DETAILED CHEMICAL ANALYSIS OF DIRT SPECKS IN CELGAR OFF-GRADE PULP

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ABSTRACT

Off-grade in Celgar NBSK pulp has been an intermittent problem since 1998. In order to fully understand the cause of the problem, more than 170 dirt specks in Celgar off-grade pulp were collected over a 4 month period starting in 2005. Each individual sample was characterized using preliminary chemical testing. More detailed analytical methods were used on selected samples. This work was able to positively identify slime/biofilm as the cause of off-grade in more than 70% of the samples examined. Prior to this work, it was not possible to clearly distinguish between slime and pitch during pulp grading at the mill, and off-grade from slime/biofilm was frequently classified as pitch.

A simple routine test was implemented to allow graders to clearly distinguish between pitch and slime.

Nitrogen isotope analysis was used to show the source of slime/biofilm in individual dirt specks. This is the first time that this has been reported in the pulp and paper industry.

Additional analytical methods used include SEM/EDS, FTIR-microscope and glycoside composition analysis.

INTRODUCTION

Zellstoff Celgar is a modern pulp mill producing approximately 460,000 admt/year of northern bleached softwood Kraft (NBSK) pulp. The mill is located in the West Kootenay region of British Columbia, and as such utilizes a wide variety of softwood species to make up its furnish basket. To compete in the market, a final pulp with a high level of brightness and cleanliness is essential.

When the mill was modernized in 1993, production increased from roughly 650 admt/day to its current level of 1400 admt/day and a significant improvement in the closure of the mill water system was implemented. Over the course of several years it became apparent that this closure was leading to increased levels of biological growth in the pulp machine area and an increase in off-grade in the final pulp. This type of problem is commonly seen in paper machine environments, but rarely in pulp mills. It was believed that this growth would slough off at times and contribute to off-grade problems in the final pulp. Since the biological growth on the pulp machine was usually a combination of pitch, talc and slime, it was difficult to know which component should be the focus of control efforts. Significant process modifications were made to reduce visible growth of biological deposits, but off-grade continued to be an intermittent problem.

The main purpose of this work was to provide an accurate representation of the types of dirt present in off-grade pulp at Zellstoff Celgar. To do this, it was necessary to collect and characterize a large number of dirt specks over a significant time interval and to collect multiple samples of each type of dirt that occurred. More than 170 samples were collected and individually examined over a four month period of time.

The initial screening procedures used only a small part of each sample to provide a significant number of very similar samples for more detailed testing. Detailed characterization generally required destructive testing and was carried out on the major dirt types identified in the initial screening.

The following analytical methods were used on individual dirt specks:

- Chemical spot tests using a microscope for preliminary identification.
- Scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDS).
- Fourier transform infrared spectroscopy (FTIR)-microscope.
- Glycoside composition analysis (sugar composition of polysaccharides).
- Natural isotope analysis ($\delta^{15}N$) by elemental analysis-isotope ratio mass spectrometry (EA-IRMS).
- Carbohydrate content, soluble and insoluble.

METHODS AND MATERIALS

Pulp samples containing dirt specks were collected by mill personnel in the grading shack. A total of 171 samples were collected from September 27, 2005 to February 4, 2006. Each sample was stamped with the time and date of collection and given an identification number. The length and width of the spot, the pulp machine (#1 or #2) and a preliminary microscope image were also recorded for each sample. All information, including links to images, was put in a spreadsheet to make the data easily accessible.

Preliminary characterization of pulp deposits was done using a stereo microscope, at 20X or 40X magnification, capable of using incident or backlight illumination. Chemical tests for dirt spot characterization were based on the methods of Isenberg [1] and Sitholé [2].

For SEM/EDS measurements, samples were coated with evaporated carbon and examined on a Philips XL30 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.

FTIR-microscope measurements were made at Econotech Services Ltd., Vancouver, BC. The FTIR spectra were collected in the mid-infrared region by using a Bomen MB-122 series spectrometer equipped with a Spectra-Tech IR Plan Analytical Microscope. The microscope was equipped with transmission and reflectance modes and also a liquid nitrogen cooled mercury-cadmium-telluride detector.

Samples were submitted to the University of Victoria for nitrogen isotope analysis by EA-IRMS. Results were obtained with a Fisons NA1500 elemental analyzer (EA) connected to a Thermo Delta Plus XL isotope ratio mass spectrometer (IRMS) with a ConFlo II interface.

Glycoside composition analysis was performed at the Complex Carbohydrate Research Center at the University of Georgia. This is the only facility in North America that can routinely perform these measurements on samples as small as 0.4 mg. This made it possible to examine the material present in individual dirt specks. Glycosyl composition analysis was

performed by combined gas chromatography/mass spectrometry (GC/MS) of the per-O-trimethylsilyl (TMS) derivatives of the monosaccharide methyl glycosides produced from the sample by acidic methanolysis.

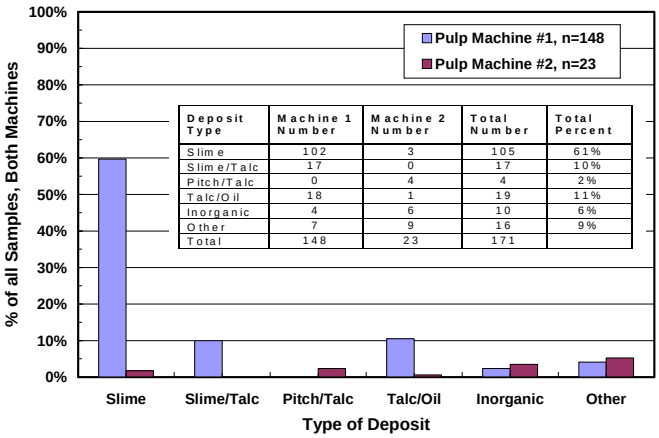
The assay for total carbohydrates was performed using a modified version of the phenol-sulphuric acid test [3]. Measurements were made in the lab of Dr. Alex Speers, Food Science Program, Department of Process Engineering and Applied Science, Faculty of Engineering, Dalhousie University, Halifax, NS.

RESULTS AND DISCUSSION

1. Preliminary Characterization

Preliminary characterization of the 171 samples collected from September 27, 2005 to February 4, 2006 is summarized in **Figure 1**. These results are based on chemical spot tests carried out using a stereo microscope. A useful modification to standard chemical spot tests was made in this work.

In **Figure 1**, the major component of the collected dirt specks (71%) contained slime (biofilm). These specks were typically very thin, brittle and appeared pale yellow to dark brown by microscope. When contacted with 5 wt% sodium hypochlorite solution and observed under the microscope, dirt specks containing slime rapidly swelled, their colour faded, and gas evolution occurred. The dirt speck was dispersed, sometimes leaving a residue of talc particles. This type of dirt speck was not affected by dichloromethane or 1M HCl solution. The ninhydrin spot test [1] was inconsistent for these samples. In contrast, pitch deposits were easily identified in spot tests as they were soluble in dichloromethane.



Deposit Type	Machine 1 Number	Machine 2 Number	Total Number	Total Percent
Slime	102	3	105	61%
Slime/Talc	17	0	17	10%
Pitch/Talc	0	4	4	2%
Talc/Oil	18	1	19	11%
Inorganic	4	6	10	6%
Other	7	9	16	9%
Total	148	23	171	

Figure 1. Preliminary Characterization of Dirt Specks.

The fading of colour on contact of slime with hypochlorite solutions is well known [1]. Concurrent gas evolution is not well known. It is likely that the gas bubbles are carbon dioxide from random cleavage of the polysaccharide chains present in the biofilm [4,5]. The combination of rapid colour fading and gas evolution results in an excellent spot test for slime/biofilm.

The high proportion of off-grade due to slime at Celgar was not expected. Previous work at the Celgar mill by industry experts had identified pitch as the major cause of off-grade. As a result, detailed analyses of the dirt specks classified as slime and slime/talc were carried out.

Dirt specks classified as talc/oil were primarily talc loosely held together by a material that was not identified by preliminary screening tests.

Inorganic dirt specks consisted of carbon or iron scale particles.

Dirt specks classified as "other" were either resin shives (9 of 16) or could not be determined.

2. SEM/EDS Results

Figure 2 shows an SEM image of a slime/talc deposit in sample 1. The image shows a cross-section cut through the pulp sheet. The deposit was 2 x 1 mm with a thickness of 0.07 mm. Talc particles were positively identified using EDS.

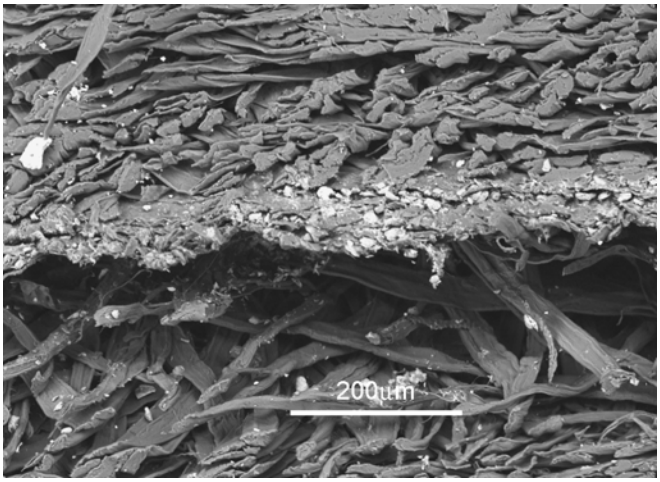


Figure 2. Back-Scattered Electron Image Showing Talc Particles (White) in Sample 1.

SEM images of a slime deposit (sample 4) were obtained over a range of magnifications. In **Figure 3**, sample 4 can be seen on a small slice of pulp fibres cut from the pulp sheet. The biofilm material is the smooth surface on the top of the pulp fibres.

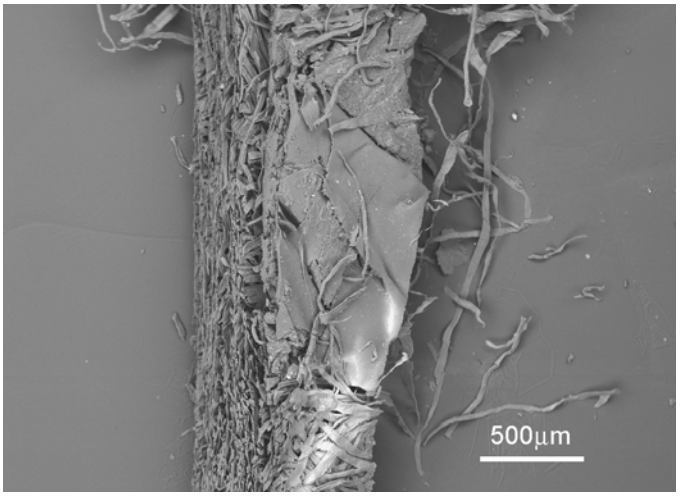


Figure 3. Back-Scattered Electron Image of Sample 4.

Figure 4 shows a magnified view of a cracked edge of the biofilm material from **Figure 3**. The box labelled 1 is shown at much higher magnification in **Figure 5**. A layered structure can be seen in **Figure 5**. There is no evidence of cellular material in these images. SEM/EDS could only show that this material was organic in origin.

These SEM images are consistent with biofilm material. It is likely that the layered material consists primarily of exopolysaccharides produced by biofilm.

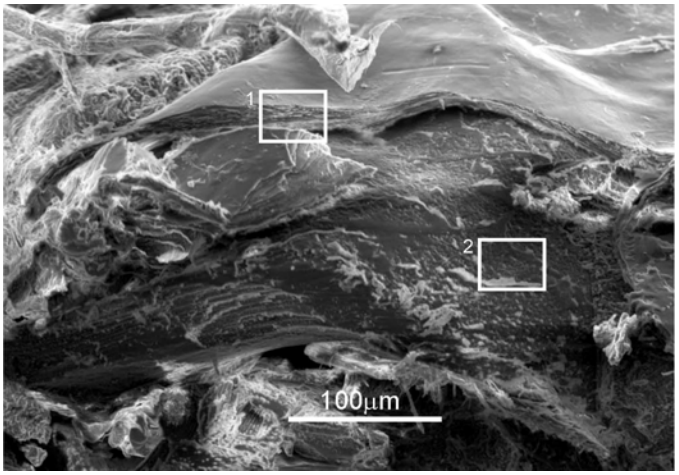


Figure 4. Secondary Electron Image of a Broken Edge in Sample 4.

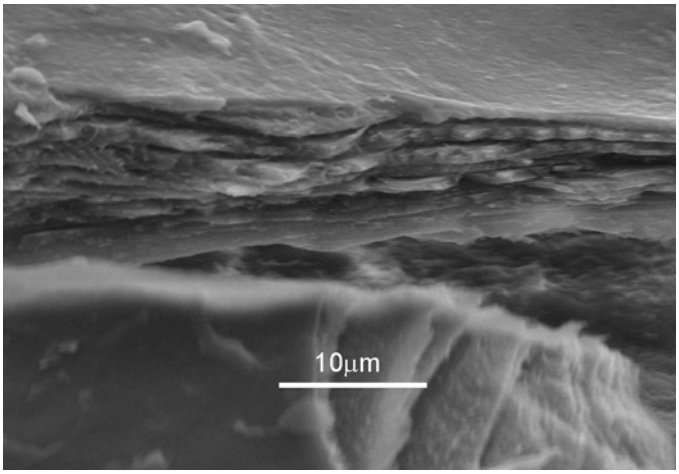


Figure 5. Secondary Electron Image of the Region Labelled 1 in Sample 4 (Figure 4).

3. FTIR-Microscope Results

Sample 89 was obtained in an off-grade pulp sample collected October 25, 2005, from pulp machine #1. This biofilm sample did not contain talc and was inside the pulp sheet, not on the surface. The deposit was carefully isolated from the pulp fibres to obtain a thin (less than 0.1 mm) sample that weighed 0.3 mg. This sample was examined by FTIR-microscope and compared with adjacent pulp in **Figure 6**.

Many features of the two spectra are similar, with two very important differences. In **Figure 6**, two strong peaks are present at 1652 and 1539 cm^{-1} in the deposit. The peak at 1652 cm^{-1} is associated with carboxylic acid groups. The peak is very strong in the deposit and weak in the pulp fibre FTIR. The peak at 1539 cm^{-1} is very strong in the deposit and absent in the pulp fibre. This peak is assigned to amide groups present in biofilms as will be described below.

FTIR spectra of biofilms have been reported by Ivnitsky et al. [6] and by Acuña et al. [7]. **Figure 7** shows the increase in FTIR absorbance over time for a growing biofilm on a stainless steel surface [7]. The y-axis is given in absorbance values, and the x-axis covers the region 900 to 1900 cm^{-1}. As the biofilm grew over 20 days, FTIR absorbance increased at 1650, 1550, 1450 and 1085 cm^{-1}.

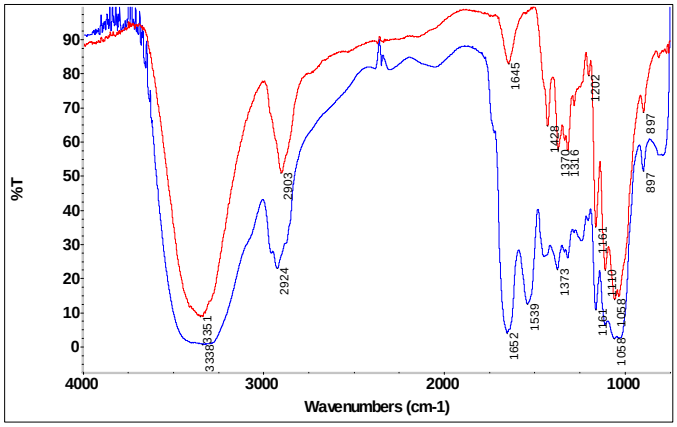


Figure 6. FTIR of Clean Pulp Fibres (upper) and Sample 89 Deposit (lower).

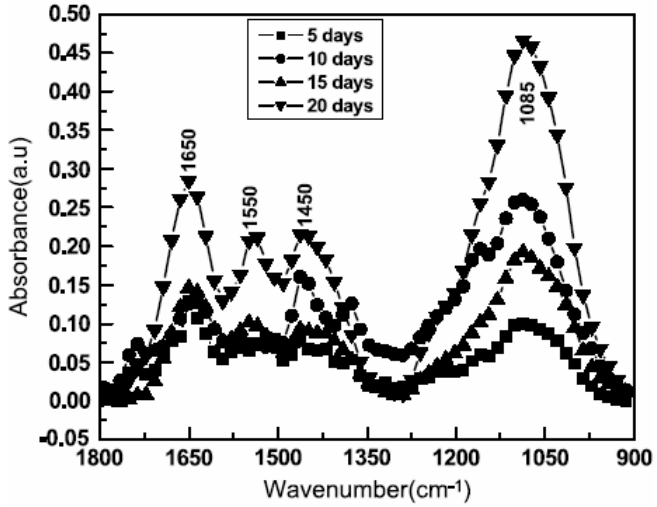


Figure 7. FTIR of Biofilm Growing on Stainless Steel [7].

In **Figure 8**, the FTIR spectrum of sample 89 is displayed in absorbance values over the same wavenumber range as shown in **Figure 7**. The 1652 and 1539 cm^{-1} peaks are very prominent in both **Figures 7** and 8. Biofilm peaks in the region of 1085 cm^{-1} may be obscured in sample 89 as a result of cellulose fibers that absorb light in that region (**Figure 6**).

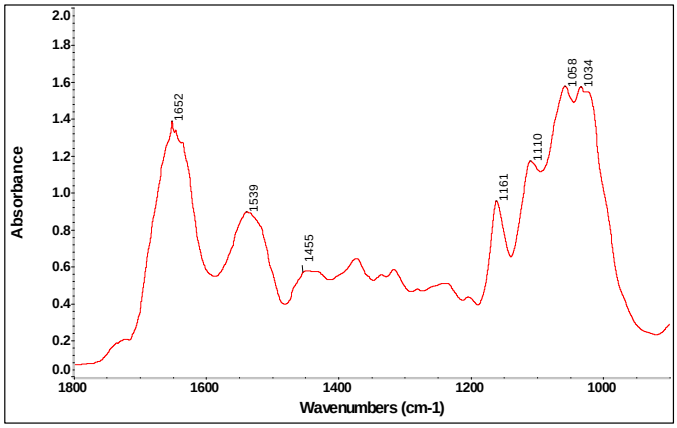


Figure 8. FTIR of Sample 89 Deposit, 900 to 1800 cm-1.

Ivnitsky et al. [6] confirmed the identification of the FTIR peaks at 1652 and 1539 cm^{-1} in biofilm samples, and provided assignments of all other major peaks in the FTIR spectrum of

a biofilm sample. The 1652 cm^{-1} peak represents the increased number of carboxylic acid groups that are present in typical biofilms, as compared to cellulose from pulp fibers. The 1539 cm^{-1} peak represents amide groups that are present in biofilms as proteins in cellular material. This type of material is absent in cellulose from pulp fibers.

The FTIR spectrum of the bleach-reactive material (slime) in sample 89 is completely consistent with a biofilm material containing both exocellular polysaccharide and cellular material.

These slime deposits can be difficult to detect by standard FTIR methods. The FTIR spectrum of the slime was very similar to that of the pulp, and great care was taken in this work to completely isolate the deposit from pulp fibres. These deposits are not soluble in dichloromethane, and will not be observed in FTIR measurements of dichloromethane extracts of deposits.

4. Stable Isotope Analysis

At Zellstoff Celgar, there are four different process streams where slime could grow and find its way into the pulp. The mill water quality was a significant concern because water from the Arrow reservoir is not filtered as it enters the mill. Stable isotope analysis was able to determine which process stream produced the slime found in the off-grade pulp.

Nitrogen isotope analysis was done on pulp machine slime deposits and individual samples of slime in off-grade pulp. These results were compared with nitrogen isotope composition of organic material collected from strainers of mill water, warm water and hot water delivered to pulp machines #1 and #2.

Both nitrogen-15 and nitrogen-14 occur naturally. Nitrogen-15 can become enriched during biological growth in nitrogen-limited environments. The variation in the absolute abundance of nitrogen-15 is small, so isotope composition is expressed as $\delta^{15}N$ in parts per thousand:

$$\delta^{15}N = (R_{sample}/R_{standard}) \times 1000\%$$

Where R_{sample} and $R_{standard}$ are the molar ratios of the heavier to the lighter isotope. The value of $R_{standard}$ is 0.0036765 [8].

In **Table 1**, $\delta^{15}N$ values of biofilm (slime) sources at the mill are reported. Organic material in mill water, warm water and hot water streams had $\delta^{15}N$ values of 2.2 to 12.5. These samples were slightly enriched with respect to nitrogen-15. Standard deviation of individual values in **Table 1** is approximately 0.2 according to UVic.

Pulp machine samples, collected from different areas of the machines and on different dates, showed $\delta^{15}N$ values ranging from -2.14 to 0.4. These samples were less enriched in nitrogen-15. This could have occurred because of higher concentrations of nitrogen present in the white water, or as a result of the different source of nitrogen present in the white water stream.

In **Table 2**, results of 15 individual dirt spots isolated from Celgar pulp are reported. These 15 samples were bleach-reactive material classified as slime or slime/talc. The values of $\delta^{15}N$ range from -1.44 to 0.51, except for one sample with a value of 1.24. Standard deviation of individual values was 0.4, due to the small sample size. Two samples of slime/talc had $\delta^{15}N$ values of 0.2 and 0.3, fitting into the middle of this range. The nitrogen content of these samples was also determined during the analysis.

TABLE 1. Nitrogen Isotope Ratios of Potential Sources of Slime in Celgar Off-Grade Pulp.

Sample Description	Pulp Machine $\delta^{15}N$	Mill Water $\delta^{15}N$	Warm Water $\delta^{15}N$	Hot Water $\delta^{15}N$
PM#1 Trim Filter, March 16/06	-	5.29	-	-
PM#1 Trim Filter, June 5/06	-	12.5	-	-
PM#2 Warm Water Tank Feed Strainer, June 5/06	-	-	2.2	-
PM#1 Felt HP Shower Oscillator Strainer, June 5/06	-	-	-	6.0
PM#1 Frame, May 2/06	-2.14	-	-	-
PM#1 Frame, May 5/06	-0.1	-	-	-
Hi-Vac Box #6, October 27/05	-0.92	-	-	-
PM #1 Machine Wire, May 5/06	0.4	-	-	-
PM#1 3rd Press Frame, May 5/06	-1.7	-	-	-
PM#1 Table Roll Doctor Board, May 5/06	-0.2	-	-	-
PM#2 Frame, May 2/06	-0.3	-	-	-

TABLE 2. Nitrogen Isotope Ratios of Slime in Celgar Off-Grade Pulp.

Sample #	Date Sampled	Size, mm x mm	$\delta^{15}N$	wt% Nitrogen
6	28-Sep-05	2x3	-0.29	2.2
29	12-Oct-05	8x3	-0.41	1.4
60	22-Oct-05	10x10	-0.2	1.1
64	23-Oct-05	7x3	-0.4	0.4
66	23-Oct-05	7x3	-0.2	0.7
70	23-Oct-05	6x5	-0.6	1.0
72	24-Oct-05	4x10	0.2	2.6
80	25-Oct-05	4x7	-1.1	0.5
84	25-Oct-05	3x7	-0.3	0.3
89	25-Oct-05	5x6	1.24	2.9
109	24-Oct-05	5x3	-0.2	1.0
148	27-Dec-05	9x3	0.51	1.7
152	30-Dec-05	5x3	-0.1	1.0
160	14-Jan-06	5x4	0.26	1.0
163	26-Jan-06	6x3	-1.44	1.7
Kraft pulp	23-Oct-05	-	Insufficient nitrogen	
Dirt speck PM#1	March-05	-	-1.6	0.3
Pitch Sample	27-Oct-05	-	1.1	0.6

Several additional sample results are shown in **Table 2**. Pure Kraft pulp did not show any nitrogen even with relatively large sample size. As a result, contamination of the dirt spots with pulp fiber is not expected to affect the results. An old slime sample from March, 2005 had a $\delta^{15}N$ value of -1.5. A pitch sample showed a $\delta^{15}N$ value of 1.1 and lower nitrogen content than most of the slime samples.

The following conclusions can be made from the results:

- Nitrogen isotope values of slime on pulp machine surfaces closely match values found in slime and slime/talc that occurred in off-grade pulp.
- The majority of slime and slime/talc in off-grade pulp appears to have grown in contact with white water. It does not appear to originate from mill water, warm water or hot water sources.
- This is the first reported use of nitrogen isotope analysis for determining the origin of slime in pulp machine dirt specks.

5. Glycoside Composition Analysis

Sample 9 was biofilm (slime) isolated from an off-grade pulp sample collected October 10, 2005 from pulp machine #1. The isolated sample was approximately 3 x 2 mm, less than 0.1 mm thick and weighed 0.4 mg. Sample 9 was sent to the University of Georgia for glycoside composition analysis. Results are summarized in **Table 3**.

Sample 9 contained glucose, mannose, xylose and trace amounts of galactose. The glucose may have come from pulp fibers that could not be removed from the sample. Pulp fiber also contains small amounts of xylose and mannose. Proportionately, there is a high amount of mannose, xylose and galactose in the sample that is consistent with an exopolysaccharide from biofilm (slime).

TABLE 3. Glycosyl Composition Analysis of Sample 9.

Glycosyl Residue	Mass (µg)	Mole %[a]
Arabinose (Ara)	n.d.	n.d.
Rhamnose (Rha)	trace	trace
Fucose (Fuc)	n.d.	n.d.
Xylose (Xyl)	5.0	39.9
Glucuronic acid (GlcA)	n.d.	n.d.
Galacturonic acid (GalA)	n.d.	n.d.
Mannose (Man)	2.6	17.3
Galactose (Gal)	0.4	2.7
Glucose (Glc)	6.1	40.0
N-acetyl galactosamine (GalNAc)	n.d.	n.d.
N-acetyl glucosamine (GlcNAc)	n.d.	n.d.
3-deoxy-d-manno-2-octulosonic acid	n.d.	n.d.
Total:	14.1	

a. Values are expressed as mole percent of total carbohydrate. n.d.= none detected. Total % carbohydrate by weight = 4%.

6. Soluble Carbohydrate Content

Sample 42 (2.3 mg) was a slime/talc sample from pulp machine #1. The isolated dirt speck was treated with a 5 wt% sodium hypochlorite solution (0.1 mL) for 12 hours, then diluted to 1.5 mL. An identical sample of adjacent pulp was treated the same way. The hypochlorite solution solubilizes the polysaccharide of the biofilm material, but does not affect the pulp fibers. Analysis showed that sample 42 contained approximately 17 wt% soluble carbohydrate, after correcting for the background response of sodium hypochlorite. This method can be used to determine slime content in a pulp or paper sample.

CONCLUSIONS

- An accurate understanding of the amount and types of dirt present in off-grade pulp at Zellstoff Celgar was obtained.
- Biofilm (slime) accounted for 71% of the total number of off-grade deposits in 171 samples collected from September 27/05 to February 4/06.
- Results showed why it can be difficult to positively differentiate slime from pitch in dirt specks.
- Nitrogen-15 isotope analysis of individual dirt specks showed that the slime most likely formed in contact with the white water and did not form in mill water, warm water or hot water systems.
- The pulp machine #1 frame was identified as the most likely source of slime found in the off-grade pulp.
- A simple spot test was implemented at the mill for identification of biofilm (slime) in dirt specks.

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