Recovery of sulfur from spent semichemical pulping liquors

Nancy J. Sell and Jack C. Norman

A combined acidification/evaporative concentration process can be used to recycle, as sulfur dioxide, about two thirds of the sulfur in spent sulfite semichemical liquors.

Introduction

Background

Though a number of sulfur recycling methods are available, chemical recovery is generally not practiced for sulfite-based semichemical pulping processes. Spent semichemical pulping liquors are often sewered to secondary waste treatment or are burned without chemical recycling. There are a number of process advantages attained by using a chemical recovery system. A recycling process reduces the amount of fresh sulfur dioxide raw material which must be used for the pulping and minimizes the amount of waste which must be processed further. However, most of the existing processes are complicated and expensive.

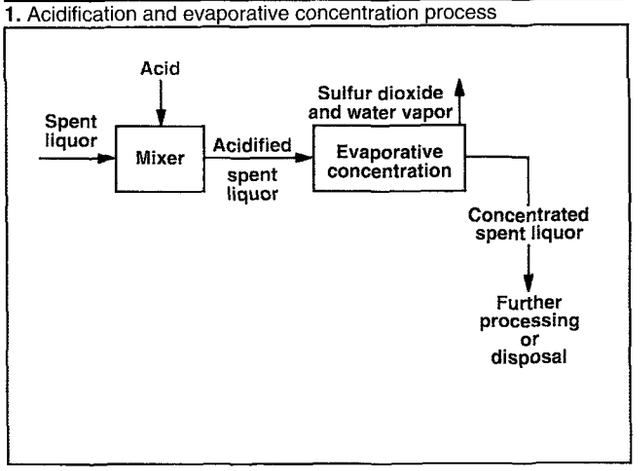
The purpose of this project was to refine and optimize a new recovery process for recycling sulfur dioxide from the spent liquor from sulfite semichemical pulping. This study optimized the treatment levels and determined the feasibility for processing a variety of liquors from different mills across the United States.

Semichemical pulping processes combine chemical and mechanical methods. Wood chips are partially softened with chemicals; the balance of the pulping is by mechanical force. The majority of commercial facilities using semichemical pulping processes are based on sodium sulfite pulping methods, often using a "neutral sulfite semichemical" (NSSC) process. The NSSC process uses sodium sulfite cooking liquor buffered with sodium carbonate to neutralize organic acids liberated from the wood during cooking.

The pulp yields from sulfite semichemical methods range between mechanical pulping yields and chemical pulping yields. That is, the yields range from 55% to 90%.

Few methods exist for the recovery of pulping chemicals used in semichemical processes. A recent report based on a National Science Foundation workshop specifically points out the need for recovery systems for semichemical pulping processes. It states, in part, "Chemical recovery technology is not practiced in these processes. . . . Research is required to develop a commercially feasible recovery or treatment process for high-yield pulping."[1]

1. Acidification and evaporative concentration process



Summary of the process

In this recovery process (**Fig. 1**), a combination of acidification and evaporative concentration expels sulfur dioxide gas from the spent liquor.

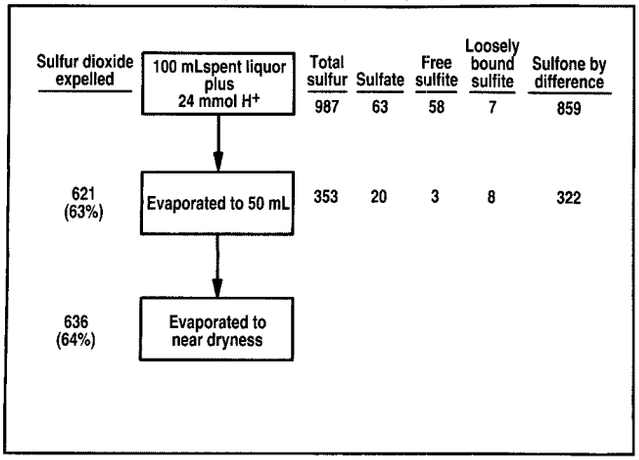
An appropriate amount of acid is mixed with spent sulfite liquor. This acidified mixture is evaporatively concentrated a predetermined amount, at or near the boiling point of the mixture. The emitted gaseous sulfur dioxide and water vapor is collected and can be recycled to regenerate white liquor. The residual spent liquor can be further processed for heat recovery, chemical recovery, or can be disposed of by waste treatment methods.

The initial tests of this process included both chemical and semichemical spent liquors. Though the treatment process is effective to a certain extent on all of the liquors tested, it is best on the semichemical liquors. This relatively simple and inexpensive treatment can remove more than 70% of the

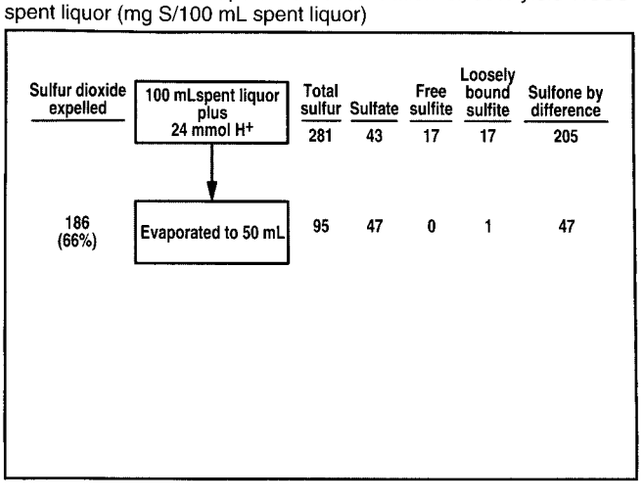
[1] Research Needs in the Pulp and Paper and Related Industries, report of an industry workshop sponsored by the National Science Foundation, July 12–13, 1988, University of Maine, U.S. Dept. of Commerce National Technical Information Service PB89-209068, p. ix.

Sell and Norman are professors at the University of Wisconsin–Green Bay, E S 317, Green Bay, WI 54311-7001.

2. Acidification and evaporative concentration of 78%-yield sodium bisulfite spent liquor (mg S/100 mL spent liquor)



3. Acidification and evaporative concentration of 83%-yield NSSC spent liquor (mg S/100 mL spent liquor)



I. Sulfur dioxide expelled from spent sulfite pulping liquors

			Sulfur dioxide (as mg S) expelled from 100 mL weak spent liquor when evaporately concentrated			
			to 50%		*to dryness*	
Pulp yield, %	*Cation*	*Total sulfur/ 100 mL spent liquor, mg*	*72 mmol H^+ per 100 mL, % of total S*	*No acid added, % of total S*	*72 mmol H^+ per 100 mL, % of total S*	*No acid added, % of total S*
85	Na^+	280	51	1	58	6
83	Na^+	738	61	9	63	16
78	Na^+	987	65	17	69	26
60	NH_4^+	557	19	15	31	17
80	Na^+	744	15	1	16	1

II. Distribution of sulfur species in "as-received" spent liquor (mg S/100 mL liquor)

Pulp yield	*Base ion*	*Total*	*Sulfate*	*Free sulfite*	*Loosely combined sulfite*	*Sulfone*
85	Na^+	280	43	17	17	205
83	Na^+	738	86	39	44	569
78	Na^+	987	63	57	7	860
60	NH_4^+	557	123	1	8	425
80	Na^+	744	285	20	19	421

sulfur as SO_2 of a sufficiently high concentration (perhaps 12% SO_2 in water vapor) to be recycled directly back to white liquor preparation. A recovery boiler is not needed for this process, which is a major advantage. An analysis of the sulfur species present in the liquor before and after treatment indicates that the process is releasing the SO_2 primarily from the lignosulfonates.

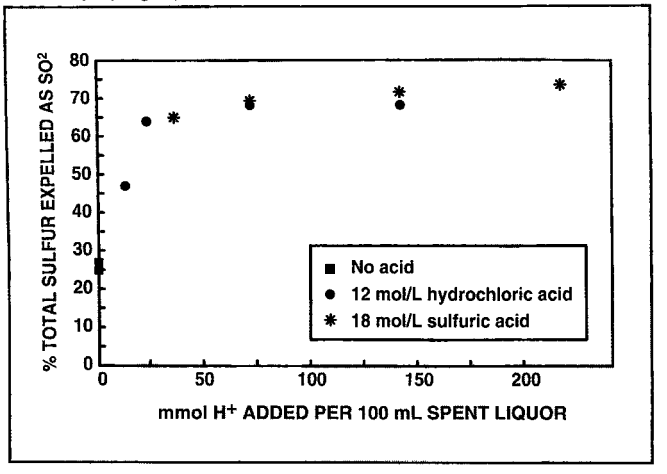
Experimental

Procedure

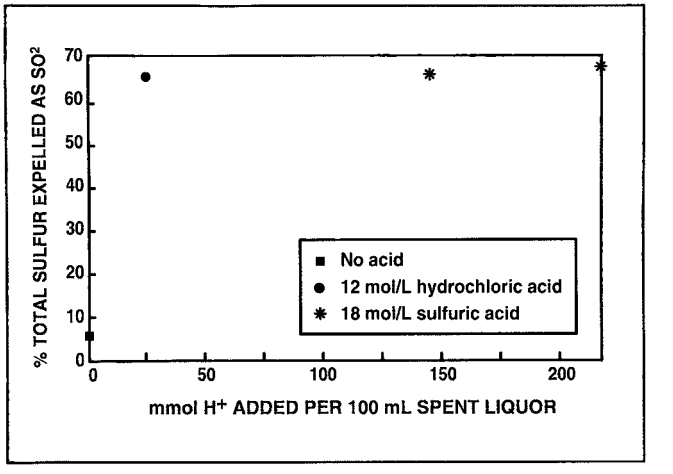
Four sodium-based and one ammonium-based spent semichemical pulping liquors were obtained from several mills across the United States.

Each liquor, as received from the pulp mill, was analyzed for total sulfur, sulfate, "free" sulfite, "loosely-bound" sulfite, and sulfone (or lignosulfonate). The analyses were conducted in accordance with TAPPI Test Method T 629 wd-80. Samples

4. Acidification and evaporative concentration of 78%-yield sodium bisulfite pulping liquor



5. Acidification and evaporative concentration of 83%-yield NSSC pulping liquor



of all of the liquors were mixed with varying amounts of acid and then evaporated to about 50% v/v or to near dryness. Gas chromatography indicated that the gas expelled contained only sulfur dioxide (SO_2) and water vapor. This gas was bubbled through a series of flasks containing 0.01% NaOH. The solution in these collection flasks was then analyzed for sulfite. For corroboration of the sulfur dioxide expulsion, the total sulfur remaining in the residue after 50% evaporation was measured and compared to that initially present.

For two of these semichemical liquors, a complete determination of all sulfur species (total sulfur, "free" sulfite, "loosely-bound" sulfite, sulfate, and sulfone) was made after evaporation to 50% v/v. These results were compared to the as-received samples to identify the sources of the expelled sulfur dioxide.

To determine if we could further expand the choice of acids, carbon dioxide (CO_2) was also bubbled through the 78%-yield sodium bisulfite spent liquor. Because the CO_2 would rapidly neutralize any dilute NaOH in the collection flasks and render them useless to absorb SO_2, the total sulfur in the pot was measured after 1 hour of bubbling at a moderate flow rate.

The bubbling of CO_2 through the spent liquor did not expel any measurable amounts of SO_2. The CO_2 appears to be too weak an acid to release any SO_2 from the lignosulfonates.

Results

Table I summarizes the amount of sulfur dioxide expelled from the five "raw" spent liquors. In all cases, either 72-mmol H^+ (2 mL H_2SO_4) were added per 100 mL spent liquor or no acid was added. Though the combined acidification and evaporation does remove sulfur dioxide in all cases, the removal is generally more effective for the higher-yield liquors.

The one exception to this trend is that of liquor no. 5, a sodium-based, 80%-yield NSSC liquor. The sulfur removal efficiency is significantly lower than might be expected. The likely reason for this can be at least partially explained by **Table II**, a summary of the various sulfur species found in the as-received liquors. This liquor is exceedingly high in sulfate. Discussions with corporate research center staff verified that their liquor typically contains about 25% sulfate. This excessively high sulfate level is due to the pressurized pulp washer used in the pulping process. A second potential reason for the lower expulsion efficiency is the pH: this liquor is initially received at a pH of about 10. It is likely that the 2 mL of concentrated H_2SO_4 that was added was insufficient to complete the SO_2 expulsion.

The sources of the sulfur dioxide generated are identified in **Figs. 2 and 3**. In these spent liquor samples, the sulfur present in the sample as sulfones decreased upon the addition of 24 mmol of hydrogen ion and evaporation to 50% of the original volume.

Acidification alone, or evaporative concentration alone, does not expel significant amounts of sulfur dioxide. It is only in conjunction with each other that these treatments lead to the massive sulfur dioxide emission that occurs.

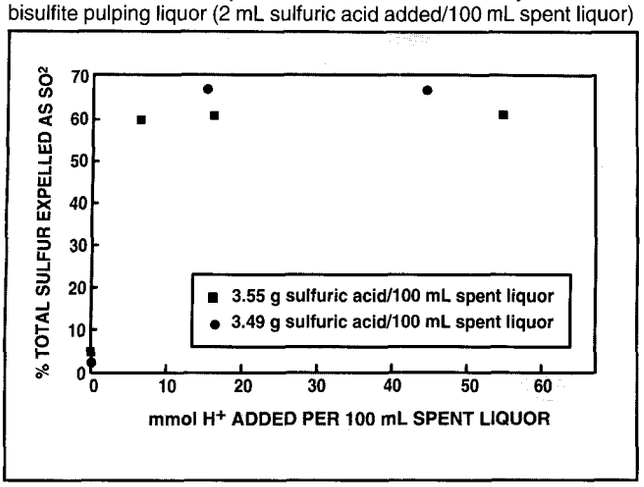
Figures 4 and 5 illustrate the effect of various amounts of acid added to these same spent sulfite liquors. In both cases, the spent liquor was evaporated to dryness.

These figures illustrate the use of two different acids: sulfuric acid and hydrochloric acid. The results can be superimposed to produce one curve, illustrating that it is the hydrogen ion concentration which is of importance, not the nature of the associated anion.

In Fig. 4, representing a 78%-yield sodium sulfite spent liquor, the acid additions varied from zero to 0.36 mmol hydrogen ion per milligram total sulfur in the untreated spent liquor. As little as 0.025 mmol hydrogen ion added per milligram of total sulfur in the untreated liquor is sufficient to expel 65% of the sulfur as sulfur dioxide, when combined with evaporation of the spent liquor to near dryness. Increasing the acid addition to about 0.15 mmol hydrogen ion per milligram total sulfur correspondingly increases the sulfur dioxide expulsion to greater than 70% of that available.

Figure 5 summarizes the amount of sulfur that can be removed from an 85%-yield sodium-based NSSC pulping system as a function of hydrogen ion addition. In this test, the acid addition varied from zero to 0.75 mmol hydrogen ion per milligram total sulfur in the untreated spent liquor. Since this spent liquor is much lower in total sulfur than in the other examples (about 280 mg sulfur/100 mL spent liquor), the ratio of mmol hydrogen ion to milligrams of sulfur is much greater. Adding as little as 24 mmol hydrogen ion per 100 mL of spent liquor provides 0.085 mmol hydrogen ion per milligram sulfur. This is

6. Acidification and evaporative concentration of 78%-yield sodium bisulfite pulping liquor (2 mL sulfuric acid added/100 mL spent liquor)



sufficient acid addition to expel the maximum available sulfur dioxide when the liquor is simultaneously evaporated to near dryness.

Figure 6 illustrates the effect of various amounts of evaporative concentration at a constant acid addition level. For this test using a 78%-yield sodium sulfite spent liquor, 50 mmol of hydrogen ion were added per 100 mL of spent liquor. Only about 5% of the sulfur was emitted as sulfur dioxide if there was no evaporative concentration. Less than 5% evaporative concentration, combined with the acid addition, increases the amount of sulfur dioxide emitted to greater than 60% of the total sulfur available.

Discussion

Acidification and evaporative concentration treatment of spent sulfite semichemical liquors expels a significant amount of the sulfur directly as sulfur dioxide. In sulfite based processes, the sulfur dioxide must be further converted to sulfite and bisulfite before reuse as cooking liquor. To do so, the sulfur dioxide is reacted with an aqueous solution such as sodium carbonate, calcium hydroxide, magnesium hydroxide, or ammonia to regenerate sulfite and bisulfite.

The gas emitted during this recovery process is a mixture of sulfur dioxide and water vapor. The relative amount of the two gases is dependent upon the amount of evaporative concentration that occurs. Assume, for example, the spent liquor is evaporated 10% and, simultaneously, 67% of the available sulfur is emitted as sulfur dioxide. If the original spent liquor contains 900 mg of sulfur per 100 mL of liquor, about 600 mg of sulfur (1.2 g of sulfur dioxide) is contained in the gaseous mixture which also contains about 8.8 g of water vapor. Thus, the emitted gas contains 12% sulfur dioxide. A typical sulfite chemical cooking liquor, prior to fortification with the sulfur dioxide from digester relief gas, is 4.0–4.2% sulfur dioxide. The sulfur dioxide and water vapor mixture from this recycling system is of an appropriate concentration to be used directly as a sulfur dioxide makeup chemical. (The remaining 40% of the sulfur dioxide required could be provided by fresh chemical or by sulfur dioxide recovered by a different, additional recovery process.)

Most pulp mills concentrate their spent liquor to be at least 50% solids (by weight) prior to waste treatment, burning, or further processing. As noted in Fig. 6, very little additional sulfur dioxide is released after 15% or 20% evaporation, so one option is to evaporatively concentrate the liquor in two stages. The first stage is described above: the spent liquor is acidified and evaporatively concentrated to an optimum level, which is determined by the amount of evaporative concentration needed to expel nearly all of the available sulfur dioxide and by the desired sulfur dioxide/water vapor ratio for the regeneration of the sulfite cooking liquor. A second evaporation then concentrates the spent liquor further, to a solids content appropriate for further treatment. This second-stage concentration is equivalent to the evaporation and concentration currently used by most mills.

The remaining spent liquor contains the sulfur compounds that were not converted to and expelled as sulfur dioxide. The remaining aqueous liquor also contains inorganic chemicals, such as carbonates, salts of the added acid (for example, sulfates), and dissolved organic compounds. This liquor can be further processed for heat or chemical recovery, or it can be disposed of by waste treatment techniques.

The acidification and evaporative concentration for sulfur dioxide recovery can be conducted in commercially available equipment. For example, the spent sulfite liquor from pulp washers can be acidified in a mixing tank. This acidified liquor would be concentrated in, for example, a multi-effect evaporator. Other commercially available evaporators and concentrators can also be used, such as cascade evaporators or falling-film-type evaporators. The gaseous sulfur dioxide and water vapor mixture is recycled to conventional cooking liquor preparation for reuse. The remaining spent liquor can be concentrated further in additional evaporators, and then further processed for chemical recovery, heat recovery, or sent to waste treatment.

Conclusions

A combination of acidification and evaporative concentration can be used to recycle much of the sulfur from spent sulfite semichemical liquors. This process appears to be successful with almost all NSSC and other higher yield, spent sulfite liquors. It can be used, but with less efficiency, on lower yield spent sulfite liquors.

Since about 70% appears to be the maximum amount of sulfur that can be recycled by this technique, this process can be combined with a reductive or oxidative burning technique to attain close to 100% recovery. □

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