CHEMICAL
WOOD PULPING
AP-42 Section 10.2
Reference Number
14

Process Modifications for Air Pollution Control in Neutral Sulfite Semi-Chemical Mills

Sergio F. Galeano and Byron M. Dillard
Owens-Illinois, Inc.

The body of information presented in this paper is directed to those individuals concerned with the air pollution control problems of the pulp and paper industry operation. Process modifications introduced at two Company mills, at Big Island, Va. and Tomahawk, Wis., where neutral sulfite semichemical pulping of hardwoods is performed at rates of 550 and 630 tons per day, respectively, are discussed. The methodology and concepts used to minimize total reduced sulfur and total sulfur oxide emissions from the recovery furnace of one of the operations are explained. In another major improvement already implemented in the Big Island Mill conventional hydrogen sulfide emissions from the sulfiting tower, on the order of 8–10 lb as sulfur per ton of pulp, have been completely eliminated by a process modification technique. Other aspects of the operations are described, and a forecast of possible emission levels for mills with a newer technology is made.

The principal chemical pulping process, known in the industry as the kraft process, accounts for 65% of the pulp produced. The semichemical process turns out about 9% of all pulp and various other chemical processes account for another 6%.

Sulfur compounds are active cooking ingredients in the production of 95% of the pulp made by chemical or semichemical process.[1] All indications are that the use of sulfur-active compounds in pulping will continue at present, or even increased, levels throughout the 1970's and beyond.

Important among the reasons for that conclusion is the fact that the industry has made tremendous capital investments over the last decade in the [illegible] [illegible] possibility of pulping without sulfur compounds in certain types of pulps other than kraft is being studied, but it would be premature to advance conclusions.

The pulping industry in recent years has made significant advances in reducing sulfur gaseous emissions at pulp mills mainly through modifications of the process and control of these gaseous emissions at the source. These advances permit anticipating compliance with foreseeable standards for ambient quality and their related source emissions standards.

Environmental Pollution Problems

In the early 1950's, the Institute of Paper Chemistry[2] designed a method of chemical recovery for NSSC mills. Our mill in Tomahawk, Wisconsin was the first installation of its kind to implement this recovery system in 1953. A similar system was installed in our [illegible] in 1954. [illegible] problems at the mills, but at the same time created new problems in air pollution. New air pollution problems arose along the recovery system as a result of emissions of particulate matter and/or gases from the recovery furnace, the evaporating units, and the sulfitation tower.

Case History

At our Tomahawk mill the conventional system depicted in Figure 1 is described as it functioned in 1955 as follows: The spent liquor (black liquor) from the cooking process was concentrated to 45% solids in multiple effect evaporators. Further concentration, to about 60–62% solids, was achieved by bringing together the hot flue gases from the recovery furnace with the black liquor. The concentrated liquor was then burned in a kraft recovery furnace with a capacity of 150 tons of kraft a day. The inorganic chemicals were recovered as smelt and dissolved in an aqueous solution (green liquor). The green liquor was reacted with gaseous sulfur dioxide in a sulfiting tower to form the sulfited liquor. The typical reaction taking place here was:

$$Na_2S + SO_2 + H_2O \rightarrow Na_2SO_3 + H_2S$$

Thus, an inherent problem of the original process was the release of one mole of hydrogen sulfide for each mole of reacted sodium sulfide.

In order to reduce these sulfur losses, we introduced a minor process change. A certain percentage of the green liquor [illegible] [illegible] produced small traces of sodium sulfide in the more diluted spent liquor (weak black liquor). When this liquor is concentrated in the conventional cascade evaporator to 60–65%

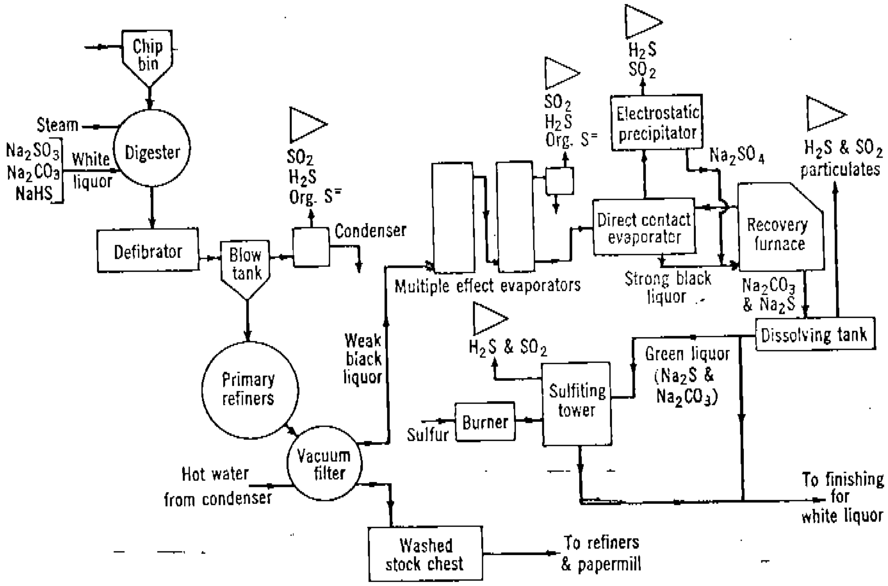

Figure 1. Flowsheet of the conventional NSSC process.

Table I. Predicted and real amounts of primary air for zero ppm sulfide emission.

Furnace's loading level		Amount of air (lb/hr)	
# solids/hr	psig nozzle	Prediction method	Real*
18,600	65	61,000	63,000
17,000	55	54,000	54,000
15,600	45	48,500	49,000
11,988	35	42,000	45,500
8,800	25	36,000	43,500

* Under field conditions of zero ppm TRS (total reduced sulfur).

Table II. Calculated and effective secondary air.

Furnace's loading level		Secondary air (lb/hr)		Ratio E/C
# solids/hr	psig nozzle	Calculated	Effective*	F
18,600	65	53,000	53,000	1.0
17,000	55	48,000	51,000	1.05
15,600	45	38,600	48,000	1.17
11,988	35	28,000	44,500	1.55
8,800	25	16,000	43,500	2.6

* For zero ppm TRS (total reduced sulfur).
F = 0.90 + 0.0955 (P/65) —3.017.

solids, the sulfide concentration increases. Then, upon contact with the hot CO_2-rich flue gases, some additional hydrogen sulfide was released.

Our present system at Tomahawk has been operating since 1968 without a cascade or direct contact evaporator. Liquors are concentrated in multiple effect evaporators to 62–64% solids. Thus, gaseous emissions from the recovery unit are limited to the furnace itself and the control of these emissions is the subject of our first process modification.

Control of Sulfur Emissions from the Recovery Furnace

The operation of a pollution-controlled furnace must be a compromise of different and sometimes contradictory requisites, which are:

1. Acceptable combustion efficiency.
2. Chemical recovery as Na_2S and Na_2CO_3.
3. Minimization of Na_2SO_4 formation.
4. Low alkali dust load.
5. Elimination of $S^=$ emissions.
6. Low SO_2 emission.
7. Control of CO in flue gases.
8. Control of NO_x.

The complex processes taking place during combustion could be simplified into a system of inorganic substances. The two existing phases in the lower zone, gas and solid, can be explained by thermodynamic postulates. Reactions and the values of the equilibrium constants are available in several publications.[3] The solution of simultaneous equations in order to obtain the partial pressures of each reacting substance at equilibrium is a rather tedious problem unnecessary for our approach.

Mapping the Zone of Compromise in the Equilibrium Diagram for Primary Air. Figure 2 is an equilibrium diagram for a Na-base pulping system based on these assumptions:

$pCO + pCO_2 = 0.15$ atm
$pH_2 + pH_2O = 0.10$ atm
$pH_2 + pSO_2 + pSO_3 + pS_2 =$ 0.01 atm
Na in excess of S as to fix all S to Na and to obtain a Na_2CO_3 residue.

Since our modification was to be achieved through air control, the partial pressure of oxygen was taken on the abscissas and the partial pressure of the remaining compounds as ordinates, all in negative logarithms.

We then proceeded to narrow down the diagram according to our requirements, in the following fashion:

1. We disregard any area to the right of the point delimiting Na_2S and Na_2SO_4 formation, log $pO_2 = -10.007$
2. The requisite of an acceptable good combustion is fulfilled by staying away from very low oxygen partial pressures. In this fashion, we disregard the area left of the point at which solid carbon will appear, log $pO_2 = -19.3$
3. Decomposition of Na_2CO_3 is avoided by staying above the horizontal line obtained at log $pCO_2 = -6.453$.
4. Alkali losses must be kept as low as possible. A compromise point is the intersection of the Na_2 and H_2S curves. This will give the new boundary on the left.
5. Since minimum H_2S emissions should take place, any area to the left of the point where the H_2S and SO_2 curves intercept will be acceptable. This point will be our boundary on the right.

The new zone of compromise is thus the rectangle marked by thick inclined lines in Figure 2. Within this zone, the left-hand side offers better fulfillment of most of the requisites, say lower H_2S and Na_2 partial pressure and less possibility of Na_2SO_4 formation.

We selected a midpoint in which we will have approximately:

58% of C as CO
42% of C as CO_2
58% of H_2 as H_2O
42% of H_2

The amount of primary air was estimated to satisfy the above mentioned ratios according to the elemental analysis of the spent liquor and common process calculations. When estimating the combustion of the auxiliary fuel oil, we considered enough air to permit its combustion to CO_2 and H_2O. The situation of the fuel oil guns discharging right in the upper limit of the primary zone was one factor in consideration. Auxiliary oil makes about 20% of the total heat input.

Table I indicates, at different operating conditions, the final values for primary air that were used to obtain experimentally zero ppm sulfide emissions in the flue gases. Also shown are the values from the prediction method already outlined. It is possible that some additional turbulence was required at the very low loading levels.

Secondary Air and Turbulence. The amount of secondary air could be calculated by substraction of the primary air from the total estimated requirements. The air required as determined stoichiometrically is the minimum needed and additional air must be supplied. Our total calculated air included a 5% excess air.

For our experiment we tried to follow an approach consisting of the increase of the secondary air injection velocity. At that moment in the study, we have been able to obtain zero ppm sulfide emission for several hours at the highest loading level. As indicated in Table II, as the input of black liquor solids to the furnace decreased, there was a need to increase secondary air above calculated amounts in order to complete the oxidation of the sulfides.

[illegible] turbulence needed in the secondary zone should include a scale of turbulence. We like to think of it as an analogy with the von Karman–Howarth

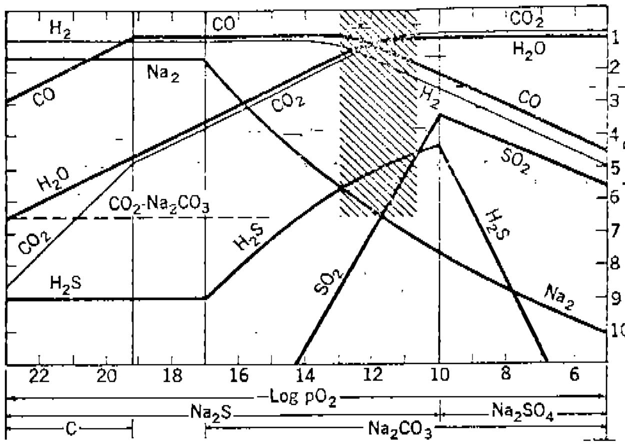

Figure 2. Logarithmic equilibration diagram for Na-base liquor.

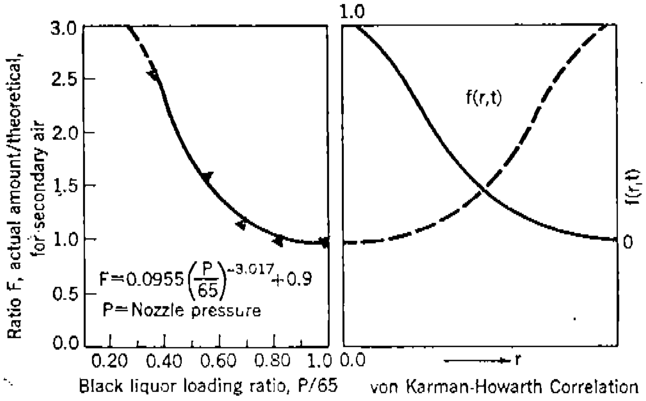

Figure 3. Analogy for the scale of turbulence in secondary zone.

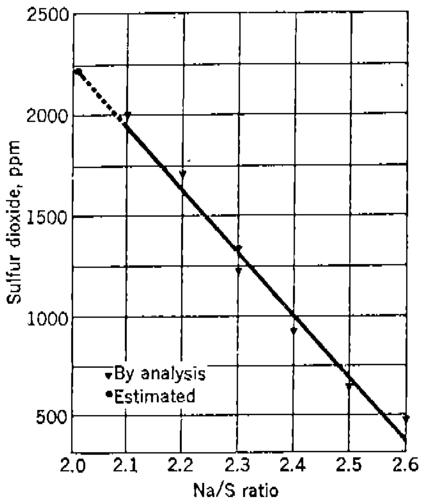

Figure 4. Sulfur dioxide reduction with increase in Na/S ratio.

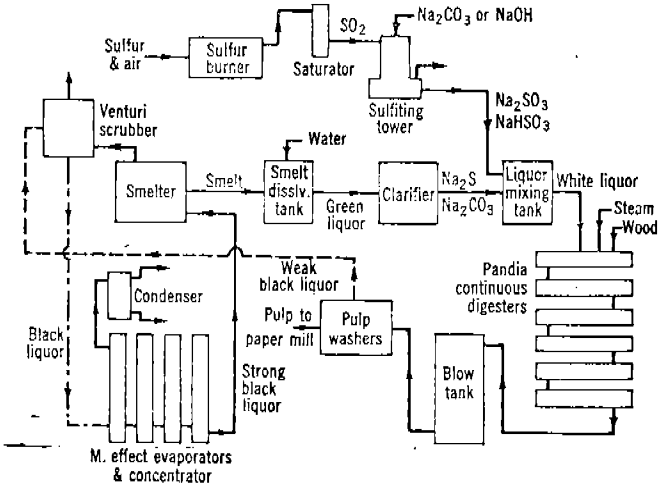

Figure 5. Modified NSSC recovery process at the Big Island Mill.

equation for the second order correlation function $f\ (r,\ t)$. If r is the distance between two points, a correlation between the fluctuation at these two points will give a measure of turbulence. Another analogous element could be introduced if we consider the secondary ports system as a grid or mesh producing the turbulence. The decay of the intensity of turbulence is also expressed by the function $f\ (r,\ t)$.

For our fixed geometric dimensions in the furnace, a decrease in the loading will bring about a decrease in the distance, r, and time, t, after the grid and, consequently, a decay in turbulence. For lower loadings to the furnace, it would be necessary to increase turbulence in the same fashion it decays. In other words, we need to trace back the curve which gives $f\ (r,\ t)$. Figure 3 indicates the high loading point (1.0, 1.0) and the reverse curve (dotted line). Point (0.4, 2.5) was determined by proportion and some trial-and-error. With these two points, an operating equation was developed and estimations for each operating level were made.

Control of Nitrogen Oxides. Two-stage combustion is one of the methods to reduce the formation of NO_x. This is the fashion in which the furnace is operated to obtain proper inorganic chemical recovery. Keeping the temperature relatively low in this process also aids in keeping the NO_x at a minimum. Generally, temperatures at the lower or primary zone are in the range of 2000–2300°F.

Recent studies of NO_x at our recovery operation at Big Island, Va., using the phenoldisulfonic acid method, indicate values in the range of 50–100 ppm NO_x, as NO_2. This corroborates our previous work at Tomahawk, Wis. in 1969. There is no indication of any scrubbing effect because of the venturi-evaporator at the Big Island operation.

Reduction of Sulfur Dioxide

There is a relationship between the sodium/sulfur ratio in the liquor and the emissions of SO_2 from the furnace itself. When total reduced sulfur (TRS) emissions are reduced, the Na/S ratio decreases. Less alkali is available for recombination with the SO_2 in the secondary zone. Figure 4 illustrates the experimental data from the Tomahawk mill, showing the relationship between Na/S ratio and SO_2 emissions. We think that there is a practical limit to the increase of the Na/S ratio. Adequate turbulence and cooling of the gases will promote efficient recombination and low alkali losses.

Elimination of Hydrogen Sulfide Emissions from the Sulfitation Tower

As a continuation of an earlier program to remove and recover SO_2 from power boilers using high-sulfur coal as fuel,[4] a modification of the IPC recovery system was devised for our Big Island operation. Sulfur dioxide from the existing sulfur burner is scrubbed with an alkaline solution of sodium base in the amount required by the Na make-up of the mill. The solution should have a molar ratio bisulfite/sulfite of 4:1 at a pH of around 7.0.[5]

The formation of the bisulfite–sulfite solution takes place in the original sulfitation tower. The bisulfite–sulfite liquor is contacted with green liquor instead of directly with the smelt as originally envisioned. Figure 5 is a schematic of the main components of this system at Big Island.

Other Improvements at the Big Island Operation

The capacity of the direct contact evaporator for removing SO_2 is an important tool in reducing the total emission of S from the smelter, since the smelter, *per se*, does not favor the best control of sulfide and sulfur oxide emissions.

Our program for further improving the control of pollutant emissions from the smelter called for replacing the existing concentrated black liquor to the venturi evaporators with weak black liquor, which contains only 12–17% solids.[6] Figure 5 also depicts this system as in operation. The increase in the liquid/gas ratio and the reduction of solids in the scrubbing solution will increase the particulate collection to 98%. Preliminary data from the on-going study indicates that an increased removal of SO_2 has been achieved by the use of weak black liquor, the concentration being below 200 ppm.

Experimental work in the existing installation on the effect of strong and weak black liquors in the release of sulfur emissions from the contact evaporators has shown a reduction of sulfide emissions when using weak liquors. At a pH on the alkaline side (around 9.7), and sulfide concentrations from 0.1 to 0.3 g/l as Na_2S, release of sulfides does not take place, but a reduction from the inlet concentrations does. Liquid-to-gas ratio, expressed as gallons per 1000 actual cubic feet of gas, is in the range of 12–13 for these results. Studies to further increase the liquid/gas ratio are under way.

Conclusions

Table III compares what we consider old and new technologies from NSSC operations. These figures indicate that significant reductions have been made, including the immediate reduction of total sulfur emissions of about 15 lb/ton of pulp, and that further reductions could be made. Differences from one mill to another are significant as indicated by Tables III and IV, and the values in Table III must be interpreted for a mill able to adopt the best one of the independent improvements. In some cases this may not be possible for existing mills.

We would like to stress the following conclusions:

A. Air pollution problems are increased in the NSSC pulping process whenever steps are taken to reduce water pollution levels by chemical recovery.

B. Through process modifications, more exacting combustion practices, and control at the sources, the air pollutant emissions in the NSSC pulping process can be reduced to levels of anticipated air quality standards.

C. The sulfite semichemical pulping process, as most commonly practiced differs substantially from one mill to another and generalizations on emissions and control levels are not to be made as in the most uniform kraft process.

Table III. Comparison of old and newer technology on gaseous emissions.

Source	Pollutant	Old technology	Newer technology
Recovery furnace or smelter	SO_2	8.20	1.40–2.45
	H_2S	4.20	1.10–0.20
	RSH	0.30	0,10–0.05
	Other	—	—
		12.70	2.60–2.70
Sulfiting tower	SO_2	0.80	0.30
	H_2S	8.55	—
		9.35	0.30
Blow tank	SO_2	0.30	0.25
	H_2S	4.20	2.10
	RSH	1.56	0.78
	Other Org S^-	3.12	1.50
		9.18	4.63
Dissolving tank	H_2S	0.10	
	SO_2	0.04	
		0.14	0.14
Evaporator	H_2S	0.13	
	Org S^-	0.09	
		0.22	0.22
Washers	H_2S	0.05	
	SO_2	0.01	
		0.06	0.06
Total		31.65	7.95–8.05

Table IV. Smelter flue gas emissions before and after venturi-evaporator (lb sulfur/ton ADP)

Pollutant	Emissions* Before	Emissions* After	Collection efficiency*	Expected emission after program
Sulfur dioxide, as S	17.2	1.5	91	1.40**
[illegible] sulfur				[illegible]
Hydrogen sulfide, as S	4.5	5.9	—30.0	1.00**

* With strong black liquor.
** From preliminary data of on-going program.

References

1. *Paper Trade J.*, **153** (22), 39 (June 2, 1969).
2. R. P. Whitney, S. T. Han, and J. L. Davis, "Direct sulfitation in a neutral sulfite recovery process," *TAPPI*, 40 (7), 587 (July, 1957).
3. U. S. National Bureau of Standards, *Circular 500*, Government Printing Office, Washington, D. C., 1952.
4. S. F. Galeano and C. I. Harding, "Sulfur dioxide removal and recovery from pulp mill power plants," *J. Air Poll. Control Assoc.* **17** (8), 536 (1967).
5. Galeano, S. F., U. S. Patent No. 3,622,443 (November, 1971).
6. C. I. Harding and S. F. Galeano, "Using weak black liquor for sulfur dioxide removal and recovery," *TAPPI*, **51** (10), 48A (Oct., 1968).

Dr. Galeano is Divisional Coordinator at the Forest Products Division, Owens-Illinois, Toledo, [illegible] Island, Va. This paper was presented at the 64th annual meeting of APCA at Atlantic City, N. J. in June, 1971, as Paper no. 71-87.