Final Report

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Biological Kraft Chemical Recycle for Improvement of Pulp Mill Efficiency and Reduction of Sulfur Emissions

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Summary

The chemicals used in pulping of wood by the kraft process are recycled in the mill in the recovery furnace, which oxidizes organics while simultaneously reducing sulfate to sulfide. The recovery furnace is central to the economical operation of kraft pulp mills, but it also causes problems. The total pulp production of many mills is limited by the recovery furnace capacity, which cannot easily be increased. The furnace is one of the largest sources of air pollution (as reduced sulfur compounds) in the kraft pulp mill.

We have studied a possible solution to these problems: a biological process for kraft chemical recycle. To augment the capacity of an overloaded recovery furnace the dust recycle and makeup saltcake (mostly sodium sulfate) would be diverted from the furnace, mixed with a portion of the weak black liquor (bypassed around the furnace) and diluted to the eventual volume of the green liquor. Sulfate-reducing bacteria in a bioreactor would oxidize fermentable organics in the black liquor while reducing sulfate to sulfide for use in pulping. After removal of biomass and excess lignin the solution would be used to dissolve the smelt from the recovery furnace. Using this process mill recycle capacity could be increased by up to 7%.

If biological kraft chemical recycle were used to process all of the kraft chemicals substantial reductions in total reduced sulfur emissions might be accomplished. An oxidizing furnace would be used to avoid production of reduced sulfur compounds, while a bioreactor reduced the sulfate produced by the furnace.

Prior to beginning this work, preliminary data showed that microbial cultures were able to reduce 0.2 M sulfate to sulfide and polysulfide, both of which are useful in pulping. Sulfate reduction continued even at sulfide levels as high as 0.14 M, higher than previously reported for biological cultures in the lab. During the last year we have set up bench-scale, sulfate-reducing bioreactors to determine the sulfate-reducing abilities of these cultures when fed kraft liquor. Staffing, technical, and operational difficulties delayed our progress in the first year, but we presently have three bioreactors running and reducing hydrogen sulfide. To date these reactors have produced sulfide at levels not exceeding 0.03 M S^{2-} . Balance in the sulfur into and out of the reactors does not support the hypothesis of significant formation of polysulfide.

During the final year of the project, mesophilic and thermophilic cultures were tested with two bioreactors operated at 35 and 50°C. Neither of these reactors was able to achieve levels of sulfide that would be useful in kraft chemical recycle. Another reactor was operated with a simplified carbon source: lactate and acetate, compounds that are well known to support sulfate reduction. All bioreactors were reinoculated with sediment and biomass from high sulfur and high temperature environments. Throughout bioreactor operation insufficient sulfide was produced for use in kraft chemical recycle. It is

concluded that biological sulfur reduction could not be used to increase kraft chemical recycle capacity.

Introduction

Economical production of pulp by the kraft process, requires sulfide and alkali recycling. Due to limitations in the capacity of the recovery furnace, many pulp mills have excess pulping capacity that cannot be used. This inefficiency limits pulp mill production and the ability to respond to changing markets.

We have proposed an alternative method for recycling kraft chemicals intended to integrate biotechnological processes with the kraft recovery process: biological reduction of oxidized sulfur to sulfide. Biological sulfur reduction could augment conventional kraft recovery furnace capacity and increase reduction efficiency. We are determining the level of sulfide achievable in kraft black liquor fermentations by biological cultures and assessing how biological systems could be integrated with other kraft chemical recycle processes and pulp production.

The central idea of biological of kraft chemical recycle (BKCR) is the use of bacterial systems to biologically degrade the low molecular organics in kraft black liquor (KBL) while reducing the oxidized sulfur produced in pulping, reconstituting the sulfide used in the kraft pulping process. Bacterial reduction of sulfate to sulfide with the simultaneous oxidation of organic compounds to carbon dioxide, is commonplace in anaerobic biological environments.

Biological sulfate reduction could be employed in several ways in kraft chemical recycle. The application with the best immediate feasibility would use a biological process to reduce sulfate in the dust recycle and in the makeup saltcake. Within the recovery process approximately 50% of the sulfur used in the pulping process is available in the form of solid sodium and potassium sulfate salts (Adams 1989). About 60% of this solid Na_2SO_4 is in the form of dust from the furnace stack and the electrostatic precipitators. The makeup salt cake (also Na_2SO_4) makes up the remainder. Presently this sulfate salt is redissolved in the heavy black liquor concentrate and reinjected into the recovery furnace. This internal cycle of sulfate salt is a deadload that is detrimental to the operation of the recovery process due to increased viscosity of the liquor and dilution of its heating value.

We propose to divert a portion of this salt to a biological fermentor separate from the recovery boiler where it will be reduced to sulfide biologically, using KBL diverted around the concentration and recovery processes. Thus the load on the recovery process will be reduced by this amount of KBL and the dead load on the furnace will also be reduced. This scheme is shown in Figure 1.

Figure 1
Schematic of Biological Augmentation of kraft Recycle

Productivity Benefits. Significant increases in mill productivity and profitability could be had using biological kraft chemical recycle. For example, to reduce the oxidized sulfur in the dust and makeup saltcake (51% of the total sulfur entering the furnace(Adams 1989)) about 6% of the weak KBL flow would be bypassed around the furnace to the fermentor to supply the necessary fermentable organics for biological reduction. Assuming a typical loading rate for anaerobic reactors (10 kg COD/m³/d) a pulp mill with a total capacity of 1200 ton pulp/d would require a fermentor with a volume of about 5,300 m³ (e.g., 2 tanks 12m dia x 24 m height). Using cost functions developed for anaerobic wastewater treatment(Rantala and Väänänen 1985) the estimated cost of the fermentor and associated sedimentation basin would be less than \$6M and would allow an increase of recycle capacity of about 6% for a mill limited by a recovery furnace bottleneck. Such an increase would yield an increase in profit on the order of \$3-6M per year, rapidly covering the cost of the BKCR system. These increases in pulp production could be had without increases in energy consumption or emissions in the recovery process.

Environmental and Energy Efficiency Benefits. Due to the diversion of the dust recycle and make-up salt cake to the BAKR bioreactor, the sulfur load in the reduction furnace will be reduced by about half (see page 1 of the proposal). It is well known that pulp mills operated with low sulfidities and lower sulfur loads on the furnace produce lower SO₂ emissions. Similarly we expect to see a substantial reduction in SO₂ emissions from the reduction furnace with BAKR.

Furthermore, a furnace with a substantially lower sulfur load could be run to take advantage of the trade-off between SO₂ and NO_x levels. By operating the furnace with less oxygen supply to the lower furnace we expect a significant reduction in NO_x emissions while maintaining substantially lower SO₂ emissions.

The energy production of the BAKR process per ton of pulp will be about the same as a conventional recovery furnace sized to the greater capacity of the BAKR process. This can be seen by drawing a materials and energy balance box around the two recovery processes and noting that they both have essentially the same composition of black liquor entering and green liquor leaving the box.

Since the energy requirements of some of the mill processes will not increase proportional to the pulp production rate, we expect a small increase in the percentage of mill energy that is generated from the recovery process. Thus the BAKR process may result in a small reduction in fossil fuel requirement per ton of pulp.

KBL as a Biological Medium. KBL is a harsh environment compared to most biological media. High pH, high temperature, high ionic strength, toxic organics such as resin acids, and high sulfide levels are toxic to many microorganisms. However, some natural environments are similar in important characteristics to black liquor. The pH of a solution of sodium sulfate and sodium carbonate with a composition of sulfur and sodium typical of pulping liquors falls in the range of 9-10, similar to that of hypersaline lakes with anaerobic depths in which sulfate reduction occurs. Soap Lake in Washington state, for example, has deep waters in which the pH exceeds 9 and sulfate reducing bacteria have generated hydrogen sulfate in excess of 0.19 M S.(Edmondson 1963) Furthermore, The ionic strength of KBL is not atypical of many natural environments, such as seawater and brackish lakes.

Sulfate reducing bacteria are more robust than other anaerobic bacteria, such as the methane producers. While methane-producing bacteria are known to be inhibited by the resin acids in KBL(Sierra-Alvarez, Kortekaas et al. 1991). Sulfate reducers are not susceptible to inhibition by similar compounds. Hydrogen sulfide has been observed to inhibit sulfate reducers, but its effect is minimized at pH greater than 9.

Preliminary Experiments Experiments at the UW prior to the beginning of this project appeared to

show that continuous-flow, fluidized-bed, sulfate-reducing bioreactors could be operated with a feed mixture of 67% KBL and 33% green liquor. This bioreactor achieved sulfide levels of 62 mM S. In other bioreactors, fed with lactate to allow control of carbon, sulfide levels of 0.060-0.14 M S have been achieved. Both reactors were operated at pH 8.5-9.5. The effluent from the lactate-fed bioreactor contained about 1 g S per L as SO_4^{2-} . The unaccounted for sulfur appeared to be present as elemental sulfur and polysulfide

($[\text{S}^0]_n\text{S}^-$, formed spontaneously from S^0 at high pH). Based on differential acidimetric titration with sulfite addition (Ahlgren 1967) we estimated that the effluent contained about 0.12-0.19 M S^0 , and gas chromatographic analysis (Borchardt and Easty 1984) confirms the presence of S^0 . Elemental sulfur was also found in the effluent of the KBL-fed reactor.

Accomplishments

During the first year of the funded project, bench-scale, continuous-flow, fluidized-bed, bioreactors were constructed and operated under conditions equivalent to those expected during augmentation of recovery furnace capacity. Three bioreactors were constructed and inoculated. These reactors (shown schematically in Figure 2 and in a photo in Figure 3) were operated for about 15 months starting in April 1998. Peristaltic pumps recycled fluid and supply influent levels of KBL and inorganic salts (Na_2SO_4 , Na_2CO_3 and nutrients). The reactor volume was about 0.4 L and was maintained anaerobic by using air-locks and frequent purging with nitrogen gas. Influent solutions were also maintained anaerobic. The attachment medium for growth of the sulfate-reducing biofilm was diatomaceous earth particles about 1 mm diameter (Cellite™). The pH of the reactors was controlled at various levels, from 8.5 to 10.

The bioreactors were inoculated with the contents of the reactors used in preliminary experimentation and with sediment samples obtained from Soap Lake in Washington State. In the last few months the reactors were reinoculated with sediment from Hot Lake, a heliothermal lake in Okanogan County, Washington State, and from a thermophilic sewage sludge digester in Tacoma, WA. A control reactor was set up using acetate/lactate as a carbon source (at 35°C) while two test reactors were operated with KBL as the carbon source simulating biological augmentation. One of the KBL-fed reactors was initially run at 35°C while the temperature of the other KBL-fed reactor was gradually increased to 50°C.

The pH of the reactors was maintained using electronic pH controllers, pH probes mounted inline in the recirculation tubing, and by pumped addition of 10N NaOH solution to increase the pH and by sparging with CO_2 gas to lower it.

Figure 3 goes here

The influent feed to the reactors was constituted to simulate augmentation of the kraft chemical recycle process running with a 5% KBL bypass. KBL was obtained from Simpson Inc, in Tacoma, WA. This level of sulfate supply was intended to result in an estimated level of sulfide production from sulfate of 0.14 M S in the fermentor.

We changed the titrant for the sulfide analysis to lead perchlorate because of problems using silver nitrate. With time silver precipitated out of the silver nitrate, reducing its strength and resulting in inaccurate high readings for sulfide. The strength of the tritrant was periodically tested against standardized sodium sulfide solutions, which were prepared fresh for each use.

Operation of the Dionex ion chromatograph for analysis of oxidized sulfur species (especially sulfate and thiosulfate) started in February 1998 (Chemical Properties Committee of the Process & Product Quality Div. 1987). Spiked recoveries were approximately 100%, indicating a lack of matrix effects or interferences in the samples.

We undertook several strategies to increase sulfide production. Based on the knowledge that sulfide reducing bacteria require high levels of metals as enzymatic cofactors, we prepared a concentrated mixture of ferrous, nickel, and cobalt salts, complexed with EDTA. This solution was manually injected each day into the reactors (1 mL) in order to overcome precipitation reactions and provide a continuously available source of these metals to the bacterial population.

Problems with declining sensitivity in the thiosulfate IC assay led to a change in ion chromatography several months after the start of bioreactor operation (1/99). A new column was installed (ASHA-SC) and the eluent was changed to 9.539 g sodium carbonate and 7.141 g sodium bicarbonate per 500 ml degassed Epure water. These changes greatly improved thiosulfate sensitivity.

Two approaches were taken to measure organic usage in the reactors. Our first efforts focused on using five-day biological oxygen demand (BOD) as a measure of biologically available organics (Greenberg, Connors et al. 1994). Conventional BOD incubations were prepared with a wide range of dilutions. Biologically active seed was either municipal sewage activated sludge or biomass from an aerobic laboratory bioreactor fed with KBL and a mineral nutrient solution. The BOD test was calibrated using conventional glucose-glutamate standard solutions. Consistent and reasonable results were difficult to obtain using the BOD test. Typically influent BODs were lower than effluent BODs. This discrepancy appeared to be caused by toxic compounds in the influent. These compounds could be partially removed by prolonged sparging with nitrogen and lignin removal prior to analysis. Discrepancies remained, however.

After the failure of the BOD approach, chemical oxygen demand analyses were set up. In order to remove nonfermentable organics, lignin was removed by adjustment of the sample pH to less than 10, the resulting suspension centrifuged, and the supernatant diluted for analysis using conventional methods (Greenberg, Connors et al. 1994). This approach yielded reasonable results that could be used to calculate the consumption of organics in the bioreactors, as discussed below.

The following table shows the changes in COD across the bioreactors. There was no correlation of COD change and sulfide production. Calculated sulfide production based upon the COD loss exceeded the observed sulfide production severalfold.

Chemical oxygen demand in reactor influents and effluents, mg/L

	R1				R2				R3			
Date	in	out	change	%change	in	out	change	%change	in	out	change	%change
5/20/1999	36,875	23,725	13,150	36%	28,400	24,650	3,750	13%	33,475	32,250	1,225	4%
5/26/1999	42,450	24,650	17,800	42%	24,300	16,450	7,850	32%	35,450	30,500	4,950	14%
6/1/1999	45,800	30,200	15,600	34%	24,000	12,100	11,900	50%	47,600	39,800	7,800	16%
6/8/1999	94,600	39,850	54,750	58%	53,300	26,400	26,900	50%	43,500	36,700	6,800	16%
6/22/1999	46,400	43,575	2,825	6%	50,475	36,950	13,525	27%	31,600	59,100	-27,500	-87%

A series of batch of tests were performed to determine the effects of pH and carbon source on sulfide production. Figure 4 shows that sulfide production was due to biological activity, since sulfide levels in controls killed with formaldehyde were close to zero. Maximum production of sulfide occurred at pH 9.5 for KBL-fed cultures. Variations in pH had little effect on acetate/lactate-fed cultures, although maximum sulfide production occurred at pH 10.5.

To determine whether KBL has toxic effects on sulfide production a series of cultures were tested with various levels of KBL ranging from 0 to 100% with acetate and lactate (known sulfate-reducing bacterial substrates) making up the remainder. KBL had little effect on sulfide production at 75% or less of the carbon source (Figure 5).

Figure 4

Figure 5

The bioreactors were inoculated from several sources during the course of this study. These were (1) bioreactors used previously in preliminary studies, (2) sediment and water column samples from Soap Lake and Hot Lake, Washington state, and (3) mesophilic and thermophilic anaerobic sewage digesters. Late in the study it appeared that some atmospheric oxygen may have been leaking into the bioreactors. Dissolved oxygen measurements indicated that oxygen levels were less than 0.1 mg/L, a very low level. However the apparent production of sulfate in some of the mass balances suggested that there may have been steady introduction of oxygen at low levels. This suggestion was also supported by the excess in carbon utilization compared to sulfide production that we observed. In order to prevent the introduction of oxygen effluent gases were passed through a saturated saltwater bath and influent solutions were sparged with nitrogen gas.

We also operated one bioreactor with a mixture of pure carbon sources known to promote sulfate reducing bacterial growth (Pfennig, Widdel et al. 1981). Acetate than lactate (1:1) were used for this reactor. In general, the acetate/lactate-fed reactor produced a slightly higher level of sulfide than the KBL-fed reactors.

Since high temperature (thermophilic, 45-80°C) sulfate-reducing cultures are usually dominated by archaea, a very different group of bacteria than the eubacteria that dominate in the mesophilic range (20-45°C); we attempted to develop a thermophilic reactor, operated at 40-50 °C. We had hopes that this culture might be less sensitive to high sulfide levels, but this was not the case. The thermophilic bioreactor always produced low levels of effluent sulfide (usually less than 0.5 g S/L).

The timecourse of sulfide levels in the bioreactors is shown in Figure 6.

Figure 6

The mass balance of total sulfur species across the reactors is shown in Figure 7. With a few exceptions, the mass balance was approximately zero.

Figure 7

Figure 8 shows the change in sulfate across the reactors. While individual observations seemed to show a decrease or an increase in effluent sulfate levels, overall sulfate did not changed significantly. We believe that the scatter in these data was due to the lag between influent and effluent sampling, caused by the relatively long retention time in the reactors and by variations in reactor conditions and influent feed composition.

Figure 8

Thiosulfate may have been the most important source of sulfur for production of sulfide in the bioreactors. Figure 9 shows a correlation between thiosulfate levels and sulfide and effluent for reactors 1 and 3. The correlation between sulfide and sulfate changes is not as clear.

Figure 9a – Correlation between Sulfate and Thiosulfate Species and Effluent Sulfide Levels

Figure 9b – Correlation between Sulfate and Thiosulfate Species and Effluent Sulfide Levels

Figure 9c – Correlation between Sulfate and Thiosulfate Species and Effluent Sulfide Levels

Despite our efforts, sulfide levels in the effluents never exceeded 2 g S/L in any reactors, and were usually at 1 g S/L or less. Calculations clearly show that biological kraft chemical recycle cannot be an effective augmentation of the conventional Tomlinson furnace unless effluent sulfide levels exceed 3 g S/L. Possible reasons for our failure to achieve higher levels of sulfide in the bioreactor effluents are as follows:

1. Toxicity of hydrogen sulfide to the bacteria. Although sulfide levels in one of our sources of inocula (Soap Lake hypolimnion) are at 3 g S/L or above, those levels may have been reached very slowly over periods of many years. The bacteria in those sources may have been adapted to low temperatures (less than 20 °C), which would not have been useful in the Kraft recycle process. The more toxic form of hydrogen sulfide is H₂S, while the ionized form, HS⁻, is thought to be less toxic. We operated the reactor in a pH range (8.5-10) in order to minimize the presence of H₂S. Bottle tests of the effects of pH yielded somewhat contradictory results, with pH effects depending upon carbon source (see Figure 4). At very high pH, toxic effects due to pH may also be expected, even though the lake sediment sources were also high pH environments.

2. Toxicity of KBL constituents. We initially operated the bioreactors with whole KBL. On the hypothesis that lignin in the KBL may inhibit sulfate reducers, we switched to using KBL from which the

high molecular weight lignin had been removed by acidification and centrifugation. This modification resulted in a somewhat higher level of sulfide production (see figure 6, after August 1998). However bottle test comparisons of KBL and acetate/lactate as carbon sources did not support the hypothesis of KBL toxicity (see figure 5). Furthermore the bioreactor operated with acetate/lactate also did not achieve sufficiently high levels of sulfide. Nevertheless, the acetate/lactate bioreactor usually had higher sulfide levels, suggesting that there was some inhibitory factor in lignin-treated KBL (e.g., resin acids), but that other factors prevented high levels of sulfide production.

3. Oxygen contamination of the bioreactors. The lack of balance between carbon utilization and sulfide production suggests that there may have been slow introduction of oxygen into the bioreactors. It is difficult to conceive of a route by which oxygen could have entered the bioreactors in sufficient amounts to oxidize several g/L of carbon. It is more likely that the carbon loss was due to fermentation. Sulfide production was unaffected by our efforts to remove pathways by which oxygen could enter the reactors.

4. Polysulfide production and toxicity. After the end of the laboratory work it has been suggested to us that polysulfide could have been produced in the reactors at levels below our ability to measure, and that this chemical could have had a strong toxic effect on the sulfate reducing bacteria.

5. Why were the sulfide levels produced in our current experiments lower than those observed in the preliminary work? Although the cultures may have changed, the bioreactors used in the preliminary experiments were used to inoculate the bioreactors we report on here, so biological factors were probably not involved. Sulfide measurements in the preliminary experiments depended upon either colorimetric titration or potentiometric titration using silver nitrate as the titrant. The former is subject to many interferences, while the latter is subject to false high readings due to dilution of the titrant by precipitation of silver. We suspect that these artifacts led to a misinterpretation of our preliminary data, suggesting higher sulfide levels than we actually had achieved.

Bibliography

- Adams, T. N. (1989). Black Liquor Combustion. Pulp and Paper Manufacture: Alkaline Pulping. M. J. Kocurek. Atlanta, GA, The Joint Textbook Committee of the Paper Industry, TAPPI. 5.
- Ahlgren, P. (1967). "An acidimetric method for the determination of hydroxide, sulfide, excess sulfur and carbonate in polysulfide solutions." Svensk Papperstidn. 70(21): 730.
- Borchardt, L. G. and D. B. Easty (1984). "Gas chromatographic determination of elemental and polysulfide sulfur in kraft pulping liquors." Jour. Chromatogr. 299: 471-476.
- Chemical Properties Committee of the Process & Product Quality Div. (1987). Analysis of pulping liquors by suppressed ion chromatography, TAPPI.
- Edmondson, W. T. (1963). Pacific Coast and Great Basin. Limnology in North America. D. G. Frey. Madison, Wisc., Univ. Wisconsin: 371-392.
- Greenberg, A. E., J. J. Connors, et al. (1994). Standard Methods for the Examination of Water and Wastewater. Washington, DC, Amer. Public Health Assoc.
- Pfennig, N., F. Widdel, et al. (1981). The dissimilatory sulfate-reducing bacteria. The Prokaryotes, Berlin, Springer-Verlag.
- Rantala, P. and P. Väänänen (1985). "Cost comparison of aerobic and anaerobic wastewater treatment systems." Water Sci. Tech. 17: 255-264.
- Sierra-Alvarez, R., S. Kortekaas, et al. (1991). "The Anaerobic Biodegradability and Methanogenic Toxicity of Pulping Wastewaters." Water Science and Technology Wsted4 24(3): 113-125.