminated with small amounts of lime mud used to pre-coat the filter, but was submitted for XRD analysis to minimize the possibility of crystallization of dissolved salts during dregs evaporation.

Pirssonite was present (34 wt%) in the sample from the clarifier floor. It was also present in the dregs (10 to 22 wt%).

Three different sodium carbonate compounds as well as calcium carbonate and magnesium carbonate are present in the clarifier deposit samples. The sodium carbonate compound thermonatrite, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, is the major component of the dregs and the clarifier floor deposits.

Quartz is present in small quantities, probably carried over from the dissolving tank. Graphite is present at concentrations up to 17 wt% in the dregs. The presence of halite (sodium chloride) in the GLC floor and dregs samples may occur from evaporation of the sample after it is collected, as it seems unlikely that it is formed in the clarifier.

TABLE 2. XRD OF GREEN LIQUOR CLARIFIER DEPOSITS AND DREGS

Phase	Ideal Formula	Wall ¹	Floor ¹	Dregs ²
Pirssonite	$\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$	-	33.9	10/22
Calcite	CaCO_3	41	2.3	1.4/19
Portlandite	Ca(OH)_2	-	-	2.7/-
No name	$\text{Na}_3\text{H(CO}_3)_2(\text{H}_2\text{O})_2$	-	15.4	-
Thermonatrite	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	-	34.6	56/35
Natrite	Na_2CO_3	-	-	8.8/-
Magnesite	MgCO_3	1.9	-	-
Sjögrenite	$\text{Mg}_6\text{Fe}_{23}(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$	-	-	-/0.4
Anhydrite	CaSO_4	-	-	1.8/-
Quartz	SiO_2	-	0.9	-/2.2
Graphite	C	-	3.5	10/17
Halite	NaCl	-	2.2	4.3/3.5
Sulfur, elemental	S	-	-	1.7/-
Hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	-	0.6	-
Erdite	$\text{NaFe}^{2+}\text{S}_2 \cdot 2(\text{H}_2\text{O})$	5.8	2.0	-
Lepidocrocite	$\text{Fe}^{3+}\text{O(OH)}$	0.6	-	-
Diopside	$\text{CaMgSi}_2\text{O}_6$	19.5	-	1.1/-
Clinocllore	$\text{Mg}_{3.75}\text{Fe}_{2+1.25}\text{Si}_3\text{Al}_2\text{O}_{10}(\text{OH})_8$	16.4	-	-
Pargasite	$\text{NaCa}_2\text{Mg}_3\text{Fe}^{2+}\text{Si}_6\text{Al}_3\text{O}_{22}(\text{OH})_2$	6.4	-	3.3/-
Vermiculite	$\text{Mg}_{1.8}\text{Fe}^{2+0.9}\text{Al}_{4.3}\text{SiO}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$	-	4.8	-/1.1
Vishnevite	$\text{Na}_{6.5}\text{KCa}_{0.1}\text{Si}_{6.2}\text{Al}_{5.8}\text{O}_{24}(\text{SO}_4)_{0.7}(\text{CO}_3)_{0.4}\text{Cl}_{0.5} \cdot 1.4(\text{H}_2\text{O})$	8.4	-	-

1. May 24, 2005

2. April 14, 2005 before rotary filter/Aug. 25 after filter.

Several iron-containing compounds were present. The mineral erdite shows that an iron sulfide can form in the clarifier, and this is one of the ways that iron can be precipitated and separated. Lepidocrocite, $\text{Fe}^{3+}\text{O(OH)}$ was another iron compound identified. Iron (III) is present, meaning that iron (II) in the green liquor was oxidized, most likely by oxygen in air.

The presence of elemental sulfur in the clarifier and dregs also suggests the oxidation of sulfide in the dissolving tank. Sulfur was not present in the August 25/05 dregs sample.

Diopside, $\text{CaMgSi}_2\text{O}_6$, was present at nearly 20 wt% in the clarifier wall sample. This magnesium silicate represents a route for loss of both magnesium and silicon from the green liquor clarifier.

The remaining compounds that were identified are all aluminosilicates. Three contain the elements magnesium and iron in addition to aluminum and silicon.

In the April 14/05 dregs sample, the XRD results are in good agreement with elemental analysis (**Table 3**) for aluminum, silicon and sodium. This indicates that diopside (1.1 wt%) and pargasite (3.3 wt%) account for most of the aluminum and silicon found in the dregs sample, and that sodium carbonate compounds were the major dregs components. The pargasite and diopside account for about 30% of the iron and 50% of the magnesium in that dregs sample. The remaining iron and magnesium must be present in amorphous compounds that are not detected by XRD. This emphasizes the role that magnesium plays in the formation of compounds containing silicon, aluminum and iron in the dregs.

TABLE 3. NPEs IN CLARIFIER DEPOSITS AND DREGS

Component, mg/kg	Wall ¹	Floor ¹	Dregs ²	
			Apr. 14	Aug. 25
Aluminum	15,800*	6,260*	1,670*	2,050*
Calcium	178,000*	45,700*	18,500*	20,700*
Chromium	67	229	33	42
Iron	84,700*	34,100*	6,590*	10,600*
Magnesium	20,600*	17,200*	8,030*	12,100*
Manganese	6,400*	8,690*	3,980	5,950*
Nickel	70	90	32	38
Phosphorus	405	77	98	78
Potassium	1,280	6,870	9,830	11,600
Silicon	44,700*	22,500*	5,380*	5,190*
Sodium	69,900	247,000	311,000	267,000
Titanium	5,580*	303	100	127
Zinc	422	1,020	269	313

1. May 24, 2005

2. April 14, 2005 before rotary filter/Aug. 25 after filter.

* indicates alkali fusion of sample required

Results in **Tables 2 and 3** show that aluminum and silicon are lost from the green liquor clarifier primarily as the magnesium silicate diopside, $\text{CaMgSi}_2\text{O}_6$, as well as the aluminosilicates pargasite, $\text{NaCa}_2\text{Mg}_3\text{Fe}^{2+}\text{Si}_6\text{Al}_3\text{O}_{22}(\text{OH})_2$, and vermiculite, $\text{Mg}_{1.8}\text{Fe}^{2+0.9}\text{Al}_{4.3}\text{SiO}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$. This can explain why clarified green liquor is deficient in magnesium (**Figure 5**). At Elk Falls mill, it appears that the concentration of magnesium in the raw green liquor is the limiting factor in the formation of dregs compounds that contain aluminum and silicon. This leads to low removal efficiency of these two elements from green liquor in the clarifier. It is likely that increasing the concentration of magnesium ion would result in increased formation of silicate and aluminosilicate compounds in the clarifier.

Filtration tests of Elk Falls clarified green liquor showed

that iron, manganese, magnesium and calcium were all present primarily as particulates. Aluminum and silicon were present in dissolved form only. Efficient green liquor clarification can reduce iron carry over to the lime cycle, but will not affect aluminum and silicon carry over.

3. NPE Components in Lime Mud, Lime and Grits

The major component of the lime mud and slaker grits was identified as calcite by XRD analysis (Table 4). Portlandite, Ca(OH)_2 , is unreacted slaked slime and was not detected. Hydroxylapatite was a major component of lime mud and slaker grits, ranging from 5 to 7 wt%. Thermonatrite, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, was found in the lime mud while pirssonite was present in the slaker grits. Both are major components of clarifier dregs and may be carried over from the clarifier. These materials are likely to be responsible for the sodium content of the lime mud and associated with lump and ring formation in the lime kiln [18,19]. Pirssonite is expected to decompose in the lime kiln at 500°C to CaCO_3 and Na_2CO_3 [20].

Hydrotalcite, $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}$, was not detected in lime mud samples. If present in amorphous form, it would not be detected by XRD. No magnesium or aluminum compounds were detected by XRD in the lime mud. Hydrotalcite is not expected in lime since it decomposes in the lime kiln at 900°C [13].

Phase	Ideal Formula	Lime Mud ¹	Slaker Grits ¹	Lime ¹
Calcite	CaCO_3	94/94	85/91	-/3.6
Portlandite	Ca(OH)_2	-	-	47/50
Lime	CaO	-	-	53/34
Periclase	MgO	-	-	-/0.8
Pirssonite	$\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$	-	9.1/1.4	-
Thermonatrite	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	1.2/-	-	-
Hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	4.6/5.9	5.8/6.8	-/10.6
Silicorbenanite	$\text{Ca}_4\text{Na}_2(\text{PO}_4)_2(\text{SiO}_4)$	-	-	3 to 5/-
Quartz	SiO_2	0.3/0.3	0.2/0.2	-
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-	-	-/1.0

1. May 18 / August 25, 2005

Identification of NPE compounds in lime was carried out using XRD as shown in Table 4. The lime contained primarily CaO and portlandite as expected. Portlandite forms from reaction of the lime with water vapour in air. Calcite (3.6 wt%) and magnesium oxide (0.8 wt%) were only detected in the lime sample collected on August 25/05.

The presence of the mineral silicorbenanite, $\text{Ca}_4\text{Na}_2(\text{PO}_4)_2(\text{SiO}_4)$, in the May 18/05 lime sample is significant. To the best of our knowledge, this compound has not been reported in kraft mill lime before. The concentration range given by XRD appears to indicate that a large part of the phosphorus and silicon in Elk Falls lime was tied up in this compound. 1 wt% phosphorus tied up in silicorbenanite will produce a dead load of 7.9 wt%. In Elk Falls lime, this is

roughly 9 wt% dead load if all phosphorus is present as silicorbenanite. However, primarily hydroxylapatite was observed in the August 25/05 lime sample.

Phase	Ideal Formula	5'	50'	120'
Calcite	CaCO_3	69.4	75.3	-
Portlandite	Ca(OH)_2	16.2	3.6	55.3
Lime	CaO	8.0	1.0	20.9
Hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	5.1	8.8	6.8
Sulfur	S	1.4	-	-
Anhydrite	CaSO_4	-	2.1	13.8
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-	4.6	2.1
Thenardite	Na_2SO_4	-	4.5	-
Quartz	SiO_2	-	0.2	0.4

Lime kiln deposits were collected at 5, 50 and 120 feet from the kiln inlet during the May 24/05 shutdown. Both XRD (Table 5) and elemental analysis were done on the samples. Results were consistent with Tran et al. [18,19] and showed that sodium in lime mud and sulfur in the fuel both contributed to deposit formation near the kiln exit.

NPE compounds from the green liquor clarifier can be carried over as suspended solids or dissolved in clarified green liquor and contribute to downstream deposits and scaling.

For instance, high concentrations of NPEs were found in material plugging white liquor filter socks. Compounds identified by XRD included diopside, $\text{CaMgSi}_2\text{O}_6$, and bemenite, $\text{Mn}_8\text{Si}_6\text{O}_{15}(\text{OH})_{10}$. Figure 6 shows a SEM micrograph of a used filter sock surface. Radiating crystals were identified as gypsum and likely formed in place. Fine-grained material ($< 2 \mu\text{m}$) forming a filter cake on the filter surface is composed primarily of NPE compounds with traces of graphite. CNCG white liquor scrubber scale contained the magnesium silicates lizardite, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, sepiolite, $\text{Mg}_4\text{Si}_6\text{O}_{15} \cdot 6(\text{H}_2\text{O})$, and diopside as major components.

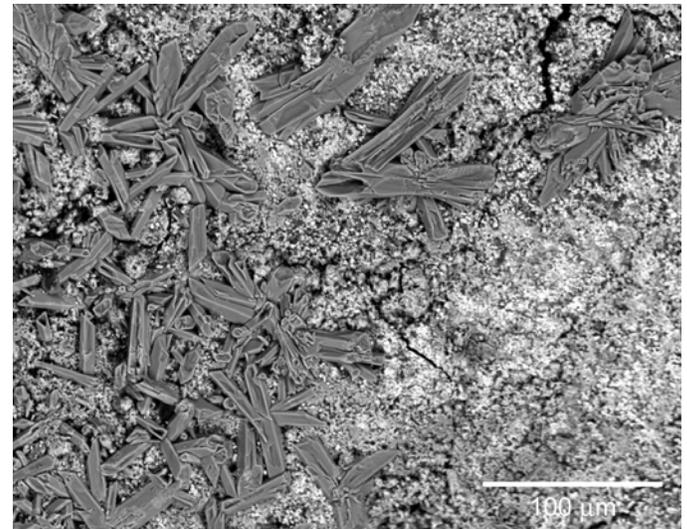


Figure 6. SEM Micrograph of White Liquor Filter Sock Sampled May 24/05 (scale bar 100 μm)

CONCLUSIONS

1. Aluminum and silicon were removed from green liquor in the dregs mainly as the compounds diopside, $\text{CaMgSi}_2\text{O}_6$, pargasite, $\text{NaCa}_2\text{Mg}_3\text{Fe}^{2+}\text{Si}_6\text{Al}_3\text{O}_{22}(\text{OH})_2$, and vermiculite, $\text{Mg}_{1.8}\text{Fe}^{2+}_{0.9}\text{Al}_{4.3}\text{SiO}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$.
2. Magnesium ion was depleted from green liquor in the clarifier. This limits the removal efficiency of aluminum and silicon compounds.
3. Phosphorus in Elk Falls lime is the major dead load component and is present primarily as the mineral silicorbenanite, $\text{Ca}_4\text{Na}_2(\text{PO}_4)_2(\text{SiO}_4)$, or as hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$.
4. Clarifier dregs contained 35 to 55 wt% thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), 10 to 20 wt% pirssonite ($\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$) and 10 to 20 wt% graphite as the major components.
5. Iron, manganese, calcium and magnesium are all present in clarified green liquor primarily as particulates, not in dissolved form. Increasing clarifier efficiency will reduce their concentration in clarified green liquor.
6. Aluminum and silicon are present in clarified green liquor in dissolved form only. Increasing clarifier efficiency will not reduce their concentration in clarified green liquor.
7. White liquor pressure filter sock plugging was due to formation of gypsum crystals and accumulation of micron-sized NPE compounds and graphite.
8. Formation of pirssonite, $\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$, in the green liquor clarifier and dissolving tank will limit the maximum TTA that can be reached in the green liquor.
9. The presence of iron (III) and elemental sulfur in some green liquor clarifier deposits indicates oxidation by oxygen in air (May 24/05 samples only).

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REFERENCES

1. TAYLOR, K. and BOSSONS, D., "Investigation of Green Lime Mud at Harmac Mill", *Pulp & Paper Canada*, 107(3): T63-66 (2006).
2. RICHARDSON, B., ULOTH, V., LOWNERTZ, P., GLEADOW, P., FORGET, C. and HOGIKYAN, R., "Behaviour of Non-Process Elements in the Kraft Recovery System", *TAPPI Proceedings, 1998 International Chemical Recovery Conference*, Tampa, FL, 1025-1039.
3. KEITAANNIEMI, O. and VIRKOLA, N.E., "Undesirable Elements in Causticizing Systems", *TAPPI*, 65(7), 89-92 (July 1982).
4. DORRIS, G.M. and ALLEN, L.H., "The Effect of Reburned Lime Structure on the Rates of Slaking, Causticizing and Lime Mud Settling", *J. Pulp Paper Sci.*, 11(4): J89-J98 (1985). Erratum: 11(6): J188 (1985).
5. BENNETT, A.J., GILLET, J.D. and WUNDER, H., "The Control of Mineral Deposits in Wet Air-Oxidation Soda-Recovery", *Appita*, 35(5), 383-394 (1982).

6. MAGNUSSON, H., MÖRK, K. and WARNQVIST, B., "Non-Process Elements in the Kraft Recovery System", *Proc. 1979 TAPPI Pulping Conference, Sept 24-26*, Seattle, WA, p. 77-83.
7. FREDERICK, W.J. Jr., "Managing Non-Process Element Flows in Pulp-Mill Operations", in: *The Impact of Energy and Environmental Concerns on Chemical Engineering in the Forest Products Industry, AIChE Symposium Series*, No. 239, Vol. 80, 21-29 (1984).
8. WANNENMACHER, P.N., FREDERICK, W.J., HENDRICKSON, K.A. and HOLMAN, K.L., "Application of Solubility Data to Predicting the Accumulation of Aluminum and Silicon in Alkaline Pulp", *TAPPI Minimum Effluent Mills Symposium Proceedings*, Atlanta, Georgia, 303-308 (1996).
9. THELIANDER, H., "Si and Al Inputs and Behaviour in the Recovery Cycle", *TAPPI Minimum Effluent Mills Symposium Proc.*, Atlanta, Georgia, 295-300 (1996).
10. ERICKSON, L.D. and HOLMAN, K.L., "Non-Process Element Flows and Control in a Kraft Pulp Mill", in: *Applications of Chemical Engineering Principles in the Forest Products and Related Industries*, Ferhan, K., Krieger-Brockett, B., Eds., AIChE Forest Products Division, New York, Vol. 1, 21-30 (1986).
11. ULMGREN, P., "Consequences of Build-up of Non-Process Chemical Elements in Closed Kraft Recovery Cycles – Aluminosilicate Scaling, a Chemical Model", *Pulp & Paper Canada*, Trans., TR 27-31 (1982).
12. CROUSE, N.E. and STAPLEY, C.E., "Dregs – Their Cause and Effect", *Pulp and Paper Canada*, 80:C, T93-8 (March 1979).
13. ULMGREN, P., "The Removal of Aluminium from the Recovery System of a Closed Kraft Pulp Mill", *Nord. Pulp Pap. Res. J.*, 2(1), 4-9 (1987).
14. BJÖRK, M., and ENGSTRÖM, I., "Handling of Non-Process Elements for Improved Runnability and Reduced Environmental Impact", *Pulp & Paper Can.*, 103(4), T102-105 (April 2002).
15. ULMGREN, P. and RÅDESTRÖM, R., "The Composition of Calcium Phosphates Precipitated from Green and White Liquors", *Nordic Pulp and Paper Research Journal*, 12(3), 167-174 (1997).
16. MCGUFFIE, B. and TAYLOR, K., "Non-Process Element Mass Balance Improves Re-caust and Lime Kiln Efficiency at Elk Falls Mill", PAPTAC Parksville Conference, April 21-22, 2006, PACWEST Conference, Jasper, AB, May 17-21, 2006.
17. FREDERICK, W.J., KRISHNAN, R. and AYERS, R.J., "Pirssonite Deposits in Green Liquor Processing", *Tappi J.*, 73(2), 135 (1990).
18. TRAN, H., MAO, X. and BARHAM, D., "Mechanisms of Ring Formation in Lime Kilns", *Journal of Pulp and Paper Science*, 19(4), J167-J175 (1993).
19. TRAN, H., GRIFFITHS, J. and BUDGE, M., "Experience of Lime Kiln Ringing Problems at E.B. Eddy Forest Products", *Pulp & Paper Canada*, 92(1), T26-T30 (1991).
20. DORRIS, G.M., "Effects of Mud Washing and Calcining Temperature on Lime Properties", *J. Pulp and Paper Science*, 29(6), 185-189 (2003).