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Development of Aqueous Processes for Removing NO$_X$ from Flue Gases - Addendum

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Development of Aqueous Processes for Removing NO$_X$ from Flue Gases - Addendum

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ABSTRACT

This report summarizes the findings of the laboratory program for "Development of Aqueous Processes for Removing NO_x and SO_2 from Combustion Flue Gases." This project is the second phase of the flue gas scrubbing work sponsored by EPA under Contract No. 68-02-0220. The results of the Phase I program are contained in report EPA-R2-72-051, entitled, "Development of the Aqueous Processes for Removing NO_x from Flue Gases."

The present report contains discussions of analytical techniques and scrubber design in addition to experimental results obtained with a vertical spray tower scrubber. The blended flue gases passed up the unpacked glass column countercurrent to the absorbing solution which was sprayed down from the top. The scrubbing experiments showed:

- NO_2 and SO_2 are effectively absorbed by 1.0 molar Na_2SO_3 solutions.

- NO_2 absorption by 1.0 molar NaOH solution is enhanced by the presence of SO_2 in the flue gas.

- Neither NO nor NO_2 is effectively absorbed by 1.0 molar NaOH solution in the absence of SO_2, and NO absorption is not improved by the presence of SO_2.

- Increasing the L/G ratio improves NO_2 and SO_2 absorption by 1.0 molar Na_2SO_3.

- Under similar scrubbing conditions $Mg(OH)_2$ slurry is not as effective as Na_2SO_3 solution for NO_2 absorption.

The data show that sulfite solutions would effectively absorb NO_x and SO_2 from flue gases provided the NO_x (mostly NO) has been oxidized to NO_2 upstream from the scrubber.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

The oxides of nitrogen (NO, NO_2) are essential components in the formation of photochemical smog in addition to being pollutants in their own right. Sulfur dioxide (SO_2) is a major air pollutant. The major sources of these oxides is the large fossil fuel fired boilers such as those found in electric power generating plants. Nitric oxide (NO) is formed in the high temperature zone of the furnace by the reaction between atmospheric nitrogen and oxygen; as the combustion gases cool, a small percentage (10%) of the NO is oxidized to NO_2. Collectively, these two oxides are referred to as 'NO_x'. If the fuels contain organically bound nitrogen, as do coal and oil, part of this nitrogen is converted to NO_x during combustion. Similarly, sulfur containing species present in the fuel provide a source for SO_2. The composition of different flue gases is shown in Table 1.

TABLE 1

TYPICAL COMPOSITIONS OF FLUE GASES

Component	Volume % Combustion Of		
	Coal[a]	Oil[b]	Gas[c]
N_2	76.2	77.0	72.3
CO_2	14.2	12.0	9.1
H_2O	6.0	8.0	16.8
O_2	3.3	3.0	1.8
SO_2	0.2	0.15	--
NO_x	——— 0.07[d] ———		
Particulates grams/ft^3	0.5[e]	0.01	--

(a) Calculated for burning with 20% excess air a typical high volatile bituminous coal of the following composition = carbon -70.1%, oxygen -6.6%, hydrogen -4.9%, nitrogen -1.4%, sulfur -3.0%, ash -12.7%, and H_2O -1.3%.

(b) Calculated a typical residual fuel oil of the following composition = 86.5% carbon, 10.3% hydrogen, 2.5% sulfur, 0.7% nitrogen with 20% excess air.

(c) Calculated for burning natural gas with 10% excess air.

(d) This is an average value. Actual values range from 0.01% to 0.15%.

(e) Assumes 90% particulates removal.

In order to remove NO_x from flue gases, Esso Research and Engineering Company carried out a flue gas scrubbing program which was sponsored by EPA. The program consisted of screening various aqueous absorbents for NO_x absorption potential. The results of the screening program are contained in the report EPA-R2-72-051. The main conclusions of the batch screening studies were:

- The addition of NO_2 to flue gas to improve NO_x (mostly NO) absorption does not appear promising. While the presence of NO_2 does improve the absorption of NO, the magnitude of the increase is insufficient to support a viable process.

- Sulfite solutions and slurries are efficient NO_2-SO_2 absorbents. Soluble sulfites (Na_2SO_3) are better NO_2 absorbers than insoluble slurries ($CaSO_3$) because of the higher level of sulfite ion in solution.

- Calcium, magnesium, and zinc hydroxide slurries are effective NO_2-SO_2 absorbers. The sulfite formed when SO_2 is absorbed is necessary for efficient NO_2 scrubbing.

- Limestone ($CaCO_3$) is also a good NO_2-SO_2 absorbent for the same reasons as for $Ca(OH)_2$.

- NO_2 scrubbing is enhanced by removing oxygen from the flue gas or by adding an anti-oxidant such as hydroquinone to the scrubbing solution.

- Sulfide solutions are excellent NO_2 and SO_2 absorbers but do generate a small amount of NO.

- Part of the absorbed SO_2 is oxidized to sulfate.

These results led to the second phase of the program which was to design, construct, and test a continuous, gas scrubbing system for simultaneous removal of NO_2 and SO_2 from blended flue gases. The underlying assumption is that flue gas NO_x (mostly NO) from a real plant could be oxidized to NO_2 upstream from the gas scrubber. This may be technically feasible using ozone or a catalyst.

The basic approach is to use the sulfite formed during SO_2 absorption to remove the NO_2 from the same gas stream.

$$SO_2 + 2OH^- \longrightarrow SO_3^= + H_2O$$

$$2OH^- + SO_3^= + 2NO_2 \longrightarrow SO_4^= + 2NO_2^- + H_2O$$
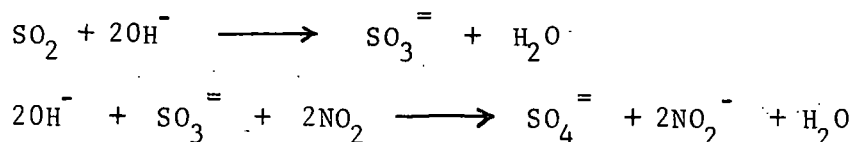
The resulting nitrite ion (NO_2^-) may subsequently be oxidized to nitrate ion (NO_3^-) by the molecular oxygen (3%) present in the flue gas.

In addition to testing sulfite ion scrubbing, certain analytical techniques needed improvement. These included the spectrophotometric procedure for analyzing solutions for nitrite and nitrate levels, and the procedure for measuring nitric oxide (NO) levels in damp flue gas.

The objectives of the program were to:

(1)   Design and construct a continuous flue gas scrubber for NO_2-SO_2 absorption.

(2)   Obtain scrubbing data using several absorbents to verify the results of the screening study.

(3)   Develop and improve the analytical procedures so that accurate material balances may be obtained.

These will be discussed in detail in the following section.

2. LABORATORY STUDIES

2.1 Analytical Techniques

This section discusses the procedures for solution analysis and for gas analysis.

2.1.1 Analysis of Solutions for Nitrite and Nitrate Levels

When absorbed by aqueous solutions NO_x is converted primarily to nitrite and nitrate ions whose levels must be accurately determined in order to insure a satisfactory NO_x material balance. J. H. Wetters and K. L. Uglum [Analytical Chemistry, 42, 335 (1970] have described a spectrophotometric technique capable of the direct, simultaneous determination of nitrate and nitrite levels in aqueous solutions. The procedure involves taking two ultraviolet absorbance readings (302 nm and 355 nm) on the solution followed by calculation of the levels using molar absorptivities determined with standard solutions of nitrite and nitrate ions. The authors claim a lower detection limit, using 1.0 cm cells, of 0.02 mg/ml for nitrite and 0.09 mg/ml for nitrate. Three molar absorptivities are required because nitrite ion absorbs at 302 nm and 355 nm whereas nitrate ion absorbs only at 302 nm. Thus, the nitrite level in an unknown solution may be determined by a single absorbance reading at 355 nm whereas the nitrate level must be calculated from readings taken at both wavelengths. For example, the nitrite level in a solution containing both nitrite and nitrate may be calculated from the absorbance reading at 355 nm using Beer's Law.

$$A = \varepsilon bC$$

A = measured absorbance
ε = molar absorptivity
b = cell path length (centimeters)
C = solute concentration (molarity)

The nitrite concentration is calculated from the following quantities.

$$A^{355} = \varepsilon^{355}_{NO_2^-} \, bC_{NO_2^-}$$

The nitrate determination is slightly more involved because the measured absorption at 302 nm contains contributions from both species.

$$A^{302} = \varepsilon^{302}_{NO_2^-} \, bC_{NO_2^-} + \varepsilon^{302}_{NO_3^-} \, bC_{NO_3^-}$$

However, the concentration of nitrite is already known from the reading taken at 355 nm.

$$C_{NO_2^-} = A^{355}_{NO_2^-} \Big/ \epsilon^{355}_{NO_2^-} \, b$$

Substituting into the expression for the total absorption at 302 nm gives, after cancelling the equal path lengths,

$$A^{302} = \left(\frac{\epsilon^{302}_{NO_2^-}}{\epsilon^{355}_{NO_2^-}} \right) A^{355} + \epsilon^{302}_{NO_3^-} \, bC_{NO_3^-}$$

$$C_{NO_3^-} = \left[A^{302} - \left(\frac{\epsilon^{302}_{NO_2^-}}{\epsilon^{355}_{NO_2^-}} \right) A^{355} \right] \Big/ \epsilon^{302}_{NO_3^-} \, b$$

Therefore, the nitrate level may be determined from three molar absorptivities, two absorbance measurements, and the cell path length.

In order to measure the molar absorptivities, stock solutions of $NaNO_2$ and KNO_3 were prepared from reagent grade chemicals and distilled water. Samples of solution were placed in 4.0 cm quartz cells which were inserted into an Optica Spectrophotometer for absorbance measurements. The results, tabulated in the Appendix, gave the following molar absorptivities and average deviations:

$$\epsilon^{302}_{NO_2^-} = 9.4 \pm 0.2$$

$$\epsilon^{355}_{NO_2^-} = 24.2 \pm 0.7$$

$$\epsilon^{302}_{NO_3^-} = 7.5 \pm 0.2$$

These values were used to test the procedure by analyzing prepared solutions containing both $NaNO_2$ and KNO_3. These results are shown in Table 2.

Table 2

Spectrophotometric Analysis of Nitrite-Nitrate Mixtures

Exp #	Actual Solution Molarity		Measured Solution Molarity		% Error	
	NO_2^-	NO_3^-	NO_2^-	NO_3^-	NO_2^-	NO_3^-
1	0.00488	0.00908	0.00500	0.00961	2.5	5.8
2	0.00488	0.00908	0.00485	0.00908	0.6	0
3	0.00975	0.00908	0.00986	0.00958	1.1	5.5
4	0.00520	0.00908	0.00525	0.00930	1.0	2.4
5	0.00520	0.00908	0.00526	0.00922	1.2	1.5
6	0.0104	0.00908	0.0102	0.00958	1.5	5.5
6a*	0.0104	0.00908	0.0104	0.00951	0	4.7

* Used a 1.0 cm cell instead of the 4.0 cm cell used in all the other experiments.

Although the nitrate measurements tended to be high, the overall results were satisfactory.

Since the bulk of the flue gas scrubbing experiments were to be carried out in the presence of sulfite ion, it was important to ascertain the effect of sulfite ion on the analysis for nitrate and nitrite levels. The spectrophotometric absorbance of sodium sulfite (Na_2SO_3) solutions exhibited a strong pH dependence as shown in Table 3.

Table 3

Effect of pH on the Molar Absorptivity of Sulfite Ion

pH	Molar Absorptivity Measured at	
	302 nm	355 nm
9.7	0.0038	0.0018
7.7	0.131	0.0035

The natural pH of 1.0 molar Na_2SO_3 is 9.7. Addition of hydrochloric acid, which does not absorb high at either wavelength, was necessary to lower the pH to 7.7. The dramatic increase in molar absorptivity at 302 nm was likely due to the formation of bisulfite ion.
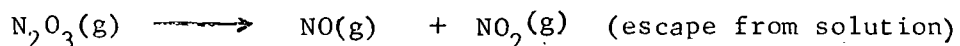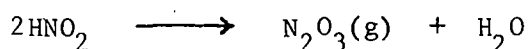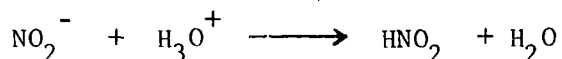
$$SO_3^= + H_3O^+ \longrightarrow HSO_3^- + H_2O$$
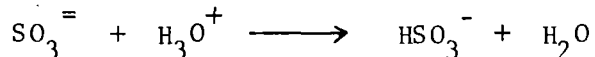
This would not seriously affect the determination of nitrite levels at the lower pH but would completely negate any attempt to measure nitrate levels. Thus, to minimize sulfite interference requires that the solution be made sufficiently alkaline (pH $>$ 9) prior to analysis. In order to verify this observation, solutions containing nitrite and sulfite were analyzed at both wavelengths. In the absence of nitrate each wavelength gives an independent measurement of the nitrite concentration and any interference should show up in the reading taken at 302 nm. Duplicate experiments on a solution containing 0.00975 molar nitrite and 0.90 molar Na_2SO_3 (pH = 9.8) produced consistent results; at 302 nm the measured nitrite level was 0.00994 molar (2% error) and at 355 nm the measured level was 0.0104 molar (5% error). Another sample of the same solution was treated with a small quantity of concentrated hydrochloric acid to lower the pH to 7.8. Spectrophotometric measurements then showed the nitrite values to be 0.0131 molar at 302 nm and 0.00894 molar at 355 nm. These values differ by +35% and -8%, respectively, from the original nitrite level. The +35% error is consistent with sulfite interference whereas the -8% error is less obvious. The dropwise addition, with stirring, of concentrated HCl produced locally high acidities in the region of drop impingement. This very low pH condition lasted momentarily until the mixing effect of stirring caused the pH to shift toward more alkaline values. However, part of the nitrite may have been lost via breakdown of the nitrous acid formed at low pH.

$$NO_2^- + H_3O^+ \longrightarrow HNO_2 + H_2O$$

$$2 HNO_2 \longrightarrow N_2O_3(g) + H_2O$$

$$N_2O_3(g) \longrightarrow NO(g) + NO_2(g) \quad \text{(escape from solution)}$$

The problem was eliminated by improved stirring and by introducing the HCl below the surface of the solution.

Alkaline scrubbing solutions will absorb CO_2 to form carbonates which may or may not be soluble depending on the cations present. Because soluble carbonate interferes with spectrophotometric determination of nitrite and nitrate, the species must be removed prior to analysis. This is easily accomplished by acidifying the solution which expels the carbonate as CO_2 gas. Subsequently, the pH must be raised to eliminate sulfite interference. In order to check the effect of pH cycling, several experiments were made with no carbonate present. Table 4 shows the results from two runs using solutions containing nitrite and sulfite ions.

Table 4

Effect of pH Cycling on Nitrite Readings

	Original Solution			After pH Cycling*				
				[NO$_2^-$]			% Error	
Exp #	[NO$_2^-$]**	[SO$_3^=$]	pH	302 nm	355 nm	pH	302 nm	355 nm
1C	0.00956	0.88	9.8	0.00924	0.00966	10.1	-3.	1.
2C	0.00953	0.88	9.8	0.00974	0.00957	11.9	2.	~1.

* The pH was lowered to 7.7 with concentrated HCl. This was followed
by addition of concentrated NaOH to raise the pH. The slight dilution
effect was taken into account in the calculations.
** All concentrations are in units of molarity.

Since the pH cycling showed no effect on nitrite measurements in the
presence of sulfite, several more experiments were made with solutions
containing nitrite, nitrate, and sulfites as shown in Table 5.

Table 5

Effect of pH Cycling on Nitrite and Nitrate Readings

	Original Solution			After pH Cycling*			% Error	
Exp #	[NO$_2^-$]**	[NO$_3^-$]	pH	[NO$_2^-$]	[NO$_3^-$]	pH	[NO$_2^-$]	[NO$_3^-$]
3C	0.00520	0.00908	9.5	0.00557	0.00892	11.6	7.1	-1.8
4C	0.00520	0.00908	9.6	0.00524	0.00936	11.7	1.	3.1
5C	0.00520	0.00908	9.4	0.00540	0.00918	11.5	4.6	1.7

* Same as in Table 4.
** Same as in Table 4. All solutions contained 0.85M Na$_2$SO$_3$.

The effect of pH cycling appears to be more pronounced in Table 5 than
in Table 4 although the only difference is the presence of nitrate ion.
Because the goal of pH cycling was to eliminate carbonate and sulfite
spectral interferences, it was decided to move on to work with solutions
containing all four ions - NO$_3^-$, NO$_2^-$, SO$_3^=$ and CO$_3^=$.

Stock solutions containing the four ions gave totally
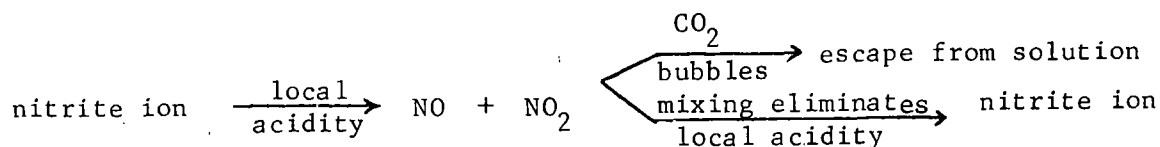unsatisfactory analyses after pH cycling as shown in Table 6.

Table 6

Effect of pH Cycling on Solutions Containing
Nitrite, Nitrate, Sulfite, and Carbonate Ions

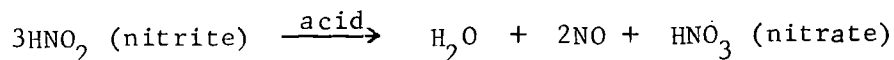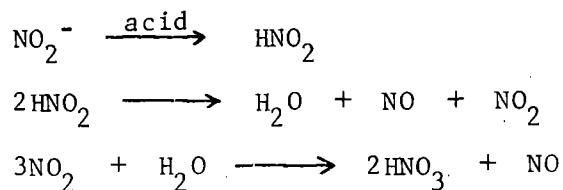| Exp #	Original Solution			After pH Cycling*			% Error	
	$[NO_2^-]$**	$[NO_3^-]$	pH	$[NO_2^-]$	$[NO_3^-]$	pH	$[NO_2^-]$	$[NO_3^-]$
6C	0.00520	0.00908	11.1	0.00143	0.0103	9.5	-73.	13.
7C	0.00520	0.00908	11.1	0.00131	0.0109	9.8	-75.	20.
8C	0.00520	0.00908	11.1	0.00384	0.0100	9.8	-26.	10.

* Same as in Table 4.
** Same as in Table 4. All solutions contained 0.85 M $SO_3^=$ and 0.85M $CO_3^=$.

These results indicate that nitrite is disappearing during
pH cycling and is not being totally converted to nitrate. It is likely that
nitrite is being stripped from the solution by the effervescence
produced during HCl addition. As discussed previously the nitrite
ion may decompose into the two gases, NO and NO_2, which may then
diffuse into a nearby bubble of CO_2 gas instead of recombining to reform
nitrite ion.

nitrite ion $\xrightarrow[\text{acidity}]{\text{local}}$ NO + NO_2 $\begin{cases} \xrightarrow{CO_2 \text{ bubbles}} \text{escape from solution} \\ \xrightarrow{\text{mixing eliminates local acidity}} \text{nitrite ion} \end{cases}$

Of the two gases, NO and NO_2, which may escape, NO_2 may react with water
to form more nitrate. Nitric oxide is very unreactive and once entrapped
in a gas bubble, will be stripped from the solution. The overall
sequence shows the possibility of one nitrate being formed for every
three nitrites which disappear.

$NO_2^- \xrightarrow{\text{acid}} HNO_2$

$2 HNO_2 \longrightarrow H_2O + NO + NO_2$

$3 NO_2 + H_2O \longrightarrow 2 HNO_3 + NO$

- -

$3 HNO_2$ (nitrite) $\xrightarrow{\text{acid}} H_2O + 2NO + HNO_3$ (nitrate)

This sequence is approximately consistent with the results of experiments
6C and 7C and accounts for the high levels of nitrate found after pH
cycling. In experiment 8C, however, we can account for only 40% of the
total excess nitrate error. Since the cycling in this experiment
lowered the pH only to 8.3 as compared to 6.5 and 7.7 for 6C and 7C,

respectively, more carbonate should remain in solution to raise the
302 nm reading (carbonate has less influence at 355 nm). The fact that
the pH was only lowered to 8.3 also explains the 1/3 less error in
nitrite level for experiment 8C. Since less acid was added, less
nitrite decomposed.

If the solutions listed in Table 6 do not undergo pH cycling, but
are analyzed directly (pH = 11.1) the resulting nitrite and nitrate values
are in excess by approximately 12%.

All further attempts at removing soluble carbonate by acid
addition failed to yield satisfactory results. At this juncture we
turned to precipitation techniques with the hope of resolving the
problem. A concentrated solution of $CaCl_2$ was added to the test
solution containing all four of the important ions. Unfortunately,
calcium carbonate and calcium hydroxide precipitates gelled the entire
sample. After breaking the gel and centrifuging the mixture the
clean solution was analyzed spectrophotometrically for nitrite and
nitrate. Unfortunately, the results were highly erratic and totally
unsatisfactory.

At this point we decided not to pursue this question any
further but concluded that a total nitrogen level would have to suffice
for those few samples containing high levels of soluble carbonate. A
complete NO_x material balance would still be possible for these samples;
only the ratio of nitrite to nitrate would be unavailable. A reasonable
approximation to the ratio could be obtained by extrapolation from
data taken from a similar absorbent in which carbonate is insoluble.

The results of this effort can be briefly summarized:

● Raising the pH to >9, effectively minimizes sulfite
   interference in the spectrophotometric determination
   of nitrite and nitrate.

● High levels of soluble carbonate interfere with
   the nitrite and nitrate measurements; no simple
   procedure was found which would eliminate this
   problem. Fortunately, a total NO_x material balance
   is still possible for those few samples exhibiting
   this problem.

2.1.2 Measurement of NO Levels in Flue Gases

Flue gases contain three gaseous pollutants:

1. SO_2
2. NO_2
3. NO

Two Dupont 400 spectrometers were used for on-line analysis of SO_2 and
NO_2. These instruments were also employed in the screening study
referred to previously. The hot (130°F), damp, flue gas flowed through
the heated gas analyzer cells where the appropriate measurements
were made. No pretreating of flue gas was necessary. The analyzer
readings were recorded continuously on strip charts.

The determination of NO levels in the flue gas was more
complicated. During the earlier screening study a Beckman NDIR (non-Dispersive
Infra-Red) was used for NO measurement. Unfortunately, the instrument
was sensitive to water vapor which required that the water be removed
prior to analysis. This was not a simple task because of the complex
reaction chemistry associated with NO, NO_2, SO_2 and liquid water. A
cumbersome yet reliable technique evolved in which the flue gas
passed through a sequence of calibrated traps designed to remove
NO_2, SO_2 and water vapor. The complexity of the system created
problems and introduced a delay time in the NDIR output.

In order to improve the analytical procedure for NO, we
discussed chemiluminescence techniques with Thermoelectron Corporation
which manufactures an instrument for NO analysis. Their conventional
instrument was unable to handle damp gases directly but it seemed
that specially heated inlet lines could resolve that problem. As
long as the water vapor did not condense in the inlet system, no
difficulties should arise. Consequently, Thermoelectron Corporation
modified a standard instrument to our specifications and loaned
it to us for test experiments.

In the first series of tests we compared the response of
the NDIR and the chemiluminescence unit (CML) to a gas blend consist-
ing of nitrogen and varying amounts of NO. Table 7 contains the
results.

Table 7

Comparison of the CML with the NDIR

Series #	NDIR Response (ppm)	CML Response (ppm)	Comments
1	287*	287*	CML inlet system
	198	202	is cold; heater not
	475	485	on
	120	115	
	360	365	
2	395*	395*	CML inlet system
	200	208	heater is on
	87	87	
	353	360	
	480	485	
3	460*	460*	Gas blend contains
	110	106	12% CO_2 in Series #
	175	185	3 runs except for
	440	450	last run
	277	290	
	265	280	steam ($\lesssim$ 5%) added
	250	265	steam ($\lesssim$ 5%) +3% O_2
	302	318	No CO_2

* At the beginning of each series, both instruments were adjusted to
give the same correct reading.

The two instruments were connected in parallel to the main line carrying the blended gas. The agreement is quite good between the NDIR and the CML which indicated satisfactory reliability for the CML.

The CML has two readout modes; one for NO only and the other for total NO_x. The second series of tests was designed to check the agreement between these two modes and to determine the influence of all the flue gas constituents on the NO reading under normal operating conditions. The NO level was fixed at 600 ppm initially and left unchanged during the entire test. The results are shown in Table 8.

<div align="center">Table 8</div>

<div align="center">Effect of Flue Gas Components on CML Reading</div>

Exp. #	NO Reading (ppm)	NO_x Reading (ppm)	Comments
1d	588	590	gas contains N_2 and NO
2d	598	598	3% O_2 added
3d	600	600	12% CO_2 added to the above
4d	600	600	10% steam added to the above
5d	600	600	one hour after steam added
6d	590	1625	$\approx$ 1000 ppm NO_2 added to above
7d	580	1500	$\approx$ 3000 ppm SO_2 added to above
8d	580	1500	SO_2 source turned off
9d	580	1500	SO_2 source turned back on

The data in Table 8 show the CML to be reliable, stable, and not significantly affected by the various constituents of flue gases. The modified instrument circumvented all the previous problems associated with the NDIR and, in addition, provided a check on our Dupont 400 NO_2 analyzer. The total NO_x readout on the CML gave the sum of NO plus NO_2 from which the NO_2 level could be calculated by subtracting the NO reading.

The final test was made with the NDIR again connected in parallel with the CML and both analyzing a hot, blended flue gas containing N_2, 3% O_2, 12% CO_2, 10% H_2O, and NO. The NDIR was equipped with the proper traps for pretreating the flue gas. The CML read 116 ppm NO and the NDIR read 111 ppm NO, which is good agreement. Based on these results, we consider the problem of measuring NO in a damp flue gas containing NO_2 and SO_2 to be resolved.

2.2 Scrubbing System

2.2.1 Flue Gas Blending

The gas blending system was capable of producing synthetic flue gas consisting of 10% steam, 12% CO_2, 3% O_2, 3000 ppm SO_2, 1000 ppm NO_2, 1000 ppm NO and N_2. The concentration of any component could be varied over a wide range. In addition, the system was capable of total flow rates of 80 to 800 SCFH. Figure 1 depicts the total scrubbing system and include a schematic of the gas blending system. All of the gases were derived from pure gas sources except for oxygen, whose source was compressed air. Nitrogen, air, and steam were available in the laboratory whereas CO_2, NO_2, NO, and SO_2 were supplied from cylinders. In order to minimize gas phase reactions between SO_2 and NO_2, each was thoroughly diluted before mixing. The pure SO_2 was blended with air, CO_2, and NO, while the pure NO_2 was diluted with N_2. After mixing the two diluted streams the blend passed into a heated steam box to receive the appropriate steam flow. The steam supplied to the lab was wet so the steam box provided the heat to dry it out. The dewpoint of the blended flue gas exiting from the steam box was approximately 115°F so that all downstream lines had to be heated.

The biggest problem encountered involved NO_2. This substance is a liquid (N_2O_4) under normal conditions which boils at 70°F under a pressure of one atmosphere. The vapor pressure rises to 17 psig at 100°F. A small heated shed was constructed just outside the laboratory to hold one cylinder each of pure NO_2 and pure SO_2. It was probably unnecessary to heat the SO_2 because of its high vapor pressure but since both cylinders had to be outdoors in winter, we decided to take the extra precaution against the possibility of unusually low temperatures. The shed temperature was maintained at 100-115°F by a thermostatically controlled electric heater. Because of its low vapor pressure, conventional corrosive gas regulators would not regulate NO_2 flow effectively. We tried to control the flow with a metering valve but temperature fluctuations in the shed generated large uncontrolled changes in gas flows. Eventually we obtained a specially modified corrosive gas pressure regulator which could effectively regulate the NO_2 pressure. However, even this controller failed once because of the highly corrosive nature of pure NO_2. The stainless steel lines carrying the pure NO_2 were heated up to the point of dilution with nitrogen. The NO_2 flowmeter was ineffective because droplets of liquid formed inside the glass barrel; we were unable to conveniently provide sufficient heat to the flowmeter. To simplify the situation, the flowmeter was replaced with a straight piece of stainless steel tubing with a metering valve. The NO_2 level in the flue gas was obtained by opening the metering valve until the proper response occurred in the Dupont 400 NO_2 analyzer. When fixing the various pollutant concentrations, the scrubber column shown in Figure 1 was by-passed and the flue gas went directly to the gas analyzers.

All lines were SS 316 stainless steel. All lines delivering gases from their sources were 1/4" i.d. except for the nitrogen and steam lines which were 1/2" i.d. Beyond the first level of blending all lines were 1/2" i.d.

Each flowmeter had a pressure gauge on the downstream side and each flowmeter was calibrated with a wet test meter.

The blending manifold functioned very well after the problems discussed above were resolved.

2.2.2 Flue Gas Scrubber

The continuous tower scrubber is shown in Figure 1. The vertical glass column is constructed of sections of glass pipe each of which is 8 inches long and 2 inches inside diameter. The sections are coupled with threaded aluminum collars. The collars and the glass pipe were obtained from the Fisher-Porter Company. The design makes it easy to change the height of the column. Each section contains a thermocouple and a port for removing samples of scrubbing fluids. The top of the column held a demister head packed with glass wool for removing entrained droplets from the gas stream. The entire column sat on a 50 liter heated flask which served as the scrubbing fluid resevoir. The flask was provided with a stirrer. Pressure gauges were located at the top and bottom of the column and a water manometer measured the pressure drop across the entire column.

A circulating pump withdrew fluid from the resevoir and pumped it up to the top to be sprayed down the column, countercurrent to the gas flow. The rough pumping rate was controlled at the pump with final adjustment being made at the flowmeter downstream from the pump. A pH electrode was situated in the pump intake for resevoir pH determinations.

The temperature of the scrubbing fluid was usually kept at 125°F. The gas and liquid flow rates were sufficiently high to maintain the glass column temperature at 125°F without additional heating or insulation. Also, it was unnecessary to heat or insulate the pump lines.

All thermocouples on the scrubbing tower and on the heated lines were connected to temperature recorders. Temperature controllers were used wherever heat was required.

When making a scrubbing experiment the following sequence was followed:

- Fix the flue gas composition and flow rate while by-passing the scrubber.

Figure 1
Flow Schematic of Scrubbing Unit

- 15 -
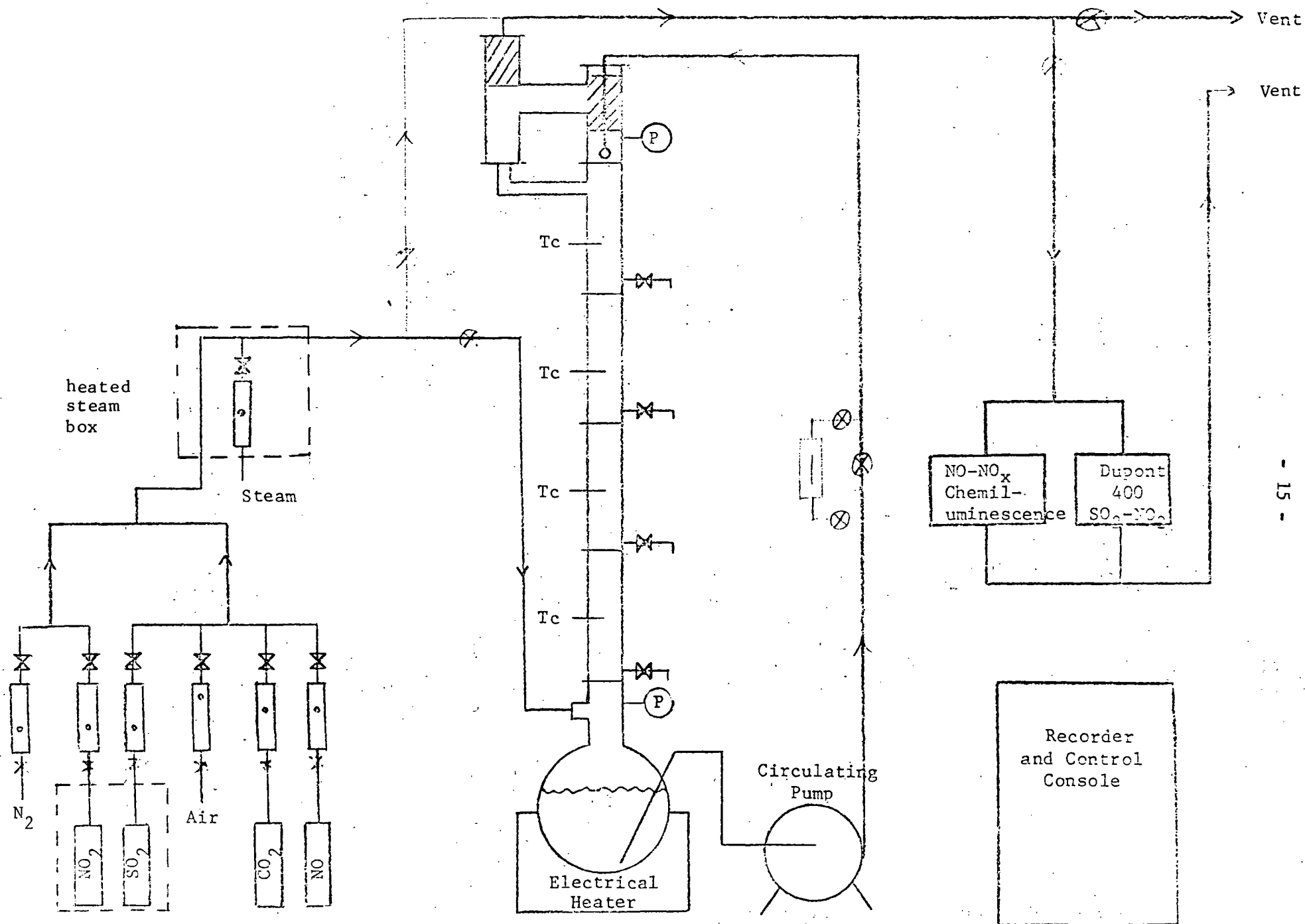
- Turn on the circulating pump and set rate to predetermined value.

- Wait 5 to 10 minutes for column temperature to stabilize.

- Switch flue gas through the scrubber.

- Monitor pH and temperatures.

- Periodically withdraw liquid samples.

- Periodically by-pass the scrubber to check the composition of the flue gas.

The system performed well; the next section discusses the results of our scrubbing experiments.

2.3 Results of Flue Gas Scrubbing Experiments

The construction, testing and trouble-shooting of the flue gas scrubbing system took much more time than anticipated. Consequently, only a small fraction of the scheduled scrubbing experiments were completed.

Despite these shortcomings, however, an important series of scrubbing experiments was completed which verified the capability of sulfite ion to effectively absorb NO_2 from flue gas. The results are shown in Table 9 and were obtained under identical conditions of temperature and flow rates. These results allow several conclusions. The first is that sulfite ion is a much better absorber of NO_2 than hydroxide ion. Unfortunately neither is effective for NO absorption which also verifies the results obtained in our previous screening study. Also the data show that the presence of SO_2 in the flue gas enhances NO_2 absorption by alkaline solutions initially containing no sulfite (see runs C1 and D1). When absorbed, SO_2 produces sulfite ion which subsequently reacts with NO_2, thereby removing it from the gas stream. A similar effect is not observed for NO; the presence of SO_2 is not significantly beneficial for NO absorption (see runs A1 and B1). Since SO_2 absorption is primarily dependent on pH, both solutions were effective for removing essentially all of the SO_2.

These experiments were made with an open column which does not provide good contacting between gas and liquid, although it does give minimum pressure drop across the column. A small amount of column packing or even some liquid distribution plates would enhance contacting and, no doubt, improve the NO_2 absorption efficiency. However, the Na_2SO_3 solution does quite well considering the poor contacting between the two phases.

Table 9

Flue Gas Scrubbing with NaOH and Na_2SO_3 Solutions

|	Input Levels (ppm)			% Absorption			Scrubbing
Exp #	NO	NO_2	SO_2	NO	NO_2	SO_2	Solution
A1	660	--	--	12.	--	--	1.0M NaOH
A2	640	--	--	0	--	--	1.0M Na_2SO_3
B1	680	--	2450	19.	--	98.	1.0M NaOH
B2	680	--	2500	6.	--	98.	1.0M Na_2SO_3
C1	--	680	--	--	12.	--	1.0M NaOH
C2	--	690	--	--	83.	--	1.0M Na_2SO_3
D1	--	690	2700	--	48.	99.	1.0M NaOH
D2	--	690	2700	--	83.	99.	1.0M Na_2SO_3

NOTES:

(1) The bulk gas composition was 10% H_2O, 3% O_2, 12% CO_2, N_2.
(2) Scrubbing solution temperature = 128°F.
(3) Gas flow rate = 5. SCFM (4.5 ft/sec in column)
(4) L/G = 20.
(5) Liquid flow rate = 4. liters per minute.
(6) Pressure inside column - 3. psig.
(7) Five glass pipe sections in column; pressure drop across entire column = 3" H_2O.
(8) Each run lasted 15 minutes; took about five minutes for system to stabilize after going on line.
(9) Resevoir initially contained 15. liters of solution.
(10) Solution pH was constant during brief runs: 1.0M NaOH, pH = 13.; 1.0M Na_2SO_3, pH = 9.
(11) No solution analyses were made.

Increasing the weight ratio of liquid flow rate to gas flow rate improves the scrubbing efficiency for NO_2 and SO_2 as shown in Figure 2.

Figure 2

Effect of L/G on NO_2 and SO_2 Scrubbing with Na_2SO_3
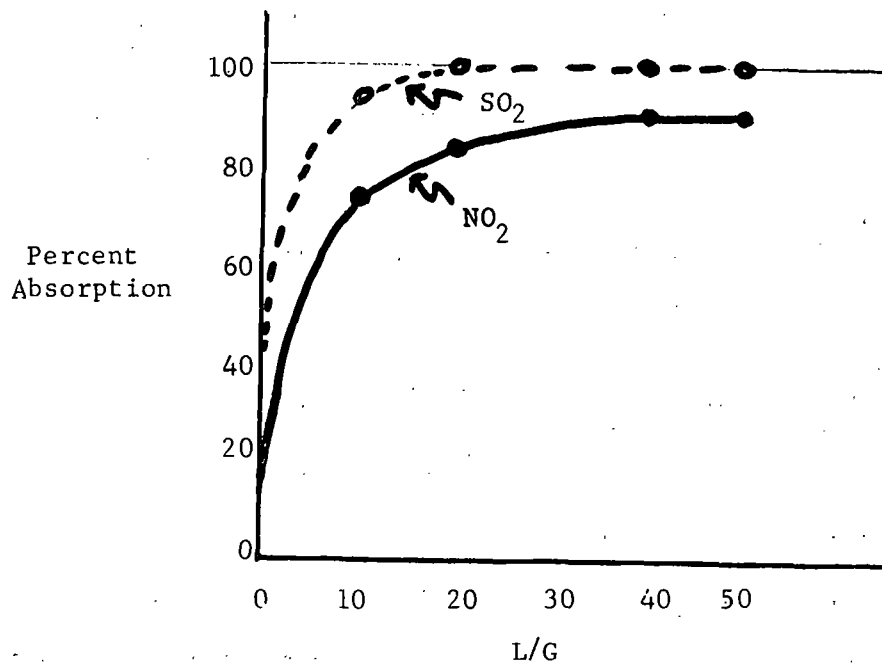
NOTES: (1) Initial NO_2 level = 620 ppm
        (2) Initial SO_2 level = 1800 ppm
        (3) Resevoir contained 13 liters of 1.0M Na_2SO_3
        (4) Total gas Flow rate = 5. SCFM
        (5) Scrubbing temperature = 125°F

Under these conditions the NO_2 absorption appears to be limited to 90% whereas the SO_2 removal, as usual, is better.

In another scrubbing experiment, using the same column configuration as before, a magnesium hydroxide slurry was employed as the absorbent for NO_2 and SO_2. Table 10 contains the results.

Table 10

Flue Gas Scrubbing Using Magnesia Slurry

Run time (min)	0	10	20	30	40	50	60
% NO_2 Absorbed	0	26.	35.	35.	34.	38.	30.
% SO_2 Absorbed	0	95.	95.	95.	99.	99.	90.
L/G	10.	10.	10.	10.	20.	20.	20.
pH	9.4	9.0	8.8	8.7	7.5	6.7	5.6

NOTES:

(1) Initial NO_2 and SO_2 levels = 920 ppm and 2600 ppm, respectively
(2) Resevoir contained 13. liters of slurry; 10. g $Mg(OH)_2$ per liter.
(3) Total pressure drop across column = 3.5" H_2O
(4) Scrubbing temperature = 125°F.
(5) Total gas flow rate - 5. SCFM.
(6) At L/G = 10, liquid flow rate was 2. liters/min.
(7) At 40 minutes on line, reset input levels to 710 ppm NO_2 and 1920 ppm SO_2.
(8) At 50 minutes, added 2. grams of hydroquinone to scrubbing fluid.

These results show that about 1/3 of the NO_2 is absorbed by the slurry. Doubling the L/G did not have any effect. In the screening program a magnesia slurry (7.4 g/l) absorbed 58% of the NO_2 from a flue gas containing 830 ppm NO_2 and 2460 ppm SO_2. The poor removal in the present experiment implies poor contacting. The screening studies also showed a marked absorption improvement with hydroquinone addition to the slurry. This was not observed in the present case, although the amount of the antioxidant added may have been too small to be effective or else the run did not last long enough for the influence to be demonstrated. In any case more data is required before any conclusions may be drawn concerning the effect of hydroquinone.

These scrubbing results verify that sulfite is a good NO_2 absorbent but a poor NO absorbent. Also, the effect of L/G is quantified for Na_2SO_3 solutions. However, these results strongly suggest that more information is required on these and other absorbing systems before engineering and economic evaluations can be initiated. The bulk of this information was to be obtained in the third and final phase of the project.

3. CONCLUSIONS AND RECOMMENDATIONS

3.1 Conclusions

The second phase of the flue gas scrubbing program was designed to realistically apply the results of the Phase I screening study to the removal of NO_2 and SO_2 from flue gases. The primary goals of the project were to design, construct and test a continuous flue gas scrubbing system which would employ sulfite species as reactive absorbents. The program required that suitable analytical procdures be developed so that accurate NO_x material balances may be obtained. The conclusions are:

(1) Analytical

    (a) Sulfite ion interferes with the spectrophotometric determination of nitrite and nitrate levels in scrubbing solutions. This interference may be minimized by raising the solution pH above 9 prior to analysis.

    (b) High levels of soluble carbonate ion will also interfere with the nitrite and nitrate analysis. This problem was not resolved. Fortunately, few samples will exhibit this condition.

    (c) Difficulties were associated with using a Non Dispersive Infra-Red instrument for analyzing NO levels in a gas stream containing NO, NO_2, SO_2 and H_2O. The problems disappeared when we changed to a chemiluminescence instrument modified with a heated inlet system.

(2) Results with continuous scrubber

    (a) The removal of NO_2 from flue gas is enhanced by the presence of sulfite in the absorbent or SO_2 in the flue gas. This verifies the results of the Phase I screening study.

    (b) NO absorption is not affected by sulfite or SO_2.

    (c) SO_2 absorption is excellent in alkaline media.

    (d) Increasing the L/G ratio improves the NO_2 absorption in 1.0M Na_2SO_3.

    (e) Only 1/3 of the NO_2 was scrubbed out by a magnesia slurry.

The results are essentially in agreement with the earlier screening study. However, much more data is required before we can effectively evaluate the overall process.

3.2 Recommendations for Future Work

Our studies have shown that flue gas scrubbing in a continuous, open column unit has promise. The following recommendations list the work which remains to be done.

- Obtain more scrubbing data using different absorbents such as lime slurry, limestone slurry, and ammonium hydroxide.

- Determine the effect of varying process parameters such as column height, superficial gas velocity, and column packing.

- Obtain complete material balances for NO_x and SO_2.

- Investigate solution regeneration techniques.

- The oxidation of NO_x to NO_2 upstream from the scrubber is vital. Studies should be instituted to optimize this reaction under flue gas conditions.

The final goal is to successfully combine NO_x oxidation, gas scrubbing, and solution regeneration into an integrated process which cleans the flue gas and minimizes the impact of scrubbing products upon the environment.

APPENDIX

TABLE A1

Measurement of Molar Absorptivities for Nitrite and Nitrate

	NO_2^-		NO_3^-
Solution Molarity	$\epsilon 302$	$\epsilon 355$	$\epsilon 302$
0.00975	9.87	25.4	--
0.00975	9.74	25.3	--
0.01040	9.52	23.7	--
0.01040	9.38	23.4	--
0.00975	9.02	24.1	--
0.00975	9.25	24.7	--
0.00975	9.28	24.7	--
0.01040	9.38	25.0	--
0.00908	--	--	7.35
0.00520	9.14	23.2	--
0.00520	9.00	23.9	--
0.00488	9.64	23.6	--
0.00488	9.48	23.7	--
0.00908	--	--	7.43
0.00908	--	--	7.43
0.01816	--	--	7.74
0.02270	--	--	7.65
0.01816	--	--	7.71

NOTES:

(1) Used standard solutions of reagent grade $NaNO_2$ and KNO_3.
(2) Used an Optica Spectrophotometer.
(3) All measurements made with 4.0 cm quartz cell.
(4) Used Beer's Law to calculate molar absorptivity.

$$A = \epsilon bc$$

A = measured absorbance
ϵ = molar absorptivity
b = cell path length in centimeters
c = solute concentration in molarity

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13. ABSTRACT

This report summarizes the findings of the laboratory program for "Development of Aqueous Processes for Removing NO_x and SO_2 from Combustion Flue Gases." This project is the second phase of the flue gas scrubbing work sponsored by EPA under Contract No. 68-02-0220. The results of the Phase I program are contained in report EPA-R2-72-051, entitled, "Development of the Aqueous Processes for Removing NO_x from Flue Gases."

The present report contains discussions of analytical techniques and scrubber design in addition to experimental results obtained with a vertical spray tower scrubber. The blended flue gases passed up the unpacked glass column countercurrent to the absorbing solution which was sprayed down from the top. The scrubbing experiments showed:

- NO_2 and SO_2 are effectively absorbed by 1.0 molar Na_2SO_3 solutions.
- NO_2 absorption by 1.0 molar NaOH solution is enhanced by the presence of SO_2 in the flue gas.
- Neither NO nor NO_2 is effectively absorbed by 1.0 molar NaOH solution in the absence of SO_2, and NO absorption is not improved by the presence of SO_2.
- Increasing the L/G ratio improves NO_2 and SO_2 absorption by 1.0 molar Na_2SO_3.
- Under similar scrubbing conditions $Mg(OH)_2$ slurry is not as effective as Na_2SO_3 solution for NO_2 absorption.

The data show that sulfite solutions would effectively absorb NO_x and SO_2 from flue gases provided the NO_x (mostly NO) has been oxidized to NO_2 upstream from the scrubber.

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Gas Scrubbing						
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Sulfites						

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15. Supplementary Notes

16. Abstracts The report summarizes the findings of a laboratory program for developing aqueous processes for removing NOx and SO2 from combustion flue gases. It discusses analytical techniques and scrubber design, as well as results obtained experimentally with a vertical spray tower scrubber: blended flue gases passed up an unpacked glass column, countercurrent to the absorbing solution which was sprayed down from the top. The experiments showed that: NO2 and SO2 are effectively absorbed by 1.0 molar Na2SO3 solutions; NO2 absorption by 1.0 molar NaOH solution is enhanced by SO2 in the flue gas; neither NO nor NO2 is effectively absorbed by 1.0 molar NaOH solution in the absence of SO2 (NO absorption is not improved by SO2); increasing the L/G ratio improves NO2 and SO2 absorption by 1.0 molar Na2SO3; and under similar conditions, Mg(OH)2 slurry is not as effective as Na2SO3 solution for NO2 absorption.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution
Nitrogen oxides
Sulfur dioxide
Combustion
Flue gases
Chemical analysis
Design
Washing
Spraying

Sodium sulfites
Absorbers (materials)
Sodium hydroxide
Nitrogen oxide
Nitrogen dioxide
Magnesium hydroxides
Sulfites
Slurries

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Stationary sources
Aqueous processes
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