SCRUBBING LIQUORS FOR NITROGEN TETROXIDE

by

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ABSTRACT

N_2O_4 scrubbing research has a considerable history, if one considers that N_2O_4 is merely a dimer of NO_2. NO_2 is a well-known health hazard and a pollutant of national concern. Once it was determined that the wet scrubbing concept was the most practical solution to the N_2O_4 emission problem, it became important to optimize the composition of the scrubbing liquor. Several reagents were cited in the literature as being advantageous in scrubbing NO_2. Experiments were conducted on a model wet scrubber in order to verify and rank the performances of these scrubbing liquors. The most efficient scrubbing liquor found experimentally was a 10% sodium sulfite solution. This was in agreement with a previous study by Exxon performed under an EPA contract.

Scrubbing Liquors for N_2O_4

Our mission, as originally conceived, was to research and develop design criteria for hardware to prevent discharge to the atmosphere of the hypergolic propellants during the pad loading operations. We were to consider any and all possible methods to accomplish the task. But the final system, of course, had to be safe, effective, economical and simple to operate. Among the concepts considered and researched were the following:

1. Cryogenic trapping of effluent
2. Adsorption towers
3. Wet scrubbers

We quickly found that cryogenic trapping could perhaps be effective, but it was uneconomical and highly dependent upon proper design. We also found that adsorption techniques were very effective on N_2O_4 contaminated effluent present in small concentrations, but the capacity of such systems are poor and regeneration is necessary. Wet scrubbers were quickly found to be overall the most advantageous in all respects. These systems are very simple in design and have large capacity.

Unlike hydrazine scrubbing, N_2O_4 scrubbing research has a considerable history if one considers that N_2O_4 is merely a dimer of nitrogen dioxide (NO_2). Nitrogen dioxide (NO_2) is a well-known health hazard and is a pollutant of national concern. It is one of six compounds for which the EPA has mandated a National Ambient Air Quality Standard. The standard is 100 ug/m^3 (0.05 ppm) annual arithmetic mean. Atmospheric NO_2 is produced by oxidation of nitric oxide (NO) generated by automobiles and power plants. Thus in the last few years there has been a significant effort in the U.S. and a great

effort in Japan to abate NO_2 atmospheric pollution. Catalytic converters perform the task in automobiles, but scrubbing is still a viable option for power plants. The power plant scrubbing problem is made more difficult because the principal oxide of nitrogen emitted is the insoluble nitric oxide (NO), rather than the soluble NO_2. Thus if power plants hope to control NOx emissions by scrubbing they must introduce a step to oxidize the nitric oxide (NO) to nitrogen dioxide (NO_2).

Actually, kinetic data has shown that the soluble NOx species is not NO_2 but N_2O_4 and N_2O_3. As mentioned before N_2O_4 is formed by combining two molecules of NO_2. N_2O_3 is formed by combining NO and NO_2. Thus we are indeed doubly fortunate in the aerospace industry to be faced with the problem of scrubbing N_2O_4 rather than NO. However, NO still presents problems.

When N_2O_3 and N_2O_4 dissolve in water, NO is released according to the equations shown below.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$
$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$
$$3HNO_2 \longrightarrow HNO_3 + H_2O + {}_2NO$$

Since this phenomenon is well known, workers in the field have attempted to minimize the NO evolution by adding oxidizing agents to the scrubbing liquor. Some of the agents tested have been potassium permanganate ($KMnO_4$), ozone (O_3), and hydrogen peroxide (H_2O_2). In general these agents were of limited value as far as adding to scrubbing efficiency is concerned.

The history of wet scrubbers for N_2O_4 in aerospace applications goes back to the Gemini program.

Hamilton Standard provided fuel-handling systems for the Gemini and Saturn programs, which included scrubbers for the removal of hypergolic propellants which would otherwise be vented to atmosphere. Gaseous nitrogen-bearing N_2O_4 vapors passed through the scrubbers, which met design specifications for contaminant concentration of less than 5 ppm N_2O_4 or less than 1 ppm MMH at the outlet of the system. This outlet was downstream of a dilution fan/mixing chamber where the scrubber effluent was mixed with fresh air in a 100:1 ratio, thus reducing contaminant concentrations by a factor of one hundred. See Figs. 1 and 2.

The scrubbers were designed to accept from 10 standard cubic feet per minute at 10^6 ppm, up to 60 SCFM at 1500 ppm, of N_2O_4-contaminated nitrogen. The scrubber, operating with a through flow of 60 SCFM, reduced N_2O_4 concentration by at least a factor of 3 (67% efficiency) and MMH concentration by a factor of 15 (93% efficiency).

Scrubbing was accomplished by a cross-flow absorber which moved the gas across sixteen cascaded filters, each with an associated fresh water spray nozzle. The cross-section of the scrubber was about 2/3 ft^2, and of each filter, about 1 ft^2. The filters were of pyrex glass wool supported by stainless steel. The length of the scrubber was about 18 ft., folded once to a "u" form. Water flow rate was 40 GPM. The scrubber and associated

Scrubber Diagram

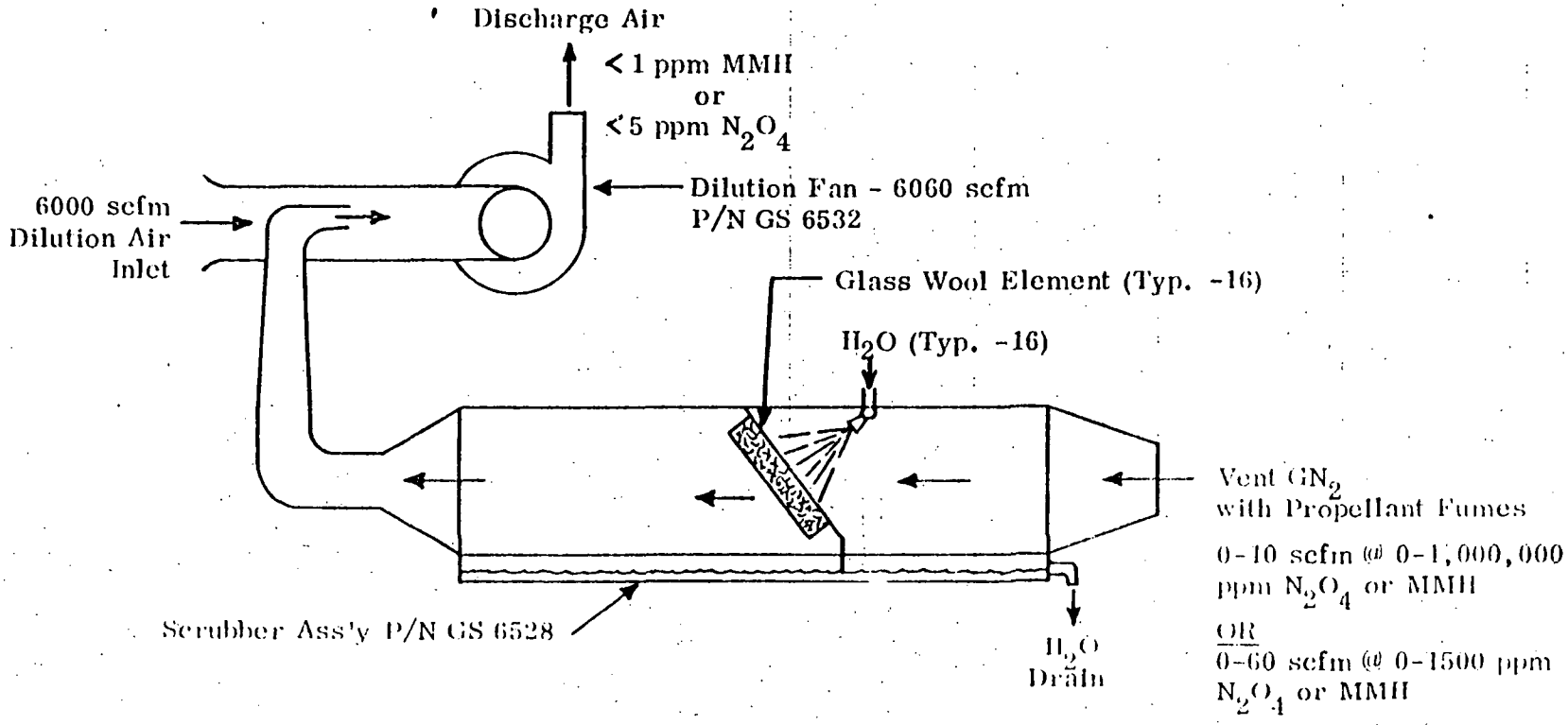


Figure 1. Side view of the Hamilton Standard (Buffalo Forge) scrubber.

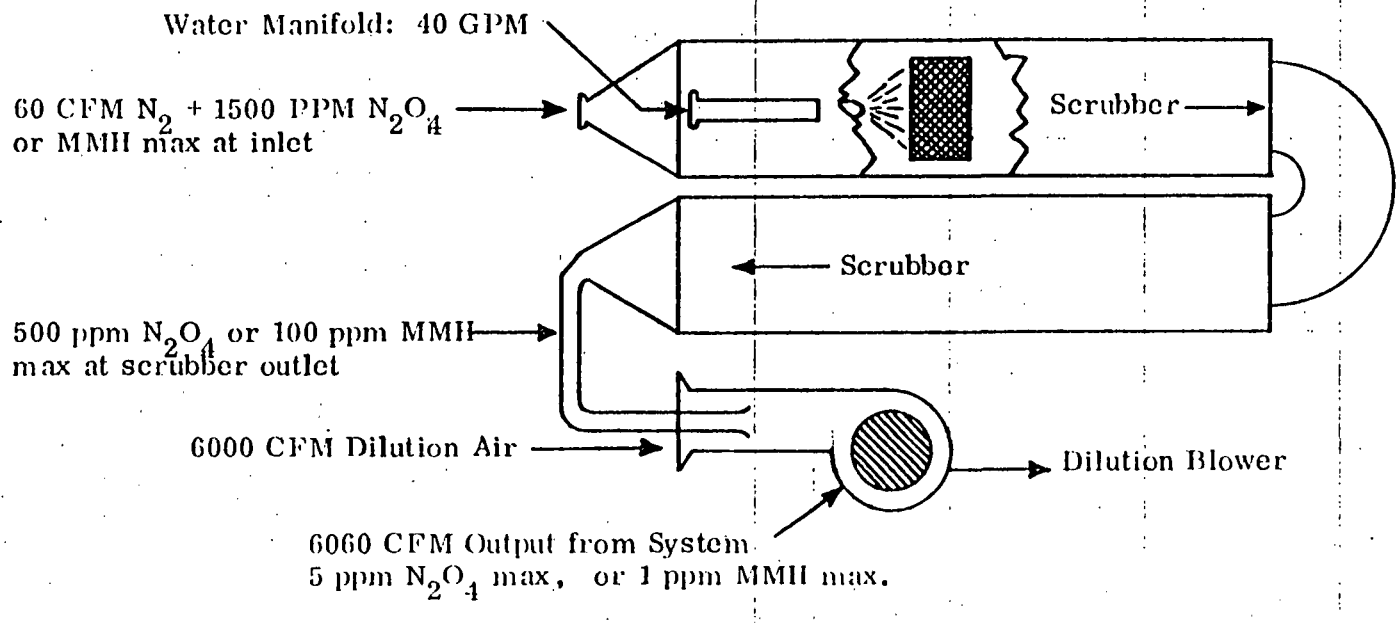


Figure 2. Top View of the Hamilton Standard (Buffalo Forge) Scrubber

dilution blower were manufacted by the Buffalo Forge Co. of Buffalo, New York. Thus, previous efforts at wet scrubbing for N_2O_4 in the Gemini program were not eminently successful.

Once it was determined that the wet scrubbing concept was the most practical solution to the N_2O_4 emissions problem, it became important to optimize the composition of the scrubbing liquor. Among the reagents suggested by the literature as being advantageous in scrubbing NO_2 were the following:

Potential Scrubbing Liquors for N_2O_4

Water	H_2O	Ammonium sulfite	$(NH_4)_2SO_3$
Sodium sulfite	Na_2SO_3	Ammonium bisulfite	NH_4HSO_3
Magnesium sulfite	$MgSO_3$	Ammonium nitrate	NH_4NO_3
Ammonium acetate	$CH_3C^{O}\text{-}O^{\ominus}NH^{\oplus}_4$	Calcium oxide	CaO
Ammonium hydroxide	NH_4OH	Magnesium carbonate	$MgCO_3$
Magnesium hydroxide	$Mg(OH)_2$	Aliphatic and aromatic amines	$R\text{-}NH_2$
Potassium permanganate	$KMnO_4$	Triethanolamine	$(HOCH_2CH_2)_3N$
Ethanolamine	$HOCH_2CH_2NH_2$	Urea	$H_2N\text{-}\overset{O}{C}\text{-}NH_2$
Nitric acid	HNO_3(20-30%)	Ferrous sulfate	$FeSO_4$
Ammonium chloride	NH_4Cl	Sodium chlorite	$NaClO_2$
Ferrous chloride	$FeCl_2$	Ozone	O_3
Sodium hypochlorite	$NaOCl$	Hydrogen peroxide	H_2O_2

Consequently, the essential problem was not to invent a scrubbing liquor but to choose one that actually performed as well as its advocates claimed and one which was truly practical.

After due consideration it was decided that insoluble reagents or reagents which resulted in the formation of a precipitate upon contact with N_2O_4 were impractical. These precipitates would perhaps clog piping and interfere with efficient operation of the recycling pumps. Thus for these reasons we eliminated from consideration calcium oxide, magnesium hydroxide, magnesium carbonate, and potassium permanganate. Reagents containing the nitrate anion were eliminated from consideration because of problems associated with ultimate disposal of the nitrate containing scrubber waste liquor. As most of you know, state regulations concerning discharge of nitrate containing wastes into bodies of water are very strict. Hence, nitric acid and ammonium nitrate were eliminated from consideration.

Although, there are various problems associated with most of the others, it was decided that at least some laboratory trials should be conducted on all the remaining reagents using a wet scrubber model system as shown in Fig. 3.

COMBINATION WET-DRY SCRUBBER SYSTEM

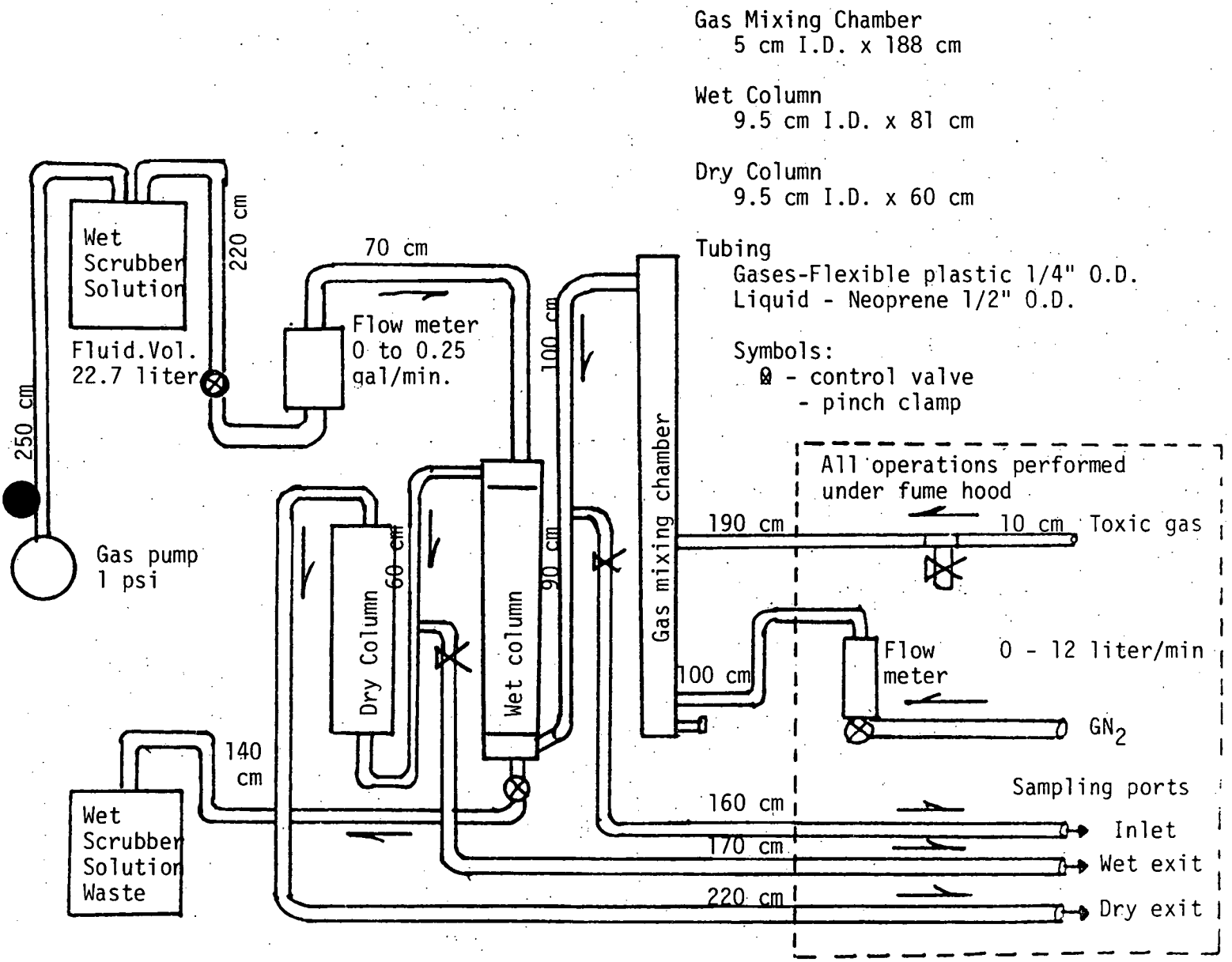


Fig. 3

The operation, sampling, and assay techniques for the scrubber system are summarized as follows:

A GN_2 flow of three to five liters per minute was established and a secondary GN_2 flow which was to be merged with N_2O_4 was set at 300 ml/min. The N_2O_4 cylinder was preheated to 20°C prior to the start of the experiment. The scrubbing solution flow is set at 12 to 90 gal/min and the scrubber was wetted down before the N_2O_4 contaminated vapor passed through. The N_2O_4 tank valve was opened and the vapor was merged with the secondary GN_2 flow. The system was allowed to equilibrate for five minutes prior to sampling.

Inlet and outlet samples were taken every five minutes during the experiment. Sampling and analysis methods used were modified methods and procedures of the Standard Analytical Method #04-507, PAA Environmental Health Laboratory for determination of Nitrite in water and nitrogen dioxide in the air. Gas samples were obtained with 10 ml gas sampling syringes at the three sampling ports, which were affixed with gas sampling bulbs. These sampling ports are located as follows:

1) The inlet sample port is located in a position upstream of the wet scrubber.
2) The mid sample port is located between the wet scrubber and the dry scrubber.
3) The outlet port is located downstream from the dry scrubber.

To determine the efficiency of any scrubbing liquor, the following formulae were used:

$$\frac{\text{Inlet ppm-Mid point ppm}}{\text{Inlet ppm}} \times 100 = \text{Efficiency of Wet Scrubber}$$

$$\frac{\text{Inlet ppm - Outlet ppm(Dry scrubber)}}{\text{Inlet ppm}} \times 100 = \text{Total efficiency}$$

A sample is taken by inserting the empty syringe's needle through the gas sampling bulb and drawing one ml of gas. This gas sample is then injected into a vial containing 10 ml of NOx absorbing solution which is principally a solution of sulfanilic acid and N-(1-napthyl)-ethylenediamine and allowed to set for 15 minutes prior to reading the absorbance at 540 nm on a spectrophotometer.

The spent liquors, as well as the inlet and outlet gases were also sampled. An assay was conducted on the scrubbing solution prior to the test. As the experiment progressed, the waste liquor assays are taken prior to recycling of the scrubber solution.

Currently, a recycling pump is now used allowing the liquid scrubber waste to be introduced back into the system with fresh solution at a constant rate.

Our first experiments were conducted using plain tap water as the scrubbing liquor. The results are shown in Table 1.

Table 1

Scrubbing N_2O_4 Vapors with H_2O

	Inlet Gas NO_x ppm	Off Gas, NO_x, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	3220-2180	32.5-5.0	5.0-0	99.9-98.5	100-99.8	35 min
Average	2787	20.8	2.5	99.1	99.9	

	Inlet Gas, NOx ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	6300-4400	163-62	5.5-2.5	98.8.96.9	100-99.2	30 min
Average	5217	84	11	98.4	99.8	

	Inlet Gas NOx ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet STage	Total	
Range	8600-6600	300-100	550-38	98.4-95.5	99.2-95.5	30 min
Average	7300	193	135	97.5	98.2	

As is seen, the results are quite satisfactory using plain water in our system.

Our next series of experiments were conducted with ammonium hydroxide solutions. Ammonium hydroxide solutions have been used experimentally in stack gas scrubbing operations because the ammonium ion converts nitrous acid formed on dissolution of N_2O_4 to environmentally innocuous products as shown. See Fig. 4.

One major problem we envisioned to be associated with use of NH_4OH as a scrubbing liquor was that if for some reason the water in the spent scrubbing liquor evaporated, it would leave potentially highly explosive

organic nitrates and nitrites as residues. Such explosive potential we believed, would be unacceptable for routine operations.

Also, as we all know, ammonia solutions have very strong pungent odors which would be repulsive to the operational personnel involved.

Reactions of Ammonium Ion and NO_2

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$HNO_2 + NH_4OH \longrightarrow NH_4NO_2$$

$$HNO_3 + NH_4OH \longrightarrow NH_4NO_3$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

Fig. 4

The results using 3% ammonium hydroxide are shown in Table 2.

Table 2

Scrubbing N_2O_4 vapors with 3% NH_4OH Solution

Inlet Gas NOx, ppm	Off Gas, NOx, ppm		Scrubber Efficiency %		Run Duration	Comments
	Wet	Dry	Wet Stage,	Total		
2800-11,000	22-157	0	99.3-99.4	100%	30 min.	Dry scrubber packed with AL_2O_3 odor at exit. Bottom 1/2 inch of packing has green color from NH_3 complex.
280-7570	16-28	0	99.4-99.6	100%	30 min.	Dry scrubber packed only with act. carbon. Packing emitted NH_3 odor

	Inlet Gas NOx, ppm	Off Gas, NOx,ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	4000-1800	60.0-27.5	10.0-2.5	98.9-98.0	99.9-99.5	30 min.
Average	2800	44.0	3.8	98.5	99.9	
Range	28000-10.0	1200-1.0	2.5-1.0	100.-75.0	100-87.5	120 min.
Average	4830	105	1.5	97.8	100.0	

The efficiencies were so high that further experiments were conducted over several hours in order to determine scrubbing efficiencies of spent scrubbing liquor. Also it was of interest to determine scrubbing efficiencies at differing concentrations of ammonium hydroxide. (See Table 3.)

As is seen, ammonium hydroxide proved to be an extremely efficient scrubbing liquor. But for reasons previously mentioned, the search for a more practical liquor had to continue.

Table 3

Scrubbing N_2O_4 vapors with 3% NH_4OH

	Inlet Gas NOx, ppm	Off Gas, NOx,ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	46000-5.0	1600-1	1	100-50	100-50	240 min
Average	8354	181	1	99.8	100	

Scrubbing N_2O_4 vapors with 10% NH_4OH

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	13,000-44,900	2.5-4250	2.5-14	81-100	0	360 min
Average	18,600	647	4.0	99.9	100	

There is a great deal of literature referring to the use of alkaline scrubbing liquors for NOx. Much of the work indicates that sodium hydroxide is inferior to plain water. In our hands, however, this did not prove to be the case. The results with sodium hydroxide seemed to be roughly equivalent to that of water. Sodium hydroxide solutions would also have the important advantage of being less corrosive to the scrubber than plain water. The results of scrubbing with sodium hydroxide solutions are shown in Table 4.

Table 4

Scrubbing of N_2O_4 vapors with 10% NaOH

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	25000-200	30-2.5	30-1.0	100-81.2	100-96.0	120 min.
Average	6722	18	11	99.6	99.8	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	150-19000	11-225	5-36	63-100	93-100	420 min.
Average	9393	46	13.8	92.2	98.9	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	4000-18000	11-28	2.5-28	63-100	92-100	720 min.
Average	10,537	17.9	11.2	93.9	95.8	

Table 5 shows that the absorption efficiency of scrubber liquor containing 0.1N H_2O_2 averages about 90% which is similar to the efficiency of runs made with plain H_2O. The small amount of H_2O_2 apparently was too dilute to rapidly oxidize NO. The efficiency of a run containing 0.25N H_2O_2 (Run 3) was approximately 2 percentage points higher. In runs containing alkali plus H_2O_2 (Runs 4 and 5) the efficiency was increased by approximately seven percentage points above the plain H_2O or dilute H_2O_2 values.

Table 5

Scrubbing of N_2O_4 with Hydrogen Peroxide

Scrubber Liquor Composition	Inlet Gas ppm NO_x	Off Gas ppm NO_x	Absorption Efficiency Percent
0.1N H_2O_2	15,700	1450	90.8
0.1N H_2O_2	16,900	1840	89.1
0.25N H_2O_2	18,000	1335	92.6
0.1N NaOH 0.1N H_2O_2	6,700	143	97.8
0.1N NaOH 0.1N H_2O_2	13,700	80	99.2

The wet scrubber system was provided with an apparatus for introducing a gaseous oxidant (O_3 and/or O_2) upstream of the column. The purpose of the oxidant was to oxidize NO (present in the feed stream mostly as a result of reaction of NO_2 with H_2O) to the more water soluble NO_2 form so as to enhance its capture in the column. The results are shown in Table 6.

It is evident from the results that averaging absorption efficiencies from the three set-ups (oxidant introduction in three different ways) the following observations can be made:

1. In plain H_2O runs, O_3/O_2 gives better results than O_2 in alkaline solution, i.e., 99.07 vs. 97.37% respectively.
2. O_3/O_2 in alkaline bath is slightly better than O_2 in alkaline solutions, i.e., 99.52 vs. 99.39% respectively.
3. The absorption efficiencies of set up #1 (O_3/O_2 fed directly to GN_2 line) and set up #2 (O_3/O_2 fed to scrubber liquor) are not significantly different.

Table 6

Scrubbing of H_2O_4 using O_3, O_2, and NaOH

O_3/O_2 Plain H_2O % Abs. Ef.	O_3/O_2 Alkaline Soln. % Abs. Ef.	O_2 Plain H_2O % Abs. Ef.	O_2 Alkaline Soln. % Abs. Ef.
99.15	99.56 (ave. of 5 runs)	98.64	99.48 (ave. of 3 runs)
99.0	99.7	96.1	99.3
----	99.3 (ave. of 3 runs)	----	----
99.07	99.52	97.37	99.39

Our next experimental scrubbing liquor was a 5% NaOCl solution. The rationale was that during the scrubbing operation, chlorine derived from NaOCl would react with the NO evolved upon dissolution of N_2O_4, and form nitrosyl chloride (NOCl) which is soluble in water as well as decomposed by water. The results were encouraging except that a highly noxious gas presumably NOCl was evolved. (See Table 7)

Table 7

Scrubbing N_2O_4 vapors with 5% NaOCl Solution

Inlet Gas NOx, ppm	Off Gas, NOx, ppm	% Scrubber Efficiency
7000	31	99.5
6590	33	99.5
5980	41	99.4

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	68000-13000	34-2.5	17.5-1.5	100-98.8	100-99.2	300 min.
Average	24000	15.5	4.6	99.9	100	

As mentioned previously, ammonium hydroxide scrubbing liquors proved to be very efficient, but one serious disadvantage of these scrubbing liquors is the strong odor. Ammonium chloride solutions do not have a significant odor if the pH is neutral or lower but they still possess the advantageous ammonium ion. Thus, scrubbing experiments with ammonium chloride solutions were conducted. The results were poor compared to other liquors. This indicates that key reactions of ammonia and N_2O_4 must take place in the gas phase to produce highly efficient scrubbing as shown in Table 8.

Table 8

Scrubbing N_2O_4 vapors with 2% NH_4Cl

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	54000-33000	7000-2500	3500-27.5	95.5-79.0	99.7-91.7	60 min
Average	42333	4833	2176	87.2	94.6	

Scrubbing N_2O_4 vapors with 10% NH_4Cl

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	28000-24000	1000-550	600-0	97.7-96.0	100-97.7	90 min
Average	26000	750	173	97.0	99.3	

$FeCl_2$ and $FeSO_4$ form a nitroso ferrous complex when reacted with nitric oxide. Thus solutions of these entities are reported to be good scrubbing liquors for NO_2. In our hands this did not prove to be the case. The scrubbing liquor turned black and evolved NOx fumes. (See Table 9.

Table 9

Scrubbing N_2O_4 vapors with 5% $FeSO_4$ Solution

Input Gas NOx, ppm	Off Gas, NOx, ppm		Scrubber Effiency %		Run Duration
	Wet Stage	Dry	Wet Stage	Dry Stage	
14,200-25,000	1900-5800	4-8000	84.5-86.7	81-99.98	30 min.

	Input Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	42000-4200	5800-1900	8000-4.25	86.7-84.5	99.98-81.0	30 min
Average	24000	3800	3100	83.8	86.8	

Urea reacts with NO and NO_2 to produce N_2, CO_2, and H_2O. The classical chemistry involved is a reaction between a primary amine and the oxides of nitrogen. Urea also reacts with HNO_3 at room temperature to form an addition compound.

$$N_2O_4 \longrightarrow 2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

$$2HNO_2 + HN_2CONH_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$$

$$NH_2CONH_2 + HNO_3 \longrightarrow NH_2CONH_2 \cdot HNO_3$$

Thus urea solutions have also been reported to be effective scrubbing liquors. In our hands this was not so, presumably because the reactions shown in this slide are favored by higher temperatures. (See Table 10)

Table 10

Scrubbing N_2O_4 vapors with 5% Urea Solution

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	8300-16000	560-720	1.0-13	92-96.5	99.92-99.99	60 min
Average	2050-10,000	13-130	0	93.7-98.9	100%	60 min

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	16000-8000	1400-560	13.0-0	96.5-86.5	100-99.9	60 min
Average	12800	796	5.4	93.8	100	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	10000-2000	680-13.0	2.5-0	99.8-90.7	100	60 min
Average	5790	193	2.5	96.6	100	

Thus, ferrous sulfate and urea proved far too inefficient to be considered further as scrubbing liquor additives.

Finally, we became aware of an NTIS document entitled, "Development of the Aqueous Processes for Removing NO_x from the Flue Gases" authored by the Esso Research and Engineering Company in September of 1972. This group conducted intensive research on wet scrubbing methods for NO_x. They concluded that the most efficient scrubbing agent for their purpose was sodium sulfite. The only interfering species they found was oxygen which converted SO_3 to SO_4. Since our experimental flows as well as the operational flows contain little oxygen, it was deduced that sodium sulfite should work very well. The experimental data was indeed very encouraging. See Table 11.

Table 11

Scrubbing N_2O_4 vapors with 4% Na_2SO_3

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	100000-19000	800-0	20.0-0	99.9-99.1	100-99.9	75 min
Average	39000	211	5	99.5	100	

Scrubbing NOx vapors with 10% Na_2SO_3

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	160000-500	77.5-10.0	47.5-0	99.5-93.7	100-94.2	360 min.
Average	33063	41.2	23.8	99.9	100	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	25000-5000	55.0-7.5	5.0-0	100-98.2	100-99.9	360 min.
Average	17,750	21.2	1.3	99.9	100	

At this time we are not able to determine any potential or actual problems concerning the use of sodium sulfite. This material can be handled without the use of any special safety equipment and can be used effectively in concentrations as high as 18%. The material or its reaction products with N_2O_4 are not potentially explosive. The spent liquor can be recycled with little or no decrease in efficiency and there is no sign of SO_2 effluent.

The chemistry of the Na_2SO_3 absorption process is not understood very well at the present time, but we can be reasonably sure that nothing of greater carcinogenicity than $NaNO_2$ is formed. Apparently the sulfite ion has a remarkable capacity to absorb NO_2. It does this over a wide pH range and at temperatures of 125°F (where little N_2O_4 exists). The classical NO_2 absorption equation does not apply since no NO is given off during the absorption process.

The mechanism of this absorption is complex but $SO_3^=$ scrubbing of NO_2 and NO has been reported to involve production of hydroxylamine (NH_2OH) derivatives.

$$N_2O_3 + 4Na_2SO_3 + 3H_2O \longrightarrow 2N(OH)(NaSO_3)_2 + 4NaOH$$

$$1/2N_2O_4 + 2Na_2SO_3 + H_2O \longrightarrow N(OH)(NaSO_3)_2 + 2NaOH$$

(Ref. Garlet, R., U.S. Patent 3,329,478, Method of Removing Nitrogen Oxides from Gases)

Ammonium sulfite solutions were also reported to be effective scrubbing liquors but in our hands these solutions proved to be unattractive.

See Table 12.

Table 12

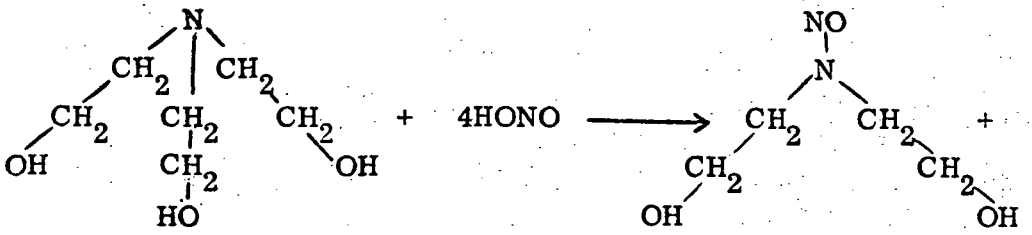
Scrubbing N_2O_4 vapors with 2% $(NH_4)_2SO_3$

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	17500-4000	8500-20.	2150-5.0	99.5-45.5	100-74.5	180 min
Average	8100	2474	689	77.0	88.2	

Triethanolamine solutions have also been reported to be effective scrubbing agents for NO_2 and this was verified in our hands.

However, there is a significant problem associated with the use of TEA. TEA reacts with N_2O_4 to form tertiary nitrosamines which decompose readily to secondary nitrosamines which are all highly carcinogenic.

NIOSH has already targeted one of the products, N-nitroso-diethanolamine as a probable carcinogen.



$$O{=}C(H)\text{-}CH_2\text{-}OH + N_2O + 3H_2O$$

(Ref. Chem. and Engineering News, October 18, 1976, page 12)

This material is present in cutting oil and has been implicated as causing cancer in machinists.

The results as a scrubbing liquor are shown in Tables 13 and 14.

Table 13

Scrubbing N_2O_4 vapors with 6% Triethanolamine (TEA)

2nd Stage Sorbent	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet Stage	Dry	Wet Stage	Dry Stage	
mixture of act. carbon act. Al_2O_3	13,000-14,500	4-40	0	99.81	100	25 min
Al_2O_3	53,000	40-157	5-49	99.70	99.97	30 min
Al_2O_3	8,350-6,400	13-4.5	2.3-0	99.84-99.93	99.97-100	30 min

Table 14

Scrubbing N_2O_4 vapors with 3% TEA

	Inlet Gas NOx, ppm	Off Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	24200-18500	3350-0	3050-0	100-85.7	100-96.8	240 min.
Average	20671	971	597	95.9	97.4	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	26000-5000	300-9.0	128-0	99.96-98.1	99.99-99.0	300 min.
Average	14500	99.3	21.6	99.3	99.4	

	Inlet Gas NOx, ppm	Off. Gas, NOx, ppm		% Scrubber Efficiency		Run Duration
		Wet	Dry	Wet Stage	Total	
Range	12800-770	180-5.0	38.0-0	99.95-76.6	99.99-99.5	420 min.
Average	9117	48.0	8.05	99.5	99.9	

Finally, Table 15 summarizes the top 15 experiments in order of decreasing scrubbing efficiency. Thus we have in the top ranking 10 liquors, sodium hypochlorite, sodium sulfite, ammonium hydroxide, sodium hydroxide, triethanolamine and water.

Table 15

SUMMARY OF N_2O_4 SCRUBBER LIQUOR DATA

	Scrubbing Agent	Average Efficiency W/T	Range W/T	Std. Dev. W/T	Break through time (min)	Run duration (min)
1	5% NaOCl	99.9 100.	0.12 0.08	0.04 0.03	300	300
2	10%$NaSO_3$	99.9 100.0	1.78 0.08	0.65 0.03	360	360
3	10%$NaSO_3$ Waste from #2	99.9 100.	5.8 5.78	2.05 2.04	300(660)	300(720)
4	10%NH_4OH	99.9 100.0	19.3 0	6.5 0	360	360
5	3%NH_4OH	99.8 100.0	50.0 50.0	17.0 17.0	240	240
6	10%NaOH	99.6 99.9	18.8 6.1	5.3 1.8	120	120
7	4%Na_2SO_3	99.5 100.0	0.8 0.1	0.32 0.04	75	75
8	6% TEA	99.5 99.9	23.35 0.49	7.7 0.16	120	420
9	20% TEA	99.3 99.4	1.86 0.99	0.7 0.37	60	240
10	H_2O	99.1 99.9	1.4 0.2	(0.53*) 0.55 0.08	35	35
11	3% NH_4OH	98.5 99.9	0.9 0.5	0.36 0.20	30	30
12	H_2O	98.4 99.8	2.0 0.8	0.8 0.32	25	30
13	3%NH_4OH	97.8 100.0	25 12.5	7.7 3.8	120	120
14	H_2O	97.5 98.2	].9 3.9	1.15 1.55	30	30
15	10%NH_4Cl	97.0 99.3	1.7 2.3	0.85 1.1	75	90

As mentioned previously sodium hypochlorite, ammonium hydroxide, and triethanolamine were dropped from further consideration for various reasons.

Thus it was recommended that the following scrubbing agents for N_2O_4 be evaluated at MMC in a full-flow testing program.

a. 4-10% Sodium sulfite (Na_2SO_3)

b. Plain Water (H_2O)

c. 3-10% Sodium Hydroxide (NaOH)