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Overview of the IPST Study of the ShockWave Power™ Technology

In this study, Hydro Dynamics' ShockWave Power™ technology was evaluated for the following purposes:

1. To determine if black liquor with high scaling tendencies could be concentrated to high solids levels without scaling
2. To determine if mass transfer rates could be increased when mixing oxygen with black liquor to improve the efficiency of the process

The test results indicate the desired objectives can be achieved.

Executive Summary:

Hydro Dynamics has a patented "controlled cavitation" technology called ShockWave Power™. Cavitation is normally considered a "destructive force" that one needs to eliminate from an industrial process. However, cavitation can be applied in a controlled manner to mix or heat fluids that are difficult to process by conventional technologies. The ShockWave Power™ technology was evaluated as a method to improve efficiency of black liquor oxidation, and to heat high solids content and difficult to process black liquor without scaling. In this study black liquor was subjected to controlled cavitation by pumping it through a mechanical device called the ShockWave Power™ generator.

The ShockWave Power™ generator is designed to create microscopic cavitation bubbles by spinning a disc containing numerous cavities in a tightly enclosed area. As the microscopic bubbles implode, shock waves are released. This action converts mechanical energy into heat that is directly absorbed by the liquid. Additionally, controlled cavitation produces efficient micromixing, for two-phase fluids. The cavitational forces created are capable of breaking down large gas bubbles into microscopic bubbles as well as breaking down the Van der Waals attraction between liquid molecules. Consequently, the surface area available for gas-liquid mixing is dramatically increased and therefore enhances mass transfer.

Economics derived from this study indicate there are numerous opportunities for using controlled cavitation in kraft pulp mills. Such applications include:

1. An alternative to low odor conversion of the recovery boiler
   - Allows mills with direct contact evaporators to meet TRS limits
   - Eliminates the expense of a low odor boiler conversion

2. Extended black liquor oxidation to increase recovery boiler capacity
   - Reduces the gross heating value of the organic matter in kraft black liquor
   - A low capital cost method of incrementally increasing black liquor processing capacity and/or pulp production

3. Increased production efficiencies due to preheating and deactivation of concentrated black liquor
   - For high solids content (high viscosity) black liquors, the rate of heat transfer is not limited by a film heat transfer coefficient that decreases as viscosity increases.
   - For black liquors with a propensity to deposit scale on heat transfer surfaces, it means no heat transfer scaling problems because there are no heat transfer surfaces to scale.

Therefore, controlled cavitation can be characterized as a "breakthrough technology" with the potential to achieve quantum improvements in certain pulp and paper operations.

ECONOMIC BENEFITS OF UTILIZING CONTROLLED CAVITATION TECHNOLOGY FOR BLACK LIQUOR OXIDATION AND HEATING

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ABSTRACT

Controlled cavitation technology was evaluated as a method to improve black liquor oxidation efficiency and to heat high solids content and difficult to process black liquor without scale deposition. In trials with a conventional kraft black liquor, sulfide was oxidized more rapidly and completely, to nondetectable residual sulfide concentrations, with either elemental oxygen or air when controlled cavitation was used. The heating value of the black liquor was reduced by 5-7% based upon an initial Na_2S concentration of 29 g/L. The selectivity of oxygen for sulfide oxidation was doubled when controlled cavitation was employed. The production increase could reach up to 8 percent based on initial Na_2S concentration.

In black liquor heating trials, a black liquor with a high propensity for calcium carbonate scaling was heated using controlled cavitation. No scale deposition was observed on the rotor or casing of the controlled cavitation device. In parallel heating tests with the same black liquor, the conventional heat transfer surface employed fouled rapidly. The decrease or elimination of scaling in the evaporators using a controlled cavitation device for heating and evaporation of high solids black liquor could increase mill production by up to 15% in mills where evaporator fouling limits capacity.

Possible applications of controlled cavitation in kraft pulp mills include oxidation of black liquor to zero residual sulfide concentration, reduction of the gross heating value of black liquor to increase recovery boiler capacity, and as a scale-free heater for high solids content black liquor or black liquor with a propensity for scaling.

The controlled cavitation device can be characterized as a breakthrough technology with the potential to achieve quantum improvements in certain pulp and paper operations.

INTRODUCTION

Cavitation is normally considered a “destructive force” that one needs to eliminate from an industrial process. However, cavitation can be applied in a controlled manner to mix or heat fluids that are difficult to process by more conventional means.

Controlled cavitation can be used to heat liquids such as black liquor directly, without a heat transfer surface. With cavitation, bubbles form, collapse, and reform in the liquid, and energy is transferred directly into the liquid as heat. The liquid is actually hotter than the surrounding metal of the rotor and housing. There is a negative ΔT between the liquid and the housing.

Controlled cavitation also serves as an efficient mixing device for two-phase fluids. When gases and liquids are subjected simultaneously to a region of controlled cavitation, large gas bubbles are broken down and dispersed in the liquid phase by the cavitational forces. At the level of micromixing achieved, diffusional limitations are eliminated. Chemical reactions such as oxidation of sodium sulfide proceed at a much more rapid rate, controlled only by the inherent chemical kinetics.

The objective of this paper is to present experimental results from pilot-scale investigations of heating, evaporating, and oxidizing kraft black liquor with controlled cavitation.

EXPERIMENTAL

In the work reported here, black liquor was subjected to controlled cavitation by pumping it through a cavity and across a specialized spinning rotor in a device called a ShockWave Power™ Generator. Figure 1 shows a small unit with a clear housing. Figure 2 shows a larger unit with its electric drive motor.

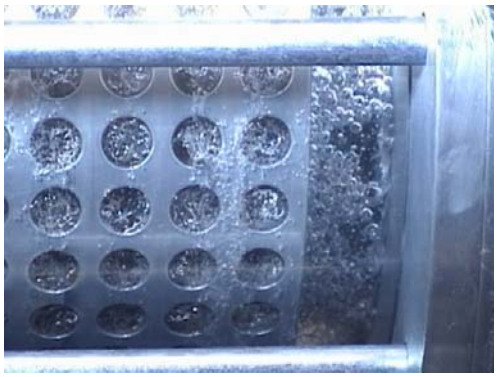

Figure 1: A small ShockWave Power™ Generator during gas / liquid mixing with a clear housing for ease of viewing.

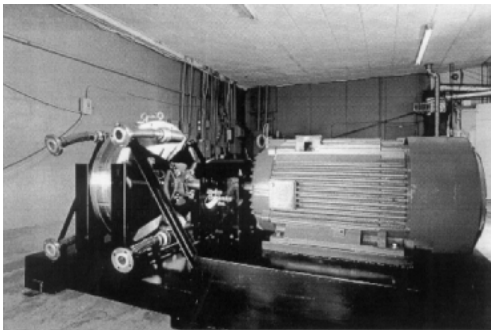

Figure 2: A commercial size ShockWave Power™ Generator complete with electric motor.

As the rotor rotates, liquid is thrown out of the cavities or dead-ended bores by centripetal force. Consequently, a

pressure drop or vacuum is created within the bores. When the negative pressure in the bore can overcome the force created by the centripetal action, the flow direction of the aqueous solution is reversed, therefore drawn into the bore. The process continually repeats itself, thereby creating millions of tiny bubbles per minute. This particular effect is commonly called "cavitation." As these bubbles implode, mechanical energy is converted to heat that is absorbed by the liquid.

The unit was designed to have the cavitation bubbles collapse within the bore of the rotor and not at the surface where cavitational damage could erode the metal. Therefore, all of the energy from the bubble collapse is transferred into the liquid in the form of heat.

Controlled cavitation also results in the efficient micromixing of two-phase fluids. The cavitational forces created break down large gas bubbles into microscopic bubbles and break down the van der Waals attraction between liquid molecules. Consequently, the surface area available for gas-liquid mixing is dramatically increased and therefore mass transfer is enhanced.

The residence time of the liquor in the pilot-scale controlled cavitation unit is 5.9 seconds at a flow rate of 71.9 L/min (19 gal/min). This paper is focused on the pilot scale controlled cavitation unit. For a commercial size unit, the residence time has a range of 2 to 3 seconds at a black liquor flow rate of 756 L/min (200 gal/min).

Oxidation of Black Liquor

In black liquor, sodium sulfide is hydrolyzed to sodium, hydrosulfide, and hydroxide ions as indicated by Equation 1.

$$Na_2S + H_2O \rightarrow 2\ Na^+ + HS^- + OH^- \qquad (1)$$

When black liquor is oxidized, HS^- is converted to thiosulfate according to Equation 2, consuming one mole of O_2 per mole of sulfur.

$$2\ HS^- + 2\ O_2 \rightarrow S_2O_3^{2-} + H_2O \qquad (2)$$

To completely eliminate TRS emissions by oxidizing black liquor, it is important to be able to oxidize to zero residual sulfide concentrations, and to oxidize organosulfur compounds (mercaptans, sulfides, and disulfides) as well.

Four different oxidation runs were made to evaluate the effectiveness of controlled cavitation on the achievable extent of sulfide oxidation and on the selectivity of oxygen for sulfide oxidation. Controlled cavitation was used to provide intense micromixing of the oxidant and black liquor. Figure 3 shows the experimental setup for black liquor oxidation.

In the 100 series run, black liquor was pumped from the feed tank, to the oxidant injection point, then through the unit, through a heat exchanger, and into a collection tank (see Figure 3). The feed and product tanks were then switched, and the liquor was processed in the same way for another pass. This procedure was repeated until all of the Na_2S was oxidized. This mode of operation provides data on the extent of oxidation per pass through the controlled cavitation unit, at different sulfide concentrations.

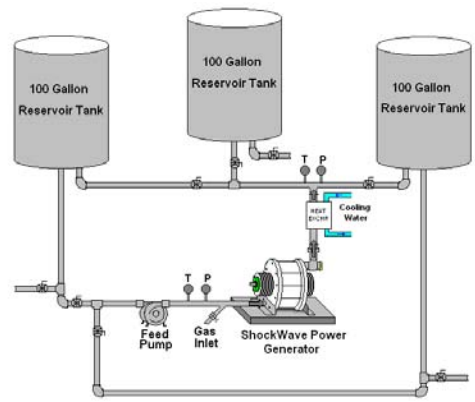

Figure 3: Experimental setup for oxidation of black liquor with elemental oxygen, using a ShockWave Power Generator for micromixing.

In the 200 and 300 series runs, black liquor was pumped continuously from the feed tank to the oxidant injection point, next through the controlled cavitation unit, then through a heat exchanger to cool it, and back to the feed tank. The runs were stopped when all of the Na_2S was oxidized. This mode of operation provided data on the extent of oxidation with continuous processing through the controlled cavitation unit as the sulfide concentration in the black liquor decreased.

Series 200 utilized pure oxygen as the oxidant while series 300 utilized air. Initially, the apparatus shown in Figure 3 was used to conduct the 300 series experiments. However, nitrogen from the oxidizing air caused uncontrollable foaming as the two-phase mixture was returned to the black liquor product tank. In order to run the experiment using air, the black liquor was pumped from a pressurized tank instead of an open reservoir, and a defoamer was added to the liquor. Figure 4 shows the apparatus used for the oxidation experiment using air as the oxidant.

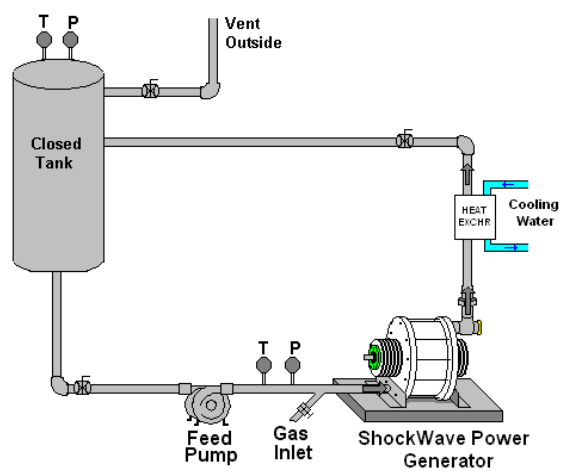

Figure 4: Experimental setup for foam control when oxidizing black liquor with air.

In a separate series of runs (designated the 000 Series), the flow loop shown in Figure 3 was used to oxidize black liquor without utilizing controlled cavitation. Black liquor was pumped from the feed tank to the oxidant injection point, through the controlled cavitation unit (with no power applied), and then into a collection tank. The feed and product tanks were then switched, and the liquor was processed in the same way for another pass.

Table I shows the experimental conditions for these four trials. These runs were all made with black liquor from a Georgia pulp mill that processes both softwood and hardwood. The liquor used in each run was a separate aliquot from a single batch of black liquor obtained from the mill. The process data collected included the total mass of black liquor in the system, the black liquor flow rate, oxidant flow rate, liquor temperature entering and exiting the unit, and the electrical current drawn by the controlled cavitation device.

TABLE I: EXPERIMENTAL CONDITIONS FOR THE FOUR BLACK LIQUOR OXIDATION TRIALS.

Series no.	010		020		030		100		200		300	
Processing mode	Single Pass						Single Pass		Recirculation		Recirculation	
Oxidant	O_2						O_2		O_2		Air	
Black liquor processed, kg	237		200		183		407		375		54	
Solids content of black liquor, wt-%	39.0		39.0		39.0		39.4		37.4		31.7	
Black liquor flow rate, L/min	76.8		75.0		70.0		72.0		70.1		67.8	
Initial sulfide content, g/L	23.0		12.6		0.73		29.2		21.6		16.0	
Oxidant input rate, L/min	56.6		62.3		68.0		54.7		56.6		56.6	
	in	out	in	out	in	out	in	out	in	out	in	out
Black liquor temperature, °C	57.4	57.4	60.8	60.8	68.6	68.6	70.0	86.8	76.2	92.0	71.0	76.5

Black liquor samples were collected during each single-pass run, and periodically during the continuous runs. They were analyzed for total solids content, inorganic sulfur species, total sulfur concentrations, gross heating value, and residual effective alkali concentration. These analyses were performed at the Chemical Analysis Laboratory at the Institute of Paper Science and Technology (IPST). Viscosities vs. shear rate measurements were also performed on the samples, using a Bohlin Controlled Stress Rheometer (Model CS-50). The viscosity measurements were performed under the direction of Dr. Skip Rochefort at the Department of Chemical Engineering, Oregon State University.

RESULTS

Single Pass Oxidation Runs

In the 100 series runs, approximately 333 L (88 gal) of black liquor at 39% solids content was pumped through the flow loop and controlled cavitation unit in the single pass operation mode at a rate of 74 L/min (19 gal/min). A total of eight single-pass runs were completed with this batch of black liquor, equating to 47.2 seconds of total residence time in the controlled cavitation unit (5.9 seconds residence time in the unit per pass).

Figure 5 shows how the sulfide concentration in the black liquor decreased per pass through the controlled cavitation unit in this series of runs. The reduction in sulfide content per pass ranged from 7.4 g/L at the highest sulfide concentration to less than 3 g/L when the sulfide concentration approached zero. The Na_2S concentration in the liquor was below the detection limit of 0.01 g/L after the eighth pass through the controlled cavitation unit. Zero sulfide concentrations were achieved in all experimental runs when controlled cavitation was employed.

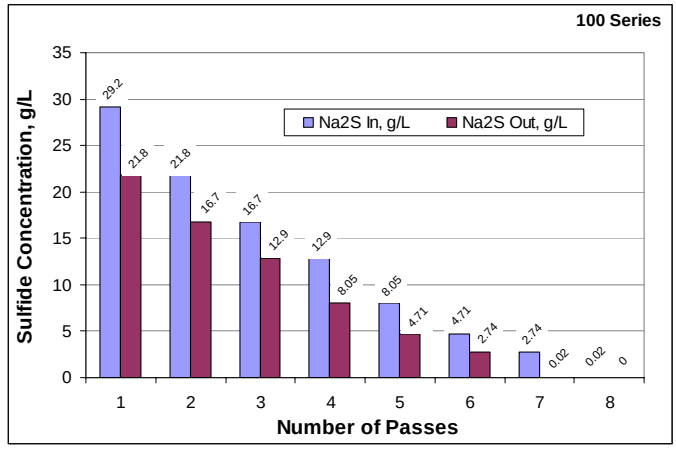

Figure 5: Sulfide concentration per pass for the 100 series run.

Figure 6 shows how the various sulfur species in black liquor changed as sulfide was oxidized. The sulfide concentration decreased and, as expected, the thiosulfate concentration increased with the number of passes of the liquor through the controlled cavitation unit, until the sulfide was depleted. The sulfite concentration remained essentially constant until the fifth pass, after which it dropped to zero. The sulfate concentration remained constant throughout the experimental runs. Polysulfide was generated during initial oxidation, but it began to deplete after the 4th pass. The total sulfur concentration in the liquor, measured independently of the concentrations of the five sulfur-containing ions, was constant during the run, within the experimental error in the measurements. Error bars in Figure 6 indicate ±10% also measured values, the expected accuracy all these measurements.

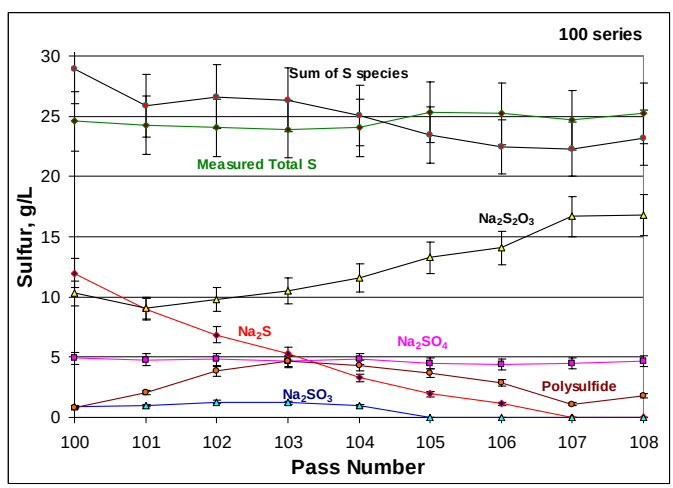

Figure 6: Concentrations of total sulfur and the inorganic sulfur-containing species in black liquor during the 100 series runs.

In order to establish a reference point for comparison, the flow loop shown in Figure 3 was used to oxidize black liquor without the controlled cavitation unit. Black liquor and oxygen were pumped through the flow loop in single pass operation, as with the 100 Series runs.

Figure 7 shows the results from runs made at three different initial sulfide concentrations. Sulfide was oxidized in these runs without controlled cavitation, but the Na_2S concentration could not be reduced below 0.38 g/L.

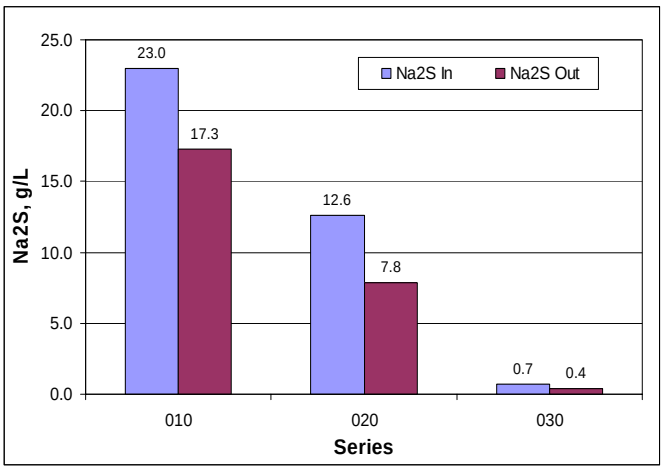

Figure 7: Change in Na_2S during oxidation without using a controlled cavitation device.

Figure 8 shows a direct comparison of low-level sulfide oxidation between the control and the controlled cavitation experiments. The controlled cavitation unit was able to fully oxidize 2.7 g/L Na_2S in a single pass. Although the control began at a much lower sulfide content (0.7 g/L), it could not fully oxidize to zero residual sulfide content despite the use of 40% more oxygen.

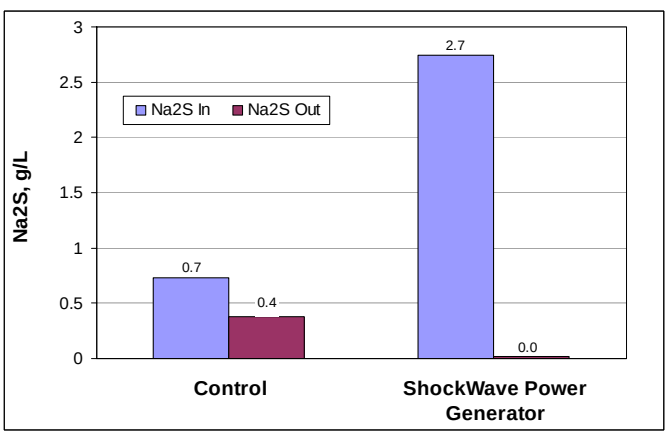

Figure 8: Comparison of polishing stage oxidation between conventional technology and the controlled cavitation device.

Figure 9 compares the sulfide concentrations vs. residence time in the cavity of the controlled cavitation unit at low Na_2S concentrations in the feed liquor for the 100 series and the 000 series runs. At Na_2S concentrations above 7 g/L, there was essentially no difference in the rate of sulfide oxidation between the two series, when compared at the same sulfide concentration in the feed black liquor. At lower sulfide concentrations, however, the rate of sulfide oxidation is much more rapid when controlled cavitation is employed, decreasing from 2.74 g/L to 0.02 g/L in one pass, and then to below the detection limit in the subsequent pass. By comparison, the sulfide concentration decreased only from 0.73 g/L to 0.38 g/L in one pass without employing controlled cavitation, even though the oxygen flow rate was 40% higher in this case. Also, as noted earlier, the residual sulfide concentration was reduced to zero only when controlled cavitation was used.

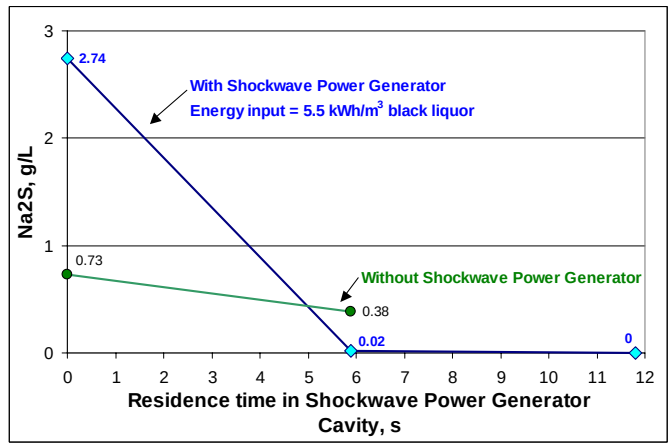

Figure 9: Sodium sulfide concentration in black liquor vs. residence time in the controlled cavitation unit cavity at nearly complete sulfide oxidation.

Continuous Flow Batch Oxidation Runs

In the 200 and 300 series runs, black liquor was pumped continuously from the feed tank to the oxidant injection point, next through the controlled cavitation device, then through a heat exchanger to cool it, and back to the feed tank. Series 200 utilized pure oxygen as the oxidant while series 300 utilized air. For the 200 series runs, the total residence time was 45 seconds (81.8 gal BL, 19 gal/min flow, 5.9 sec residence time in the unit per pass). For the 300 series runs, the total residence time was 268 seconds (4.5 minutes) (11.9 gal BL, 19 gal/min flow, 5.9 sec residence time in the unit per pass).

Figure 10 is a graph of sodium sulfide concentrations vs. cumulative residence time in the controlled cavitation unit. In all three series, the sulfide was ultimately oxidized completely, to below the detection limit. Plotting the data this way allows us to compare changes in sulfide concentration on a basis that is independent of the black liquor flow rate or total volume of black liquor processed. When plotted this way, the data suggests that the rate of sulfide oxidation in the 100 and 200 series runs is very similar. The rate during the 300 series run is apparently slower, by a factor of about five. This is roughly the same as the ratio of oxygen input rates to black liquor throughput rates in these three series.

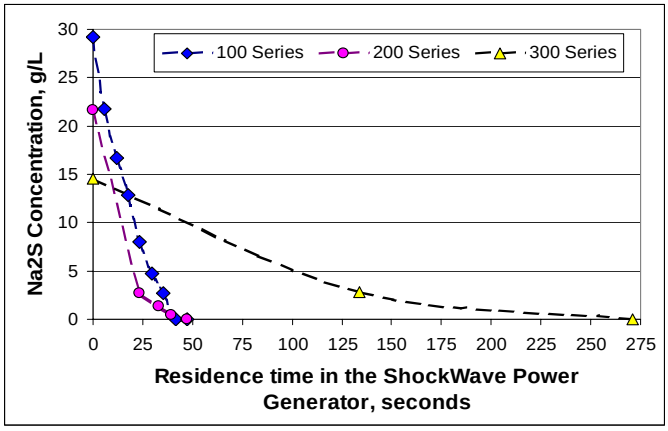

Figure 10: Sulfide concentrations vs. cumulative residence time in the controlled cavitation device for the 100, 200, and 300 series runs.

Figure 11 compares the oxygen selectivity for the oxidation of sulfide to thiosulfate as a function of the average sulfide concentration per pass during oxidation. The theoretical oxygen consumption for oxidation of sulfide was based on the stoichiometry indicated by Equation 1. The selectivity of oxygen for sulfide oxidation, $\mathbf{S_{S/OX}}$, is defined in Equation 3.

$$S_{S/OX} = O_2 \text{ consumed by } Na_2S/\text{total } O_2 \text{ consumed} \qquad (3)$$

Three conclusions can be drawn from the data in Figure 11. One is that using controlled cavitation to create micromixing increased the selectivity of oxygen for sulfide oxidation. The second is that the selectivity of oxygen for sulfide oxidation decreased linearly with the Na_2S concentration. The selectivity approached zero as Na_2S became completely oxidized. The third is that the linear decrease in oxygen selectivity apparently began at a much higher Na_2S concentration (>20 g/L) without controlled cavitation than with it (<7 g/L).

The data at higher Na_2S concentrations suggests that the selectivity of oxygen use for sulfide oxidation is 1 or greater. This is believed to be due to the generation of polysulfide during initial oxidation as shown in Figure 6. The polysulfide that was generated initially began to deplete after the 4th pass. At that point the selectivity of oxygen for sulfide oxidation was less than 1.

After the 4th pass, the selectivity for sulfide oxidation began to decrease. By sample 109, 55% of the decrease in heating value is attributable to oxidation of organic matter. The trend of the heating value data in Figure 12 indicates that further oxidation will continue to decrease the heating value. All of the change will be due to oxidation of organic matter, since the sulfide had been oxidized earlier.

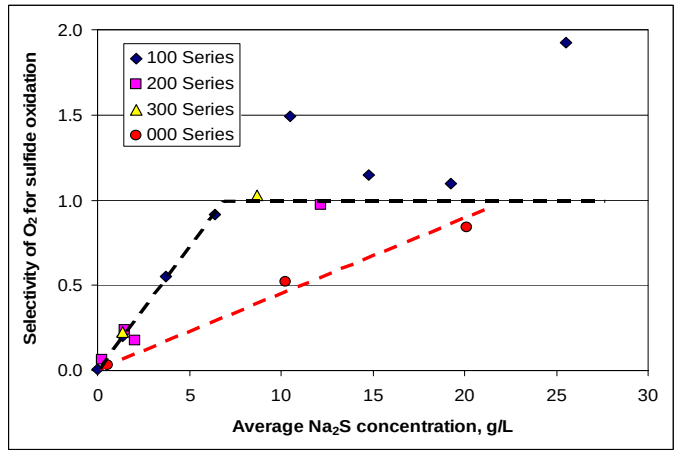

Figure 11: Oxygen selectivity for oxidation of sulfide to thiosulfate for all run series.

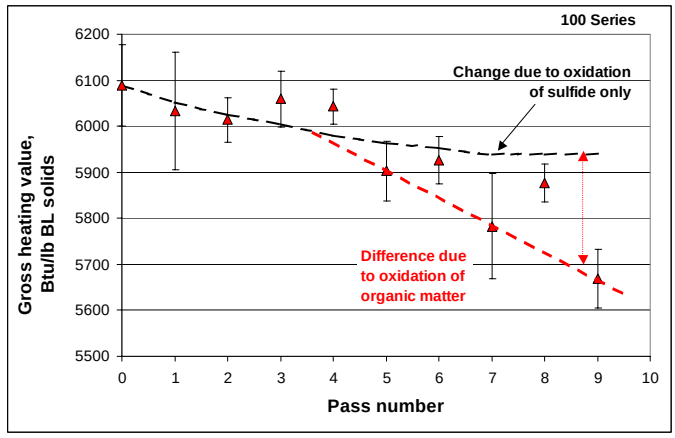

Figure 12: Na_2S concentration and gross heating value per pass for the 100 series runs.

Figure 13 shows how the residual effective alkali concentration in the black liquor changed during oxidation. The effective alkali concentration change very little in the first 20 - 25 seconds of residence time (approximately 4 passes). After that it decreased by as much as 3 to 4 g/L as Na_2O.

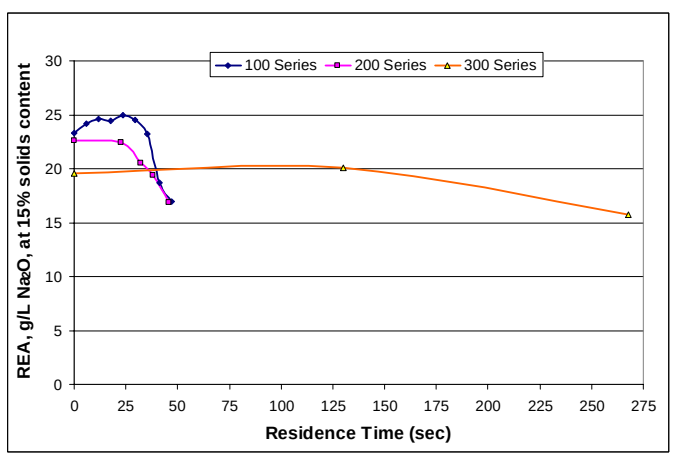

Figure 13: Residual effective alkali concentrations in black liquor vs. cumulative residence time for the oxidation run series.

Impact of Oxidation on Black Liquor Viscosity

The impact of oxidation on the rheological behavior of black liquor is illustrated in Figure 14. Each curve in this figure represents a series of viscosity measurements at different shear rates (5.3 to 85 s^{-1}). The viscosity vs. shear rate curves show the shear thinning behavior that is typical of black liquors. Oxidation generally shifts the curves upward. This is seen more clearly in Figure 15, where the viscosity at one shear rate is plotted vs. the sample number for each run series. The viscosity increases by as much as 35% percent with oxidation, generally following a trend inverse to the residual effective alkali concentration.

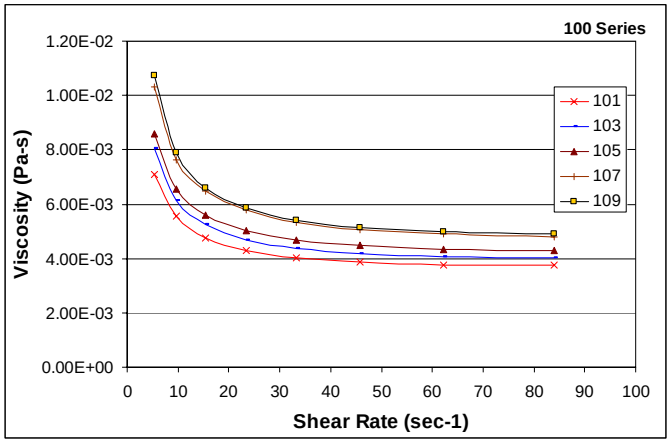

Figure 14: Black liquor viscosity at 90°C vs. shear rate for the 100 series runs.

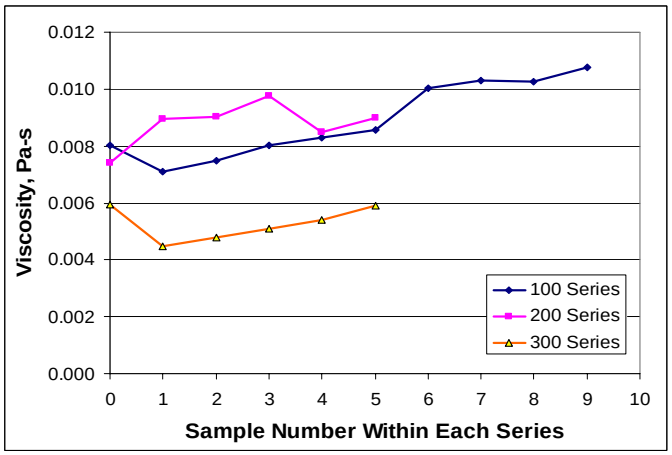

Figure 15: Black liquor viscosity at a shear rate of 5.3s^{-1} for each sample for all the 100, 200, and 300 series runs.

Evaluation of Fouling During Black Liquor Heating

Fouling of heat transfer surfaces by calcium carbonate, sodium carbonate/sulfate scale can be a problem when heating black liquor. The tendency for calcium carbonate scale deposition was evaluated by operating the controlled cavitation unit as a liquor heater, operating at liquor temperatures from 220 to 260°F. Black liquor that was known to cause severe soluble scale and calcium carbonate scale problems was obtained from a pulp mill in Arkansas. This liquor had a very high soluble calcium content, 1400 mg/kg black liquor solids, and a total calcium content of 1800 mg/kg black liquor solids. We first ran heat transfer fouling experiments in an annular flow heat transfer fouling test cell at IPST to demonstrate that the liquor would indeed foul a heat transfer surface. These experiments were run with the heat transfer surface at temperatures from 104 to 149°C (220 to 300°F) with a liquor temperature of 116°C (240°F). Figure 16 shows the temperature of the heat transfer surface and the calculated heat transfer coefficients as a function of time. These data indicate that the heat transfer surface began to foul about 40 minutes into the run, when the surface temperature was at 129°C. Fouling continued throughout the run, as indicated by the plot of d (1/U)/dt in Figure 17. At the end of the run, the scale was removed from the heat transfer surface and analyzed for total mass and inorganic composition. The scale density on the heat transfer surface was 220 g/m^2. Chemical analysis of the scale indicated that it contained 31% Na_2/K_2CO_3, 15% Na_2/K_2SO_4, 9% $CaCO_3$, and 2% $MgCO_3$. The K/Na mass ratio in the scale was 0.12.

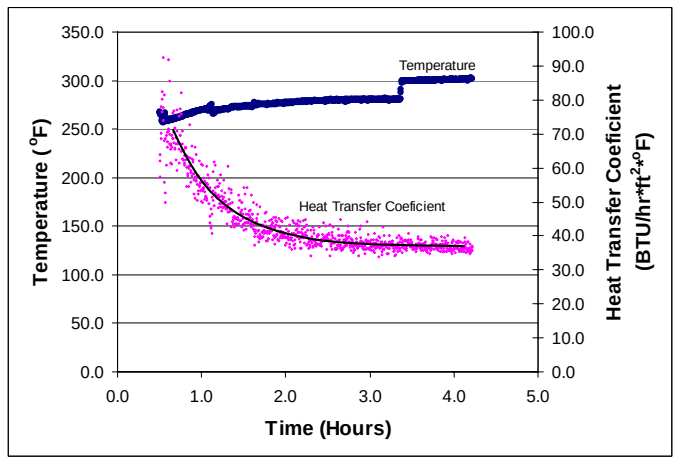

Figure 16: Heat transfer surface temperature and heat transfer coefficients vs. time for a high $CaCO_3$ scaling tendency black liquor processed in the IPST annular flow heat transfer fouling test cell.

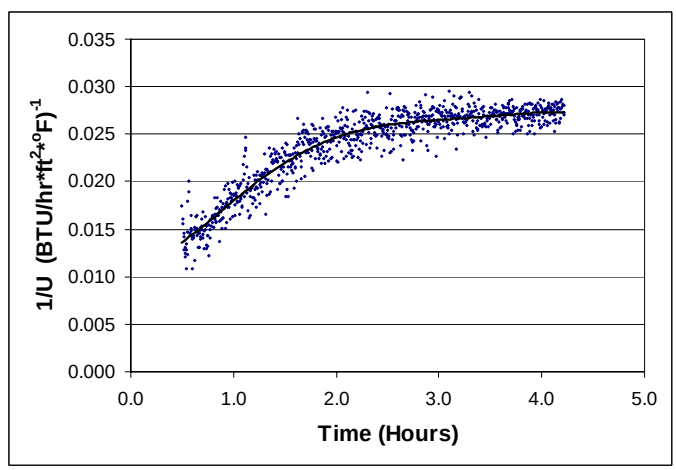

Figure 17: Heat transfer fouling rate, d (1/U)/dt, vs. time for the transfer data for a high $CaCO_3$ scaling tendency black liquor processed in the IPST annular flow heat transfer fouling test cell.

In the liquor heating experiments made using controlled cavitation, black liquor at 44% total solids content was fed to the device at 104°C (220°F) and exited at 110°C (230°F). The liquor was process continuously for five hours. The liquor temperatures were then increased to 122°C (251°F) entering the device and exiting at 127°C (261°F). The liquor was processed continuously for an additional 5 hours with a power input of 2.6 kWh/m^3. At the end of this period, liquor was drained from the controlled cavitation unit, and its surface was examined. There was no sign of any scale having been deposited on the surface of the rotor or casing.

IMPLICATIONS FOR PULP MILL APPLICATIONS

There are a number of possible applications for controlled cavitation in kraft pulp mills. In this section, we consider three applications and the implications to the economics of kraft pulp production.

An alternative to low odor conversion: One obvious application for controlled cavitation is in oxidizing Na_2S in kraft black liquor to a nondetectable residual sulfide concentration. The most important opportunity may be in kraft pulp mills with direct contact evaporators. As TRS emissions limits become more restrictive, it may be impossible for recovery boilers with direct contact evaporators to meet those limits. The conventional method of overcoming this problem is a low odor conversion: replace the direct contact evaporator with a high solids concentrator and install an economizer on the recovery boiler. Low odor conversion is expensive, costing in the range of $7000-$9,000 per daily ton of pulp production supported by the recovery boiler.

By comparison, a black liquor oxidation polisher employing controlled cavitation is a low capital cost alternative. Table II shows the annual oxygen and electrical energy requirements and costs to operate a black liquor oxidation polisher with controlled cavitation, to process 50% solids content black liquor in a 1500 ODT/day kraft pulp mill.

TABLE II: ANNUAL OXYGEN AND ELECTRICAL ENERGY REQUIREMENTS FOR A BLACK LIQUOR OXIDATION POLISHER WITH CONTROLLED CAVITATION TO ACHIEVE ZERO RESIDUAL SULFIDE CONCENTRATION.

Low Odor Conversion	Investment	Annual cost
Installed cost of capital equipment	$12,000	
Cost of lost pulp production	$9,100	
Total Year 1 investment	$21,100	
Annual maintenance cost		$600
Annual power cost		$40
Total annual operating cost		$640
Black Liquor Oxidation Polisher		
Installed cost of capital equipment	$1,300	
Cost of lost pulp production	$0	
Total Year 1 investment	$1,300	
Annual maintenance cost		$65
Annual oxygen costs		$38
Annual power costs		$351
Total annual operating cost		$454
Savings	$19,800	$186

$ in 000's

BASIS: 50% SOLIDS CONTENT BLACK LIQUOR, 1500 ODT/DAY KRAFT PULP MILL.

According to Table II, a controlled cavitation black liquor polisher costs 19.8 million dollars less in capital than a low odor conversion, as well as $189,000 less in annual operating expenses.

Extended black liquor oxidation to increase recovery boiler capacity: Many recovery boilers are limited by thermal load in their capacity to support additional pulp production. One way to increase the pulp production capacity supported by recovery boiler is to reduce the gross heating value of the black liquor. Extended black liquor oxidation is a low capital cost method of reducing the heating value of the black liquor.

In this study, the gross heating value of the black liquor was reduced by 470 kJ/kg BL solids (200 Btu/lb BL solids). This 5-7% decrease in the gross heating value of black liquor solids (based upon an initial Na_2S concentration of 29 g/L) would translate directly into a 5-7% increase in pulp production capacity supported by the recovery boiler. Table III shows the annual oxygen and electrical energy requirements and costs to operate a black liquor extended oxidizer with controlled cavitation on 50% solids content black liquor for a 1500 ODT/day kraft pulp mill. The production increase could reach as high as 8 percent based on a higher initial Na_2S concentration.

TABLE III: ANNUAL OXYGEN AND ELECTRICAL ENERGY REQUIREMENTS FOR EXTENDED OXIDIZATION OF BLACK LIQUOR WITH CONTROLLED CAVITATION TO INCREASE RECOVERY BOILER CAPACITY.

Black liquor GHV		6036 Btu/lb BLS	
GHV of organic		5887 Btu/lb BLS	
Decrease in GHV of organic matter		0.47 MJ/kg BLS (203) Btu/lb	
O_2 applied	$0.044 - $0.09/kg	4444 kg/hr	$1,600 - $3,200* /year
Electrical Power	$0.02 - $0.044/kWh	3700 kWh	$600 - $1,300 /year
Mill production		1500 ODT/day	
Increase in pulp capacity 5 - 7%		75 - 105 ODT/day	
Value of increased pulp capacity		$5,000 - $7,000 /year	
Annual Operating Cost		$2,200 - $4,600 /year	

$ in 000's

** Includes $750.00 / month facility fee for delivered oxygen*

BASIS: 50% SOLIDS CONTENT BLACK LIQUOR, 1500 ODT/DAY KRAFT PULP MILL.

As stated before, the gross heating value of the black liquor was reduced by 470 kJ/kg BL solids (200 Btu/lb BL solids). This 5-7% (based upon an initial Na_2S concentration of 29 g/L) decrease in the gross heating value of black liquor solids would translate directly into a 5-7% increase in pulp production capacity supported by the recovery boiler. However, this is based upon total oxidation of black liquor. It was determined that the largest decrease in GHV (~70%) occurs using controlled cavitation for partial black liquor oxidation, where oxidation efficiencies are extremely high. Table IV shows the annual oxygen and electrical energy requirements and costs to operate a partial black liquor oxidizer with controlled cavitation on 50% solids content black liquor for a 1500 ODT/day kraft pulp mill. This maximizes the reduction in GHV without the expense of fully oxidizing black liquor.

TABLE IV: ANNUAL OXYGEN AND ELECTRICAL ENERGY REQUIREMENTS FOR PARTIAL OXIDIZATION OF BLACK LIQUOR WITH CONTROLLED CAVITATION TO INCREASE RECOVERY BOILER CAPACITY.

Black liquor GHV		6036 Btu/lb BLS	
GHV of organic		5887 Btu/lb BLS	
O_2 applied	$0.044 - $0.09/kg	1034 kg/hr	$370 - $760* /year
Electrical Power	$0.02 - $0.044/kWh	1850 kWh	$300 - $660 /year
Mill production		1500 ODT/day	
Increase in pulp capacity 3.5 - 5%		52.5 - 75 ODT/day	
Value of increased pulp capacity		$3,500 - $5,000 /year	
Annual Operating Cost		$670 - $1,400 /year	

$ in 000's

** Includes $750.00 / month facility fee for delivered oxygen*

BASIS: 50% SOLIDS CONTENT BLACK LIQUOR, 1500 ODT/DAY KRAFT PULP MILL.

Heating of high solids/ scaling black liquors: Controlled cavitation is an effective way to heat black liquor at high solids content and/or black liquors with a propensity to deposit scale on heat exchanger surfaces. The advantages of controlled cavitation are that black liquor is heated by dissipation of mechanical energy within the bulk liquor, not by transfer of heat from a hot surface. For high solids content (high viscosity) black liquors, the rate of heat transfer is not limited by a film heat transfer coefficient that decreases as viscosity increases. For black liquors with a propensity to deposit scale on heat transfer surfaces, it means no heat transfer scaling problems because there are no heat transfer surfaces to scale. Specific applications of controlled cavitation for heating would include: preheating of high solids content black liquor prior to a high solids concentrator effect to eliminate preheater fouling; post-concentrator evaporation of black liquor by heating with controlled cavitation and flashing; heating of as-fired black liquor to firing conditions (replacing conventional heat exchangers); and a simplified thermal deactivation process, replacing the heat exchanger and recycle loop with controlled cavitation heating.

Table V compares the energy and cleaning requirements for controlled cavitation heating of black liquor by 15°C (e.g. from 120 to 135°C) with those for a conventional heat exchanger. The increase in solids content achievable by heating black liquor at 80% total solids content and flashing to the initial temperature is 1.4% (to 81.4%).

TABLE V: ENERGY AND CLEANING REQUIREMENTS FOR CONTROLLED CAVITATION HEATING OF BLACK LIQUOR BY 15°C VS. THOSE OF A CONVENTIONAL HEAT EXCHANGER.

Heat exchanger	Controlled Cavitation	Conventional
Mill production	1500 ODT/day	1500 ODT/day
Electrical power, kW	1316	6.4
Annual power cost	$471	$2.30
Steam use, kg/hr	0	1900
Annual steam cost	$0	$104
Weekly cleanings	0	0.5 - 2
Annual cleaning cost	$0	$50k - $100k
Solids content with controlled cavitation heating plus flash @ 80% solids content feed	81.40%	
Production Increase	5 – 10%	
Value of production increase	$15 - $30 /day	
Annual production value	$5400 – $10,100 /year	

$ in 000's

BASIS: 80% SOLIDS CONTENT BLACK LIQUOR, 1500 ODT/DAY KRAFT PULP MILL.

CONCLUSIONS

Controlled cavitation was found to be effective in improving black liquor oxidation efficiency. Sulfide in black liquor oxidized very rapidly with the level of micromixing that was produced by the controlled cavitation device, using either elemental oxygen or air. Residual sulfide concentrations below the detection limit were attained. Oxygen was consumed completely until all of the sulfide had been oxidized. The selectivity of oxygen for sulfide oxidation when controlled cavitation is employed was double the selectivity without controlled cavitation. The heating value of the black liquor was decreased by 7 percent (based upon an initial Na_2S concentration of 29 g/L) at the point when sulfide had been oxidized completely. The production increase could reach up to 8 percent based on initial Na_2S concentration (Tables III and IV).

Controlled cavitation is also an effective way to heat high viscosity black liquor. Fouling of heat transfer surfaces is avoided because heating by controlled cavitation requires no heat transfer surfaces. The decrease or elimination of scaling in the evaporators using the controlled cavitation device could increase mill production by up to 10% (Table V).

A logical application of the controlled cavitation device in the recovery area of a kraft pulp mill is to decrease TRS below the detection limit as an alternative to low odor conversion: installing a high solids concentrator and economizer for mills with direct contact evaporators (Table II). Additionally, the controlled cavitation device can be used to increase the pulp tonnage supported by a recovery boiler by efficiently decreasing the heating value of the black liquor via controlled cavitation. This application could increase mill production by as much as 8 percent (Tables III and IV). The controlled cavitation device could also be utilized for scale free heating of black liquor or concentrating high solids content black liquor. By decreasing downtime, scale-free heating or concentration can increase mill production by up to 10% (Table V).

The controlled cavitation device can be characterized as a breakthrough technology with the potential to achieve quantum improvements in certain pulp and paper operations.