BEHAVIOUR OF NON-PROCESS ELEMENTS IN THE KRAFT RECOVERY SYSTEM

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ABSTRACT

The behaviour of non-process elements in the chemical recovery and recausticizing areas of four kraft mills and one acid sulphite mill was studied. Enrichment factors in the precipitator dust were found to average 2.69, 1.68, and 2.44 for the elements chloride, potassium, and zinc, respectively. Good green liquor clarification will be required for metals removal, if a kraft mill is considering recycling of bleach plant effluents. Results from an acid sulphite mill indicate that the build up of Ca, Al, Mg, Mn, Fe, and Zn may be controllable through the dregs output. Bleeding lime mud from recausticizing will reduce the levels of Al, Mg, Mn, and Fe in white liquor and in the mills' liquor system as shown by both mill and lab data.

INTRODUCTION

The non-process elements (NPE) present in a kraft mill include Al, Fe, Mg, Mn, Si, K, Cl, P, and N. These elements originate mainly from the wood and mill water. Other sources of NPE input include make-up chemicals (i.e. purchased saltcake, lime or limestone), and erosion and corrosion products of metal and refractory surfaces [I]. The amount of NPE introduced to the liquor cycle depends mainly on the type of wood pulped. Birch chips, and sawmill chips in general, contain more calcium, potassium, and magnesium than do pine chips [2]. Whole-tree chips contain about 3.5 times as much aluminium, silicon, and iron and 2.5 times as much calcium and magnesium as sawmill chips because of the higher bark content (15-20% compared to 0.5-2%) [2]. Limestone and purchased lime can introduce Mg, Fe, and, in particular, aluminium and silicon into the liquor system [l]. The amount of NPE introduced in the causticizing system with the make-up lime is of the same order of magnitude as the amount introduced with the smelt [2,3]. Oxygen delignification of pulp can also contribute to the input of magnesium ($MgSO_4$).

Effluent system closure will require the mill to recycle their bleach plant effluents, increasing the load of NPE in other areas of the mill, or to have a separate facility for handling the disposal of these effluents. Because the kraft process recycles the cooking chemicals, the efficiency and operation of each unit process inherently affects that of the next and all subsequent operations. The introduction of a stream from the bleach plant into another part of the mill, carrying with it certain inherent impurities, will thus have an impact on the whole process. NPE in the kraft chemical recovery system represent a dead load, reducing the efficiency and capacity of the recovery equipment, increasing fuel consumption in the lime kiln, reducing the causticizing efficiency, and accelerating corrosion rates [4]. In addition, higher impurity levels impair lime mud settling rates and both the green and white liquors clarification steps [5].

The tendency of the various elements to accumulate in an alkali cycle has been reported to decrease in the following order: K, Cl, Al, Fe, Si, Mn, Mg, and Ca [2]. Fe, Mn, Mg, and Ca do not build up dramatically with increasing closure, since they form insoluble compounds in the green and white liquor cycle [6]. These insoluble compounds are removed from the cycle in the green liquor clarifier or the slaker. K, Cl, Al, and Si form soluble species in the liquor system [6]; they have no distinct discharge point from the recovery system and tend to accumulate in the alkali cycle [2]. Ca, Mg, P, and Mn are transferred from the alkali cycle to the lime cycle and accumulate there [2]. The accumulation of NPE in the lime cycle has been reported to decrease in the following order: Mg, Al, Fe, Mn, Si, Na, K, S, and Cl [2]. The most undesirable elements in the lime cycle are aluminum, iron, magnesium, and silicon. Increasing the silicon concentration in the lime mud may reduce the reactivity of the lime, because the silicon compounds melt on the surface of the lime pellets, decreasing porosity [2]. The maximum acceptable concentration of silica in lime is considered to be 4% [2]. Separation of white liquor from lime mud is hampered by the presence of magnesium and iron. Magnesium enters the lime cycle with makeup lime and smelt from the alkali cycle. Magnesium hydroxide is gelatinous and plugs the wire mesh on the lime mud drum filter. The maximum acceptable content of MgO in lime is considered to be 2% [2]. In well designed and operating green and white liquor clarification operations, Ca, Mg, and heavy metals will be substantially reduced by removing the dregs and grits or by lime losses [2, 3]. In fact, iron, silicon, manganese and magnesium are generally found in white liquor in lower quantities per tonne of pulp than those introduced into the chemical recovery system. Calcium has the greatest tendency of all elements to remove itself from the alkali cycle [2]. Low alkali losses tend to increase Ca and Mg concentrations in black liquor.

It is generally believed that dregs have a detrimental effect on liquor, lime mud, and calcined lime quality. Recycling of a metal-laden stream, such as an acid stage bleach plant filtrate, back to recaust can increase inorganic dregs production by a factor of 2 to 3. Moreover, the solids loading or flux in the green liquor clarifier is increased as the dregs concentration is increased and calcium losses increase with an increase in dregs concentration [7, 8]. High dregs carryover also causes high soluble sodium in the lime mud which results in non-uniform pellet formation and decreased lime reactivity [9]. An excess of dregs in the lime cycle can double the sodium loading to the kiln [7].

Possible purges of NPE include washing losses, liquor spills, bleach plant effluents, flue gas particulates, dust, grit, dregs, precipitated inorganic salts and scales, and deposits [1, 10]. Lime mud used for effluent neutralization and as a precoat on the dregs filter also constitutes a bleed from the system [1]. As mill closure increases, the ability of the recausticizing plant to remove NPE becomes increasingly important.

The concentrations of non-process chemical elements in most black liquors are usually quite low and would normally have little impact on recovery boiler operation. However, this may not be true for a totally closed kraft mill with internal recycle of its bleach plant effluents.

The purpose of this study is to assess the behaviour of non-process elements about major unit operations in the recovery and recausticization areas in a kraft mill and to compare them with extreme case results from a sulphite mill.

EXPERIMENTAL

Collection of Samples

Four different kraft mills were sampled extensively throughout the fibreline, recovery and recausticizing [11]. More than 75 samples were collected in each mill and analyzed for various elements and compounds. Mill operating data was collected on each sampling day either from the digital control system (DCS) or by manual collection from control room information. Process flows were collected from the DCS or using a portable ultrasonic flow meter; some flow data from the DCS were also checked against the portable meter.

Mill A is an interior mill; Mill B is a coastal mill; Mill C is modern interior mill; and Mill D is a recently modernized coastal mill. Both Mill A and B started up in the late 1960's. Mill A pulps mostly spruce, pine and fir wood chips and produces fully bleached pulp using a $D_CE_{OP}DED$ bleaching sequence. Mill B pulps mostly spruce and fir wood chips and produces semi-bleached pulp. Mill C, a modern mill built in the early 1990's, produced fully bleached market pulp with a $C_DE_{OP}DED$ bleaching sequence, and alternates between both hardwood and softwood chips. Mill D is a fully modernized softwood mill, producing fully bleached market pulp via a $D_CE_{OP}D_ND$ bleaching sequence. Further information about these mills is shown in Table I.

Samples (one day composites) from an acid sulphite mill (Mill H) were also obtained throughout the fibreline and chemical recovery system with the help of mill personnel.

Table. I
Kraft mills sampled.

	Mill A	*Mill B*	*Mill C*	*Mill D*
Location	*Interior BC*	*Coastal BC*	*Alberta*	*Coastal BC*
Wood Species	*Softwood*	*Softwood*	*Hardwood*	*Softwood*
Vintage	*mid 60s*	*late 60s*	*early 90s*	*late 80s*
*Fibreline Configuration**	*Conventional Dig.* $D_{C(70\%)}E_{OP}DED$	*Conventional & Sawdust Dig.* $D_{C(55\%)}E_OHH$	*EMCC, O_2 Delig.* $C_{D(30\%)}E_{OP}DED$	*EMCC, O_2 Delig.* $D_{C(60\%)}E_{OP}D_ND$
Production Rate	*750 ADt/d*	*400 ADt/d*	*1190 ADt/d*	*1045 ADt/d*
Blowline Kappa	*34*	*29*	*14*	*30*
Recovery Boiler Type	*B&W*	*B&W*	*B&W*	*B&W*
Heavy BL Solids	*61%*	*66%*	*70%*	*70%*
Kiln Emission Control	*Scrubber*	*ESP*	*ESP*	*Scrubber*

** Value in the brackets indicates the level of chlorine dioxide substitution in the first stage of bleaching.*

Laboratory Studies

Samples of green liquor and lime mud were collected from three other Canadian kraft mills (identified as Mills J, K, and L, respectively) that were characterized by very different levels of non-process elements. The dried lime muds were calcined in the lab to produce reburned limes with available lime contents of 92.7%, 93.6%, and 95.9% for Mill J, K, and L, respectively. The amount of available lime after calcining was found by the rapid sugar method [12]. Green liquors were recausticized with limes for 90 minutes at 90-95 °C; the resulting mixture (white liquor and lime mud) was placed in a settling column heated by an air bath maintained at 80 °C. The settling behaviour of the lime muds were observed and recorded. The white liquors were collected from the bottom of the settling column by filtering each liquor through the settled lime mud and the washed (with hot water) lime muds were analysed for metal concentrations. In all experiments 44 grams of ground reburnt lime was causticized in 750 mL of green liquor for 90 minutes with constant agitation using a turbine impeller operating at 800 rpm.

RESULTS

Enrichment of NPE in Precipitator Catch

As illustrated in Table II, Cl, K, and, Zn were all enriched in the precipitator catch of the kraft recovery boilers. The split (enrichment) factor was defined as: element/sodium ratio in the precipitator dust divided by the element/sodium ratio in the heavy black liquor. There were no statistically significant differences in the enrichment factors for K, and Zn between coastal and interior mills or between old recovery boilers and new recovery boilers firing at higher solids. Interior mills were found to have a slightly higher enrichment factor for Cl, a value of 3.0 versus 2.4 for coastal mills.

Table II.
Enrichment factors (precipitator dust/heavy black liquor) with reference to sodium (all on a dry basis) for four kraft mills.

	Cl	K	Ca	Fe	Mg	Mn	Zn
Mill A	3.05	1.38	---	---	---	---	---
Mill B	2.33	1.80	0.42	*	0.08	0.53	2.55
Mill C	2.98	1.98	0.14	0.98	0.34	0.84	2.11
Mill D	2.39	1.55	0.18	0.59	0.25	0.26	2.65
Average for 4 Mills	2.69	1.68	0.25	0.79	0.22	0.54	2.44
Std Dev	0.38	0.26	0.16	0.28	0.13	0.29	0.29
Average for Interior Mills	3.02	1.68	0.14	0.98	0.34	0.84	2.11
Average for Coastal Mills	2.36	1.68	0.30	0.59	0.16	0.40	2.60

* *Contaminated with flakes of rust (iron).*

For comparison, enrichment factors for seven elements on a dry solids weight ratio basis, obtained from studies carried out in the mid 1970s [13] are presented in Table III. In each case, the black liquor was sampled after the direct contact evaporators. The data for Mill E is an average of two samples, on different days, three days apart. The data for Mill F is an average of fifteen samples, taken 2-3 times a day over a six day period. The data for Mill G is an average of nine samples except where noted, sampled 1-2 times a day over a seven day period. Both Mill E and Mill F had Babcock & Wilcox type recovery furnaces and Mill G had a Combustion Engineering (now ABB) recovery furnace. The enrichment factors in Tables II and III are very comparable considering the changes made in recovery boiler operations over the last 15 years (i.e. higher fired black liquor solids, higher operating temperatures and better dust recovery) [14,15]. Zinc, chloride and potassium had the highest enrichment factors; as both K and Cl lower the melting points for recovery boiler deposits, these elements will be of concern as kraft mills become more closed. It seems that zinc should also be considered when modelling the recovery boiler and that the precipitator catch provides a natural bleed for this element from the recovery cycle. The generally higher enrichment factor for K, and lower enrichment factors for Ca, Fe, Mg, Mn, Zn, and perhaps Cl, in the current study, probably reflect the changes in recovery boiler operation over the last 15 years (higher fired solids, higher furnace temperatures and greater production of sodium fume).

Table III.
Enrichment factors (precipitator dust/heavy black liquor) with reference to sodium (all on a dry basis) for inland mills [13].

	Enrichment Factors, Precipitator Dust/Black Liquor						
	Cl	K	Ca	Fe	Mg	Mn	Zn
Mill E	4.24	1.31	0.56	0.84	1.18	1.19	4.61
Std Dev	0.60	0.12	0.48	0.31	0.52	0.33	2.74
Mill F	2.25	1.36	0.58	0.77	1.14	0.75	4.06
Std Dev	0.40	0.02	0.10	0.26	0.23	0.09	0.91
Mill G	3.37[1]	1.29	2.05[1]	1.71[1]	1.47[1]	0.34	4.60
Std Dev	0.53	0.13	1.55	0.84	1.32	0.09	1.61

[1] *An average of eight samples.*

Bleeding Non-Process Elements from the Liquor Cycle

Mill H employs an acid sulphite pulping process with a Stora chemical recovery system [16]. Pulping and brownstock washing are conducted under acidic conditions, and the various metals (or NPE) are, thus, expected to be washed from the pulp and leave as dissolved species with the liquor going to the chemical recovery system. As alkaline conditions similar to those in a kraft chemical recovery system are encountered in this mills' green liquor system, metals behaviour about the green liquor clarifier will offer insights for predicting how high NPE levels could increase in a closed-cycle kraft mill.

Although the input levels of Ca, Mg, Fe, and Zn with Mill H chips are equal or lower than in the four kraft mills (Table IV), Ca, Mg, Mn, and Zn in Mill H raw green liquor are at much higher concentrations than those found in kraft mills (Table V). These elements are, however, removed very effectively, most likely as carbonates or sulphides, with the dregs as illustrated in Figure 1. Comparing the raw green liquors and clarified green liquors further, the levels of NPE in Mill H clarified green liquor are generally very comparable to those in the four kraft mills. Levels of Mg and Mn in Mill H clarified green liquor, for example, are at most 2 to 4 times higher than those in the kraft mills although the levels in the raw green liquors are up to 10 times higher. Table A-1 in the Appendix provides a comparison of dregs composition on a dry basis for Mill H and the four kraft mills. It should be noted that Mill H green liquor is not identical to a kraft green liquor; it has a higher pH and sulphide content. These results are, however, encouraging as they indicate that the build up of Ca, Al, Mg, Mn, Fe, and Zn may be controllable through the dregs output. The relatively low removal efficiencies for Al and Si in Table IV and the fairly broad range in removal efficiencies and in clarified green liquor concentrations should be noted. Ca, Mg, and Mn can be further reduced if the clarified green liquor is filtered as illustrated in Figure 2. A sample of Mill Ds' clarified green liquor was filtered in the lab through a Whatman #42 filter paper to provide a sample free of suspended solids. These elements, presumably in the form of carbonates, seem to remain partly suspended in solution after settling. The results in Figures 1 and 2 suggest that the green liquor clarification process at Mill D may benefit from optimization (i.e. flow and TTA stabilization, flocculant use, decreased rise rate for the overflow, or installation of a filtration unit) [17].

Table IV.
Input level of elements from chips.

Sample		*Mill Chips*				
Mill		*Mill A*	*Mill B*	*Mill C*	*Mill D*	*Mill H*
Moisture	*%*	*47*	*54.6*	*44.5*	*49.7*	*45.1*
Ash	*mg/kg**	*0.36*	*0.367*	*0.386*	*NR*	*NR*
Na	*mg/kg**	*119*	*772*	*2.16*	*183*	*22.9*
K	*mg/kg**	*259*	*406*	*674*	*204*	*341*
Ca	*mg/kg**	*419*	*647*	*1280*	*480*	*396*
Al	*mg/kg**	*9*	*8.6*	*6*	*16.5*	*2.92*
Mg	*mg/kg**	*83.7*	*140*	*190*	*95.8*	*82.7*
Mn	*mg/kg**	*39.2*	*37.2*	*3.51*	*24.3*	*91.5*
Fe	*mg/kg**	*11.1*	*21.5*	*8.74*	*15.7*	*9.28*
Zn	*mg/kg**	*5.3*	*3.57*	*11.4*	*3.8*	*4.1*
Cr	*mg/kg**	*0.29*	*12.7*	*0.21*	*<0.3*	*0.31*
Pb	*mg/kg**	*0.24*	*1.2*	*<0.004*	*0.74*	*<0.007*
Si	*mg/kg**	*41*	*ND*	*18*	*20.4*	*9.7*
Cl	*mg/kg**	*9*	*722*	*13*	*206*	*ND*

** mg/kg as received*
NR = Analysis not requested
ND = Not-detected

Table V.
Removal of elements during green liquor clarification.

Sample		*Raw Green Liquor**					*Clarified Green Liquor*					*% of Element Removed*				
Mill		*Mill A*	*Mill B*	*Mill C*	*Mill D*	*Mill H*	*Mill A*	*Mill B*	*Mill C*	*Mill D*	*Mill H*	*Mill A*	*Mill B*	*Mill C*	*Mill D*	*Mill H*
Density	*@ 20 °C*	*1.169*	*1.249*	*1.173*		*1.203*	*1.17*	*1.251*	*1.172*		*1.193*					
Suspended Solids	*%*		*14.53*	*0.083*	*0.108*		*0.019*	*1.14*	*0.018*	*0.032*	*0.015*		*92.2*	*78.3*	*70.4*	
C	*mg/kg*	*39*	*53.3*					*10.2*					*80.9*			
Na	*mg/kg*	*63460*	*94740*	*68330*	*78100*	*96130*	*67640*	*90350*	*57790*	*77850*	*87760*	*-6.6*	*4.6*	*15.4*	*0.3*	*8.7*
K	*mg/kg*	*4388*	*6925*	*14310*	*4000*	*4310*	*4638*	*6903*	*15410*	*4260*	*4240*	*-5.7*	*0.3*	*-7.7*	*-6.5*	*1.6*
Ca	*mg/kg*	*68*	*104*	*139*	*99.6*	*955*	*23*	*6.7*	*2.13*	*28*	*21*	*66.2*	*93.6*	*98.5*	*71.9*	*97.8*
Al	*mg/kg*	*7.3*	*22.2*	*3.84*	*27.8*	*17.7*	*7.7*	*8.4*	*1.28*	*18.3*	*8.38*	*-5.5*	*62.2*	*66.7*	*34.2*	*52.7*
Mg	*mg/kg*	*12*	*68.6*	*132*	*41.6*	*291*	*2.5*	*3.99*	*5.53*	*15.8*	*8.92*	*79.2*	*94.2*	*95.8*	*62.0*	*96.9*
Mn	*mg/kg*	*8.2*	*27.8*	*2.05*	*13.4*	*266*	*2.8*	*2.38*	*0.3*	*5.5*	*9.85*	*65.9*	*91.4*	*85.4*	*59.0*	*96.3*
Fe	*mg/kg*	*22*	*57.7*	*11.2*	*42.9*	*26.7*	*11*	*6.51*	*4.3*	*7*	*5.03*	*50.0*	*88.7*	*61.6*	*83.7*	*81.2*
Zn	*mg/kg*	*24*	*2.07*	*6.95*	*1.71*	*15.2*	*1.4*	*1.21*	*0.77*	*1.02*	*1.13*	*94.2*	*41.5*	*88.9*	*40.4*	*92.6*
Cr	*mg/kg*	*0.9*	*0.75*	*0.85*	*0.51*	*1.25*	*0.64*	*0.089*	*0.73*	*0.43*	*0.63*	*28.9*	*88.1*	*14.1*	*15.7*	*49.6*
Pb	*mg/kg*	*0.39*	*0.16*	*2.09*	*5.93*	*0.055*	*0.16*	*0.083*	*2.6*	*6.18*	*0.003*	*59.0*	*48.1*	*-24.4*	*-4.2*	*94.5*
Si	*mg/kg*	*77*	*62.8*	*179*	*214*	*70.7*	*64*	*62.8*	*119*	*225*	*67.1*	*16.9*	*0.0*	*33.5*	*-5.1*	*5.1*

** Results based on as received basis.*

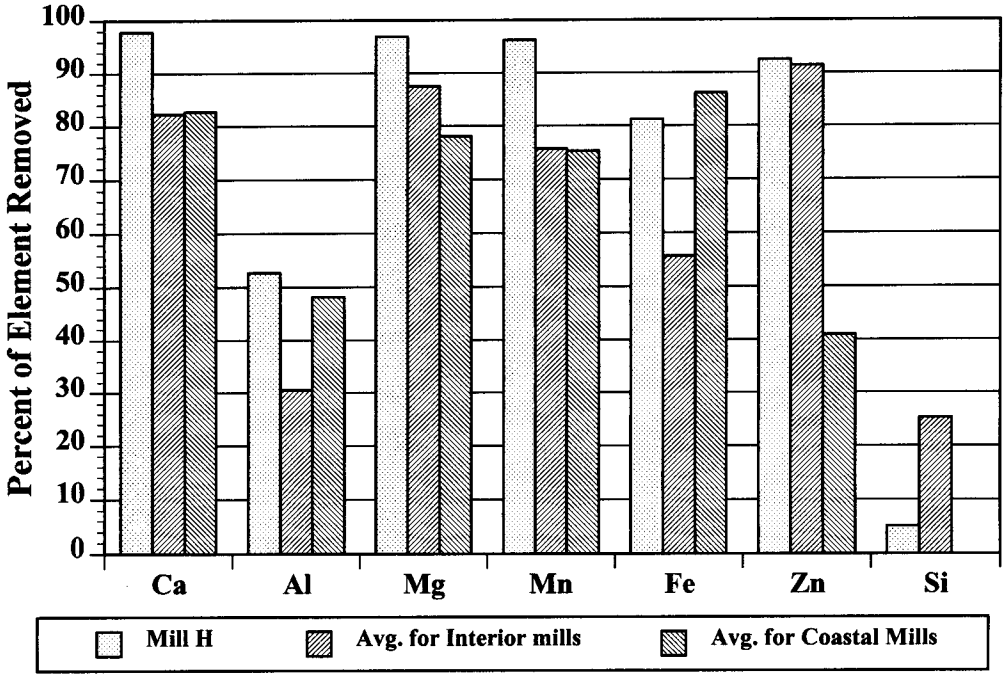


Figure 1. Percent removal of elements during green liquor clarification.

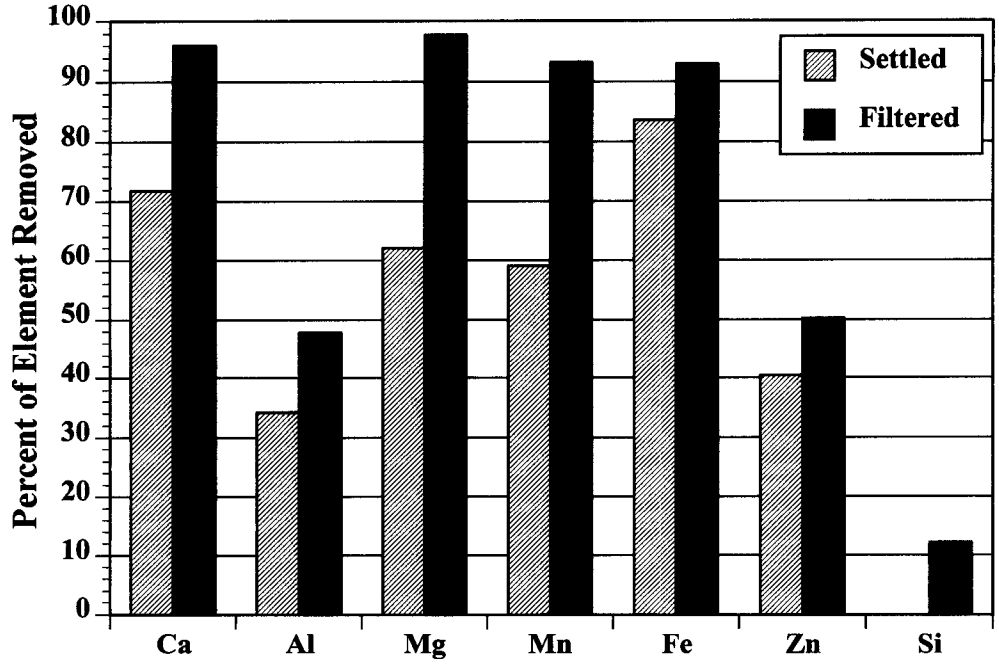


Figure 2. Percent removal of elements in settled and filtered clarified green liquor samples from Mill D.

Accumulation of Elements

Accumulation factors were calculated for three of the sampled mills and compared in Table VI to Finnish data from the early 1980's [2]. Flow data is summarized in Table A-2 of the Appendix. The high accumulation factors for potassium and chloride in the alkali loop show the high degree of solubility of these elements. The generally higher accumulation factors for Cl and K in this study (20-26 for K, 35-48 for Cl) largely reflect recent efforts to improve brown pulp washing efficiencies and the incorporation of oxygen delignification systems. The results are very similar to those reported in more recent U.S. studies (24 for K, 28 for Cl) [18]. Controlling the concentration of these elements will likely be necessary for a mill considering closure.

Table VI.
Accumulation of undesirable elements.

	*In the alkali loop**					*In the lime loop***				
Element	*A*	*B*	*C*	*D*	*Z*†	*A*	*B*	*C*	*D*	*Z*†
Ca	0.02	0.01	0	0	0.02	---	---	---	---	---
Mg	0.02	0.02	0	0.01	0.1	4.2	7.9	1.8	4.7	7.5
Mn	0.08	0.16	0.07	0.23	0.3	0.67	8.6	1.6	2.0	2.3
Al	1.3	0.4	0.6	1.0	1.2	1.6	5.2	0.6	4.7	6
Si	1.7	0.55	5.7	7.3	0.5	0.6	0.46	3.3	3.1	0.6
K	22.6	20.4	33.7	26.3	11.6	0.37	0.04	0.04	0.1	0.2
Cl	42.2	34.8	48.0	46.7	3.7	0.37	0.01	0.06	0.22	0.04
S	---	---	---	---	---	0.08	5.1	0.5	2.7	0.1

** Accumulation factor = concentration in white liquor (kg/adt of pulp) divided by the total amount introduced to the chemical recovery system (kg/adt of pulp).*

*** Accumulation factor = concentration in the lime mud fed to the kiln (kg/adt of pulp) divided by the total amount introduced to the chemical recovery system (kg/adt of pulp).*

† Data from Keitaanniemi [2].

Except for Mg, K, and Cl, the accumulation factors for the other elements are very similar to those observed in the earlier Finnish study [2]. The magnesium input from the chips for the Canadian mills is higher than that in the Finnish chips. The high variability of the accumulation factors for magnesium, particularly in the lime loop shows the importance of the relative contribution of the various sources (chips & makeup lime or limestone) at the time of sampling on the estimated accumulation factor. An examination of the accumulation factors for several other elements indicates that they are too variable to be used in modelling NPE behaviour in the liquor or lime cycle.

Behaviour of NPE in Mill Recausticization Systems

Gravimetric flows of NPE in white liquor (WL) and lime mud (LM) for the four sampled kraft mills are illustrated in Table VII. The weight percent values in this table represent the partioning of the element between the mud and the liquor; they were calculated as the amount of NPE in the mud divided by the NPE in both the white liquor and lime mud (using liquor flowrates and an estimated average of ≈120g mud per litre of WL). Over 99% of the Mg and 86% of the Mn remained in the settled lime mud for all four mills. Removal of Al, Si, and Fe varied dramatically between mills (i.e. by a factor of 2 or more). Only 21-39% of the SiO_2 remained with the lime mud. The slightly better separation efficiencies for Mill B are due to its' under utilization of the recausticizing system as this mills' liquor system was designed to handle a throughput of double its normal daily operation. As expected, potassium was found to be completely soluble and remained with the white liquor.

Table VII.
Metal analysis of mill white liquors and lime muds.

		Al	*SiO_2*	*Mg*	*Mn*	*Fe*	*K*
	WL, mg/kg	*8.9*	*70*	*1.4*	*2.3*	*14*	*4308*
Mill A	*LM, mg/kg*	*134*	*287*	*3009*	*200*	*178*	*740*
	*%**	*57.1*	*26.6*	*99.5*	*88.5*	*52.9*	*1.5*
	WL, mg/kg	*4.27*	*63.5*	*1.11*	*5.08*	*8.5*	*7003*
Mill B	*LM, mg/kg*	*570*	*428*	*5352*	*1711*	*2315*	*71.2*
	*%**	*92.6*	*38.9*	*99.8*	*96.9*	*96.2*	*0.1*
	WL, mg/kg	*3.88*	*133*	*0.9*	*0.26*	*51.7*	*11600*
Mill C	*LM, mg/kg*	*33.2*	*53*	*2910*	*45.4*	*179*	*87.4*
	*%**	*47.8*	*30.8*	*99.7*	*94.9*	*27.1*	*0.1*
	WL, mg/kg	*15.0*	*170*	*0.43*	*4.48*	*5.78*	*4730*
Mill D	*LM, mg/kg*	*550*	*500*	*3250*	*300*	*747*	*118*
	*%**	*76.5*	*20.8*	*99.8*	*85.7*	*92.0*	*0.2*

** % partitioning with the mud.*

Effect and Behaviour of NPE on Recausticizing in Lab Studies

As shown in Tables VIII and IX, the levels of NPE in green liquor and lime mud samples from these three kraft mills varied quite significantly. The lime muds were calcined at 1000°C in the lab to produce reburnt lime with available lime contents of 92.7%, 93.6%, and 95.9% for Mills J, K, and L, respectively. Green liquors and limes were recausticized for 90 minutes at 90-95°C; the resulting mixture (white liquor and lime mud) was placed in a settling column heated by an air bath maintained at 80°C. The settling behaviour of the lime muds were observed and recorded. The white liquors were collected from the bottom of the settling column by filtering each liquor through the settled lime mud and the lime muds (washed with hot water) were analysed for metal concentrations (Table X).

Laboratory results of metal partitioning with the lime mud were found to be in good agreement with actual mill results (compare Tables VII & X). Over 86% of the Al, Mg, Mn, and Fe remained in the settled lime mud in all lab experiments. In contrast to the mill tests, Fe was almost completely removed with the lime mud. As with the mill results, the lab data showed that magnesium was almost completely removed (>99%) from white liquor. Only 19-28% of the SiO_2 remained with the lime mud in these lab tests, whereas the mill results were slightly higher (21-39%).

Table VIII.
Metals analysis for original green liquors in mg/L.

	Al	SiO_2	Mg	Mn	Fe	Zn	K	Ca
Mill J	12.4	402	0.02	ND	ND	ND	7820	2.72
Mill K	4.34	189	0.03	ND	ND	ND	5410	3.47
Mill L	6.02	185	ND	ND	ND	ND	10890	3.90

ND = non-detect

Table IX.
Metals analysis for original lime muds in mg/kg (dry basis).

	Al	SiO_2	Mg	Mn	Fe	Zn	K	Na
Mill J	319	899	2311	96.8	141	ND	51.6	5025
Mill K	114	1115	2808	334	186	ND	94.5	6111
Mill L	325	745	4198	289	426	ND	296	7322

ND = non-detect

Table X.
Metal analysis of the resulting white liquors and lime muds after causticizing and settling/clarification.

Run*		Al	SiO_2	Mg	Mn	Fe	K
	WL, mg/L	1.47	451	0.03	0.96	0.3	8400
Mill J/J	LM, mg/kg	398	1067	2278	86.7	123	128
	%**	96.4	19.0	100	89.9	97.6	0.15
	WL, mg/L	2.91	432	0.03	0.53	0.5	8640
Mill J/L	LM, mg/kg	417	1308	4151	283	410	97.3
	%**	93.6	23.7	100	98.2	98.8	0.12
	WL, mg/L	2.2	305	0.04	1.73	0.5	6130
Mill K/K	LM, mg/kg	124	834	2795	322	159	52.1
	%**	85.9	22.9	100	95.3	97.2	0.09
	WL, mg/L	2.07	227	0.03	0.61	0.3	12060
Mill L/J	LM, mg/kg	340	1047	2265	95.2	132	155
	%**	93.3	28.1	100	93.0	97.4	0.11
	WL, mg/L	0.5	265	0.04	0.46	ND	12240
Mill L/L	LM, mg/kg	350	1089	4231	295	421	178
	%**	98.4	26.5	100	98.2	100	0.13

** Mill L/J refers to Mill L's green liquor causticized with Mill J's lime.*
*** % partitioning with the mud.*

As depicted in Table XI, the settling rates of the lime muds were unaffected by the level of NPE (Table VIII & IX) studied in these experiments.

Table XI.
Effect of intermixing green liquor and calcined lime muds from three different mills on white liquor composition.

Run	Sample (Green or White Liquor)	Liquor Composition in grams/L as Na_2O			Causticizing Efficiency %	Sulphidity based on TTA, %	Settling Rate cm/min
		Na_2S	NaOH	Na_2CO_3			
Mill J/J	GL	27.9	13.4	78.4			
	WL	30.2	77.4	15.7	80.3	24.5	2.9
Mill J/L	GL	27.9	13.4	78.4			
	WL	32.6	77.1	18.5	77.5	25.4	2.9
Mill K/K	GL	28.3	12.5	75.4			
	WL	26.3	72.5	17.7	77.2	22.6	2.6
Mill L/J	GL	29.2	9.7	76.8			
	WL	36	67.1	8.2	87.5	32.3	4.0
Mill L/L	GL	29.2	9.7	76.8			
	WL	34.2	68.2	10.2	85.1	30.4	2.9

** Mill L/J refers to Mill L's green liquor causticized with Mill J's lime.*

CONCLUSIONS

- In a mill wide sampling program at four kraft mills, the enrichment factors in the precipitator dust were found to average 2.69, 1.68, and 2.44 for the elements chloride, potassium, and zinc, respectively. Precipitator catch should be considered as a bleed point for these three elements.
- Ca, Mg, Mn, Fe, and Zn were removed effectively from the chemical recovery system during green liquor clarification. Good green liquor clarification or filtration will be required for metals removal if a kraft mill is considering recycling of bleach plant effluents.
- Filtering clarified green liquor greatly increased the removal efficiency of calcium, magnesium, and manganese and slightly increased the removal of aluminum and silica.
- The build up of Ca, Al, Mg, Mn, Fe, and Zn can be controllable through the dregs output. Although the input levels to the chemical recovery system of the acid sulphite mill were up to 10 times those observed in kraft mills, the NPE concentrations in clarified green liquor were quite comparable to those observed in the four sampled kraft mills.
- Purging lime mud from recaust is a bleed point for Al, Mg, Mn, and Fe as 86% or more of these elements remained with the lime mud. Only small amounts of SiO_2 (21-39%) could be removed by sewering or landfilling lime muds.
- The settling rates of the lime muds were unaffected by the level of non-process elements studied.

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REFERENCES

1. Dorris, G.M., "The Role of Non-Process Elements in Recausticizing Cycle", Paprican Seminar, Pointe Claire, Spring, 1989.

2. Keitaanniemi, O. and Virkola, N.E., "Undesirable Elements in Causticizing Systems", Tappi J. 65(7), p.89-92, July 1982.

3. Magnusson, H., Mörk, K., and Warnqvist, B., "Non-Process Elements in the Kraft Recovery System", Proceedings of the 1979 TAPPI Pulping Conference, p.77-83, November 1979.

4. Blackwell, B., "Dead Load Reduction in the Kraft Pulping Process: Memorandum 1, Recausticizing", Unpublished Report by the Environmental Protection Service, Environment Canada, October 1984.

5. Bristow, O.J. and Kunz, C.C., "The Problems of Impurities Build-Up in Causticizing Systems at Low Lime Make-Up", Southern Pulp & Paper Manufacture, p.62-66, February 1961.

6. Ulmgren, P., "Consequences of Build-up of Non-process Chemical Elements in Closed Kraft Recovery Cycles - Aluminosilicate Scaling, A Chemical Model", Proceedings of the 1981 TAPPI International Chemical Recovery Conference, p.39-44, September 1981.

7. Crouse, N.E. and Stapley, C.E., "Dregs - Their Cause and Effect", Pulp & Paper Canada, 80:C, p.T93-8, March 1979.

8. Campbell, A.J., "Factors Affecting White Liquor Quality: Green Liquor Concentration, Dregs Concentration and Lime Dosage", Pulp & Paper Canada, 82:4, p.T121-6, 1981.

9. Adams, T.N., "Lime Reburning", TAPPI Kraft Recovery Operations Seminar Notes, p.73-86, 1988.

10. Frederick, W.J., "Managing Non-process Elements Flows in Pulp-Mill Chemical Cycles", The Impact of Energy and Environmental Concerns on Chemical Engineering in the Forest Products Industry, AIChE Symposium Series, p.21-9, 80(239), 1984.

11. Tower, M., Richardson, B., Uloth, V., Singbeil, D., Hogikyan, R., Turner, P., Forget, C., Lowenertz, P., Gleadow, P., Swaney, J., Wasik, L., Yu, J., Hastings, C., Constantin, E., Yuen, T., "Mill-Wide Sampling at Four Canadian Kraft Mills. Part 1: Process Stream Analysis", PPR13XX, 1997.

12. CPPA Standard Methods, Analysis of Lime by the Rapid Sugar Method, Method J5.

13. Nguyen, X.T. and Rowbottom, R.S., "An Investigation of Kraft Recovery Furnace Particulate Properties and Alternative Low Energy Collection Devices", CPAR project report 576-1, 1977, Environment Canada Library, Place Vincent Massey, 351 St. Joseph Blvd., Hull, K1A 0H3.

14. Vakkilainen, E.K., Frederick, W.J., Reis, V.V. and Wåg, K.J., "Potassium and Chloride Enrichment during Black Liquor Combustion. Laboratory and Mill Measurements and a Mechanistic Model", Proceedings of the 1995 International Chemical Recovery Conference, p.B63-75, April 1995.

15. Shenassa, R., Reeve, D.W., Dick, P.D. and Costa, M.L., "Chloride and Potassium Control in Closed Kraft Mill Liquor Cycles", Pulp & Paper Canada, 97:5, p.T173-9, 1996.

16. Sulfite Science and Technology, edited by Ingruber, O.V., Kocurek, M.J. and Wong, A., Published by the Technical Section of CPPA, p.284-6, 1985.

17. Cornell, C.F., "Current Recausticizing Practice - Parts I and II", TAPPI Kraft Recovery Operations Short Course, p.13-40, 1991.

18. Jordan, J.M. and Bryant, P.S., "Cluster Rule Impact on Recovery Boiler Operations: Chloride and Potassium Concentrations in the Kraft Liquor Cycle", Proceedings of the 1995 TAPPI Pulping Conference & Exhibits, p.613-21, October 1995.

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Table. A-1.
Comparison of dregs composition.

Sample		*Dregs analyses on wet basis*					*Dregs analyses on dry basis*				
Mill		*Mill A*	*Mill B*	*Mill C*	*Mill D*	*Mill H*	*Mill A*	*Mill B*	*Mill C*	*Mill D*	*Mill H*
Moisture	*%*	*41.2*	*45.1*	*74.4*	*80.9*	*69.5*					
Tot Solids	*%*	*48.8*	*54.9*	*25.6*	*19.2*	*30.5*					
Sus Solids	*%*			*7.15*	*3.75*						
C	*mg/kg*	*19490*	*9828*	*1480*	*10870*	*2116*	*33150*	*17900*	*5780*	*56760*	*6938*
Na	*mg/kg*	*49470*	*9276*	*63960*	*6170*	*93320*	*84140*	*16900*	*249800*	*32220*	*305970*
K	*mg/kg*	*3746*	*523*	*13250*	*3750*	*4160*	*6370*	*953*	*51760*	*19580*	*13640*
Ca	*mg/kg*	*158290*	*232200*	*11700*	*4550*	*12075*	*269200*	*422950*	*45700*	*23760*	*39590*
Al	*mg/kg*	*1730*	*2333*	*271*	*326*	*65*	*2942*	*4250*	*1060*	*1700*	*213*
Mg	*mg/kg*	*14950*	*30970*	*9430*	*1725*	*2835*	*25420*	*56410*	*36840*	*9010*	*9295*
Mn	*mg/kg*	*10180*	*8627*	*212*	*635*	*2545*	*17310*	*15720*	*828*	*3320*	*8344*
Fe	*mg/kg*	*5300*	*8627*	*803*	*584*	*166*	*9014*	*15710*	*3140*	*3050*	*544*
Zn	*mg/kg*	*1530*	*286*	*502*	*35*	*126*	*2600*	*521*	*1960*	*182*	*413*
Cr	*mg/kg*	*345*	*31.1*	*24.7*	*8.22*	*5.42*	*586*	*56.6*	*96.5*	*42.9*	*17.8*
Pb	*mg/kg*	*0.43*	*8.19*	*6.41*	*8.65*	*0.29*	*0.73*	*14.9*	*25*	*45.2*	*0.95*
Si	*mg/kg*	*679*	*1644*	*3770*	*623*	*68.9*	*1154*	*2995*	*14730*	*3256*	*226*

Table A-2.
Mill flow data at the time of sampling.

Stream	*Mill A*	*Mill B*	*Mill C*	*Mill D*	*Mill H**
Chips, t/d	*2499*	*2059*	*4415*	*4791*	*1140*
Moisture, %	*47*	*54*	*54.5*	*49.7*	*45.1*
Cooking Liquor, t/d	*3309*	*2551*	*3571*	*5599*	*2605*
Digester Yield, %	*45.8*	*39.2*	*50.6*	*43.1*	*45*
Liquor to Evaps, t/d	*7967*	*7024*	*7887*	*14277*	*1277*
Fired Liquor as BL S, t/d	*1680*	*1019*	*909*	*2212*	*620*
Raw Green Liquor, t/d	*3809*	*2957*	*5294*	*7076*	*398*
Bleached Pulp, ADBt/d	*750*	*400*	*1073*	*1096*	*542*

** Sulphite mill*