Detailed characterization of poor settling green liquor dregs

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ABSTRACT: At a northern bleached softwood kraft (NBSK) mill in western Canada, poor settling green liquor dregs caused high non-process element levels in lime mud and white liquor pressure filter plugging. Dregs samples were collected during poor settling and normal settling conditions. Samples were examined by qualitative analysis, elemental analysis, quantitative X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscope/energy dispersion X-ray (SEM/EDX) spectroscopy. Poor settling dregs were caused by an inorganic gelatinous material. The inorganic gel was determined to be an amorphous magnesium silicate compound of approximate composition $Mg_2(Si_{1-x}Al_x)O_4$, with a molar ratio of silicon to aluminum of approximately 5:1. The density of the inorganic gel was only slightly higher than the green liquor, causing it to settle very slowly. When calcite particles were trapped by the gel, the average density increased, which increased the settling rate. The inorganic gel was present during normal settling, but contained more aluminum (silicon to aluminum ratio of approximately 2:1). During normal settling, the gel was more dense and contained more trapped particles of calcite.

Application: This work shows how the chemical composition of dregs can result in poor settling at an NBSK mill, outlines options to improve settling, and helps process engineers to understand dregs behavior and improve the settling efficiency of green liquor clarifiers.

At a northern bleached softwood kraft (NBSK) mill in western Canada, high levels of suspended solids occurred in clarified green liquor on a regular basis (once or twice a week). This resulted in higher non-process element (NPE) levels in lime mud, and increased pressure drop across the white liquor pressure filter. The mill uses oxygen delignification with magnesium sulfate addition. Flocculating anionic polymer was used in the green liquor clarifier, but varying the type and concentration did not correct the settling problem. Lime mud addition to the dissolving tank was used to improve dregs settling.

Mills with oxygen delignification and high magnesium levels in black liquor often suffer from poor dregs settling properties and high clarifier rake torque [1,2]. An excess of magnesium ion has been reported to lead to the formation of brucite, $Mg(OH)_2$, and poor dregs settling [1]; however, there is little evidence to support this mechanism.

Ulmgren [3] investigated magnesium precipitation chemistry in green liquor. He proposed that magnesium ion coprecipitates with aluminum ion in green liquor to form hydrotalcite-like compounds, $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot nH_2O$, where the Mg:Al ratio can vary from 2:1 to 5:1 in different samples. Brucite and hydrotalcite have closely related crystal structures [4]. Brucite contains octahedral layers of $Mg(OH)_2$. In hydrotalcite, aluminum ions substitute for some of the magnesium ions in brucite. Hydrotalcite formation has been proposed as a mechanism for aluminum ion removal from green liquor [3].

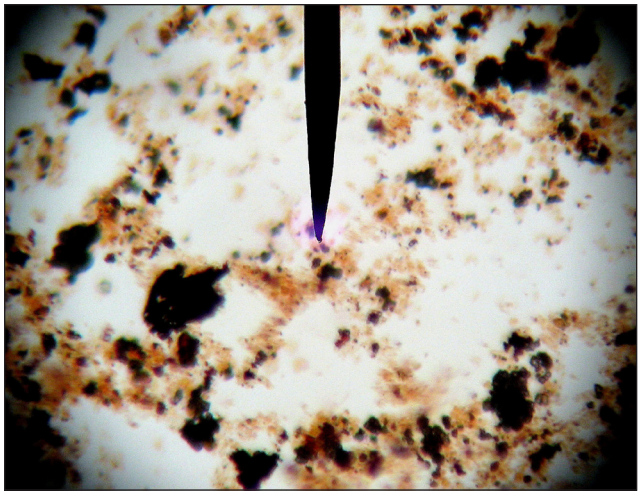
The literature contains very little detailed information on dregs composition. Published dregs data contain primarily the overall elemental composition (Richardson et al. [5]), not the distribution of compounds that are present. Some work has identified crystalline dregs components by XRD [6], but not amorphous components.

The goals of this project were to fully characterize and identify the suspended solids that occur in green liquor during periods of poor and normal settling. This allowed a good understanding of the factors leading to high suspended solids content in clarified green liquor at the mill.

MATERIALS AND METHODS

Step-scan, X-ray powder-diffraction (XRD) data using the quantitative Rietveld method were collected on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer at the University of British Columbia (UBC) Department of Earth and Ocean Sciences, Vancouver, BC, Canada, in the laboratory of Dr. Mati Raudsepp.

For scanning electron microscope/energy dispersion X-ray (SEM/EDX) spectroscopy analysis, the green liquor dregs sample was prepared by first washing the sample with deionized water to remove soluble sodium compounds. The sample was filtered and dried at 100°C to give a fine powder. The powder sample was prepared in epoxy, and the hardened mixture was polished in stages down to 6 µm diamond polish and mounted as a thick section slide by Vancouver Petrographics. This mounted sample was examined at UBC in variable-pressure mode in a Hitachi S-3000N SEM (Hitachi; Tokyo, Japan), producing back-scattered electron images. The EDX measurements were made with a light-element-capable Quartz X-One



1. Clarified green liquor dregs (P1), transmitted light, 100x magnification. Gel material dyed light brown, dark particles are opaque solids.

system (Quartz Imaging Corp., Vancouver) at the UBC Department of Earth and Ocean Sciences.

Metal concentrations (by inductively coupled argon plasma spectroscopy) and Fourier transform infrared (FTIR) spectroscopy measurements were carried out by Econotech Services Ltd., Delta, BC.

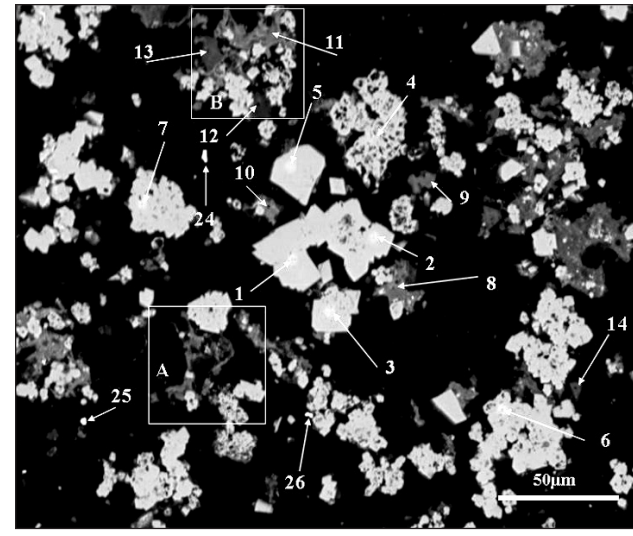
RESULTS

Preliminary characterization of samples

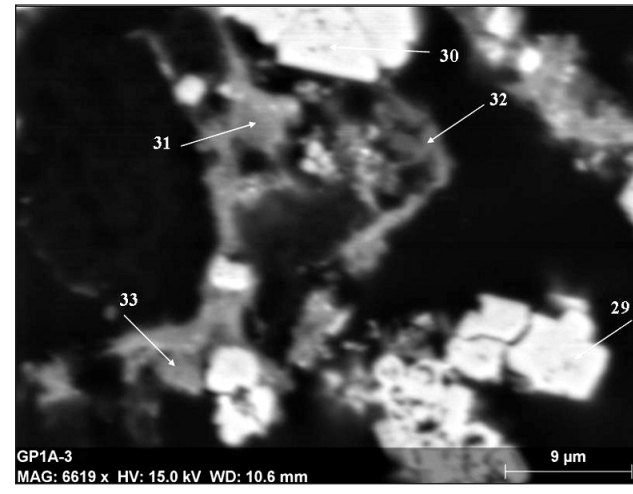
Sample P1 contained dregs material carried over in clarified green liquor during poor green liquor clarification. Sample P1 was collected on April 13, 2011, and contained small particles that were very slow to settle. A stereomicroscope was used at a magnification of 40x to examine sample P1. A clear, gel-like material was observed that contained crystalline particles. **Figure 1** shows the gelatinous material of sample P1, as viewed using transmitted light at 100x in a microscope. The gelatinous material appears light brown in the image from the use of a red dye (allura red AC) in the sample. The dark particles in Fig.1 are opaque to transmitted light and many of them are attached to the gelatinous material. The particles in sample P1 rapidly reacted with 1M hydrogen chloride (HCl) with effervescence, and are likely calcite; 1M HCl appeared to disperse or destroy the gel-like material in the sample.

A small amount of sample P1 was washed five times with deionized water to remove water-soluble sodium compounds. This treatment did not appear to affect the behavior of the gelatinous material in the sample. The washed sample was acidified with 1M HCl and tested positive for silicate using a silica test kit (Hach's, molybdate reagent and amine F).

Sample P2 contained dregs from the green liquor clarifier collected on April 13, 2011. Sample P2 was dispersed in water and found to settle more rapidly than sample P1. At 40x magnification, sample P2 still contained the gelatinous material but there were more crystalline solids attached to the gel. This likely increased the settling rate.



2. Backscattered electron scanning electron microscopy (SEM) image of sample P1a, clarified green liquor dregs. Energy dispersion X-ray (EDX) analyses of different particles are indicated. Closeup of box area A is shown in Fig. 3. Magnification approximately 350x.



3. P1a, clarified green liquor dregs. Backscattered electron SEM image of box area A in Fig. 2. Magnification approximately 1900x.

Sample N1 (dregs from green liquor clarifier, normal operation) was collected as a composite sample on September 21, 2011. Dregs particles slowly settled in this sample. At a magnification of 40x under a stereomicroscope, the sample contained some gel-like material with a large amount of crystalline particles. The gel-like material in sample N1 appeared more dense than in sample P1, and also contained more trapped particles. The gel-like material in sample N1 was dispersed by 1M HCl. A sample of N1 washed with water did not test positive for silicate using a silica test kit.

The clarified green liquor dregs (sample P1) were examined by FTIR. The FTIR spectrum is consistent with dregs containing some carbon. There was no indication of organic compounds. The primary purpose of the FTIR analysis was

to determine if any organic compounds were present that might contribute to slow dregs settling.

XRD analysis

Table I shows the XRD results for the dregs samples. All of the samples contained calcite as the major crystalline component. XRD does not detect amorphous material, however, and it was expected that the gelatinous material in the dregs would be amorphous on drying. During poor dregs settling, the clarified green liquor dregs (P1) and clarifier dregs (P2) were similar in composition. Dregs from the green liquor clarifier (P2) contained more calcite than the clarified green liquor dregs sample P1 (65 wt% versus 56 wt%). Both samples (P1 and P2) contained a similar amount of gaylussite, $Na_2Ca(CO_3)_2 \cdot 5H_2O$. Gaylussite is an insoluble sodium compound formed in the dissolving tank that is closely related to pirssonite, $Na_2Ca(CO_3)_2 \cdot 2H_2O$. Thermonatrite, $Na_2CO_3 \cdot (H_2O)$, is present from evaporation of trapped green liquor in the filtered dregs sample. Vermiculite was previously reported in green liquor clarifier samples by Taylor and McGuffie [7].

Clarifier dregs collected during normal operation (sample N1) contained calcite as the major component (Table I). Results are also shown for a sample of N1 (N1a) that was washed with water to remove soluble sodium compounds. When compared with samples P1 and P2, sample N1 contains similar amounts of calcite, gaylussite, brucite, and quartz. Less thermonatrite is present. A significant difference is the presence of 16 wt% manganotychite in sample N1. This compound likely formed during the drying of the sample at 100°C; it is not present in the water-washed N1a sample and has low solubility in water. In N1a, brucite and hydrotalcite-like material made up about 25 wt% of the sample. Thermonatrite, trona, and gaylussite were not present in N1a because of the water washing procedure. The high concentration of brucite in sample N1 contradicts the idea that brucite is responsible for poor dregs settling [1].

XRD analyses of lime mud and weak wash mud (April 13, 2011) were similar in composition, containing approximately 97 wt% calcite, 1.8 wt% brucite, and 0.4 wt% quartz (SiO_2).

Elemental analysis

Unclarified green liquor samples

Elemental analyses of unclarified green liquor samples were conducted during poor dregs settling (April 13, 2011). Results for selected NPEs were compared with average values from other mills [5]. The unclarified green liquor contained levels of aluminum, magnesium, and manganese that were similar to average values of other kraft mills within British Columbia's interior. Calcium and silicon concentrations were at the high end of the range; iron concentration was below the range of values reported by Richardson et al. [5]. The magnesium concentration was similar to levels in other mills, even though it is considered a problem NPE at the mill in this work. During poor settling, the magnesium to aluminum ratio was 6.2:1 on April 13 and 4.5:1 on April 20, 2011. On September 21, 2011, the ratio was 10.0:1, but dregs settling was normal.

Phase, wt%	Ideal Formula	P1 Clarified GL Dregs	P2 Dregs from GLC	N1 Dregs from GLC	N1a Dregs from GLC[a] (water-washed)
Calcite	$CaCO_3$	56.0	65.0	48.6	74.3
Gaylussite	$Na_2Ca(CO_3)_2 \cdot 5H_2O$	11.0	8.6	9.7	-
Thermonatrite	$Na_2CO_3 \cdot (H_2O)$	29.9	24.7	10.8	-
Trona	$Na_3(CO_3)(HCO_3) \cdot 2H_2O$	-	-	5.2	-
Brucite	$Mg(OH)_2$	0.8	0.9	2.7	13.3
Hydrotalcite-like[b]	$(Mg_{0.83}\ Al_{0.17})\ (OH)_2\ (CO_3)_{0.08}\ (H_2O)_{0.75}$	-	-	3.0	11.8
Manganotychite	$Na_6(Mn,Fe,Mg)_2(CO_3)_4(SO_4)$	-	-	16.4	-
Sjoegrenite	$Mg_6Fe_2^{3+}(CO_3)(OH)_{16} \cdot 4H_2O$	-	-	3.4	-
Vermiculite	$(Mg,Fe^{2+},Al)_3(Si,Al)_4O_{10}\ (OH)_2 \cdot 4H_2O$	1.2	0.5	-	-
Dolomite	$CaMg(CO_3)_2$	0.8?	-	-	-
Manganite	$Mn^{3+}O(OH)$	-	-	-	0.4?
Quartz	SiO_2	0.4	0.2	0.2	0.2

? Tentative.

[a] Water-soluble sodium compounds removed in sample preparation.

[b] Magnesium aluminum hydroxide carbonate hydrate. Diffraction pattern from Bellotto et al. [4].

I. Quantitative X-ray diffraction (XRD) analysis of poor and normal settling dregs (GL = green liquor; GLC = green liquor clarifier).

Element, mg/kg	P1 Clarified GL Dregs	P2 Dregs from GLC	N1 Dregs from GLC	N1a Dregs from GLC[a] (water-washed)
Aluminum, Al	2,550	2,210	6,160	9,360
Barium, Ba	171	167	389	682
Boron, B	62	42	30	19
Cadmium, Cd	15.9	13.6	42	64
Calcium, Ca	188,000	214,000	140,000	198,000
Chromium, Cr	85	73	71	106
Copper, Cu	110	95	231	352
Iron, Fe	1,620	1,240	3,460	4,800
Magnesium, Mg	29,200	26,300	71,500	110,000
Manganese, Mn	7,550	6,540	17,700	27,100
Nickel, Ni	17	12	37	52
Phosphorus, P	303	408	460	890
Potassium, K	13,100	9,710	12,700	390
Silicon, Si	11,800	10,200	16,000	20,100
Sodium, Na	121,000	114,000	107,000	4,310
Strontium, Sr	136	148	168	234
Sulfur, S	45,400	37,600	45,900	14,400
Titanium, Ti	40.3	39.7	83	125
Zinc, Zn	1,100	972	2,550	3,880

[a] Water-soluble sodium compounds removed in sample preparation.

II. Elemental analysis of dregs samples (GL = green liquor; GLC = green liquor clarifier).

Clarified green liquor dregs and dregs from the green liquor clarifier

Table II shows the elemental analyses of the clarified green liquor dregs (P1) and green liquor clarifier dregs (P2) during poor settling. Values for P1 and P2 were very similar. Calcium concentration in P2 was somewhat higher than in P1, suggesting that the settled dregs particles contained more calcite from lime mud.

Table II also shows the elemental analysis of clarifier dregs during normal settling (N1). The increase in magnesium and aluminum concentration in green liquor dregs sample N1 during normal settling is very significant. In contrast with previously reported results [1,2], good settling of the dregs occurs with high levels of magnesium. The aluminum concentration was approximately 2.5 times higher in green liquor dregs sample N1 than in clarified green liquor dregs sample P1. The weight ratio of silicon to aluminum was 4.6:1 for sample P1 and 2.6:1 for sample N1. At other kraft mills, the silicon to aluminum weight ratio in dregs is typically 2:1 to 1:1 [7]. This supports the idea that low aluminum levels contributed to the formation of gel-like, poor settling dregs at the mill in April 2011.

The sodium concentration of sample N1a was much lower because of the water wash during sample preparation. Comparing the concentrations of calcium and magnesium between samples N1 and N1a, approximately 30 wt% of sample N1 was made up of soluble sodium compounds (as carbonates, sulfates, and chlorides). This is consistent with the XRD results (Table I). These results support the idea that a component of the dregs of the mill in this work is gelatinous in nature, retaining a large amount of green liquor after filtration.

Comparing calcium concentrations in the XRD and elemental analysis results, it was estimated that 22% of sample P1 and 32 wt% of sample N1 was amorphous (noncrystalline) or water. All of the calcium was present as either calcite or gaylussite, $Na_2Ca(CO_3)_2 \cdot 5H_2O$.

Clarified green liquor

Elemental analysis of clarified green liquor was carried out during normal dregs settling, and the results were compared with reported values for other mills [5]. NPE values were comparable to other mills for calcium, magnesium, silicon, manganese, chromium, and zinc.

Concentrations of aluminum and iron in clarified green liquor were significantly lower than reported values at other mills. Low iron concentration suggests efficient green liquor clarification, because most of the iron is present in dregs particles [7]. The low aluminum concentration can contribute to the formation of poor settling dregs. Many mills with normal recausticizing operations have aluminum levels of 10-25 mg/L in clarified green liquor, compared with only 2 mg/L at the mill in this work.

Lime mud

NPE concentrations in lime mud during poor dregs settling were compared with average values of three interior British Columbia kraft mills. The lime mud showed significantly higher values of magnesium and manganese than other mills. Magnesium concentration was more than double the three mill average, while manganese concentration was more than four times higher. Higher magnesium and manganese concentrations are likely the result of carryover of dregs.

SEM-EDX analysis

Poor settling dregs

Sample P1 was washed to remove water-soluble sodium compounds (such as Na_2S and Na_2CO_3), as described in the experimental section. The procedure did not appear to change the observed properties of the suspended dregs particles when examined at 40x magnification. After drying, the sample was labeled P1a and was a fine powder. **Figure 2** shows the SEM image of the P1a particles at approximately 350x magnification, after setting the powder in epoxy and polishing the surface. Black areas in Fig. 2 are the epoxy mounting material; bright particles have the composition of lime mud by EDX (**Table III**). Seven different EDX spot measurements were made (spots 1-7), all with similar composition. All of the lime mud particles were calcium carbonate with traces of phosphorous, magnesium, and sodium, similar to bulk lime mud analysis.

The light grey areas of Fig. 2 appear to be the dried residue of the gelatinous dregs particles. Higher magnification SEM images support this assumption. These gray areas contain numerous particles of trapped calcite. The EDX analysis of spot 11 is shown in **Table IV** and is very similar for spots 8-10. Magnesium, silicon, and oxygen are major components. Some aluminum and manganese are present. Spots 12-14 were very similar to the composition shown in Table IV, but with 50% to 100% more aluminum present. Carbon in the epoxy mounting material can increase the EDX measured carbon concentration of small particles. The epoxy also contains oxygen and traces of chlorine. The sodium shown by EDX is likely from residual green liquor that was not washed from the sample. The sulfur may be present as iron sulfide or manganese sulfide.

Element	Weight%	Atom%
Oxygen	45.3	59.8
Calcium	45.2	23.8
Carbon	9.2	16.1
Sodium	0.2	0.2
Magnesium	0.1	0.1
Phosphorus	trace	trace
Silicon	trace	trace

III. Energy dispersion X-ray (EDX) analysis of spot 3 in Fig. 2, lime mud (results are typical for particles at spots 1-7 in Fig. 2).

Element	Weight%	Atom%
Oxygen	49.8	55.5
Carbon	15.4	22.9
Magnesium	17.3	12.7
Silicon	7.4	4.7
Manganese	4.0	1.2
Sulfur	1.8	0.9
Aluminium	1.4	0.9
Sodium	0.6	0.5
Iron	1.3	0.4
Calcium	0.5	0.2

IV. EDX analysis of spot 11 in Fig. 2 (results are typical for particles at spots 8-10 in Fig. 2).

Element	Weight%	Atom%
Oxygen	41.4	48.5
Carbon	15.1	23.7
Magnesium	21.0	16.1
Silicon	8.6	5.7
Manganese	6.5	2.2
Calcium	3.8	1.7
Aluminium	1.6	1.1
Sulfur	1.6	0.9
Sodium	0.5	0.4

V. EDX analysis of spot 31 in Fig. 3 (results for spot 33 are very similar).

Three small, bright spots in Fig. 2 (24-26) were identified as copper compounds by EDX. These are a trace component.

Box area A of Fig. 2 is expanded in **Fig. 3** to a magnification of approximately 1900x. EDX analyses of the bright spots 29 and 30 were very similar to Table III, lime mud. The EDX analysis of spot 31 is shown in **Table V** (spot 33 is very similar) with a silicon to aluminum molar ratio of 5.2:1. The EDX analysis of spot 32 showed a molar ratio of Si to Al of 1.9:1. Gray areas in Fig. 3 are consistent with dried residue of the gelatinous dregs particles.

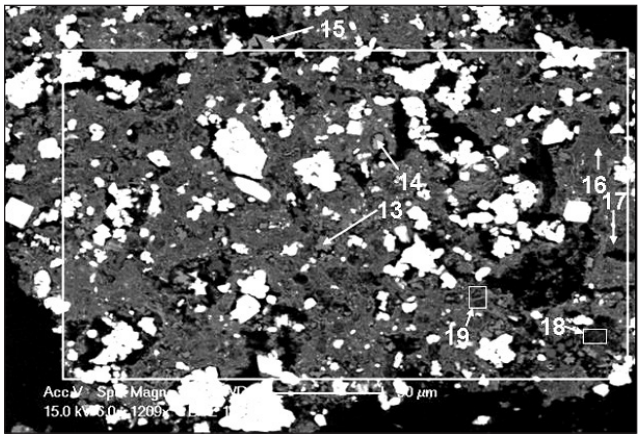
Box area B of Fig. 2 was examined at a magnification of 1900x. Bright areas are lime mud particles. EDX analyses were very similar to values at lower magnification.

In general, the inorganic gel appeared to be a magnesium silicate compound. The approximate composition was $Mg_2(Si_{0.83}Al_{0.17})O_4$ for most of the silicate material present in poor settling dregs. The average silicon to aluminum molar ratio was approximately 5:1.

SEM/EDX measurements in a different area of sample P1a showed lime mud particles, as well as particles of composition

Element	Weight%	Atom%
Oxygen	48.4	46.7
Carbon	33.6	43.1
Magnesium	10.6	6.7
Aluminium	3.6	2.1
Silicon	0.8	0.5
Iron	1.0	0.2
Manganese	0.5	0.1
Calcium	0.4	0.1
Sulfur	0.3	0.1

VI. EDX analysis of spot 17 (high Al).



4. Backscattered electron SEM image of sample N1a, green liquor dregs. EDX analyses of different particles are indicated. Magnification approximately 350x.

similar to those in Tables IV and V. An additional particle with high aluminum concentration was observed (**Table VI**). There is much more aluminum than silicon in this particle, with a molar ratio of silicon to aluminum of 0.24:1. The molar ratios of magnesium, silicon, and aluminum are approximately $Mg_2(Si_{0.3},Al_{0.7})O_4$ in this particle. This shows the range of composition of the magnesium silicate gel, which is expected for this type of material.

Normal settling dregs

Green liquor clarifier dregs collected during normal settling were examined by SEM/EDX as water-washed sample N1a. **Figure 4** shows a representative area of sample N1a. This area of the sample contains a large number of bright particles identified as calcite, with a size distribution similar to lime mud. Bulk EDX of the entire area of box F is shown in **Table VII**. The bulk composition shown in Table VII was comparable to a bulk EDX measurement made at a magnification of 55x for magnesium, aluminum, silicon, calcium, sulfur, and manganese. This indicates that the material in Fig. 4 is representative of the bulk sample. It is also important to compare the EDX spectrum with the elemental analysis of N1 in Table II. Within experimental error, the silicon to aluminum ratio, the magnesium to silicon ratio, and the magnesium to

Element	Weight%	Atom%
Carbon	26.8	38.0
Oxygen	44.7	47.6
Sodium	0.2	0.1
Magnesium	8.9	6.2
Aluminium	0.7	0.5
Silicon	1.4	0.9
Sulfur	1.0	0.5
Calcium	10.8	4.6
Manganese	3.1	1.0
Zinc	2.0	0.5

VII. Bulk EDX analysis of box F in Fig. 4.

Element	Weight%	Atom%
Carbon	21.3	28.8
Oxygen	59.1	60.0
Sodium	0.0	0.0
Magnesium	9.5	6.3
Aluminium	0.7	0.4
Silicon	5.2	3.0
Sulfur	0.6	0.3
Calcium	0.2	0.1
Manganese	2.0	0.6
Iron	1.0	0.3

VIII. EDX analysis of spot 13 in Fig. 4 (results for spot 14 are very similar).

aluminum ratio are all comparable between the EDX measurements in Table VII and the bulk elemental analysis. The silicon to aluminum molar ratio of sample N1a is 1.8:1 by EDX (Table VII) and 2.1:1 by elemental analysis of sample N1 (Table II).

In general, EDX measurements of sample N1a suggest an approximate gel composition of $Mg_2(Si_{0.65}Al_{0.35})O_4$, with additional $Mg(OH)_2$ present.

The EDX analysis of spot 13 in Fig. 4 is shown in **Table VIII** and is similar to spot 14. These two spots have a molar ratio of silicon to aluminum of 7.5:1. Spot 15 was identified as brucite by EDX. The EDX spectrum of spot 16 is shown in **Table IX** and is similar to box 19. The silicon to aluminum molar ratio in spot 16 and box 19 is 1.25:1.

The EDX analysis of spot 17 in Fig. 4 is shown in **Table X** and contains more aluminum than most other areas examined. The silicon to aluminum molar ratio of spot 17 is 0.6:1. However, the amount of magnesium is very high. Box area 18 also contains more aluminum than silicon, with a molar ratio of silicon to aluminum of 0.9:1.

By EDX, hydrotalcite-like material identified in Table I is expected to show a molar ratio of magnesium to aluminum

Element	Weight%	Atom%
Carbon	28.6	38.1
Oxygen	51.7	51.6
Sodium	0.0	0.0
Magnesium	10.5	6.9
Aluminium	0.6	0.4
Silicon	0.8	0.5
Sulfur	1.2	0.6
Calcium	0.3	0.1
Manganese	4.1	1.2
Zinc	1.9	0.5

IX. EDX analysis of spot 16 in Fig. 4 (results for box area 19 are very similar).

Element	Weight%	Atom%
Carbon	24.7	32.8
Oxygen	56.5	56.4
Magnesium	10.7	7.0
Aluminium	2.0	1.2
Silicon	1.2	0.7
Sulfur	1.5	0.8
Calcium	0.4	0.2
Manganese	2.9	0.8

X. EDX analysis of spot 17 in Fig. 4.

of approximately 4.9:1, with no silicon present. The closest match was a particle with a molar ratio of magnesium to aluminum of 6.0:1 and very little silicon. In this particle, the molar ratio of silicon to aluminum was 0.1:1.

DISCUSSION

Calcite was the major solid component of poor settling (P1) and normal settling (N1) green liquor dregs sampled at the mill in this study. Both types of dregs contained a gel-like inorganic compound that was a major component of the liquid samples.

Poor settling clarified green liquor dregs particles (sample P1, April 13, 2011) contained a soft, gel-like inorganic compound with the approximate composition $Mg_2(Si_{1-x}Al_x)O_4$. On drying, the gel-like material was amorphous and not detected by XRD. In the green liquor, this material contained a significant amount of liquid phase and the density was only slightly higher than the green liquor itself. The majority of the gel particles identified by SEM/EDX measurements in a dried sample contained much more silicon than aluminum, with an approximate composition of $Mg_2(Si_{0.83},Al_{0.17})O_4$. The typical silicon to aluminum molar ratio in the gel-like material of P1 was 5:1. A minor amount of similar material with much more aluminum was present with an approximate composition of $Mg_2(Si_{0.3},Al_{0.7})O_4$.

During normal dregs settling (sample N1, September 21, 2011), dregs particles were gel-like but appeared more dense than in sample P1 and contained more calcite particles. By SEM/EDX, significantly more magnesium and aluminum were present in the gel-like material of sample N1 than in P1. The approximate composition of the gel-like material in sample N1 was $Mg_2(Si_{0.65}Al_{0.35})O_4$, with additional $Mg(OH)_2$ present. In this case, the $Mg(OH)_2$ might be present as a separate phase (brucite). The typical silicon to aluminum molar ratio in the gel-like material of sample N1 was 2:1.

The gel-like magnesium silicate compound likely formed in the dissolving tank. This type of gel is easily formed by mixing sodium silicate solution with dissolved magnesium ions. Gels can be formed at sodium silicate concentrations as low as approximately 1000 mg/L [8]. Calcium ions will form a similar gel, but all of the calcium in the dregs preferentially forms calcite as $CaCO_3$ or gaylussite. This type of silicate gel has been extensively studied in other industries to prevent the flow of fluid in dirt and rock formations [9].

It is proposed that when $Mg_2(Si_{1-x}Al_x)O_4$ forms in the dissolving tank, the relative amounts of silicon and aluminum will determine the properties of the dregs. With a high ratio of silicon to aluminum (5:1), soft, gel-like dregs particles are able to form. With a lower ratio of silicon to aluminum (2:1), gel-like particles will be more rigid and dense. High magnesium concentrations appear to promote the formation of brucite and hydrotalcite-like particles that may be incorporated into the gel-like dregs particles. Metal ions such as iron and manganese are also incorporated into the gel-like magnesium silicate compound.

Smelt normally contains silicon as silicates or SiO_2. The normal source of silicon in black liquor is the wood itself. An additional source of sodium silicate in the smelt could be from silica (sand) in the black liquor. This could originate from sand in the wood chips or from precipitation/scaling of dissolved silica. A second possible silicate source is silicone defoamer. The silicone defoamer decomposes to silicate compounds in the recovery boiler. Spikes in usage of silicone defoamer could lead to spikes in gel formation in the dissolving tank. Calculations suggest that the amount of silicon from silicone defoamer could be significant during upset conditions with high defoamer addition.

Mills with oxygen delignification and high magnesium levels in the black liquor often suffer from poor dregs settling properties and high clarifier rake torque [1,2]. Dregs settling problems were reported to occur at magnesium to aluminum weight ratios greater than 3:1 in unclarified green liquor. At the mill in this study, the magnesium to aluminum ratio was 6.2:1 on April 13 and 4.5:1 on April 20, 2011. On September 21, 2011, the ratio was 10.0:1, but dregs settling was normal. This suggests that more factors than just the magnesium to aluminum ratio are involved. (Note, however, that Lidén [1] and Löwnertz [2] did not report silicon concentrations in their studies.)

To reduce dregs settling and filterability problems at a mill in Sweden, aluminum sulfate was added to the weak wash in the dissolving tank [2]. Addition of aluminum ion to the dissolving tank of the mill in this work is expected to reduce the formation of poor settling dregs.

CONCLUSIONS

Dregs samples collected during poor settling and normal settling conditions both contained a gel-like inorganic material in addition to calcite particles. The gel-like material was transparent and soft under the microscope (40x magnification). The density of the material was similar to that of green liquor because water was a major component. Trapping of calcite particles caused the gel to slowly settle by increasing the average particle density.

The gel-like material in sample N1 (normal operation) appeared more dense and contained more trapped lime mud particles than sample P1 (poor settling). As a result, N1 dregs settled more rapidly.

The inorganic gel was identified by SEM/EDX as an amorphous magnesium silicate compound. The approximate composition was $Mg_2(Si_{0.83}Al_{0.17})O_4$ in the poor settling dregs (P1). In sample N1 (normal operation), the approximate composition was $Mg_2(Si_{0.65}Al_{0.35})O_4$.

More aluminum was present in sample N1 (normal settling). The molar ratio of silicon to aluminum was 5:1 in poor settling sample P1, compared to 2:1 in sample N1 (normal operation).

In sample N1 (normal operation), the magnesium silicate gel likely becomes more rigid and dense because of higher aluminum concentration. This allows it to trap more calcite particles to increase its average density and settle more rapidly.

Much more magnesium was present in dregs sample N1 (normal settling) as brucite, $Mg(OH)_2$, and the hydrotalcite-like compound $(Mg_{0.83}Al_{0.17})(OH)_2(CO_3)_{0.08}(H_2O)_{0.75}$.

Most of the manganese and iron in the suspended dregs was present in the inorganic gel.

The major solid component of the dregs was calcite particles, most likely from lime mud. Calcite particles made up approximately 50-55 wt% of the dried dregs samples.

Green liquor at the western Canadian NBSK mill (clarified and unclarified) was deficient in aluminum ion relative to other mills and this contributed to the formation of poor settling dregs. **TJ**

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ABOUT THE AUTHOR

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We chose to study this topic because poor dregs settling at the mill did not respond to polymer addition and was not caused by mechanical issues. A detailed description of dregs composition was not available in the literature.

Previous studies of dregs composition in the literature examined elemental composition only, or composition of crystalline components by X-ray diffraction. This work complements previous studies by providing additional composition information on crystalline and amorphous components of green liquor dregs during different settling conditions.

Sample preparation was difficult because of the complex nature of green liquor dregs. A new procedure was used to make the dregs suitable for analysis by SEM/EDX.

It was very surprising to find that a gel-like material was present in the dregs during poor settling and normal settling conditions. This explains some unusual dregs behavior, including very slow settling, high water content of dregs, and slow filtration properties.

The work might help mills to understand dregs behavior and improve settling efficiency in green liquor clarifiers. The next step will be a mill trial of aluminum sulfate addition to the dissolving tank.

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