CALCIUM BASED SULFUR RECOVERY PROCESS FOR KRAFT BLACK LIQUOR GASIFICATION - PROOF OF CONCEPT

Christopher L. Verrill, Post Graduate Fellow* Adriaan R. P. van Heiningen, Professor**
Dr. Jack McKenzie Limerick Pulp and Paper Research and Education Centre
University of New Brunswick, Fredericton, New Brunswick, Canada E3B 6C2
* Now a Research Chemical Engineer with Westvaco Corp., Charleston, South Carolina 29423
** Now the Ober Chair of Chemical Engineering at the University of Maine, Orono, Maine 04469

ABSTRACT

This paper describes a novel process for use in black liquor gasification systems to recover sulfur from the product gas by reaction with lime. A sulfur-rich white liquor stream is produced by reaction of the resulting calcium sulfide with sodium hydroxide. Equilibrium calculations suggest that industrial feasible conditions will result in a concentrated solution of NaHS and NaOH with insignificant byproduct formation. Bench-scale experiments were conducted to investigate the sulfur removal and conversion operations. Eighty-percent conversion of CaS to NaHS was achieved in 60 minutes at 95°C with 100 g/L initial NaOH concentration. Complete conversion was attained within 240 minutes at 90-95°C with 50-100 g/L alkali. Only trace amounts of oxidized sulfur species were detected by ion chromatography. Industrial lime samples of 79 to 595 μm were reacted with H_2S to form 62-69% CaS, compared with the commercial 99.2% pure CaS powder (sub-44 μm) used in most of the experiments. Conversion of the industrial lime was as good or better than the commercial CaS; suggesting the proposed sulfur recovery process will operate well with bed material from a fluidized, product gas desulfurizer.

INTRODUCTION

Recovery of chemicals and energy from kraft black liquor is currently accomplished with the recovery boiler and recausticization plant. While commercially proven, these technologies present a number of problems. Inadvertent contact of boiler water and molten smelt has resulted in serious explosions. The corrosive environment in the recovery boiler limits maximum steam temperature and pressure. Efficiency of electrical generation is limited by the steam turbine thermodynamic cycle. The calcining operation is the most energy intensive process in the pulp mill. The sodium and sulfur balance is also difficult to control with the present technology.

Black liquor gasification (BLG) is a partial combustion process in which the organic compounds are converted into fuel gases. If the system is pressurized, and the fuel gas burned in a gas turbine, gasification can provide more efficient utilization of the black liquor fuel value, and produce more electrical power than recovery boiler technology [1, 2]. This is an attractive feature for future pulp and paper mills where higher on-site electrical generation will be desired to operate mechanical pulping and pollution control equipment. Moreover, most BLG concepts avoid the risk of smelt-water explosions. BLG is currently envisioned as the full-scale kraft recovery technology of choice for the next century [3].

In all BLG processes, some of the sulfur content of the black liquor ends up as hydrogen sulfide (H_2S) and other reduced sulfur compounds in the product gas. Most of the sodium and the remaining sulfur leave the gasifier as molten smelt, or as dry solids in the case of fluidized bed processes. The smelt contains mostly sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S); these chemicals are easily recovered by dissolution in process water streams. Separate recovery of sulfur and sodium facilitate control of white liquor composition. This may become a significant attribute of BLG in future kraft pulp mills [4].
Various processes have been proposed to recover H_2S from the product gas by absorption in alkaline process streams. However, there is an inherent difficulty in these sulfur recovery schemes because the

carbon dioxide is also subject to absorption. For example, when using a solution containing Na_2CO_3, carbon dioxide is removed by the reaction:

$$Na_2CO_3 + H_2O + CO_2 \leftrightarrow 2\ NaHCO_3 \quad \textbf{(1)}$$

Sodium bicarbonate, $NaHCO_3$, presents a potential problem because it increases the lime requirement relative to Na_2CO_3 as can be inferred from the stoichiometry of the relevant causticizing reactions:

$$2\ NaHCO_3 + 2\ Ca(OH)_2 \leftrightarrow 2\ CaCO_3 \downarrow + 2\ NaOH + H_2O \quad \textbf{(2)}$$

$$Na_2CO_3 + Ca(OH)_2 \leftrightarrow CaCO_3 \downarrow + 2\ NaOH \quad \textbf{(3)}$$

Carbon dioxide coabsorption therefore increases the lime requirement in the causticizing process, which, at a minimum, would require additional heat input to calcine the lime mud, $CaCO_3$, or in the event of calcining capacity limitations, require significant equipment upgrades.

A potential solution to this problem is gasification of the black liquor in the presence of certain amphoteric metal oxides. These metal oxides form double salts with sodium that prevent the formation of Na_2CO_3. Sodium hydroxide can then be regenerated by hydrolysis of the sodium-metal double salt and the inorganic residue is recycled to the gasifier. One such "direct causticizing" process using iron oxides has been proven at commercial scale for a sulfur-free soda liquor [5].

Research at McGill University [6, 7] and the University of New Brunswick [8] has shown that titanium oxides work well for sodium recovery in fluidized-bed gasification of kraft black liquor. However, the conditions of gasification result in significant sulfur volatilization as H_2S. While lime demand can be reduced by the addition of titanium to the BLG process, alkaline scrubbing of the H_2S from the product gas will absorb CO_2 and still require causticizing to regenerate white liquor. A number of industrial sorbents have been developed for removal of H_2S from reducing gas streams [9, 10]. In these processes, the sulfided sorbent is normally considered a hazardous waste material and must be oxidized or otherwise chemically altered before regeneration or disposal can occur [11, 12]. Obviously, this is not an option in the present case, since the goal of recovery is to regenerate white liquor. Therefore, the objective of the present work was to remove and recover sulfur as Na_2S, the desired form for the kraft pulping process.

SULFUR RECOVERY FOR BLACK LIQUOR GASIFICATION

Fig. 1 illustrates integration of the sulfur recovery process with a direct causticizing kraft black liquor gasifier. The main pieces of equipment are the black liquor gasifier, the hydrolysis reactor, the raw gas desulfurizer, and the sulfur conversion reactor. The focus of this paper is on the lime-based sulfur recovery process. Black liquor gasification with direct causticizing is described in detail elsewhere [8].

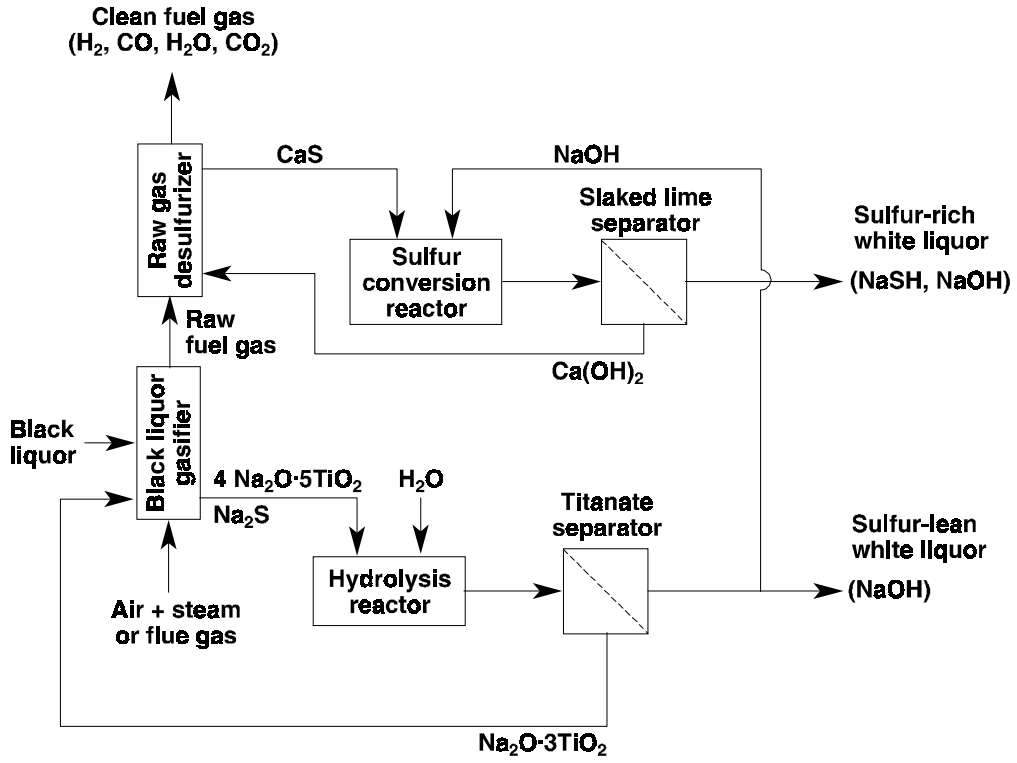

Fig. 1. Schematic of sulfur recovery process integrated with kraft black liquor gasification with direct causticization.

Reduced sulfur gases can be removed from the hot gasifier product gas by dry scrubbing with lime in a fluidized bed reactor. As discussed below, the primary product of this reaction is calcium sulfide (CaS), regardless of which form of calcium is used as sorbent. Equilibrium calculations indicate the effective capture of H_2S by lime at industrially feasible conditions of temperature and pressure. The solid phase at these conditions is nearly pure CaS.

Calcium sulfide is separated from the fuel gas stream and conveyed to a stirred-tank reactor. The reaction between NaOH, formed by hydrolysis of sodium titanates, and solid CaS produces aqueous Na_2S and precipitates sparingly soluble $Ca(OH)_2$:

$$CaS\ (s) + 2\ NaOH \rightarrow Ca(OH)_2 \downarrow + Na_2S \qquad \textbf{(4)}$$

The sulfur-rich liquor is separated from the hydrated lime and can be blended with the sulfur-lean stream from the hydrolysis reactor and fresh water to produce white liquors of varied sulfidity and total alkali concentration. Hydrated lime solids would be washed with fresh NaOH and/or water to increase conversion of CaS and/or to remove soluble Na_2S and NaOH. An indirect heater may be used to dry the $Ca(OH)_2$ before returning it to the raw gas desulfurizer. Steam blanketing may be required to protect the hydrated lime from carbonization by reaction with CO_2 in air.

This calcium-based sulfur recovery process can also operate in other configurations, with or without black liquor gasification as well as direct causticization, the only requirement being that NaOH is made available, for example by an existing lime cycle (**Fig. 2**).

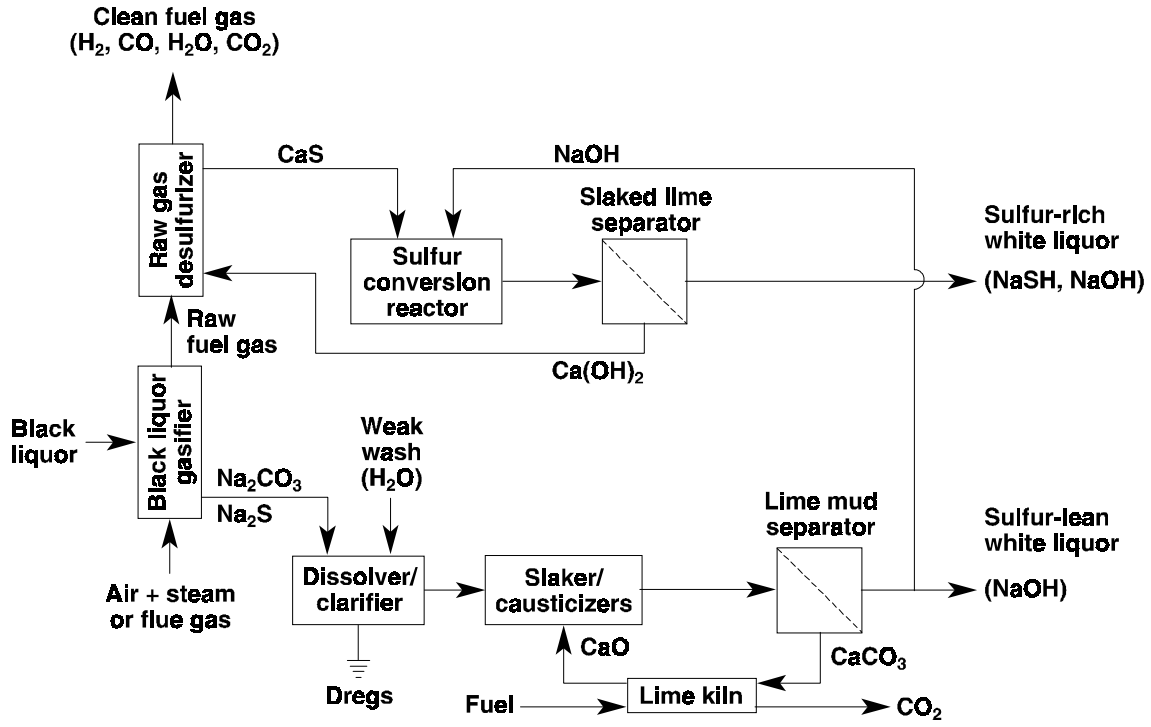

Fig. 2. Schematic of sulfur recovery process integrated with kraft black liquor gasification with conventional recausticization.

Equilibrium Analysis of Raw Gas Desulfurization

A parametric equilibrium analysis of the desulfurization reaction was conducted using the product gas from BLG in the presence of TiO_2 [13]. The equilibrium raw fuel gas contained nearly 1% vol. reduced sulfur gases. In the absence of molecular oxygen, CaS is the thermodynamically favored product of desulfurization by all forms of lime:

$$CaO\ (s) + H_2S \leftrightarrow CaS\ (s) + H_2O \quad \textbf{(5)}$$

$$Ca(OH)_2\ (s) + H_2S \leftrightarrow CaS\ (s) + 2\ H_2O \quad \textbf{(6)}$$

$$CaCO_3\ (s) + H_2S \leftrightarrow CaS\ (s) + H_2O + CO_2 \quad \textbf{(7)}$$

Which of the three forms of lime will exist depends on the conditions in the desulfurizer.

A maximum desulfurization of 99.3% is obtained at approximately 750°C, atmospheric pressure, and 15% molar excess Ca. This condition results in 64 ppm H_2S and less than 3 ppm carbonyl sulfide (COS) in the outlet gas and a solid product of 90% CaS (**Fig. 3**). At 20 atmospheres, a maximum desulfurization is obtained at about 900°C. No liquid products were predicted over the wide range of conditions investigated. A liquid phase would indicate potential difficulty in maintaining a fluidized bed of lime particles.

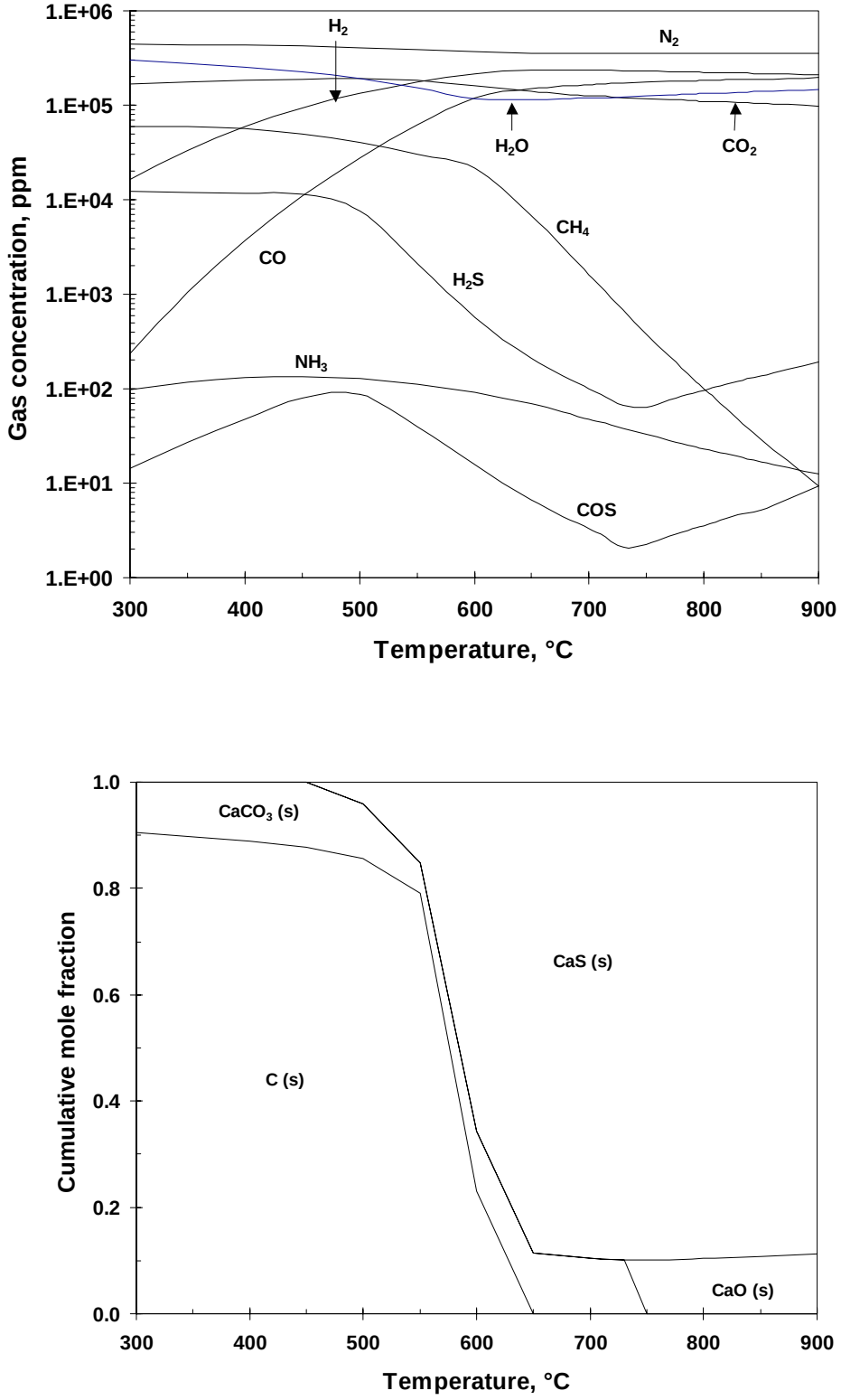

Fig. 3. Equilibrium predictions for raw gas desulfurizer as a function of temperature at 1 atm and a Ca/S molar ratio of 1.15: gas phase - top; condensed phase - bottom (from Zeng et al., [13]).

These equilibrium results suggest that, for industrially practical gasifier operating conditions (800-1000°C, 1-20 atm), a thermally-coupled fluidized bed of lime can be used for desulfurization. Operating the fluidized bed sulfidation reactor above the calcining temperature can control $CaCO_3$ build-up in the system. This temperature ranges from 700-950°C, depending primarily on CO_2 partial pressure [13].

Equilibrium Analysis of Calcium Sulfide Conversion

Reaction 4 is unlikely to proceed as written because the solubility of calcium sulfide is less than that of the hydroxide; however, CaS does react with water to form the soluble hydrosulfide:

$$2\ CaS\ (s) + 2\ H_2O \rightarrow Ca(OH)_2 \downarrow + Ca(SH)_2 \qquad \textbf{(8)}$$

The calcium hydrosulfide can then react with sodium hydroxide to form sodium hydrosulfide (NaHS), which exists in equilibrium with Na_2S:

$$Ca(SH)_2 + 2\ NaOH \rightarrow Ca(OH)_2 \downarrow + 2\ NaHS \qquad \textbf{(9)}$$

$$Na_2S + H_2O \leftrightarrow NaHS + NaOH \qquad \textbf{(10)}$$

Equilibrium calculations indicate that nearly complete conversion of CaS to Na_2S can be achieved in a strongly alkaline solution. Because the solubility of calcium hydroxide decreases with increasing temperature, CaS conversion is favored at higher temperature (**Fig. 4**). As long as the reaction mixture is maintained at a high pH by excess alkali, and contact with oxygen and CO_2 is avoided, byproduct formation is unlikely as indicated by the equilibrium results in Fig. 4, and borne out by the experimental findings given below.

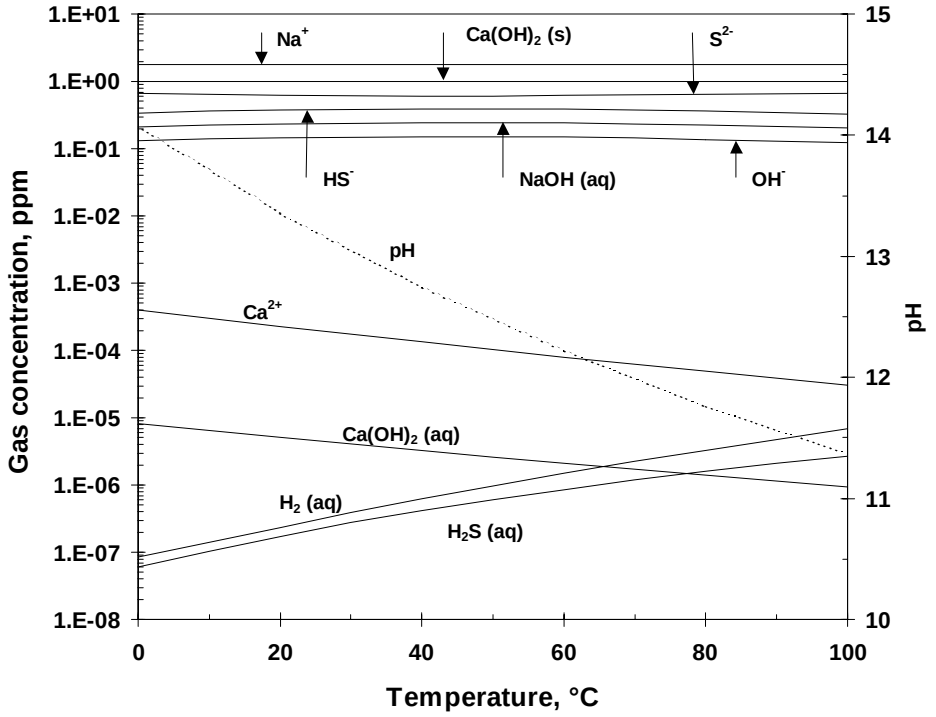

Fig. 4. Equilibrium prediction of aqueous CaS conversion reaction product composition and pH as a function of temperature for 1 atm and initial Na/Ca molar ratio of 2.0. (from Zeng et al., [13]).

EXPERIMENTAL

Experiments were performed to investigate the conversion of CaS to Na_2S using both NaOH and Na_2CO_3 as alkali reactants. The effects of temperature, alkali concentration, and sodium-sulfur molar ratio (Na/S) were investigated. Most experiments in this study were performed at 50-200 g/L initial alkali concentration with commercially available CaS (Johnson-Matthey). Additional experiments were conducted to investigate sulfur conversion with sulfided industrial lime samples (runs 33-35 in **Table I**).

In each experiment, weighed amounts of NaOH or Na_2CO_3 were added to a 250 ml three-necked reactor flask. Approximately 160 ml of purified and degassed water was added and the weight of the flask and contents was recorded. The flask was fitted with a reflux condenser and a thermometer, and heated by an electric mantle. When the solution reached the desired temperature, two 1.00 ml aliquots were taken and titrated with standardized HCl solution. Based on the initial alkali charge, the amount of CaS required for the desired Na/S ratio in the reaction mixture was calculated. The approximate amount of CaS powder was transferred to a covered weighing dish in a nitrogen-purged glove box. The conversion reaction was initiated by rapid addition of the CaS to the alkali solution, followed by addition of 25 ml hot solution that was pipetted from the reaction flask to wash down any CaS powder adhering to the funnel. The exact amount of CaS added was determined by difference of the initial and final weights of the weighing dish. The initial concentration of sodium and charge of CaS were controlled within 5% of the target values for most of the experimental runs listed in Table I.

The reaction mixture was stirred magnetically and continuously sparged with 1.00 L/min oxygen-free nitrogen. The reaction was continued for four hours with samples taken every hour for analysis. Each sample was forced through a 0.45 μm nylon filter to remove all particles. NaOH and Na_2S concentrations of the samples were measured by acidimetric titration with a standardized HCl solution. This titration, known as the ABC procedure, is commonly employed for industrial determination of the strength of green and white liquors [14]. **Fig. 5** shows how the species concentrations changed with reaction time for a typical experiment. The molar conversion of CaS at each reaction time was calculated as moles of sulfide in solution divided by initial number of moles of CaS charged to the reactor. Sulfide was determined from the Na_2S concentration by ABC titration, multiplied by the reaction volume at the time of sampling. The reaction volume was estimated from the initial amount of water charged, corrected to the reaction temperature, and the total volume of samples taken.

Table I. Summary of experimental conditions in CaS conversion experiments.

Run #	Target initial NaOH, g/L	Actual initial NaOH, g/L	% diff. actual from target	Target temp., °C	Actual average temp., °C	Target initial Na/S, mol/mol	Actual initial Na/S, mol/mol	% diff. actual from target
10	50	51.8	3.5	80	80	2.10	2.17	3.3
19	50	50.4	0.9	80	80	2.10	2.15	2.4
8	50	49.9	-0.2	90	90	2.10	2.35	11.9
15	50	50.8	1.5	90	89	2.10	2.21	5.2
32 [b]	50	48.4	-3.2	90	88	2.50	2.56	2.4
9	50	51.9	3.8	95	95	2.10	2.18	3.8
18	50	51.5	3.0	95	96	2.10	2.21	5.2
33 [c]	50	49.4	-1.2	90	90	2.50	2.59	3.6
34 [d]	50	47.6	-4.8	90	89	2.50	2.16	-13.6
35 [e]	50	46.8	-6.4	90	90	2.50	2.40	-4.0
13	100	104.3	4.3	80	77	2.10	2.13	1.4
20	100	101.1	1.1	80	79	2.10	2.14	1.9
11	100	91.0	-9.0	90	89	2.10	2.12	1.0
12	100	97.2	-2.8	95	93	2.10	2.07	-1.4
16	100	102.8	2.8	95	94	2.50	2.57	2.8
17	100	102.2	2.2	95	96	2.10	2.12	1.0
25 [a]	100	97.3	-2.7	80	80	2.10	2.20	4.6
23 [a]	100	91.2	-8.9	90	90	2.10	2.14	1.9
26 [a]	100	96.5	-3.5	90	90	2.10	2.18	4.0
24 [a]	100	91.5	-8.5	95	95	2.10	2.09	-0.4
21	200	194.3	-2.8	80	80	2.10	2.06	-1.9
14	200	195.2	-2.4	90	89	2.10	2.06	-1.9
31 [b]	200	200.9	0.4	90	91	2.10	2.10	0.0
22	200	199.4	-0.3	95	96	2.10	2.08	-1.0

[a] Runs 23-26 Na_2CO_3 used as reagent, all other runs with NaOH.
[b] Runs 31-32 commercial CaS lot #2, runs 8-28 CaS lot #1.
[c] Run 33 CaS from 74-149 μm sulfided lime sample produced at UNB.
[d] Run 34 CaS from 149-297 μm sulfided lime sample produced at UNB.
[e] Run 35 CaS from 297-595 μm sulfided lime sample produced at UNB.

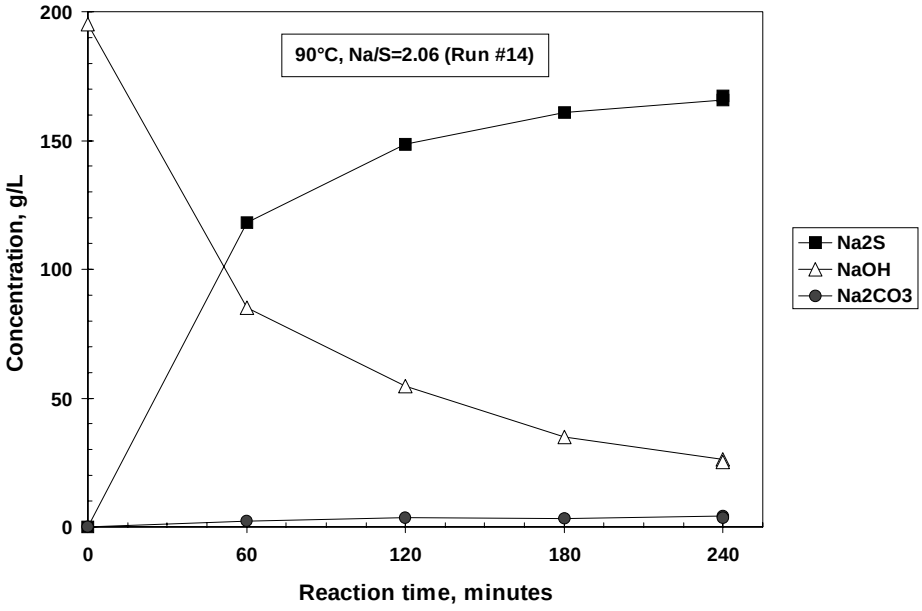

Fig. 5. Typical change in alkali species concentrations during sulfur conversion reaction, determined from ABC titration procedure.

Determination of Na_2S by the ABC procedure was compared with a $HgCl_2$ titration using an $S_2^{=}$ ion selective electrode (ISE), the latter procedure given by Papp [15]. Comparison of these results in **Fig. 6** indicates good agreement over the concentration range from 15-40 g/L Na_2S, and confirmed that the simpler acidimetric titration could be employed to monitor sulfur conversion during the experiments.

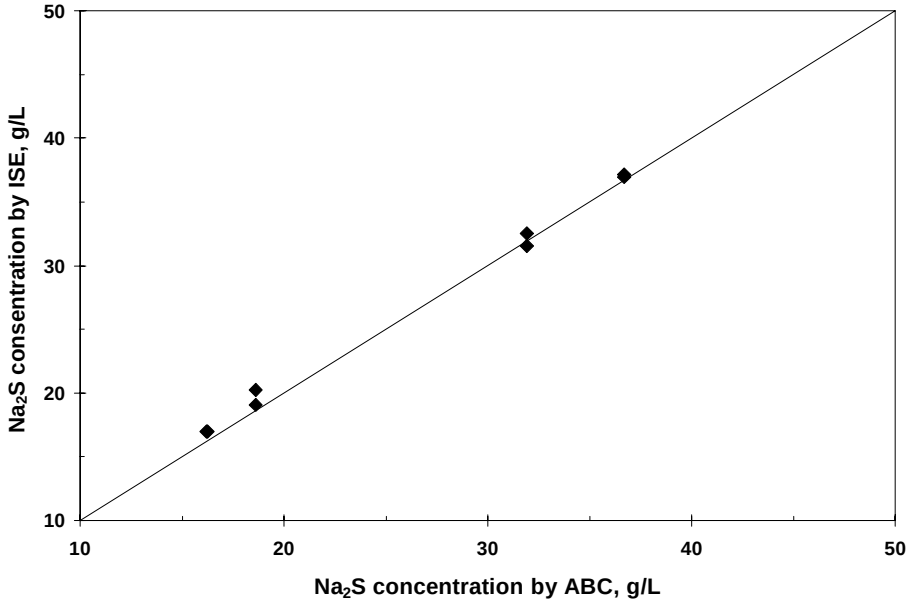

Fig. 6. Comparison of Na_2S determined by two methods.

In three runs, diluted samples of the supernatant product solution were analyzed by ion chromatography (IC) to determine the amount of sulfur in the form of sulfite ($SO_3^=$), sulfate ($SO_4^=$), and thiosulfate ($S_2O_3^=$) [16]. Corresponding samples were oxidized with hydrogen peroxide to convert all sulfur species to sulfate, and allow total sulfur determination by IC [17]. A Dionex Model DX 300 ion chromatograph with AS4A Ion Pac^R separation column and 2.00 ml/min of 1.806 mM Na_2CO_3 and 1.704 mM $NaHCO_3$ eluent was used. The sulfur ion concentrations were determined with a pulsed electrochemical detector, operated in the conductivity mode. Stock calibration solutions were prepared using analytical reagent grade Na_2SO_3, Na_2SO_4, and $Na_2S_2O_3$. Standard dilutions of each species were prepared from the stock solution on a weekly basis. Standards were run daily to establish a calibration curve before analyzing the samples. Each unknown sample was injected through 0.22 or 0.45 μm filters.

The above analysis results show 88.1-91.3% of total sulfur in filtrate accounted for as $S^=$ by ABC titration, with only small concentrations of all three oxidized sulfur compounds (**Table II**). The oxidized sulfur ions amount to less than 1.6 % of the total sulfur measured in the fully oxidized reaction product. The formation of polysulfide or other sulfur-oxygen compounds, such as di- or tri-thionates, or a systematic error between the ABC and IC procedures could account for the difference of approximately 8-10%. Note that sulfide determination by IC was not attempted due to extensive dilution required for detection and the high likelihood of oxidation of both sample and standards in solution. Results of these sulfur species measurements demonstrate that minimal oxidation occurred during the experiments.

Table II. Forms of sulfur in CaS conversion reaction product.

Run	Units	Total S by IC	$S^=$ by ABC	$SO_3^=$ by IC	$SO_4^=$ by IC	$S_2O_3^=$ by IC
7	mmol S/L	562.7	496.0	3.56	1.40	4.14
	% total S	-	88.2	0.63	0.25	0.74
8	mmol S/L	553.0	501.3	1.11	0.94	1.47
	% total S	-	90.7	0.20	0.17	0.27
9	mmol S/L	617.5	564.0	1.03	1.04	1.70
	% total S	-	91.3	0.17	0.17	0.28

After four hours, filtering the insoluble lime mud from the aqueous product stopped the reaction. The filtrate was diluted with degassed water and the lime mud was returned to the three-necked flask fitted with a dropping funnel and N_2 purge line. Concentrated HCl was slowly added to decompose the lime mud. The evolving gases passed through a gas-washing bottle containing a 1.0 N NaOH scrubbing solution to capture H_2S. The decomposition was continued for several hours to ensure complete removal of sulfur from the lime mud. Samples were taken from the diluted filtrate, the scrubbing solution, and the decomposition residue; all were then fully oxidized with hydrogen peroxide [17]. The sulfate content of all oxidized samples was then determined by the IC procedure described above [16].

Sulfur balance closure was determined as the sum of the total number of moles of sulfur in the filtrate, scrubbing solution, and decomposition residue by IC as a percentage of the number of moles of sulfur present in the solution at the end of the reaction, as determined by the ABC titration method. Closure falls between 92.7 and 104.1% for all cases with 50-200 g/L initial alkali concentration and commercially prepared CaS (**Fig. 7**). This result confirms that, with 50-200 g/L alkali as reagent, sulfur measured by the ABC titration was in the form of hydrosulfide ions, and that the product of the proposed conversion reaction is a strong solution of NaHS.

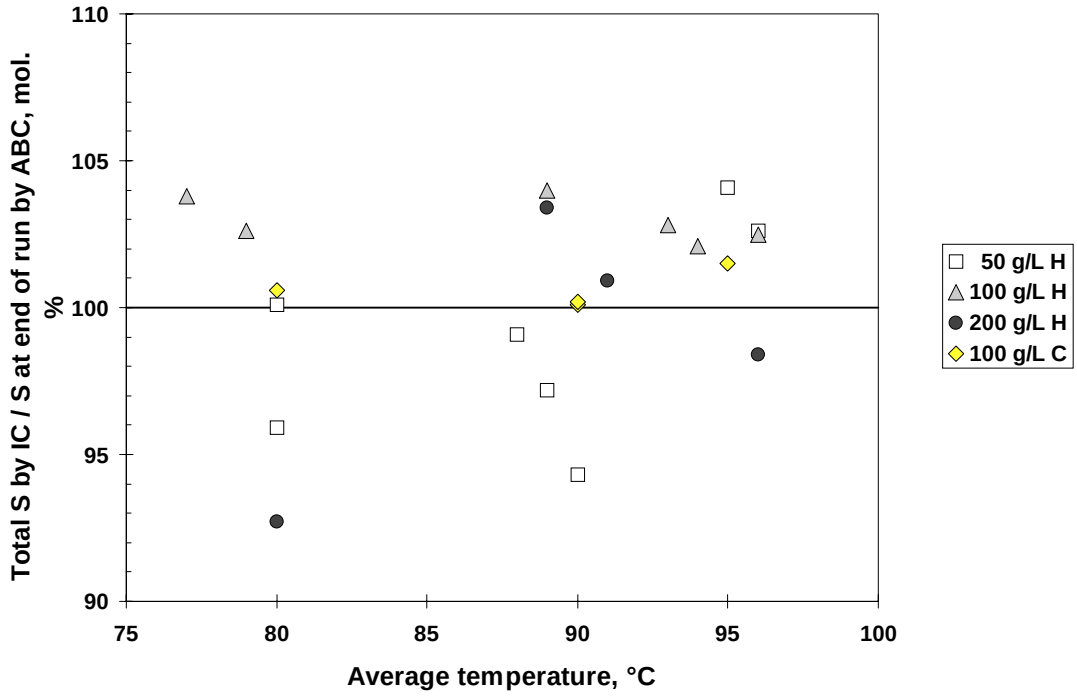

Fig. 7. Sulfur balance closure for all runs with commercial CaS and 50-200 g/L initial alkali concentration.

In runs 33-35, CaS was formed by reaction of H_2S with lime from a Canadian kraft pulp mill. The industrial lime sample was first sieved into three size fractions: 74-149 μm, 149-297 μm, and 297-595 μm. Batches of lime were loaded into alumina boats and heated to 900°C in a quartz tube furnace under a fast stream of nitrogen. After drying, the lime samples were exposed to a gas mixture containing 2.0% by volume H_2S and 3.7% H_2 for 240 minutes. Each batch was stirred once during sulfidation. The samples were cooled and stored under nitrogen. Based on recommended methods [18-20], we developed the following iodometric analysis method for determining the sulfide content of CaS. 50.00 ml of a 0.100 N iodine solution was pipetted into an Erlenmeyer flask. The solution was diluted with 150 ml of water and acidified with 20 ml of 1 N HCl. Approximately 0.1 g of CaS was accurately weighed and transferred to the flask. The flask was stoppered and stirred for 30 minutes. The mixture was then buffered with excess sodium bicarbonate (about 11 g). The contents was then titrated with a standard As_2O_3 solution. The titration was continued until the mixture was a straw yellow color, at which point 2 ml of starch indicator was added. The titration was continued until the blue-purple color was just destroyed.

The yield of CaS in the sulfided lime samples was found to be 62.3% for the smallest particle size fraction, 64.1% for the intermediate fraction, and 69.0% for the largest fraction. With these values, the sulfur conversion after four hours of reaction was calculated to be 107-113%. All calculated conversions using commercial CaS never exceeded 105%, suggesting that the iodometric analysis may have been in error. As a check, the commercial powder was analyzed and yielded 92.6% CaS or 6.7% lower than the guaranteed assay of the reagent (99.2% CaS). When calculated conversions for the sulfided lime samples were adjusted by systematically increasing the CaS assay by 6.7%, then the final conversion fell between 99 and 105%, in accordance with the other experiments.

RESULTS AND DISCUSSION

Seven preliminary experiments were performed for which the initial concentration of NaOH ranged from 42.1 to 45.2 g/L and the Na/S molar feed ratio from 1.7 to 3.1. The results in **Fig. 8** show a dramatic increase in the reaction rate between 60 and 80°C. The explanation for this behavior is that, unlike most compounds, slaked lime has a lower solubility at higher temperatures. Therefore, the driving force for the conversion reactions (Eqs. 8-10) increases with temperature. Based on these initial results, the remaining experiments were conducted at 80-95°C, which are feasible temperatures for liquor processing equipment.

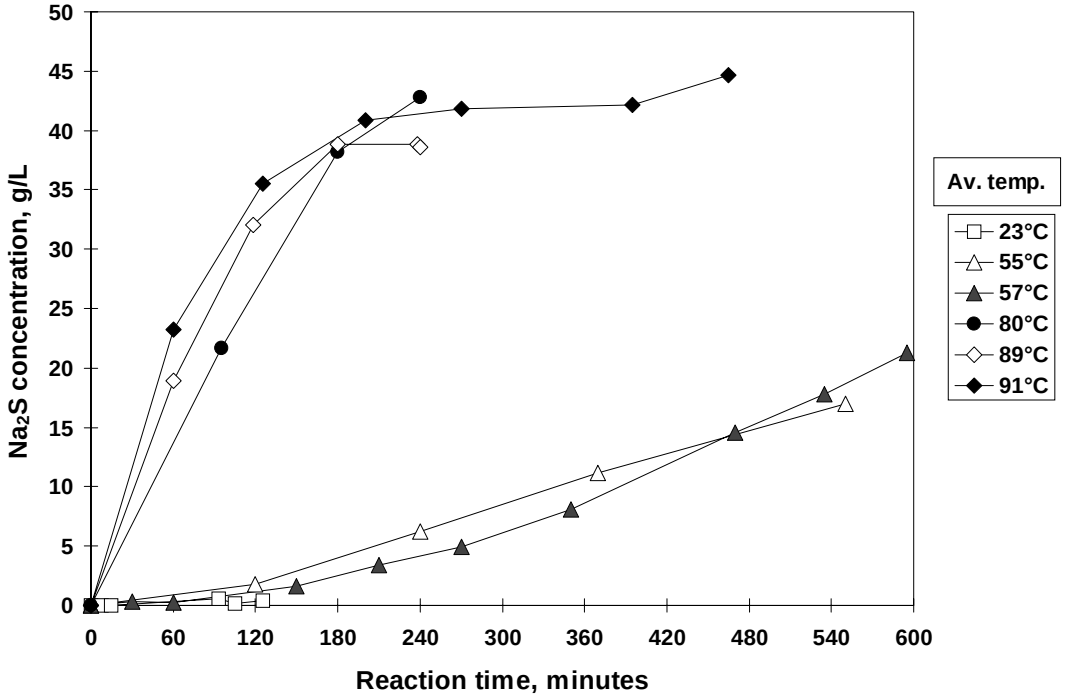

Fig. 8. Na_2S concentration as a function of reaction time and temperature at 42-45 g/L initial NaOH concentration.

Results plotted in **Fig. 9** show that increasing temperature from 80 to 95°C increased the initial rate of reaction when commercial CaS was reacted with 50 g/L NaOH. After four hours, the sulfur conversion was essentially complete at the higher temperatures, but required an additional two hours at 80°C. There was no significant effect of initial Na/S mole ratio, which ranged from 2.15 to 2.56 (Table I), because sodium hydroxide was in excess for all runs. The effect of temperature was similar at 100 g/L NaOH, as can be seen in **Fig. 10**. The higher alkali strength did result in a 30% higher initial reaction rate.

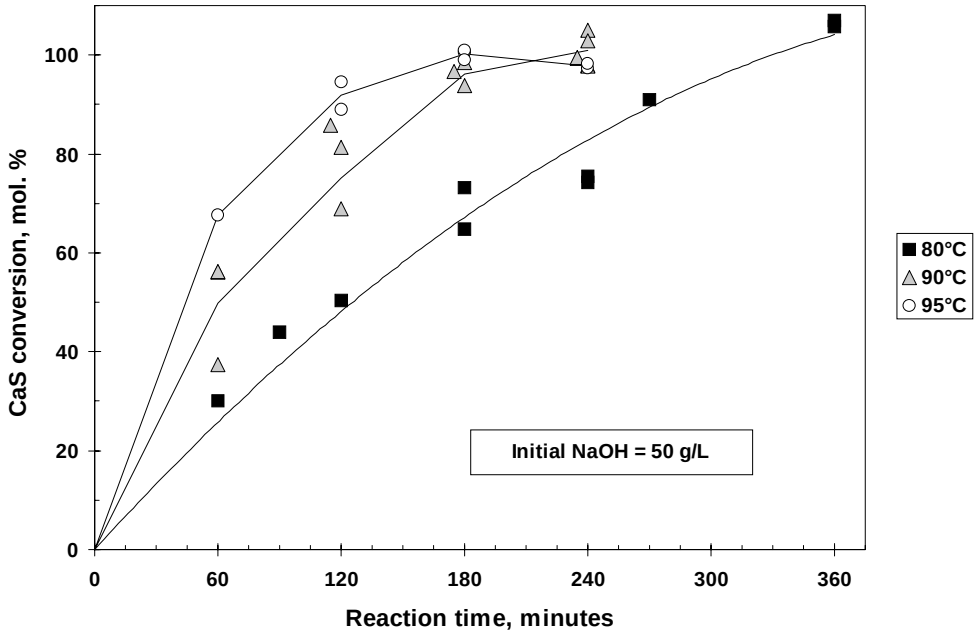

Fig. 9. Molar conversion of CaS to Na_2S as a function of time and temperature for 50 g/L initial NaOH concentration.

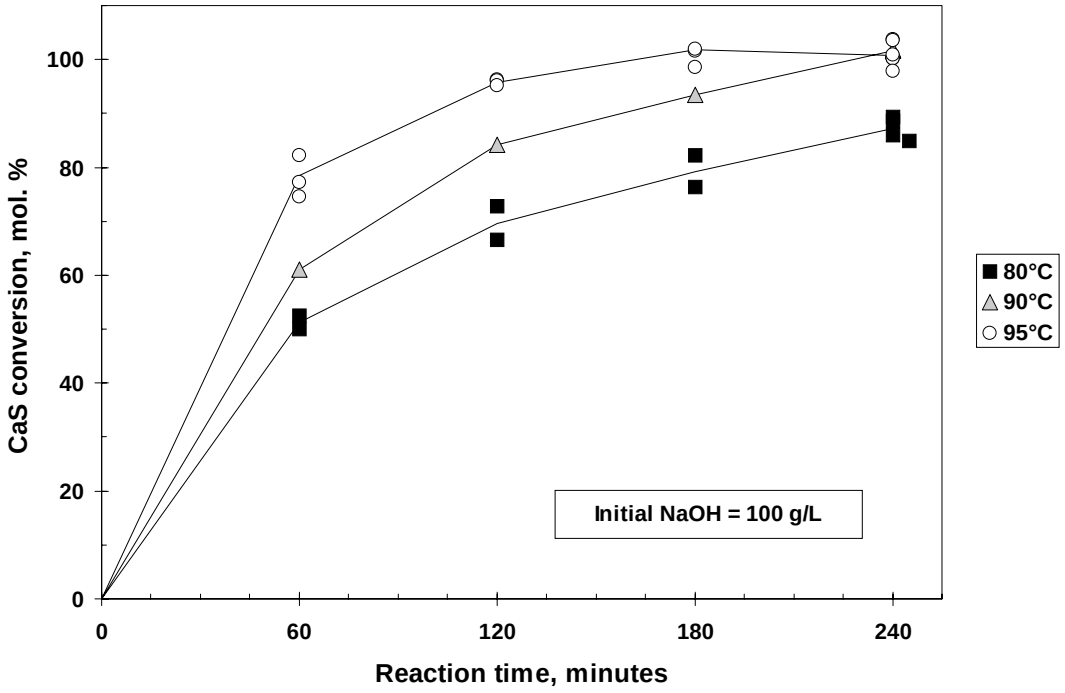

Fig. 10. Molar conversion of CaS to Na_2S as a function of time and temperature for 100 g/L initial NaOH concentration.

Pulping liquors prepared by conventional recovery systems typically contain 100 g/L NaOH. Soda black liquor gasification with direct causticizing can potentially double the NaOH concentration in the feed liquor to the conversion reactor [21]. The effect of a higher alkali charge was therefore investigated. The results in **Fig. 11** show that the initial reaction rate at 200 g/L NaOH was not significantly different than that at 100 g/L; however, the higher concentration appears to limit the ultimate sulfur conversion.

For industrial systems, the alkali reagent stream will contain some Na_2CO_3 and sulfur species in addition to NaOH. In the case of a low-temperature gasification process with no causticizing of the dissolved inorganics, the alkali reagent will be primarily Na_2CO_3. Therefore, an experiment was conducted to measure conversion of commercial CaS with Na_2CO_3 at an initial concentration of 100 g/L. The results in **Fig. 12** show that a maximum conversion of 80% was achieved at 90°C after 240 minutes. The rate of reaction with Na_2CO_3 is lower than similar runs conducted with pure NaOH (Fig. 10). However, the trend of the data suggests that 100% conversion could be achieved given sufficient reaction time. This conclusion is supported by the fact that the reaction product, $CaCO_3$, has an order of magnitude lower solubility than $Ca(OH)_2$.

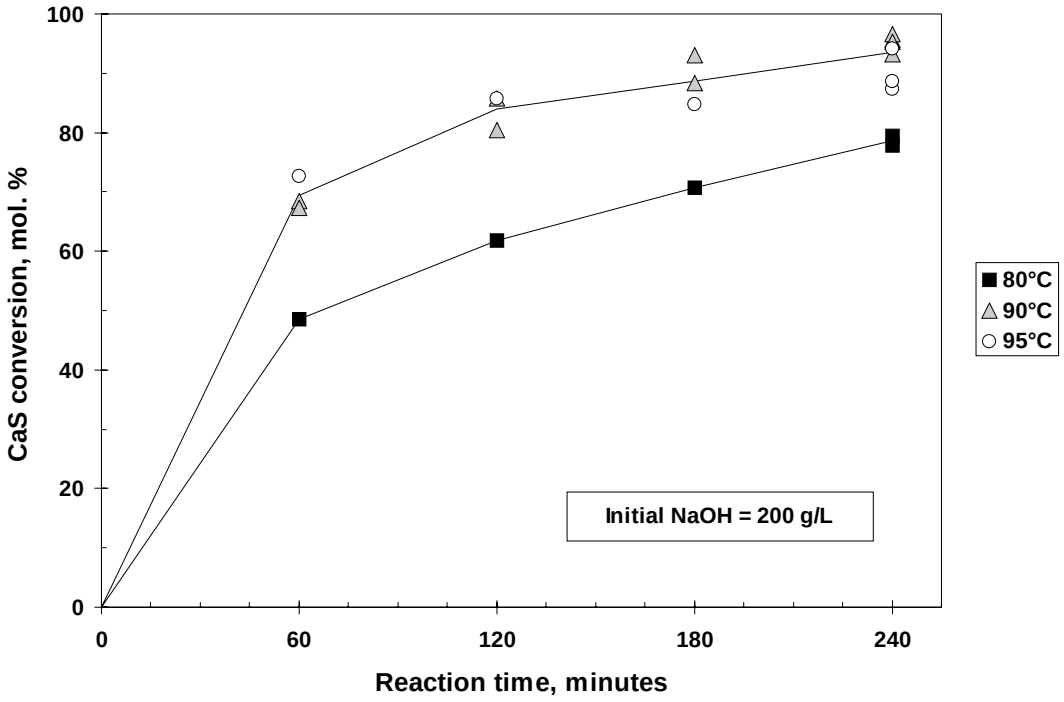

Fig. 11. Molar conversion of CaS to Na_2S as a function of time and temperature for 200 g/L initial NaOH concentration.

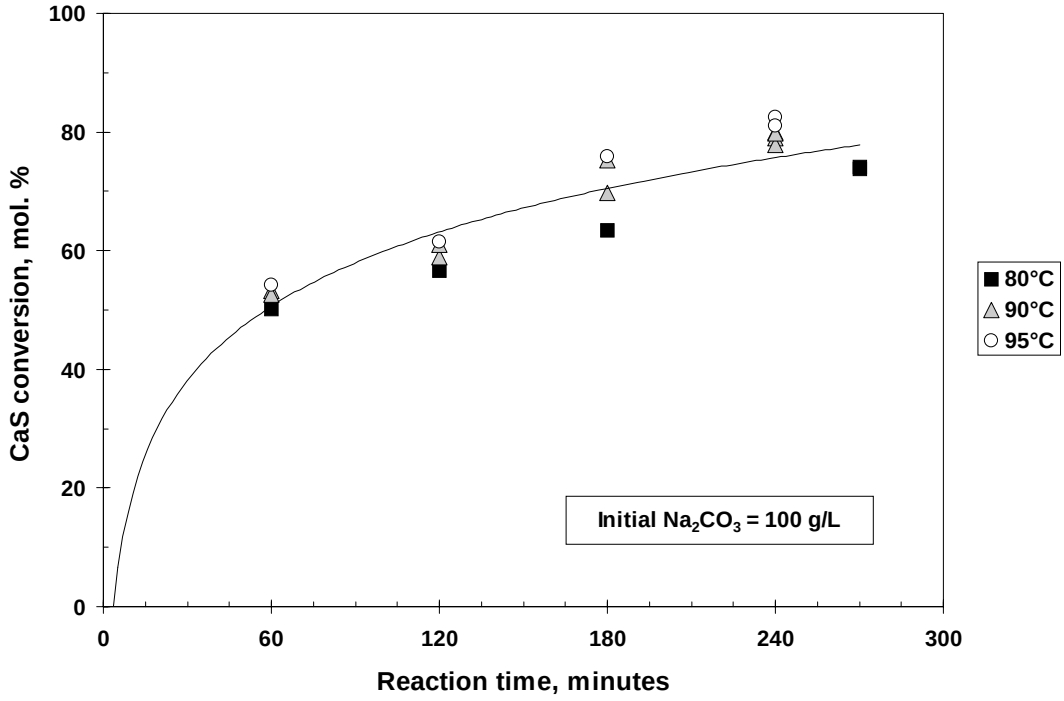

Fig. 12. Molar conversion of CaS to Na_2S as a function of time and temperature for 100 g/L initial Na_2CO_3 concentration.

The results in Figs. 9 through 12 suggests that 100% conversion of CaS can be achieved within 240 min. at 90-95°C and an initial NaOH concentration of 50-100 g/L. These results typically exhibit a lower initial rate of reaction but ultimately reach a higher conversion than in the causticizing reaction (Eq. 3). Industrial conditions used for causticizing green liquor are typically 90-100°C, with 120-240 minutes of retention time, which results in approximately 80% conversion of Na_2CO_3 to NaOH [22, 23]. To be practical for an industrial process, the extent of CaS conversion must be balanced against retention time. Comparison of results at 60 minutes reaction time in **Fig. 13**, suggests that 95°C and a 100 g/L NaOH concentration could be the optimum conditions for industrial conversion of CaS to Na_2S. Also of note in Fig. 13, is the relatively small effect of temperature on CaS conversion by Na_2CO_3. This latter result suggests that formation of Na_2CO_3 must be controlled to maximize sulfur conversion.

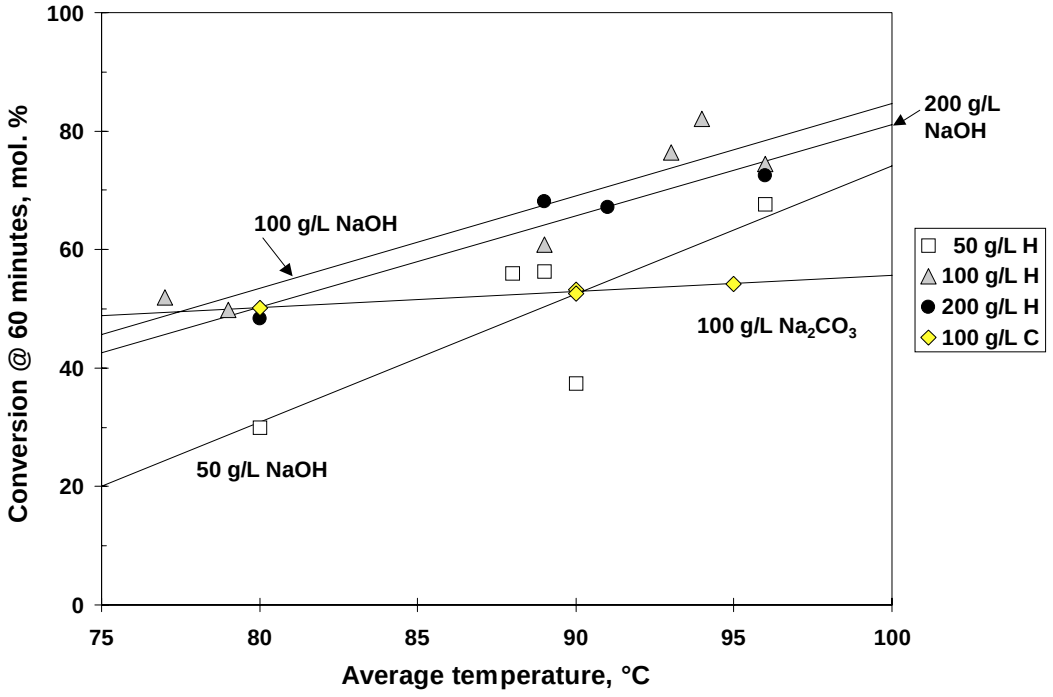

Fig. 13. Comparison of conversion at 60 minutes for all runs with commercial CaS and 50-200 g/L initial alkali concentration: H = NaOH, C = Na_2CO_3.

The commercial CaS was in the form of a fine powder: 96.6% by mass less than 44 μm. In the proposed industrial process, a larger particle size would be required to minimize elutriation from the fluidized bed sulfidation reactor. Depending on equipment type, size and process conditions, the particle size could be expected to vary from 50 to 1000 μm. If the liquid-phase reaction were diffusion limited, then particle size would be expected to affect the conversion rate. Experiments with varying CaS size were therefore conducted to investigate mass transfer limitation effects. As described in the experimental section, three size fractions of CaS samples were prepared by reacting sieved industrial lime with H_2S at 900°C. The size of the produced CaS samples was not determined but was assumed to be approximately equal to that of the initial fractions. Conversion based on the sulfided industrial limes (67-74% CaS adjusted assay) with 50 g/L NaOH is shown in **Fig. 14**. No significant effect of particle size can be noticed for these results. Comparison with the commercial CaS results in Fig. 14 shows that conversion of the sulfided lime is on average 17% higher at 60 minutes and 1% higher at 240 minutes. This important result suggests that the performance of partially-sulfided lime particles, typical in size and composition for an industrial desulfurization reactor, is equal or superior to fine, commercially prepared CaS as a reactant in the proposed sulfur recovery process.

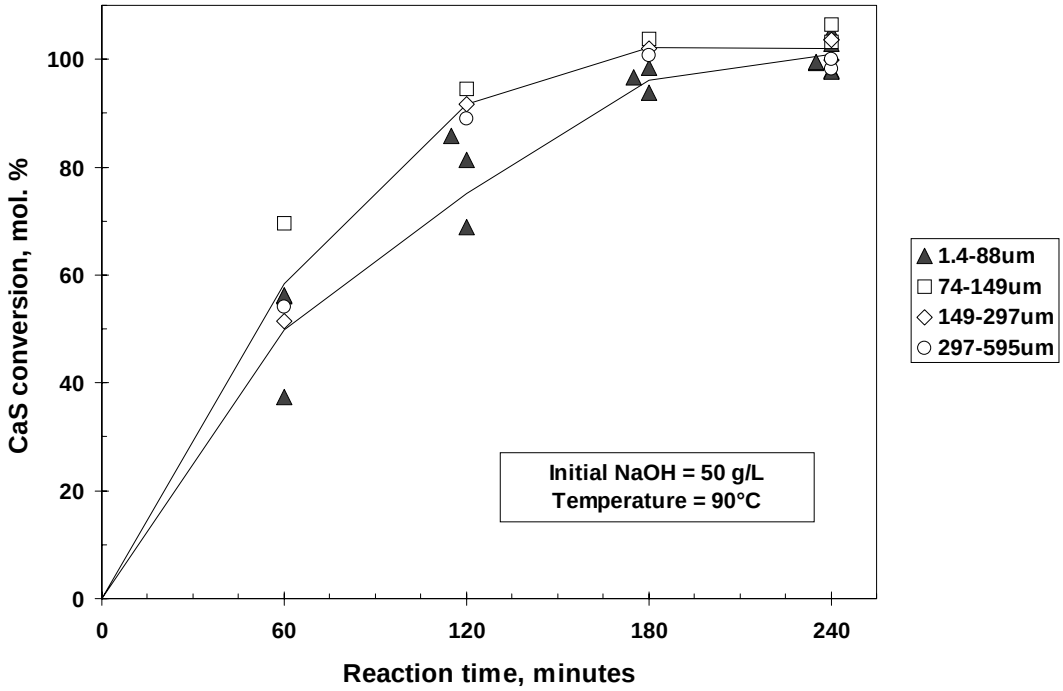

Fig. 14. Conversion of CaS to Na_2S as a function of time and particle size at 90°C with 50 g/L initial NaOH concentration. Commercial CaS: 1.4-88 μm (99.2% assay); prepared CaS: 74-149 μm (66.7% adjusted assay); 149-297 μm (68.7% adjusted assay); 297-595 μm (73.9% adjusted assay).

CONCLUSIONS

The experimental results confirm the equilibrium predictions that 100% conversion of CaS to NaHS can be achieved at industrially practical conditions. It is proposed that the negative temperature coefficient of solubility for the reaction byproduct, $Ca(OH)_2$, is responsible for the dramatic increase in reaction rate when the temperature is increased from 60 to 80°C.

The optimum reaction conditions were found to be an initial alkali of 100 g/L NaOH with a slight molar excess of Na_2 relative to S. A conversion of 80% was achieved in 60 minutes at 95°C; 100% conversion was attained within 240 minutes at 90-95°C with 50-100 g/L alkali. Higher alkali concentrations decreased the conversion slightly.

Conversion of CaS to primarily Na_2S was confirmed with ion chromatography, and sulfur balances closed within ±5%. Only trace amounts of oxidized sulfur species were detected at the end of 4-6 hours of reaction with initial alkali levels of 50-200 g/L.

Neither particle size (79-595 μm) nor extent of sulfidation (67-74%) of industrial lime samples adversely affected conversion at 90°C with 50 g/L alkali; this suggests the proposed process will operate well with bed material from a fluidized bed raw gas desulfurizer.

The level of Na_2CO_3 in the liquor cycle of the sulfur recovery process must be minimized. CaS does react with Na_2CO_3; however, the reaction is slower than with NaOH and results in unconverted CaS even after 4 hours of reaction time. Calcium carbonate formed by this reaction can be converted back to CaS in the raw gas desulfurizer as long as it is operated above the calcination temperature.

A potential advantage of the proposed process is that standard pulp mill recausticizing equipment; e.g., causticizer vessels, clarifiers, and lime mud filters can be employed for sulfur recovery.

ACKNOWLEDGMENT

The authors wish to thank Dr. Le Zeng who conducted extensive equilibrium calculations to support the experiments. Special thanks goes to Ms. Sherri Griffin for her diligence and care conducting the majority of the experimental work and her help in developing the analysis procedures.

REFERENCES

1. Larson, E. D., "Biomass-Gasifier/Gas Turbine Cogeneration in the Pulp and Paper Industry," *J. Eng. Gas Turbines and Power* 114:665 (1992).
2. Rickard, J. C., "The 2020 Mill-Utility Requirements for Market Kraft Pulp," *Tappi J.* 78(3):175 (1995).
3. Grace, T. M., "Where Does Gasification Fit?" *PIMA* 76(11):54 (1994).
4. Lownertz, P. P. H., and Herschmiller, D. W., "Kraft Cooking with Split White Liquors and with High Initial Sulfide Concentration--Impact on Pulping and Recovery," *1994 TAPPI Pulping Conference Proceedings.*, Tappi Press, Atlanta, p.1217.
5. Scott-Young, R. E., and Cukier, M., "Commercial Development of the DARS Process," *1995 International Chemical Recovery Conference Proceedings*, CPPA, Montreal, p. B263.

6. Zou, X., Avedesian, M. M., and van Heiningen, A. R. P., "Kraft Black Liquor Combustion and Direct Causticization with Titanium Dioxide," *1991 Pulping Conference Proceedings*, Tappi Press, Atlanta, p. 299.
7. Zou, X., Avedesian, M. M., and van Heiningen, A. R. P., "Kinetics of the Direct Causticizing Reaction between Sodium Carbonate and Titanium Dioxide," *1991 AIChE Forest Products Symposium Proceedings*, Tappi Press, Atlanta, p. 1.
8. Zeng, L., and van Heiningen, A. R. P., "Pilot Fluidized-Bed Testing of Kraft Black Liquor Gasification and its Direct Causticization with TiO_2," *J. Pulp Paper Sci.* 23(11): J511 (1997).
9. Yumura, M., and Furimsky, E., "Comparison of CaO, ZnO, and Fe_2O_3 as H_2S Adsorbents at High Temperatures," *Ind. Eng. Chem. Process Des. Dev.* 24(4):1165 (1985).
10. Gangwal, S. K., Harkins, S. M., Woods, M. C., Jain, S. C., and Bossart, S. J., "Bench-Scale Testing of High-Temperature Desulfurization Sorbents," *Env. Prog.* 8(4):265 (1989).
11. Jagtap, S. B., and Wheelock, T. D., "Regeneration of Sulfided Calcium-Based Sorbents by a Cyclic Process," *Energy & Fuels* 10(3):821 (1996).
12. Brooks, M. W., and Lynn, S., "Recovery of Calcium Carbonate and Hydrogen Sulfide from Waste Calcium Sulfide," *Ind. Eng. Chem. Res.* 36(10):4236 (1997).
13. Zeng, L., Verrill, C. L., and van Heiningen, A. R. P., "Thermodynamic Study of Calcium Based Sulfur Recovery for Kraft Black Liquor Gasification," *Proceedings of the 1998 International Environmental Conference and Exhibition*, Tappi Press, Atlanta, p.1217.
14. Clayton, D. W., Easty, D. B., Einspahr, D. W., Lonsky, W., Malcolm, E. W., McDonough, T. M., Schroeder, L., and Thompson, N. S., "Chemistry of Alkaline Pulping," in *Pulp and Paper Manufacture, Vol. 5: Alkaline Pulping*, 3rd ed., Joint Textbook Committee of the Paper Industry, Montreal, 1989, pp. 15-22.
15. Papp, J. , "Determination of Sulfur Compounds in Alkaline Pulping Liquors with a Sulphide Ion-Selective Electrode," *Svensk Papperstid.* 74(10):310 (1971).
16. TAPPI Official Test Method T 699 om-87, "Analysis of Pulping Liquors by Suppressed Ion Chromatography," Chemical Properties Committee of the Process and Product Quality Division, Technical Association of Pulp and Paper Industries, TAPPI Press, Atlanta, 1987.
17. TAPPI Classic Method T 624 om-85, "Analysis of Soda and Sulfate White and Green Liquors," Chemical Properties Committee of the Process and Product Quality Division, Technical Association of Pulp and Paper Industries, TAPPI Press, Atlanta, 1984.
18. Vogel, A. I., *Quantitative Inorganic Analysis*, 3rd ed., Longmans, London, 1961, p. 370.
19. Borgwardt, R. H., and Roache, N. F., "Reaction of H_2S and Sulfur with Limestone Particles," *Ind. Eng. Chem. Process Des. Dev.* 23(4):742 (1994).
20. AOAC Test Method 940.32, "Sulfides in Depilatory Powders," *Official Methods of Analysis*, 15th ed., Association of Official Analytical Chemists, Arlington, VA, 1990, p. 365.
21. Maddern, K. N., "Mill-Scale Development of the DARS Direct Causticization Process," *Pulp Paper Can.* 87(10):78 (1986).
22. Wernqvist, A., and Theliander, H., "On the Kinetics of the Causticizing Reaction," *J. Pulp Paper Sci.* 20(10):J301 (1994).
23. Holman, K. L., Carlson, K. R., and Warrick, R.P., "Application of Reaction Kinetics to Recausticizing System Design," *AIChE Symp. Ser.* 92(311):122 (1996).

Received for review: December 3, 1998
Accepted: March 31, 1999

Presented at the 1998 TAPPI International Chemical Recovery Conference.

This paper was accepted for abstracting and publication in the July issue of TAPPI Journal