



Project Summary

Evaluation and Application of SO_x Measurement Procedures for Kraft Recovery Furnaces

A. K. Jain, R. O. Blosser, D. B. Newport, and H. S. Oglesby

A research program was initiated to determine sulfuric acid ($\text{SO}_3/\text{H}_2\text{SO}_4$) and sulfur dioxide (SO_2) emissions from kraft recovery furnaces using an extractive sampling system. The Goksoyr and Ross controlled condensation technique, which uses a modified Graham condenser, was chosen because of its reported accuracy. Equipment was designed and fabricated to evaluate the effect of coil length, frit porosity, temperature, flow rate, and concentration on the efficiency of H_2SO_4 capture.

Laboratory tests were conducted to determine the optimum design and operating conditions to minimize $\text{SO}_3/\text{H}_2\text{SO}_4$ losses in filter holders used in the sampling train for particulate separation. The effects of recovery furnace particulate on $\text{SO}_3/\text{H}_2\text{SO}_4$ losses were investigated. The alkaline particulate from the recovery furnace reacted with a part of $\text{SO}_3/\text{H}_2\text{SO}_4$ in the sample. Although the losses could not be correlated with the alkalinity of the particulate, they were not considered significant.

Field studies were conducted on five representative kraft recovery furnaces to determine $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 concentrations in flue gases. The $\text{SO}_3/\text{H}_2\text{SO}_4$ concentrations varied from 0 to 2.98 ppm, and the range of SO_2 concentrations varied from 14 to 416 ppm. A comparison of these emissions with the $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 emissions from oil- and coal-

fired utility boilers shows the kraft recovery furnace emissions to be much lower.

Introduction

Because of their adverse effect on respiratory functions, acid sulfate aerosols in the ambient air are of special concern in air quality management programs. One of the precursors of ambient acid sulfate aerosols is sulfur trioxide (SO_3), which is formed during the combustion of sulfur containing fossil fuels.

In the kraft pulping industry, the concentrated spent cooking liquor (black liquor), which consists of wood components, inorganic chemicals, and sulfur compounds, is sprayed into a furnace and combusted. Although the kraft recovery furnace burns black liquor in a manner to minimize sulfur dioxide (SO_2) generation, the presence of high concentrations of sulfur in the black liquor has raised the question of the possible presence of sulfur trioxide (SO_3)/sulfuric acid (H_2SO_4) in kraft recovery furnace flue gas.

The objective of this investigation was to determine representative SO_2 and $\text{SO}_3/\text{H}_2\text{SO}_4$ levels in kraft recovery furnace emissions. Sampling flue gases from the kraft recovery furnace is difficult because the flue gases are about 20 percent moisture and contain alkaline particulate which can react with $\text{SO}_3/\text{H}_2\text{SO}_4$ during sampling. The

investigation was divided into four areas:

1. Development and laboratory testing of a suitable method to measure SO₃/H₂SO₄ concentration in a particulate-free gas stream,
2. Determination of the effect of the presence of kraft recovery furnace particulate on the measurement of SO₃/H₂SO₄,
3. Selection and testing of a suitable particulate separation device to minimize particulate interaction with SO₃/H₂SO₄ in the sampling train if particulate is found to interfere in SO₃/H₂SO₄ measurement, and
4. Measurement of SO₂ and SO₃/H₂SO₄ levels in kraft recovery furnaces from five representative sources in the southeast

Conclusions

The kraft recovery furnace SO_x study results can be divided into two parts laboratory investigation and field measurements of SO_x emissions

Laboratory Investigation

A study of the Goksoyr and Ross method for SO₃/H₂SO₄ measurement showed that the efficiency of SO₃/H₂SO₄ capture in the modified Gramh condenser was dependent upon the frit porosity and coil length (Table 1) A condenser with Type C (Ace Glass) frit and a 200-cm coil maintained at 75° to 85°C (167-195°F) was the most suitable for use in the sampling train because of its ability to provide high H₂SO₄ capture efficiency and acceptable sampling rate in the range of 6-8 L/m

Tests to find a suitable filter holder for removing particulate from the gas stream prior to SO₃/H₂SO₄ measurement showed that the conventional EPA Method-5 type of filter holders could not withstand the desired temperature of 260°C (500°F) A quartz filter assembly, developed for another EPA project, was fabricated and tested in the laboratory The study showed no significant loss of H₂SO₄ in the filter support assembly maintained above 260°C (500°F)

The effect of kraft recovery-furnace particulate upon the passage of SO₃/H₂SO₄ through the filter holder

Table 1. Effect of Frit Porosity Upon SO₃ Condenser Efficiency.

No.	Frit Type*	Max. Pore Dia. Range (μM)	Length of Condensing Coil (cm)	Flow Rate (Lpm)	% H ₂ SO ₄ Capture
1	B	70-100	100	2	20-40
2	D	10-20	200	2	99
3	C	25-50	200	2-8	90-99

*Ace Glass

Table 2. H₂SO₄ Losses in Tests With Recovery Particulate

H ₂ SO ₄ Conc., ppm	H ₂ SO ₄ Loss,		H ₂ SO ₄ Loss*		Difference	
	ppm	Percent	ppm	Percent	ppm	Percent
20.0	3.4	17	1.4	7	2.0	10
23.0	6.0	26	1.6	7	4.4	19
28.8	4.3	15	1.4	5	2.9	10
32.3	0.3	1	1.0	3	-0.7	-2
8.8	1.4	16	3.1	35	1.7	-19
11.1	4.1	37	3.2	29	0.9	8
22.2	2.4	11	0.7	3	1.7	8
19.4	2.7	14	0.6	3	2.1	11
17.7	2.5	14	0.5	3	2.0	11

*If all alkalinity present was neutralized

was determined by continuously loading the quartz filter with recovery-furnace particulate while passing a gas stream containing H₂SO₄ through the filter The results (Table 2) show substantially higher losses of H₂SO₄ than were expected based upon the alkalinity of the particulate and may be due to the adsorption of H₂SO₄ on the particulate surface. The absolute values of H₂SO₄ losses were, however, low and, for purposes of estimating emission levels from kraft recovery furnaces, of little significance

The alkaline particulate present in the kraft recovery furnace stack gas offered a potential for SO₃/H₂SO₄ loss from the sample To minimize the contact between the gas and the collected particulate and to reduce the potential for SO₃/H₂SO₄ loss, tests were conducted with an electrostatic precipitator

obtained from the EPA Environmental Sciences Research Laboratory Tests showed that the precipitator removed 99 percent of the particulate present in a stack gas following a precipitator, and there was no conversion of SO₂ to SO₃ in the precipitator

Field Measurement of SO_x Emissions

The SO_x emissions from five kraft recovery furnaces were measured Included were two furnaces with direct contact evaporators (DCE) and three without any contact evaporators One of the non-contact furnaces was a cross-recovery furnace in which 30 percent of the liquor was from the sodium-based semichemical cooking process

The sampling train is shown in Figure 1 Table 3 summarizes test results by

furnace type and sample conditioning techniques. The data for all the tests show a $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration range of 0 to 2.98 ppm, with an average value of 0.81 ppm. When separated according to the type of furnaces, the data show that DCE furnaces have an average $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration of 0.24 ppm in stack gases; non-DCE furnaces have a slightly higher average concentration (1.07 ppm). Non-DCE furnaces had an average concentration of 356 ppm of flue gas SO_2 , substantially higher than the average concentration in furnaces with DCE (80 ppm).

The data in Table 3 indicate that non-DCE furnaces have an average $\text{SO}_3/\text{H}_2\text{SO}_4$ level of 0.90 ppm when a quartz filter was used in the sampling train, a lower average than the $\text{SO}_3/\text{H}_2\text{SO}_4$ concentration of 1.62 ppm obtained with a miniature electrostatic precipitator (ESP) in the sampling train

for particulate separation. These differences, too small to be of any importance, may be due to source variability, oxidation of SO_2 to SO_3 in the ESP during sampling, or lower losses of $\text{SO}_3/\text{H}_2\text{SO}_4$ in the ESP.

The lower SO_2 concentrations in DCE furnaces were anticipated and are generally due to SO_2 scrubbing in the DCE.

To determine any linear correlation between the $\text{SO}_3/\text{H}_2\text{SO}_4$ and the SO_2 concentrations, the values of coefficient

Table 3. $\text{SO}_3/\text{H}_2\text{SO}_4$ Emission Data Summary

Samples	No.	$\text{SO}_3/\text{H}_2\text{SO}_4$ Conc., ppm			SO_2 Conc., ppm
		Max.	Min.	Avg.	
All Samples	26	2.98	0	0.81	260
<i>Types of Furnaces</i>					
-DCE Furnaces	9	1.10	0	0.24	80
-non-DCE Furnaces	17	2.98	0.17	1.07	356
<i>Non-DCE Furnaces</i>					
-Quartz Filter Only	13	2.63	0.17	0.90	430
-ESP Only	4	2.98	0.91	1.62	305

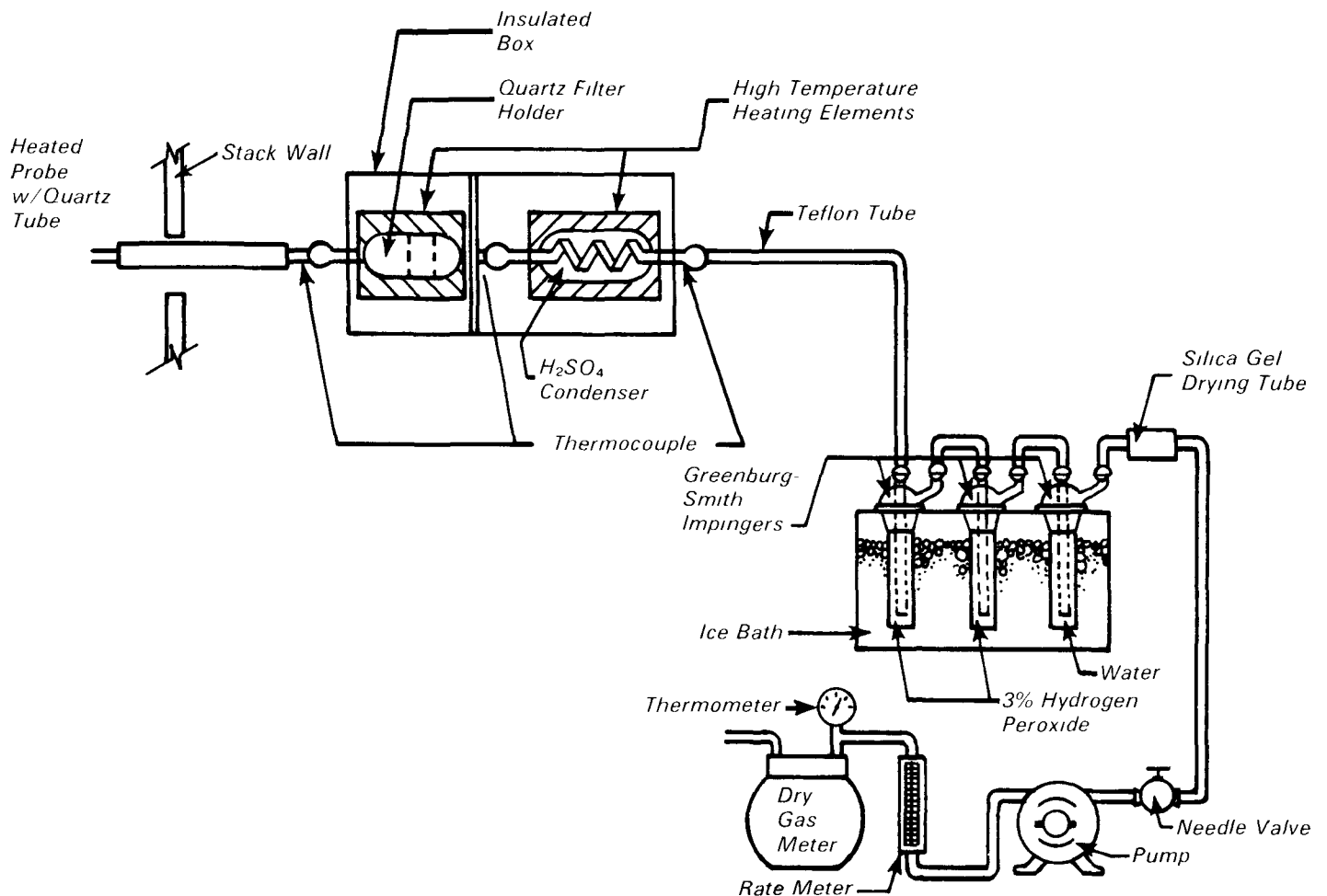


Figure 1. SO_x sampling train

of correlation (r) between $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 were determined for each recovery furnace and are tabulated in Table 4. These results, except for recovery furnace C, show a very poor correlation between $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 . If a high level of SO_2 is noted in a particular furnace's stack gas, it should not be assumed that the same furnace also emits a high concentration of $\text{SO}_3/\text{H}_2\text{SO}_4$.

Table 4. Coefficient of Correlation $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 .

Recovery Furnace	Coefficient of Correlation
A	-0.33
B	-0.50
C	0.99
D	-0.42
E	-0.46

To understand the relative significance of the SO_x levels in kraft recovery furnace stack gases, these levels must be compared to emissions from oil- or coal-fired utility or industrial boilers. Some of the recently published SO_2 and H_2SO_4 emission data from oil- and coal-fired boilers show that both the SO_2 and the H_2SO_4 concentrations in flue gases from oil- and coal-fired boilers are much higher than the levels in kraft recovery furnace stack gases.

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Michael D. Strutz is the EPA Project Officer (see below). The complete report, entitled "Evaluation and Application of SO_x Measurement Procedures for Kraft Recovery Furnaces," (Order No. PB 81-109092; Cost: \$7.00, subject to change) will be available from:

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