

# EFFECT OF NON-PROCESS ELEMENTS ON KRAFT MILL EFFICIENCY

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## ABSTRACT

This paper examines the effects that non-process elements (NPEs) can have on Kraft mill efficiency. These include increased lime kiln fuel consumption, reduced lime mud filtration efficiency and increased scaling of heat exchangers. Procedures to address these problems are discussed along with mill case studies.

At the Harmac mill in Nanaimo, reduction of NPE inputs into the lime cycle significantly reduced serious incidents of lime mud filter plugging and maximized secondary sludge burning in the recovery boiler. This resulted in cost savings of approximately \$2,000,000/year.

At the Elk Falls mill in Campbell River, high NPE concentrations resulted in low solids content in filtered lime mud. Kiln dead load from NPE compounds was nearly 10 wt%. It was estimated that the low solids content and high kiln dead load resulted in additional lime kiln fuel costs of more than \$350,000/year. NPE specifications were developed for lime rock, fuel oil, salt cake and clarified green liquor. A cost-effective solution was developed to monitor and control NPEs in the lime cycle.

## INTRODUCTION

The accumulation of non-process elements (NPEs) in Kraft mill process streams is becoming increasingly important as mills move toward effluent system closure.

The effects of NPEs on Kraft mill operation have been extensively reviewed [1-13] and include increased lime kiln fuel use, reduced filtration efficiency, reduced lime mud settling and increased scaling of heat exchangers. The most important NPEs are aluminum, silicon, phosphorus and iron.

Lime kiln fuel use is strongly affected by the amount of water and NPE dead load that is present in lime mud. McGuffie and Taylor [14] estimated the incremental cost of 5 wt% water in lime mud and 8 wt% dead load from NPE compounds. The result was an incremental lime kiln fuel cost of more than \$350,000/year, based on a fuel oil cost of US\$32/barrel and a Kraft mill capacity of 830 t/d.

In the lime kiln, phosphorus has been shown at several different mills to be the most significant cause of dead load [1,14,15,]. In lime and lime mud, phosphorus can be present as calcium phosphate compounds such as hydroxylapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  [14,15]. 1 wt% phosphorus will result in a dead load of 5.4 wt% as hydroxylapatite or up to 8 wt% for other phosphate compounds [14].

Dregs carryover to lime mud is known to significantly reduce lime mud solids content [12]. Taylor and McGuffie recently identified a number of previously unreported silicate and aluminosilicate NPE compounds in green liquor clarifier deposits and dregs [16]. McGuffie and Taylor [14] also showed that high NPE concentrations correlated with low lime mud solids content. They showed that reducing NPE

concentrations in lime mud decreased kiln dead load and increased lime mud solids content.

The most likely cause of low solids content from NPEs in lime mud is the formation of high surface area aluminosilicate compounds [1,14]. Kaolinite, a high surface area aluminosilicate clay, was identified in Harmac lime by XRD analysis [1].

Recent work by Taylor and Bossons suggested that high surface area aluminosilicate compounds in lime mud could also lead to reduced filtration efficiency [1]. A good understanding of the effect of NPEs at the Harmac mill resulted in cost savings of up to \$2,000,000/year from reduced lime plant upsets and increased burning of secondary treatment sludge [1].

Aluminosilicate scaling of black liquor evaporators reduces heat transfer efficiency. These scales are also very difficult to remove [8,9,11].

All of the above areas can affect Kraft mill efficiency and operating costs.

This paper looks in more detail at the following topics:

1. Evidence for NPE aluminosilicate compounds in lime mud.
2. Summary of two mill studies where NPEs had a significant effect on filtration efficiency and lime kiln fuel use.
3. NPE reduction strategies.

## 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.

Kaolin clay was obtained from Feldspar Corp. (Florida) as EPK Kaolin and contained 97 wt% kaolinite. Surface area was 24 m<sup>2</sup>/g and average particle size was 1.4 microns. Synthetic green liquor contained 1.1M sodium carbonate (ACS grade) and 0.5M sodium sulphide (ACS grade).

## RESULTS AND DISCUSSION

### 1. Cause of Green Lime Mud - Aluminosilicates

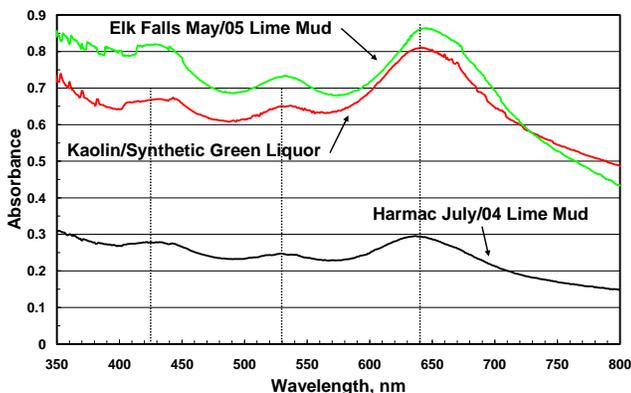
XRD analysis of a 2004 Harmac lime sample showed the presence of kaolinite (0.2 wt%) and gehlinitite (0.9 wt%) [1]. Kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot (\text{OH})_4$ , is an aluminosilicate compound with very high surface area and small particle size. It is the most common of the clay minerals. Gehlinitite,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , is a calcium aluminosilicate that can be formed from heating kaolinite with calcium oxide at temperatures

above 1000°C [17]. It is likely that the gehlinites in Harmac lime was produced in the lime kiln from kaolinite in the lime mud. The total concentration of these two minerals, 1.1 wt%, is significant. The occurrence of kaolinite in Harmac lime is important because its small particle size and high surface area could contribute to lime mud filter plugging.

There are three possible sources of the kaolinite in the lime: the kiln brick lining, clay impurities in makeup lime rock or formation in the recaust area of the mill. The lime kiln brick was ruled out as a possible source of this kaolinite, since it contained primarily the refractory ceramic mineral mullite. Aluminum concentrations in lime rock samples were low (<100 mg/kg), indicating low clay concentrations. Formation of kaolinite in green or white liquor has been suggested by other researchers. Magnusson et al. [6] used equilibrium calculations to show that kaolinite could be precipitated from white or green liquor at high silicon concentrations and relatively low (<9) pH values. Hem and Lind [18] reported kaolinite synthesis at 25°C in alkaline solutions. It is possible that aluminosilicate gels, the precursors to crystalline aluminosilicates, are involved with filter plugging [19].

The dark green colour of both Harmac and Elk Falls lime mud samples supports the presence of aluminosilicates in these process streams. Green compounds formed from sulphides and aluminosilicate compounds are well known [21-23]. Sulphide species combine in varying amounts with the aluminosilicate mineral sodalite to form the intensely coloured pigments aquamarine green, blue and red [21]. Kaolinite reacts with sulphides in a similar way. Sodalite is known to form in Kraft mill green and white liquor [8,20].

Kaolinite (from kaolin clay) became dark green in either Harmac green liquor or synthetic green liquor [1]. Visible light reflectance measurements were made of the green kaolin and green Harmac lime mud. Results are shown in **Figure 1** [1,16]. 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 in color [16]. The green color is composed primarily of a blue color (absorption at 640 nm) and a yellow color (absorption at 425 nm).



**Figure 1. Reflected Light Spectrum of Lime Mud**

It was previously reported [21-23] that the blue component absorbing light at 640 nm is the  $S_3^-$  radical anion and the yellow component absorbing light at 425 nm is the  $S_2^-$  radical anion. The minor absorption at 530 nm is caused by

the red-coloured  $S_3^-$  anion. It is likely that the green lime mud found at Harmac and Elk Falls mills is caused by the interaction of sulphides with aluminosilicate compounds such as kaolinite or hydroxysodalite [1,21,23].

## 2. Harmac Mill

The Harmac pulp mill, located on the east coast of Vancouver Island, is operated by Pope & Talbot. Harmac lime mud was typically very white in color until 2001. Since then, lime mud color has varied from nearly white to dark green. Recaust upsets such as plugging of pressure and rotary lime mud filters seemed to occur when the lime mud was dark green in color. These incidents of poor lime mud quality were serious enough to reduce mill output due to insufficient white liquor production. The mill operates with a capacity of 1120 ADt/d of fully bleached market Kraft pulp. The recaust was modernized in the mid 80's and combined into a single line. Harmac disposes of the waste secondary sludge from its effluent treatment process by three means: dewatering and burning in the power boiler, dewatering and sending to landfill or direct mixing with the weak black liquor and burning in the recovery boilers. NPE results discussed in this paper were originally reported by Taylor and Bossuns [1].

A strong economic incentive exists to burn sludge in the recovery cycle at Harmac as it reduces operating costs by approximately \$2 million a year. Incineration of secondary sludge in the recovery boiler has been of interest to the pulp industry for some time [24]. Economics are favourable but the sludge is known to contain mill-specific NPEs that can affect mill operation [25].

By comparing Harmac NPE values with other mills, and from historical mill data, NPEs of primary interest included iron, magnesium, aluminum, silicon and phosphorus [1].

A mass balance of iron in the lime plant showed that a major source of iron was the lime rock. Iron concentrations in the lime rock were found to vary from 300 to more than 1000 mg/kg between lime rock shipments. When iron input to the lime plant exceeded losses to the white liquor and grits, iron levels in the lime increased rapidly. Iron concentrations in the lime rock of less than approximately 500 mg/kg did not result in a build-up of iron in the lime plant and significantly improved recaust operation. High iron concentrations were associated with the occurrence of green lime mud and lime mud filter plugging at Harmac.

Magnesium concentration in the lime rock also varied significantly. High magnesium concentrations tended to occur with higher iron concentrations in the lime rock. Magnesium concentration in lime rock shipments varied from a low of approximately 1000 mg/kg to more than 9000 mg/kg. Aluminum concentrations were generally less than 100 mg/kg.

At Harmac, it appears that the increasing magnesium concentration in the lime since 2001 has occurred with a concurrent increase in aluminum concentration in the lime and in green and white liquor. This contrasts with other studies showing that the addition of magnesium can reduce aluminum levels in the liquor system [7,14,16,25].

The silicon concentration in lime, lime mud, green liquor and white liquor was significantly higher at Harmac than reported values for other mills. Silicon concentrations were not significantly affected by sludge burning and were relatively stable since 2001.

Phosphorus accumulated rapidly in Harmac lime during sludge burning. At other times, phosphorus levels were comparable with other mills. Phosphorus in the lime mud was identified by XRD as hydroxylapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , and was identified as the major contributor to kiln dead load.

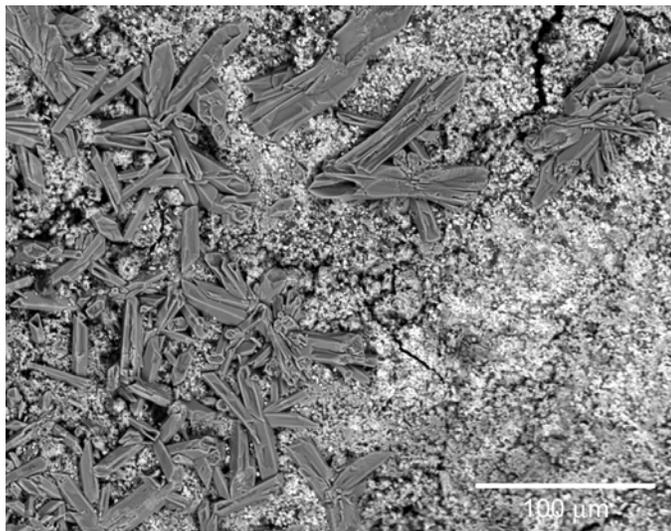
A good understanding of the effect of NPEs at the Harmac mill resulted in significant cost savings from reduced lime plant upsets and increased burning of secondary treatment sludge [1].

### 3. Elk Falls Mill

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. 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 was 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.

NPE compounds and chemistry occurring in the green liquor clarifier and lime cycle of the Elk Falls mill were studied in detail by Taylor and McGuffie [16]. This information allowed the design of a successful NPE mass balance mill trial that is reported in a separate paper [14].

At Elk Falls, hydroxylapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , was identified by XRD as the primary phosphorus-containing component of lime mud. Phosphorus-containing compounds were the most important dead load component in the lime kiln, present at more than 10 wt% in one lime sample [16].



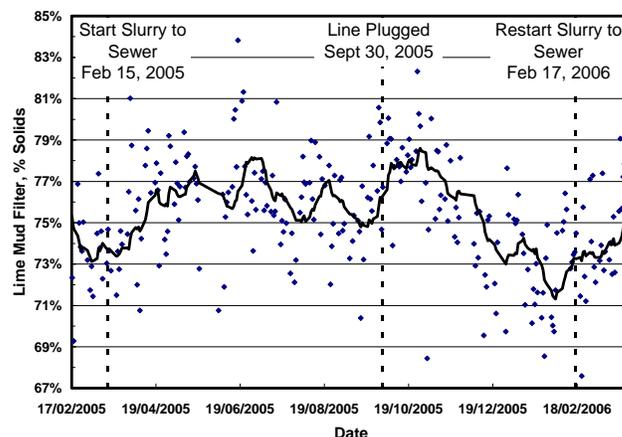
**Figure 2. SEM Micrograph of White Liquor Filter Sock Sampled May 24/05 (scale bar 100  $\mu\text{m}$ ) [16].**

High concentrations of NPEs were found in material plugging white liquor pressure 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 2** 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 surface were composed primarily of NPE compounds with traces of graphite [16]. These NPE compounds are not acid-soluble.

A non-process element mass balance was conducted at Elk Falls mill [14]. The study was implemented to provide a clear picture of NPE accumulation in the Elk Falls lime cycle. The study resulted in NPE specifications for lime rock, fuel oil, salt cake and clarified green liquor. Fuel oil was identified as an important source of P, Fe and Zn in the lime cycle. In contrast to the Harmac mill, lime rock did not significantly contribute to NPE input at Elk Falls.

Sewering of kiln precipitator catch had a definite positive impact on solids content of lime mud as shown in **Figure 3**. Sewering had the additional benefit of effluent pH adjustment. Precipitator catch slurry initially flowed to sewer beginning in February 2005 and ending September 20, 2005. During this period, lime mud solids averaged 76.2% with a standard deviation of 2.3%. The slurry line plugged on September 20 and was not put back into operation until February 17, 2006. While the line to sewer was out of commission, lime mud filter solids continuously declined, averaging 72.9% with a standard deviation of 1.9% from January 17 to February 17, 2006. After February 17, slurry flow was restarted at a high rate. Average slurry flow rate was 55 L/minute from February 17 to March 31, 2006, replacing an estimated 40% of the lime mud inventory. Lime mud solids from March 16 to March 31, 2006, averaged 76.4% with a standard deviation of 1.8%. These results show a significant improvement in lime mud solids content. Phosphorus, zinc, iron and aluminum concentrations in the lime mud all decreased significantly by March 2/06 as shown in **Figures 4 and 5**.



**Figure 3. Lime Mud Solids Content, 10 Day Average**

### 4. NPE Reduction Strategies

Results from the Harmac and Elk Falls mills showed very different NPE inputs and outputs [1,14,16]. Since significant variations can occur in each mill, a mass balance of NPEs can quickly pinpoint the most cost-effective strategies for NPE management [14].

The first step is to compare NPE concentrations in lime mud, green liquor and white liquor with average values of other mills [1,14].

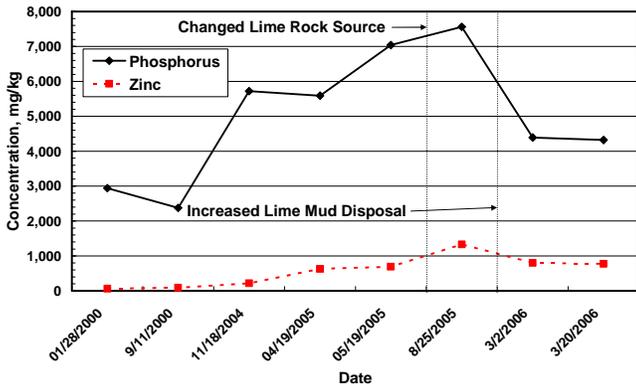


Figure 4. Trends in P and Zn in Elk Falls Lime Mud

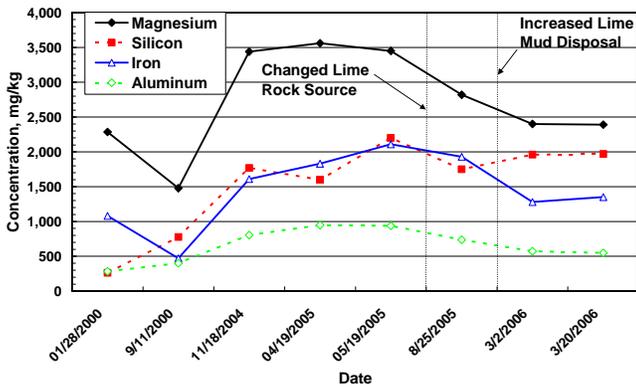


Figure 5. Trends in Mg, Si, Fe and Al in Elk Falls Lime Mud

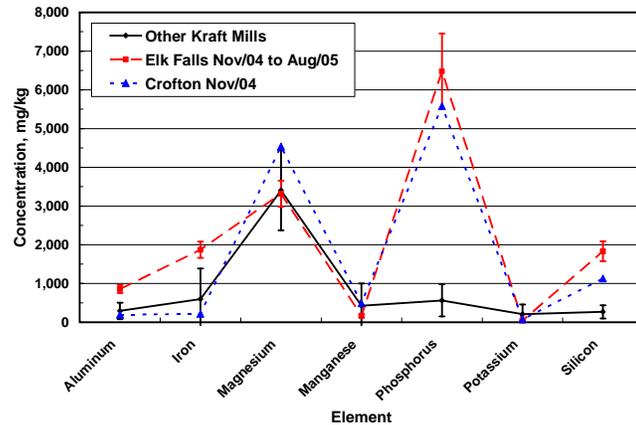


Figure 6. Comparison of NPE Levels in Lime Mud

Figure 6 shows that aluminum, iron, phosphorus and silicon concentrations in Elk Falls lime mud were all significantly higher than reported values at other mills [2,4]. Magnesium, potassium and manganese concentrations were within the range of values reported at other mills by Richardson et al. [2]. Sodium concentration is not shown, but was within the range of values seen at other mills.

For comparison, results for the Crofton mill are also shown in Figure 6. The Crofton Kraft mill is on Vancouver Island south of the Harmac mill in Nanaimo. 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.

Historical trends in NPE concentration in a mill are also important, as shown in Figures 4 and 5. It is important to look for long term trends in the concentration of individual NPEs.

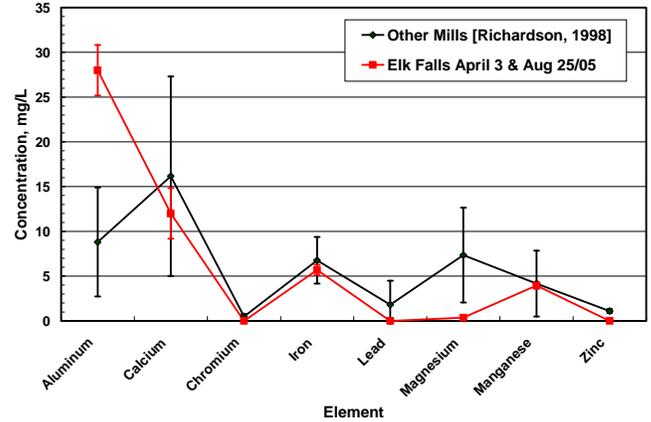


Figure 7. NPEs in Elk Falls Clarified Green Liquor

Figure 7 shows that the aluminum concentration in Elk Falls clarified green liquor was significantly higher than average values for other mills [16]. In addition, the magnesium concentration was much lower and was almost zero. It was shown by Taylor and McGuffie [16] that at Elk Falls mill, removal efficiency of both aluminum and silicon in the green liquor clarifier was reduced because of insufficient magnesium ion concentration in the raw green liquor.

Several studies have shown that magnesium addition to the dissolving tank can reduce aluminum concentration in clarified green liquor [5,26]. In their studies of wet air-oxidation (WAO) soda recovery, Bennett et al. [5] intentionally added magnesium from dolomite to make-up limestone to reduce aluminum concentration in the white liquor. Ulmgren [26] reported a successful mill trial where aluminum concentration in green liquor was reduced by the addition of magnesium sulphate to the dissolving tank.

It is possible that a mill might have an excess of magnesium in the raw green liquor. In that case, it might be possible to remove magnesium by addition of aluminum ion. The Skoghall mill in Sweden has added aluminum ion to the dissolving tank to reduce excess magnesium ion in green liquor [25].

Significant cost-savings can sometimes be achieved by using a mill waste stream that contains significant amounts of a required ion, such as magnesium ion in bleach plant effluents.

## CONCLUSIONS

1. NPE compounds in lime mud can significantly increase lime kiln fuel use, both by increasing dead load and by decreasing solids content.
2. Aluminosilicate compounds in lime mud may be present as high surface area clays that can significantly decrease solids content and lead to filter plugging.

3. Phosphorus in Elk Falls and Harmac lime is the major dead load component and can tie up more than 5 times its own weight in calcium phosphate compounds.
4. White liquor pressure filter sock plugging can be caused by the accumulation of micron-sized acid-insoluble NPE compounds and graphite.

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