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REMOVAL OF Nu[SUB]X AND SO[SUB]2 FROM FLUE GAS USING OXIDIZING COMPOUNDS

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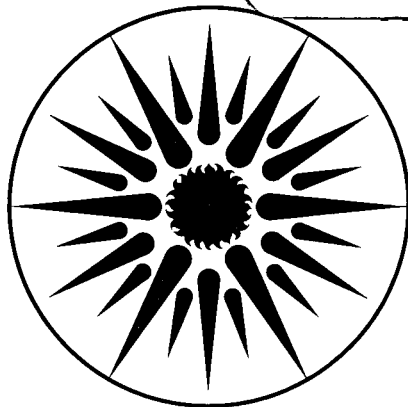
### Removal of NO<sub>x</sub> and SO<sub>2</sub> from Flue Gas Using Oxidizing Compounds

D. Littlejohn and S.G. Chang

June 1988

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**Removal of NO<sub>x</sub> and SO<sub>2</sub> from Flue Gas  
Using Oxidizing Compounds**

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June 1988

## REMOVAL OF NO<sub>x</sub> AND SO<sub>2</sub> FROM FLUE GAS USING OXIDIZING COMPOUNDS

David Littlejohn and S.G. Chang\*

There are several general methods of NO<sub>x</sub> and SO<sub>2</sub> from flue gas using chemical reactions. The pollutants can be oxidized, reduced, complexed or dissolved. Oxidation of NO<sub>x</sub> and SO<sub>2</sub> will ultimately yield nitrate (NO<sub>3</sub><sup>-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>) when in solution. Reduction will lead to N<sub>2</sub> and elemental sulfur. Complexation has generally been applied to NO<sub>x</sub> to generate nitrosyl complexes. Since NO<sub>x</sub> is not highly soluble in aqueous solution, dissolution has been generally applied to SO<sub>2</sub> to generate HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup>. It is desirable to develop a single process which acts on both SO<sub>2</sub> and NO<sub>x</sub> to minimize the complexity of the scrubbing system for the power plant. A suitable oxidizing or reducing system could meet this criterion. We have investigated several peroxy compounds to determine their usefulness in removing NO<sub>x</sub> and SO<sub>2</sub> from flue gas by oxidation.

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is known to be effective in removing SO<sub>2</sub> from flue gas, rapidly oxidizing it to sulfate. However, it is not very effective in removing NO<sub>x</sub>, which consists primarily of nitric oxide (NO)<sup>1</sup>. There are a number of peroxy compounds, and in particular, a number of simple peroxyacids (or peracids) that hold promise for effectively removing NO<sub>x</sub>. The peroxyacids studied are shown in Figure 1. They are generally prepared by mixing concentrated H<sub>2</sub>O<sub>2</sub> with the concentrated acid and allowing the system to equilibrate<sup>2</sup>. Other preparations are also shown on Figure 1 for peracetic acid and persulfuric acid.

In the preparation of performic acid and peracetic acid adding a small quantity (1% or less) of sulfuric acid hastens the equilibration process. The equilibria and formation

rates for the formation of performic and persulfuric acid were studied by Monger and Redlich<sup>3</sup>. They obtained a measure of the equilibrium quotient  $K' = [\text{peracid}] \bullet [\text{H}_2\text{O}]/[\text{acid}] \bullet [\text{H}_2\text{O}_2]$ , which is a crude approximation of the equilibrium constant. Their values of  $K'$  for performic acid is shown in Figure 2. This approximation can be improved somewhat by including activity coefficients for  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ ;  $K'' = (\gamma_{\text{H}_2\text{O}}/\gamma_{\text{H}_2\text{O}_2}) \bullet K'$ . This was done for persulfuric acid and their data are shown in Figure 3. From these figures, it can be seen that concentrated acid and  $\text{H}_2\text{O}_2$  are needed to obtain high concentrations of peracid in solution. Data from work done by Greenspan<sup>4</sup> indicate similar behavior for peracetic acid. Increasing the temperature of the mixtures decreases the equilibrium quotient for the peroxy acids, but increases the rate of formation.

The pKs of the peracids are generally higher than the acids from which they are formed<sup>5</sup>. The pKs are listed in Figure 4. Monger and Redlich<sup>3</sup> indicate that persulfuric acid is appreciably weaker than sulfuric acid and the value listed is only an estimate.

The concentrated peroxyacids are unstable, particularly at high temperatures or in the presence of certain impurities. Performic acid is less stable than the other acids. At one time, a 40% solution of peracetic acid was commercially available, stabilized by a small amount of sodium pyrophosphate<sup>4</sup>. The stability of persulfuric acid appears to be similar to peracetic acid.

For the studies done on  $\text{NO}_x$  and  $\text{SO}_2$  removal, 35%  $\text{H}_2\text{O}_2$  was used to prepare the peracid solutions.  $\text{H}_2\text{O}_2$  at concentrations above 70% are not readily available, but more concentrated solutions can be prepared by removing water from the  $\text{H}_2\text{O}_2$  solution on a vacuum line. Concentrated formic acid (88%), acetic anhydride, and concentrated sulfuric acid (97%) were used with  $\text{H}_2\text{O}_2$  to prepare the solutions. Generally, 35%  $\text{H}_2\text{O}_2$  was used in the preparations.

The  $\text{NO}_x$  and  $\text{SO}_2$  removal capabilities of the peracids were studied using a wet scrubbing system and a small spray drying system. The wet scrubbing system is shown in Figure 5. The desired mixture of gases is prepared and passed through a fine frit in the bottom of the scrubbing column. Gas flow rates of 1-2 l/min were generally used. The column has a volume of about 250 ml. Typically, 50 ml of the peroxyacid solution was used. The column temperature was adjusted by either using electrical heating tape or a circulating water bath. A condenser was used in some experiments at higher temperatures to reduce the amount of evaporated liquid transferred to the cold trap. After passing through the cold trap, the gas was directed to a chemiluminescent  $\text{NO}_x$  analyzer and a pulsed fluorescent  $\text{SO}_2$  analyzer. Some experiments were done without a cold trap to insure that none of the pollutants were removed by the trap. The cold trap was maintained at  $-73^\circ\text{C}$  when used. The  $\text{NO}$  concentrations ranged from 150 to 1050 ppm and the  $\text{SO}_2$  concentrations, when used, ranged from 220 to 2500 ppm. Since  $\text{SO}_2$  was always removed by the  $\text{H}_2\text{O}_2$  in the peracid preparation it was not always included in the gas to be scrubbed.

The spray drying system is shown schematically on Figure 6. The gas mixture was mixed and heated to the desired temperatures before entering the spray dryer. The spray drying chamber has a volume of 350 l and gas flow rates used were about 600 l/min. A cyclone on the exhaust from the chamber collected most of the particulate matter. A small amount of the exhaust gas was passed through a filter and cold trap and then to the  $\text{NO}_x$  and  $\text{SO}_2$  analyzer. The peracid solution was dispersed into the spray drying chamber by a rotary atomizer operating at 25,000 rpm. For the spray drying experiments,  $\text{NO}$  concentrations ranged from 550 to 850 ppm and the  $\text{SO}_2$  concentrations, when used, ranged from 240-2740 ppm.

In both the wet scrubbing system and the spray drying system, the scrubbing efficiency of the peracid solutions was unaffected by the presence of oxygen, as would be expected. This is one advantage an oxidizing approach to flue gas clean-up has over a reducing approach.

Experiments were done with peroxyacid solutions, as well as with hydrogen peroxide and formic acid, acetic acid and sulfuric acid as controls. In the wet scrubbing system,  $H_2O_2$  and the peracid solutions all removed 100% of the  $SO_2$  present. The  $SO_2$  absorbed by  $H_2O_2$  solutions was converted to  $H_2SO_4$ , which reacted with  $H_2O_2$  to produce persulfuric acid. Thus, the removal of NO by  $H_2O_2$  solutions would gradually increase with time as the persulfuric acid built up. To simplify interpretation of the results, most of the wet scrubbing runs were done with NO alone.

All of the peroxyacid solutions showed improved NO removal at higher temperatures, in spite of having lower equilibrium concentrations than at room temperature. A series of runs were done using the peracids to remove NO. No sulfuric acid was added to the performic acid or peracetic acid mixtures so that only the desired peracid would be present. 60 ml solutions containing roughly equimolar amounts of the parent acid and  $H_2O_2$  were prepared approximately 1 hour before use. Each of the solutions, in turn, was added to the scrubbing column, and 1000 ppm NO in  $N_2$  was passed through the column. The temperature of the bath surrounding the column was raised from 25 °C to 65 °C. The NO removal efficiency vs temperature for performic acid is shown in Figure 7. The maximum removal occurs at about 55 °C and decreases at higher temperatures. This decrease is believed to be due to the decomposition of performic acid, which occurs more rapidly as temperature increases. A similar plot for peracetic acid is shown in Figure 8. No decrease in removal efficiency is observed at the higher temperatures. Since peracetic acid has a fairly slow equilibration rate, the solution is likely to have had somewhat



better performance if it had been prepared a day in advance. The plot of NO removal efficiency vs temperature for persulfuric acid is shown in Figure 9. Its removal efficiency increases as the temperature increases. Under these conditions, it proved to have somewhat better removal rates than the other two peracids tested. Under suitable flow rates, temperature and peracid concentration, NO removal rates in excess of 90% have been achieved by all three of the peracids.

The products of the NO removal reaction have been found to be primarily nitrate ( $\text{NO}_3^-$ ) and  $\text{NO}_2$ . Raman spectra of the solutions were collected after use and showed the presence of  $\text{NO}_3^-$  as a result of NO removal. The other product,  $\text{NO}_2$ , is released from the solution after it is formed from NO. The amount of  $\text{NO}_2$  released is proportional to the acidity of the solution. Persulfuric acid released more than performic acid, while the peracetic acid released only small amounts. The amount of  $\text{NO}_2$  released is not large. In the case of persulfuric acid, less than 20% of the NO removed was released as  $\text{NO}_2$ . The release of  $\text{NO}_2$  can be eliminated by neutralizing some of the acid in the solution. This will also reduce the potential corrosion problems of using acidic solutions.

Using the peracids in the spray drying system did not provide removal efficiencies as high as those obtained in the wet scrubbing system. A number of runs were done with performic acid with 600 ppm and, optionally, 1100 ppm  $\text{SO}_2$ . The spray dryer inlet temperature was 170 °C and the outlet temperature was 95 °C. 20 to 30% of the NO was removed and 30 to 40% of the  $\text{SO}_2$  was removed when it was included in the gas mix. From the results of the runs done, higher feed rates of the peracid solution would have removed more of the pollutants. The temperature at which these runs were done are above those found to be optimum in the wet scrubbing experiments.

Reference runs were made using formic acid alone and  $\text{H}_2\text{O}_2$  alone with the same conditions mentioned above. Formic acid removed very little of either NO or  $\text{SO}_2$ .  $\text{H}_2\text{O}_2$

was found to remove very little ( $< 5\%$ ) of NO when the gas contained NO alone. However, when the gas contained both NO and SO<sub>2</sub>, substantial amounts (30 to 40%) of these pollutants were removed. We attribute this to the formation of persulfuric acid from H<sub>2</sub>O<sub>2</sub> and SO<sub>2</sub>. The formation would occur rapidly at the high temperatures in the spray dryer. The persulfuric acid formed can oxidize the NO to NO<sub>2</sub>.

To investigate this process, a series of runs were done under a range of conditions. The NO concentration was maintained at 850 ppm. The SO<sub>2</sub> concentration was varied from 240 to 2740 ppm. Two temperature conditions were used. The first condition was with a spray dryer inlet temperature of 110 °C and an outlet temperature of 50 °C. The second condition was with an inlet temperature of 165 °C and an outlet temperature of 75 °C. Figure 10 shows NO removal as a function of initial SO<sub>2</sub> concentration for the two conditions. The H<sub>2</sub>O<sub>2</sub> flow rate into the atomizer was 9.5 ml/min. NO removal is more effective at higher temperatures, particularly at lower SO<sub>2</sub> concentrations. This is similar to what is observed in the wet scrubbing system.

Figure 11 shows the effect of H<sub>2</sub>O<sub>2</sub> flow rate on NO and SO<sub>2</sub> removal for initial concentrations of NO = 850 ppm and SO<sub>2</sub> = 730 ppm. The NO removal rate increases only slightly as the H<sub>2</sub>O<sub>2</sub> flow rate is raised. Figure 12 shows the NO and SO<sub>2</sub> removal with a higher initial concentration of SO<sub>2</sub> of 1460 ppm. NO removal is higher and SO<sub>2</sub> removal is lower than in the preceding figure on a percentage basis.

For a given H<sub>2</sub>O<sub>2</sub> flow rate, the amount of SO<sub>2</sub> removed did not change much as the initial SO<sub>2</sub> concentration was increased, suggesting that H<sub>2</sub>O<sub>2</sub> is the limiting factor. The amount of NO removed was closely tied to the amount of SO<sub>2</sub> removed over a range of H<sub>2</sub>O<sub>2</sub> flow rates and initial SO<sub>2</sub> concentrations. The ratio of NO removed to SO<sub>2</sub> removed averaged 1:3 over a number of runs. This ratio may be related to the sulfuric acid - persulfuric acid equilibrium. The basic reactions for the removal are shown in

Figure 13. Most of the NO removed in the spray drying experiments appeared as NO<sub>2</sub>.

The ratio of NO and SO<sub>2</sub> removed to H<sub>2</sub>O<sub>2</sub> added for the experiments shown in Figures 10 and 11 was between 1:5 and 1:10. While this ratio is not too low, use of peracids in a spray drying system does not appear to be exceptionally promising. The gas from the spray dryer would require treatment to remove NO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> and any excess H<sub>2</sub>O<sub>2</sub>. One run was done with a mixture of H<sub>2</sub>O<sub>2</sub> and ammonia. The process generated solid ammonium sulfate. The filtering in the gas stream before the analyzers was insufficient to remove all of the finely divided solid and it interfered with the analyzers' operation. While the readings were not very accurate, it appears that a solution of H<sub>2</sub>O<sub>2</sub> and ammonia was capable of removing significant amounts of SO<sub>2</sub> and NO.

In conclusion, our results indicate the peracid solutions used in wet scrubbing systems are capable of removing substantial amounts of NO<sub>x</sub> and SO<sub>2</sub>. The primary products of this process are NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. Use of these solutions in a spray drying system appears to be less advantageous, as it requires post-treatment to remove the NO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> products.

### References

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3. J.M. Monger and O. Redlich (1956) *J. Phys. Chem.* 60, 797.
4. F.P. Greenspan (1946) *J. Am. Chem. Soc.* 69, 907.
5. A.J. Everett and G.J. Minkoff (1953) *Trans. Faraday Soc.* 49, 410.

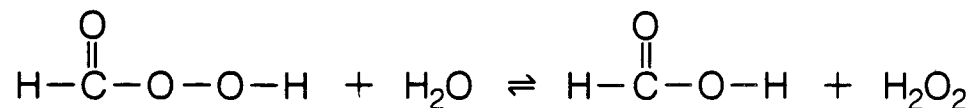
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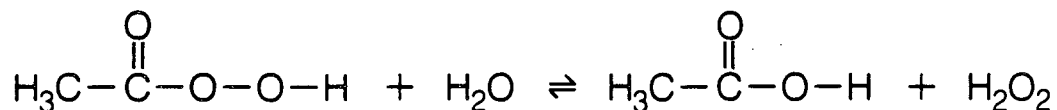
### Figure Captions

- Figure 1.** Peroxyacids used in this study.
- Figure 2.** Equilibrium quotient for performic acid and peracetic acid
- Figure 3.** Corrected equilibrium quotient for persulfuric acid
- Figure 4.** pKs for acids and peracids used in the experiments
- Figure 5.** Wet scrubbing system used in testing peracid solutions
- Figure 6.** Laboratory-scale spray drying system
- Figure 7.** NO removal efficiency *vs* temperature for performic acid
- Figure 8.** NO removal efficiency *vs* temperature for peracetic acid
- Figure 9.** NO removal efficiency *vs* temperature for persulfuric acid
- Figure 10.** NO removal efficiency as a function of SO<sub>2</sub> concentration in the spray drying system.
- Figure 11.** Effect of H<sub>2</sub>O<sub>2</sub> flow rate on NO and SO<sub>2</sub> removal in the spray drying system. [NO]<sub>initial</sub> = 850 ppm [SO<sub>2</sub>]<sub>initial</sub> = 730 ppm
- Figure 12.** Effect of H<sub>2</sub>O<sub>2</sub> flow rate on NO and SO<sub>2</sub> removal in the spray drying system [NO]<sub>initial</sub> = 850 ppm [SO<sub>2</sub>]<sub>initial</sub> = 1460 ppm
- Figure 13.** Reactions involved in the removal of NO and SO<sub>2</sub> in the spray drying system

Performic Acid  
(Peroxyformic Acid)

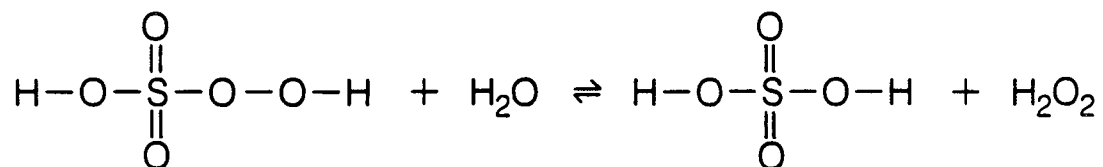


Peracetic Acid  
(Peroxyacetic Acid)



Also formed from  $\text{H}_2\text{O}_2$  + acetic anhydride

Persulfuric Acid  
(Peroxomonosulfuric Acid, Caro's Acid)



Also formed from  $\text{H}_2\text{O}_2$  +  $\text{HSO}_3\text{Cl}$  and hydrolysis of  $\text{H}_2\text{S}_2\text{O}_8$

XBL 884-8863

Figure 1

$$K' = \frac{[\text{peracid}] [\text{H}_2\text{O}]}{[\text{acid}] [\text{H}_2\text{O}_2]}$$

Performic acid data from  
J.M. Monger and O. Redlich (1956), J. Phys. Chem. 60, 797.

Peracetic acid data from F.P. Greenspan (1946),  
J. Am. Chem. Soc. 69, 907.

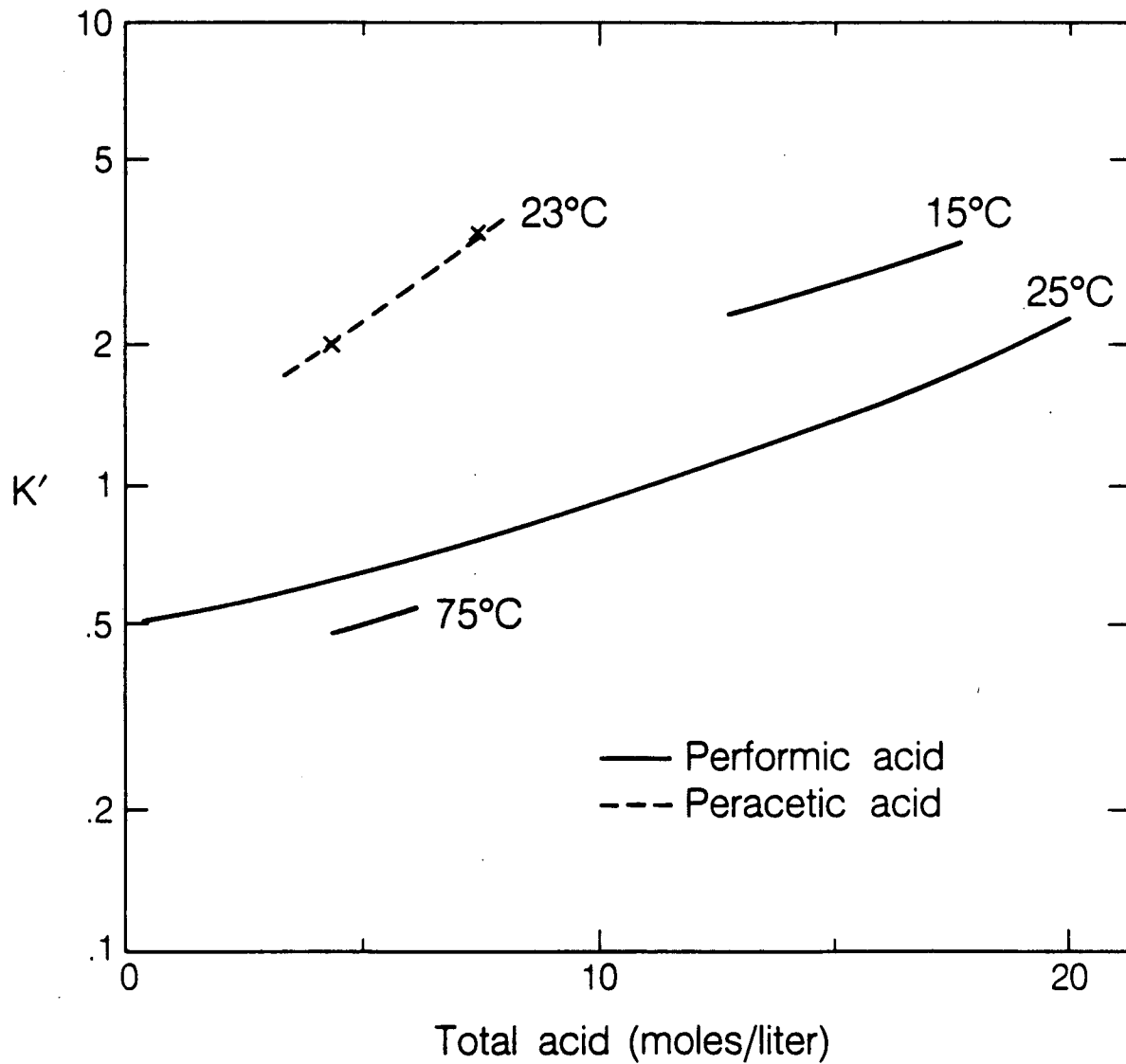
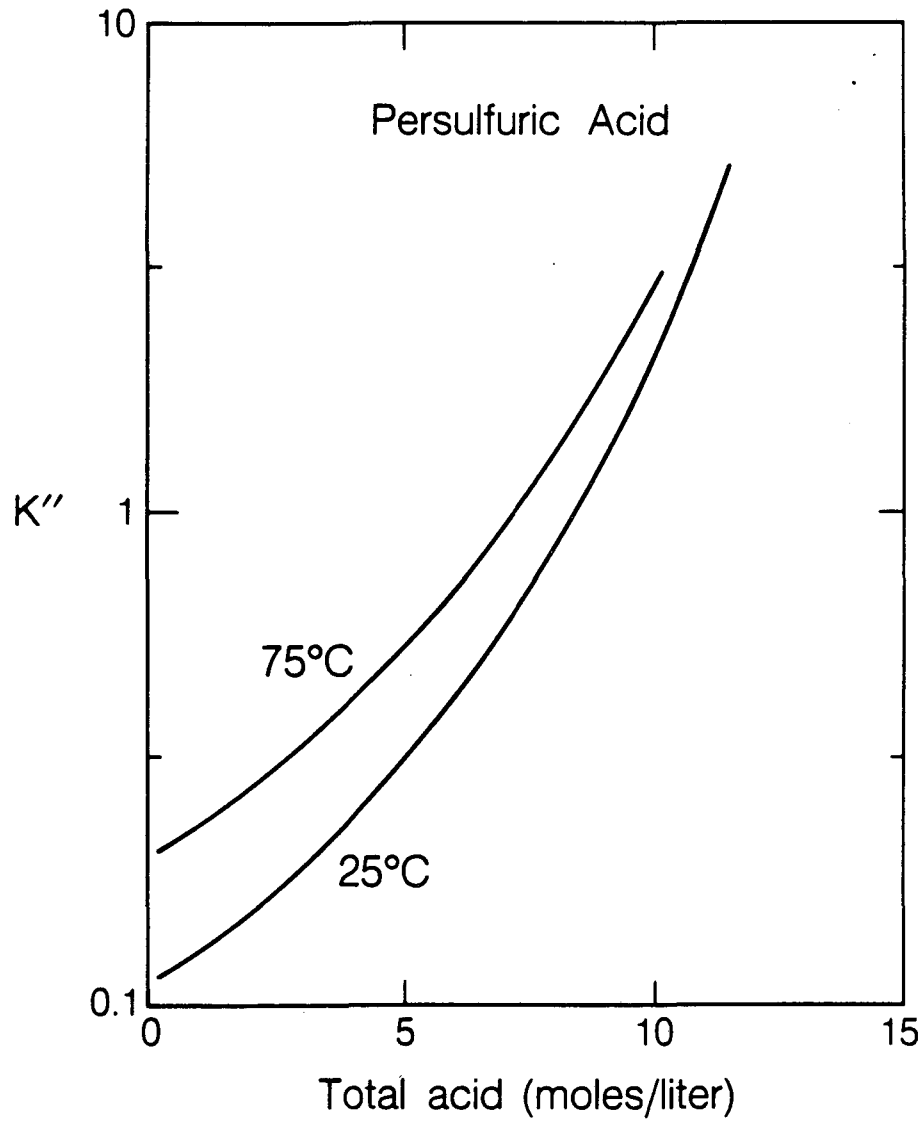


Figure 2

XBL 884-8862

$$K'' = \frac{\gamma_{\text{H}_2\text{O}}}{\gamma_{\text{H}_2\text{O}_2}} \times \frac{[\text{peracid}] [\text{H}_2\text{O}]}{[\text{acid}] [\text{H}_2\text{O}_2]}$$



XBL 884-8861

Figure 3



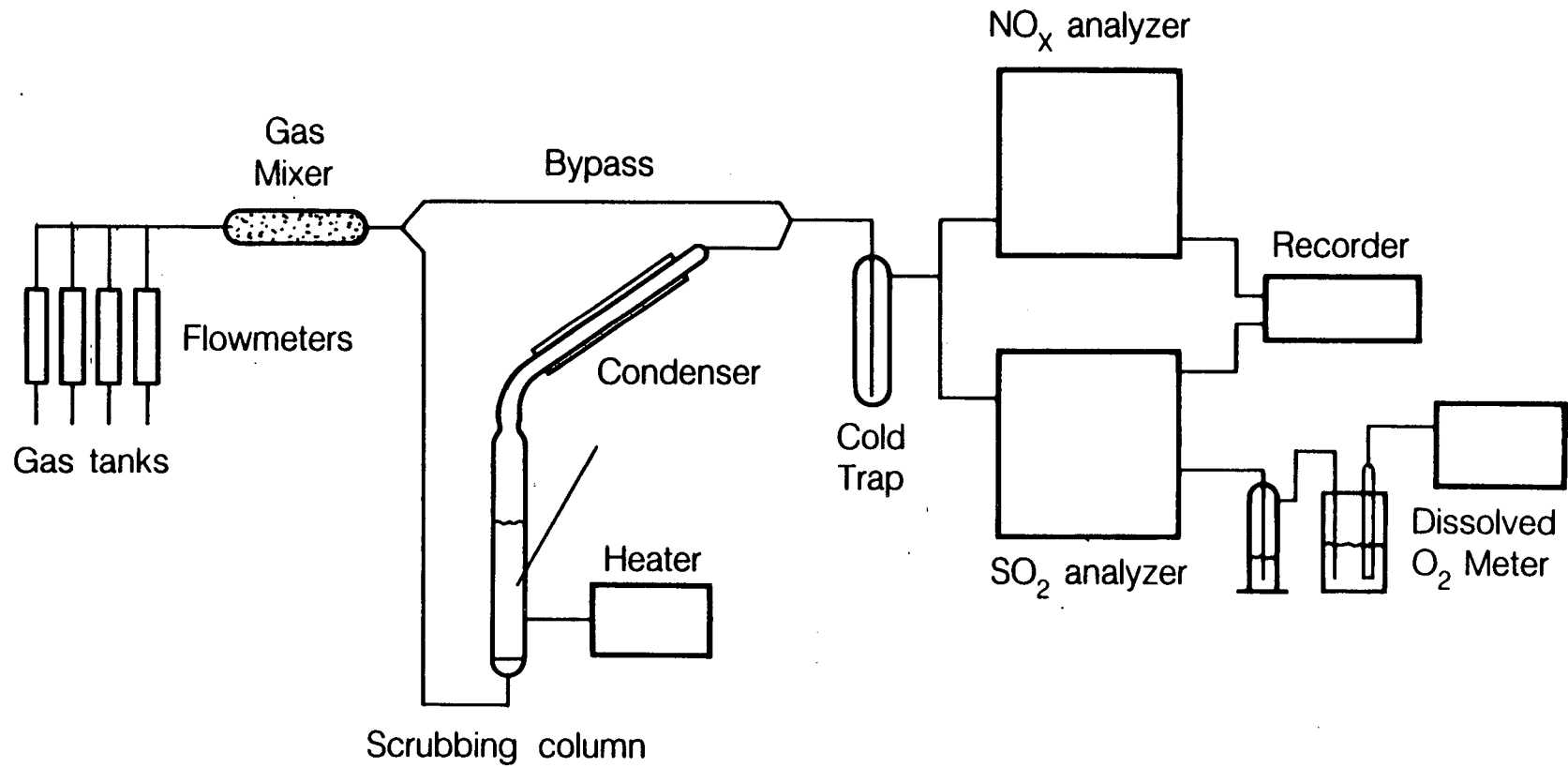
ACID	PK	PERACID	PK
FORMIC ACID	3.8	PERFORMIC ACID	7.1
ACETIC ACID	4.8	PERACETIC ACID	8.2
SULFURIC ACID	1.9	PERSULFURIC ACID	~5?

Acid  $pK_a$  values from the CRC Handbook of Chemistry and Physics, 60th edition.

Performic acid and peracetic acid  $pK_a$  values from A.J. Everett and G.J. Minkoff (1953) Trans. Faraday Soc. 49 410.

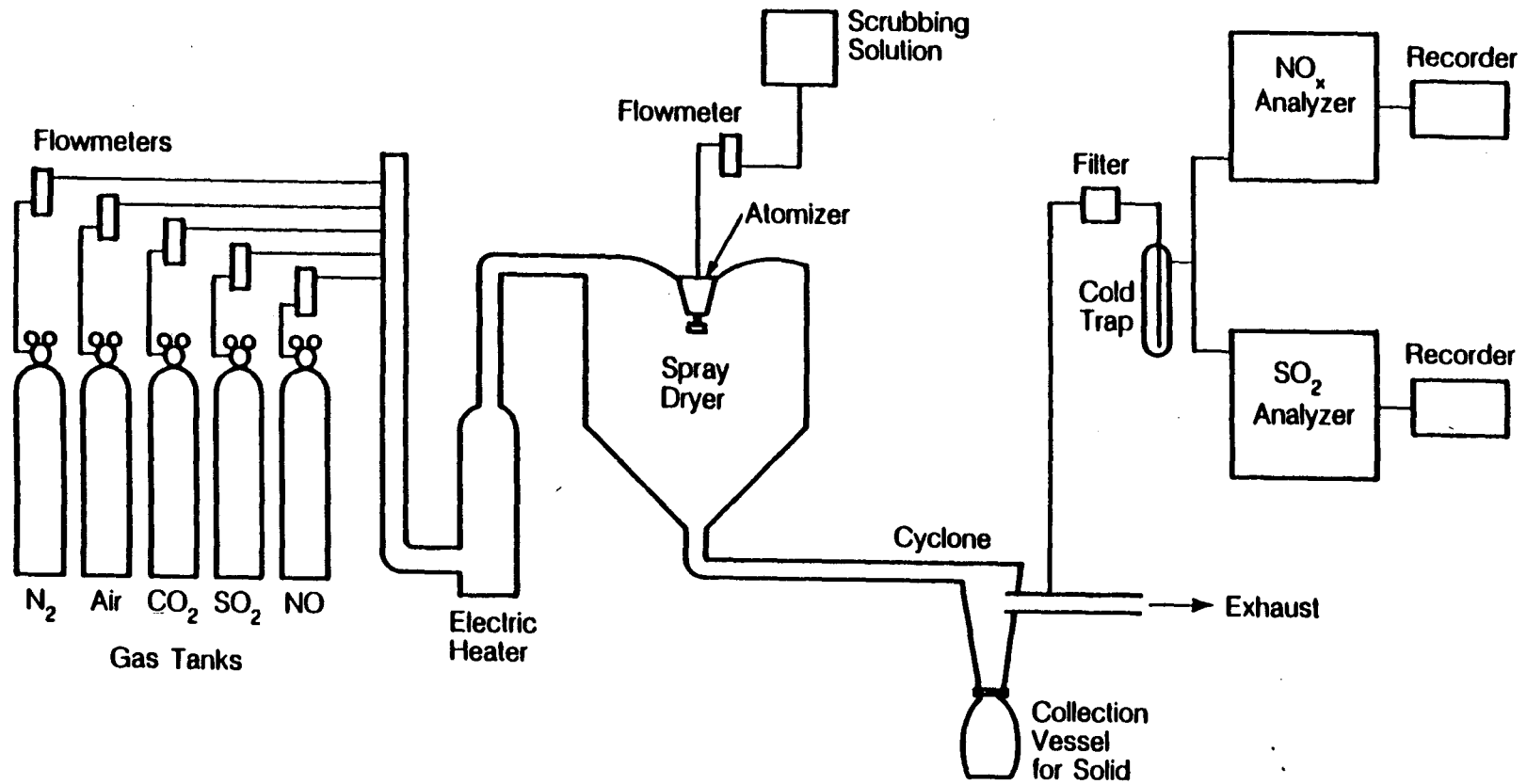
Figure 4

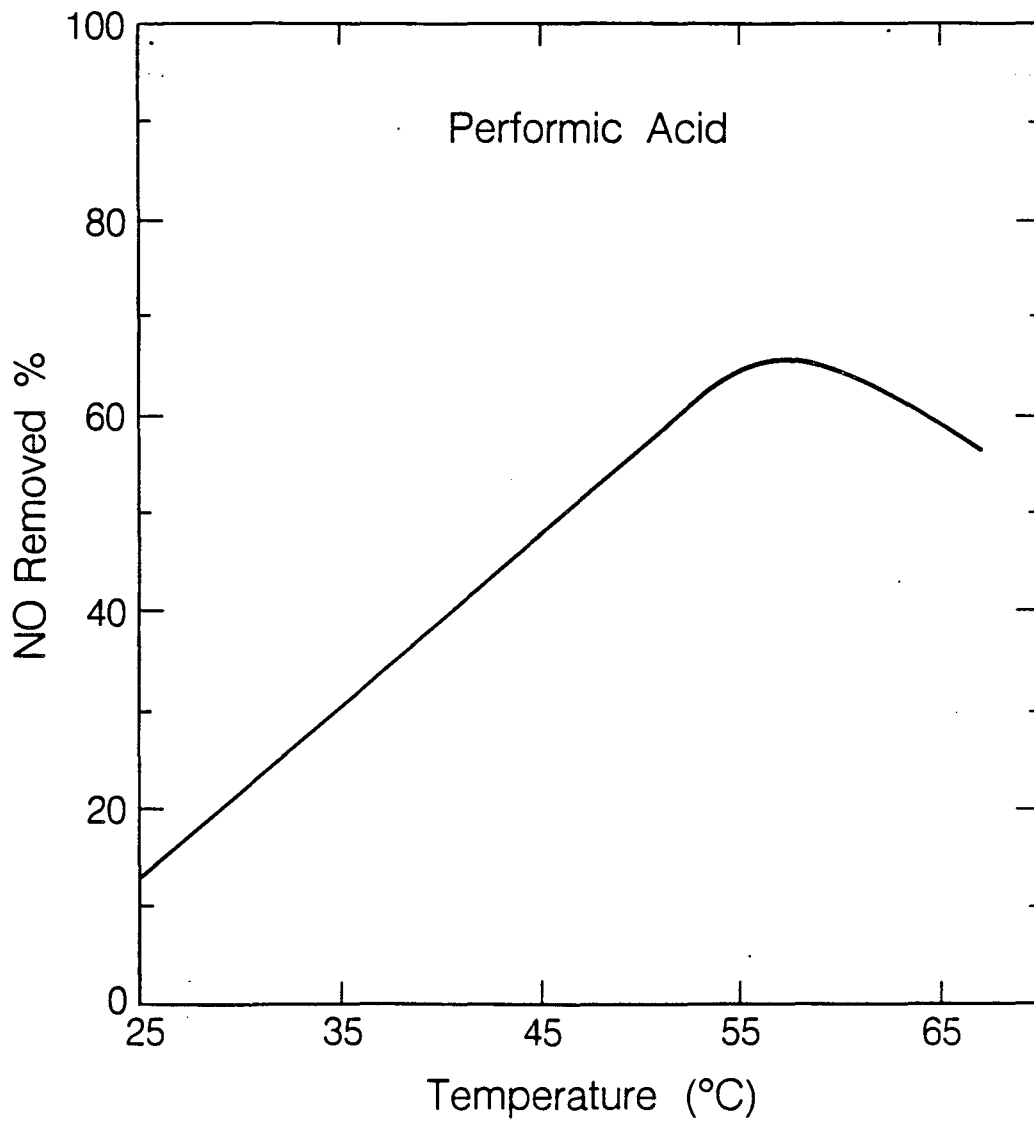
Figure 5



XBL 884-8864

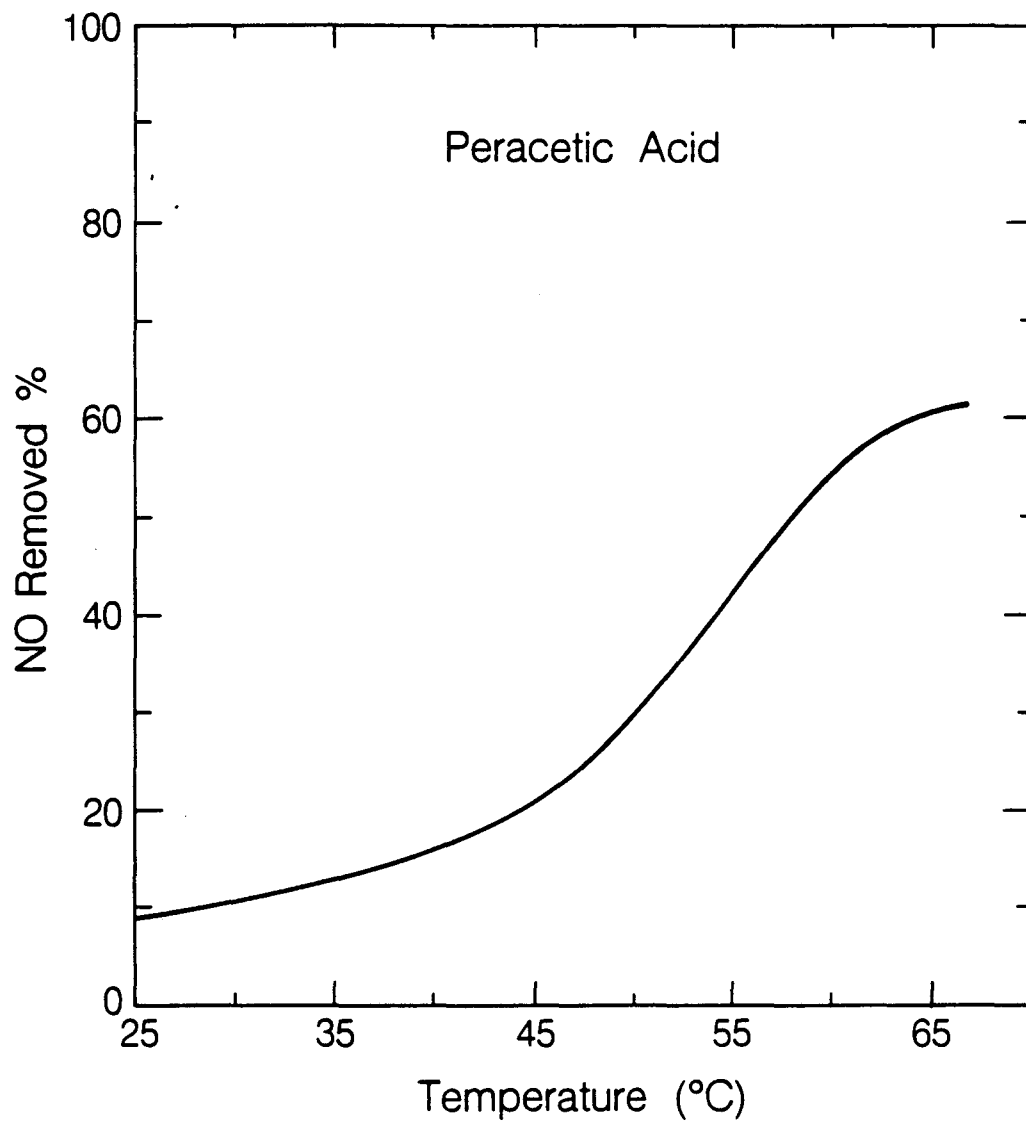
Figure 6





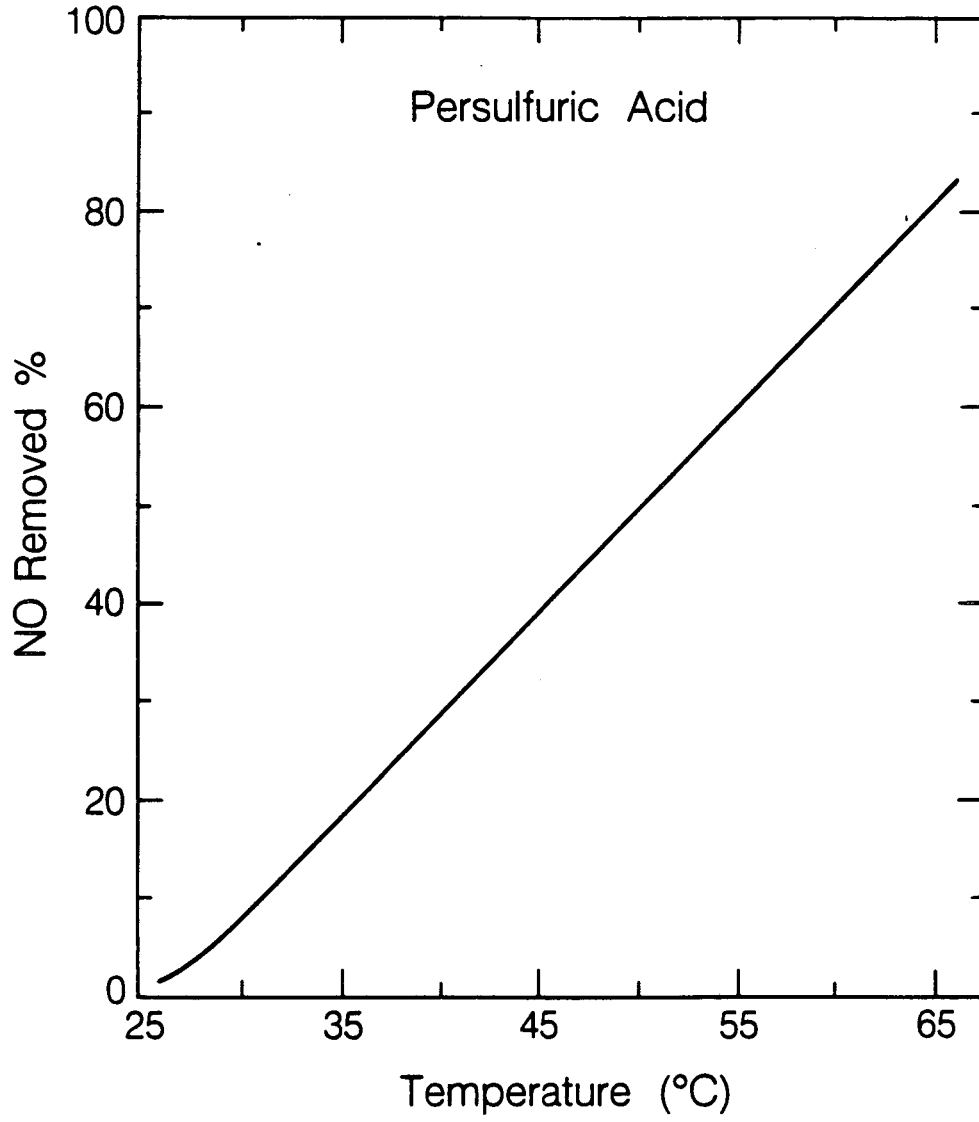
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Figure 7



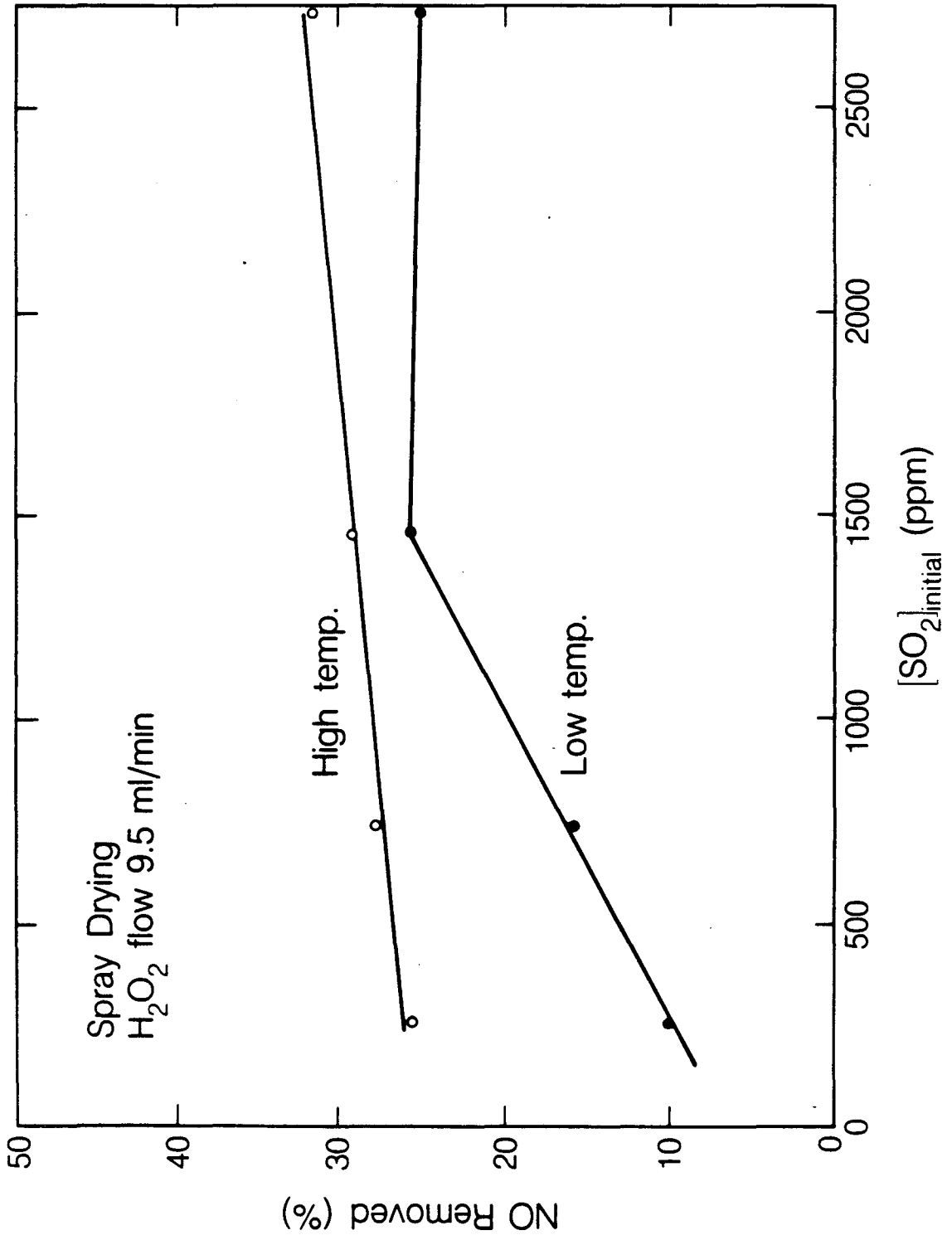
XBL 884-8859

Figure 8



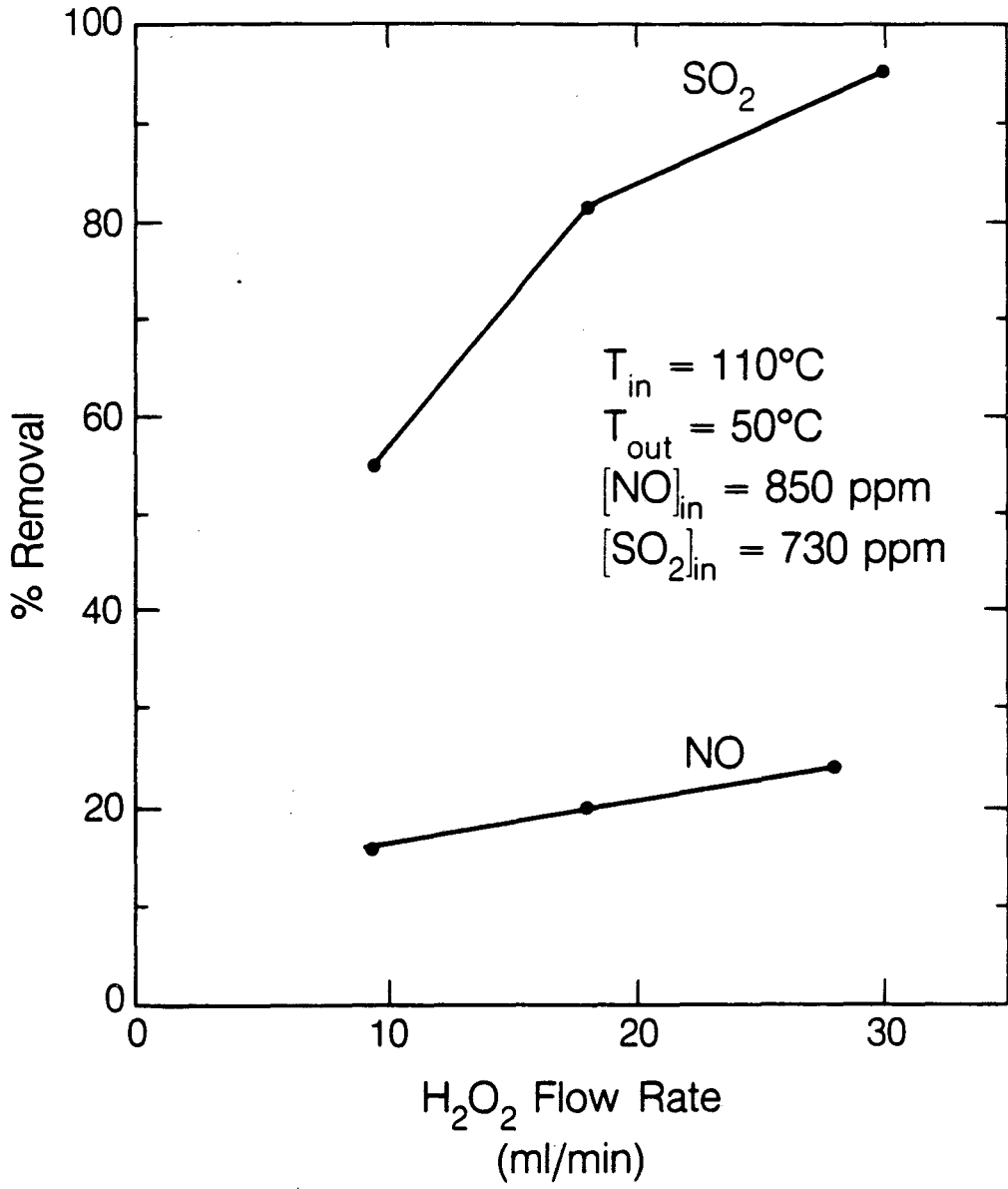
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Figure 9



XBL 884-8857

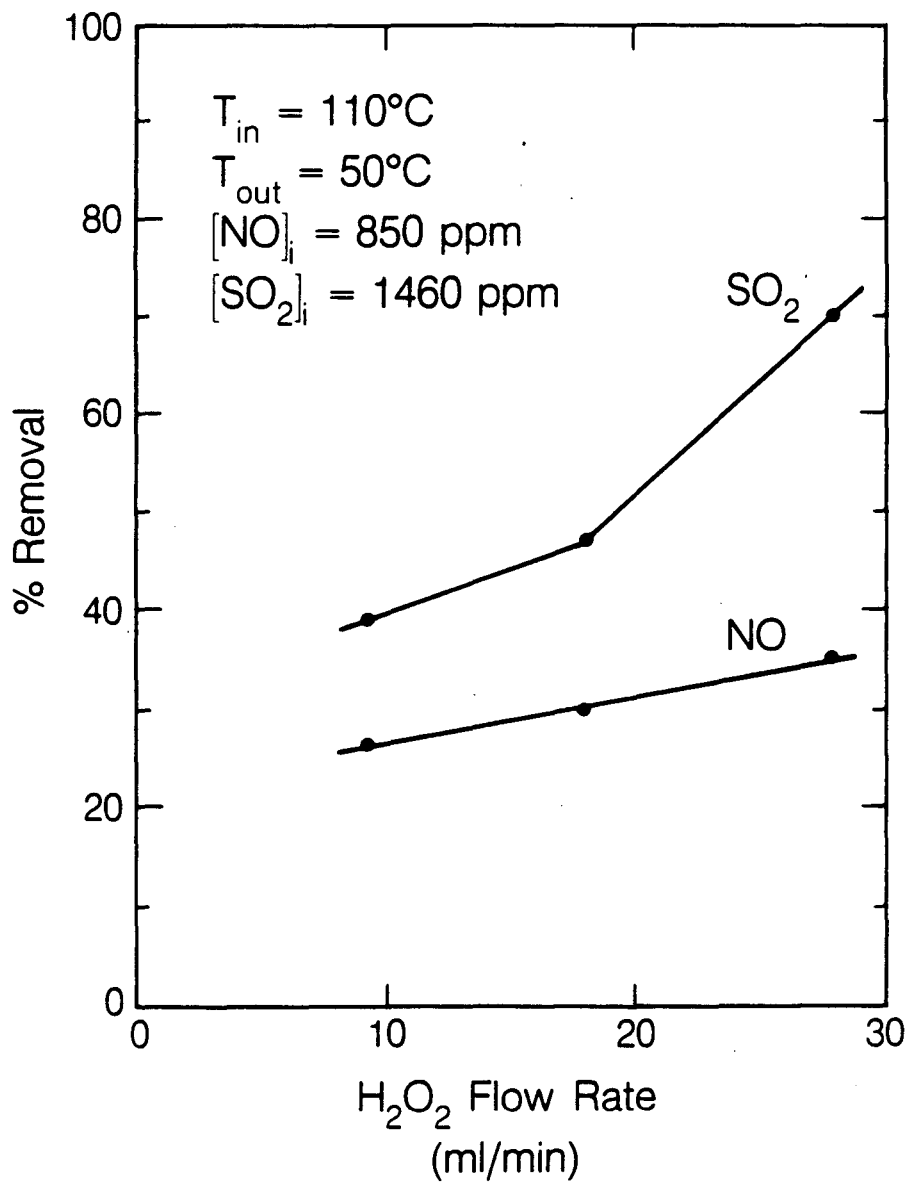
Figure 10



XBL 884-8856

Figure 11





XBL 884-8855

Figure 12

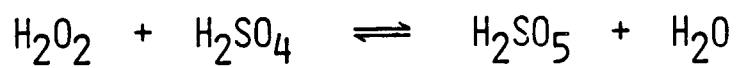
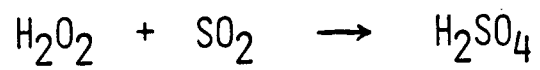


Figure 13

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