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# Removal of $NO_x$ and $SO_2$ from Flue Gas by Peracid Solutions

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# Abstract

Treatment of water-soluble carboxylic acids with concentrated hydrogen peroxide generates solutions of peracids. These compounds can rapidly oxidize $NO_x$ and $SO_2$ to their respective oxyanions, making them useful in flue gas treatment. The properties of performic acid, peracetic acid, and perpropionic acid are reported and are compared with peroxymonosulfuric acid. The chemistry of $NO_x$ and $SO_2$ removal by these compounds is dicussed.

A number of oxidizing compounds have been studied to determine their effectiveness in removing $NO_x$ and $SO_2$ from flue gas.(Kobayashi et al, 1977) A process exists using hydrogen peroxide to remove $NO_x$ and $SO_2$ from flue gas, but it is only effective under very acidic conditions (Cooper, 1984). The process developed by Cooper requires an acidic medium because hydrogen peroxide is a much more effective oxidizing agent in the form of $H_3O_2^+$, which exists in acidic conditions (Purcell and Kotz, 1977). The process needs an alkaline wash of the treated gas to remove volatilized nitrogen oxides from the acidic peroxide solution. We have made further studies of oxidizing compounds to determine their usefulness in flue gas clean-up systems. One class of compounds that has been found to be effective in $NO_x$ and $SO_2$ removal is that of peroxyacids, or peracids. Peracids have been found to function over a much wider pH range than hydrogen peroxide alone. They are formed by a reaction of hydrogen peroxide and some compounds containing a carboxylic acid group. Performic acid (PFA), peracetic acid (PAA), and perpropionic acid (PPA) were studied and compared with peroxymonosulfuric acid (PMSA), also known as Caro's acid.

**Experimental Section**

Techniques for preparation of peracids were pioneered by D'Ans and Frey (1912). Other methods of preparation have been reviewed by Swern (1949). Solutions of peracids were prepared by the reaction of 30% or 50% hydrogen peroxide with the concentrated acid or acid anhydride.

$$H_2O_2 + R\text{-}COOH \Longleftrightarrow R\text{-}COOOH + H_2O \qquad (1)$$

$$2H_2O_2 + (R\text{-}CO)_2O \rightarrow 2R\text{-}COOOH + H_2O \qquad (2)$$

In some cases, a small amount of sulfuric acid was added as a catalyst. Sufficient time was allowed for equilibration to occur. The equilibration time depends on the acid involved, the temperature of the solution, and the concentration of the reactants, as well as the presence of catalysts. The equilibration of PFA and PMSA was studied by Monger and Redlich (1956) and the equilibration of PAA and PFA has been reported by Greenspan (1946). Swern reports additional data from which equilibrium quotients can be determined. The equilibrium quotient,

$$K = [\text{peracid}]\cdot[H_2O] / [\text{acid}]\cdot[H_2O_2],$$

is shown in Figure 1 as a function of total acid concentration. The data were compiled from values reported by Monger and Redlich (1956), Greenspan (1946), and Swern (1949). The equilibrium quotients for PFA tend to be smaller at higher temperatures, but the rate of formation is faster. Data for the temperature dependence of the equilibrium quotients of PAA and PPA are not available, but they also appear to form more quickly at higher temperatures. PAA and PPA can be concentrated by distillation. PFA can be concentrated by distillation also, but it is more unstable and concentrated solutions can explode (Swern, 1949).

Most of the studies on $NO_x$ and $SO_2$ removal by peracids were done with the bench-scale wet scrubber shown in Figure 2. A gas mixture with the desired concentrations of NO and $SO_2$ was prepared and passed through a fine frit at the bottom of the scrubbing column containing the peracid solution. NO was used instead of a mixture of NO and $NO_2$, since it is generally more abundant in flue gas and is more difficult to remove. Gas flow rates of 1 to 2 liters/min were generally used. The temperature of the column was regulated by a water bath. A condenser was used in some experiments to minimize loss of the scrubbing liquid at high temperatures. The gas was then directed to $NO_x$ and $SO_2$ analyzers. Some experiments were also performed with a small spraying system from Niro Corporation, using a rotary atomizer to disperse the peracid solution into the spraying chamber. An air flow of 600 liters/min was used, with an inlet temperature of 160 - 190°C and and outlet temperature of 75 - 95°C. An NO concentration of 600 ppm were used and the $SO_2$ concentration was varied from 0 to 1600 ppm.

The stability of the peracid solutions was studied as a function of temperature and pH. The concentrations of peroxides in the solutions were monitered by colorimetry and by Raman spectroscopy. Most of the work was done by colorimetry, which involved diluting a fraction of the solution under test and observing the amount of ferrous ion oxidized to ferric ion via the ferric thiocyanate complex absorption at 460 nm. Colorimetry was found to be a simpler analytical method than Raman spectroscopy for this work. Most of the Raman peaks of the peracids were fairly weak. Many of these peaks overlapped with the peaks of hydrogen peroxide or the parent acid. Colorimetry provided a direct measure of the total amount of peroxides present. This is useful since the peracid is in equilibrium with hydrogen peroxide.

**Results and Discussion**

Hydrogen peroxide solutions are effective in removing $SO_2$ from gas streams under a wide range of conditions. However, they can remove significant amounts of $NO_x$ only under highly acidic conditions (Cooper, 1984). Peracid solutions were tested in a survey of the capabilities of oxidizers in removing $SO_2$ and $NO_x$ from flue gas. The peracids were found to have the potential for removing a large fraction of $NO_x$ and $SO_2$ from flue gas. The reactions involved in the removal process are shown below:

$$\text{R-COOOH} + SO_2 + H_2O \rightarrow SO_4^{2-} + \text{R-COOH} + 2H^+ \qquad (3)$$

$$\text{R-COOOH} + NO \rightarrow NO_2 + \text{RCOOH} \qquad (4)$$

$$\text{R-COOOH} + 2NO_2 + H_2O \rightarrow 2NO_3^- + \text{R-COOH} + 2H^+ \qquad (5)$$

Peracids will also deprotonate at moderate pHs,

$$\text{R-COOOH} \Longleftrightarrow \text{R-COOO}^- + H^+ \qquad (6)$$

Measurements of the $pK_a$s for the peracids used in this work were made by Everett and Minkoff (1953). While the value of $pK_{a1}$ for PMSA does not appear to be known (Ball and Edwards, 1956), Monger and Redlich (1956) suggest that it is a significantly weaker acid than sulfuric acid. The $pK_a$s of the acids and their respective peracids are listed below.

| | | | |
|---|---|---|---|
| Formic acid | pK = 3.8 | Performic acid | pK = 7.1 |
| Acetic acid | 4.8 | Peracetic acid | 8.2 |
| Propionic acid | 4.9 | Perpropionic acid | 8.1 |
| Sulfuric acid | 1.9 | Peroxymonosulfuric acid | 3 - 4 (est.) |

The ability of peracid solutions to remove NO and $SO_2$ was tested in the small wet scrubbing system. Typically, 60 ml of solution, containing about 22% $H_2O_2$ and 30-40% of the parent acid on a weight basis, was used with gas containing about 500 ppm of NO and 2000 ppm of $SO_2$ flowing through at about 1 liter/min. It was found that peracid solutions were capable of removing up to 95% of NO and 100% of $SO_2$ in simulated flue gas. Maximum NO removal was obtained with temperatures of 50 to 60°C and NO concentrations of 500 ppm or less. $SO_2$ is effectively removed by solutions of $H_2O_2$ alone, so most tests were done with gas mixtures of only NO and air or NO and $N_2$. Since oxidizers are the active compounds of the scrubbing solution, oxygen in the flue gas had no effect on the removal efficiency.

The temperature dependence of NO removal by peracid solutions was studied by observing the amount of NO removal by heating the solution from 25°C to 65°C. The measurements were made with 60 ml of 1:1 mixtures of the concentrated parent acid and $H_2O_2$. A gas mixture of 1050 ppm NO in $N_2$, flowing at 1.2 liters/min, was used. The pHs of the solutions were not adjusted after mixing and all of them were fairly acidic ($pH < 2$). The results are shown in Figure 3. All the peracids showed improved removal efficiencies at elevated temperatures. PFA shows a decrease in removal efficiency above 55°C, possibly due to decomposition of the compound. It has been reported to be less stable than PAA and PPA (Greenspan, 1946). PMSA shows behavior similar to that of PAA and PPA.

The pH of the scrubbing solution influenced the NO removal efficiency. Since PFA and PMSA are stable only in fairly acidic solutions ($pH < 2$), their pH dependence was not studied. The NO removal efficiency of PAA and PPA was found to increase with pH. The percent removal of NO by a PPA solution as a function of pH is shown in Figure 4. The measurements were made at 60°C with a 1.2 liter/min flow of 1050 ppm NO in $N_2$ through 60 ml of PPA solution. A PPA solution was prepared by mixing 30% $H_2O_2$ and propionic anhydride in a 1.5:1 volume ratio. After letting the solution react for 24 hours, it was diluted with an equal volume of water, giving a final PPA concentration of about 1.5 M. The pH of the solution was adjusted by the slow addition of concentrated NaOH while stirring.

The fractional NO removal efficiencies, $E_f = 1 - ([NO]_{out}/[NO]_{in})$, at 25°C and 55°C for the peracid solutions are listed in Table 1, along with those for hydrogen peroxide and sodium chlorite. The latter two compounds have been included to provide a comparison with the results obtained by Kobayashi et al (1977). The solution concentrations for these two compounds were 3% $H_2O_2$ and 0.4 M $NaClO_2$ in our study. The peracid data were obtained from the runs shown in Fig. 3. The measurements were made using 1.2 liter/min of 1050 ppm NO in $N_2$ passing through 60 ml of solution in a water bath. Kobayashi et al used 250 ppm NO in $N_2$ flowing at 820 ml/min and 100 ml of solution in their studies.

Table 1

| Reagent | $E_f$ (25°C) |  | $E_f$ (55°C) |
|---|---|---|---|
|  | a | b | b |
| $H_2O_2$ | 0.13 | 0.05 | 0.03 |
| $NaClO_2$ | 1.00 | 1.00 | 1.00 |
| PFA | - | 0.25 | 0.65 |
| PAA | - | 0.08 | 0.43 |
| PPA | - | 0.07 | 0.40 |
| PMSA | - | 0.09 | 0.51 |

a - Kobayashi et al (1977)
b - this study

The NO removal efficiencies for the compounds studied by Kobayashi and co-workers were correlated with the redox potentials of the compounds. The redox potentials for the peracids do not appear to be available, but would be expected to be similar to that for hydrogen peroxide, since they exist in equilibrium. It should be noted that the redox potentials in basic conditions can differ substantially from those in acidic conditions. Table 2 provides a comparison of redox potentials for $H_2O_2$, $ClO_2^-$, and $ClO^-$ in acidic and basic solutions, along with the values used by Kobayashi et al. The values for acidic and basic conditions were obtained from Latimer and Hildebrand (1959). Since there is considerable variation in redox potential with pH, as well as other solution conditions, caution should be used when relating these values to NO removal ability.

Table 2

| | |
|---|---|
| **Acidic Solution** | |
| $2H_2O = H_2O_2 + 2H^+ + 2e^-$ | -1.77v |
| $HClO + H_2O = HClO_2 + 2H^+ + 2e^-$ | -1.64v |
| $0.5Cl_2 + H_2O = HClO + H^+ + e^-$ | -1.63v |
| **Basic Solution** | |
| $3OH^- = HO_2^- + H_2O + e^-$ | -0.88v |
| $ClO^- + 2OH^- = ClO_2^- + H_2O + 2e^-$ | -0.66v |
| $Cl^- + 2OH^- = ClO^- + H_2O + 2e^-$ | -0.89v |
| **Kobayashi et al** | |
| $4OH^- = H_2O_2 + 4e^-$ | -0.88v |
| $Cl^- + 4OH^- = ClO_2^- + 2H_2O + 4e^-$ | -1.55v |
| $Cl^- + 2OH^- = ClO^- + H_2O + 2e^-$ | -0.89v |

Some experiments were performed using a small spraying system to test the peracid solutions under spraying conditions. In most of the experiments, the spraying system was operated at an air flow rate of about 600 liters/min with an inlet temperature of 170°C and an outlet temperature of 95°C. The NO concentration used was 600 ppm and the $SO_2$ concentration ranged from 0 to 1600 ppm. In some cases, no $SO_2$ was added to the gas stream. Only performic acid (containing an equilibrium concentration of about 1 M PFA) and 30% hydrogen peroxide solutions were tested in the spraying system. Flow rates of the peroxy compounds into the atomizer were in the range of 10 to 25 ml/min. It was found that PFA oxidized NO to $NO_2$ and $SO_2$ to sulfate ion and sulfuric acid. The $SO_2$ appears to react rapidly with $H_2O_2$ to form PMSA, which, in turn, oxidizes NO to $NO_2$. When $SO_2$ was added to the gas, NO oxidation increased from 2 - 4% to 20 - 40%. $SO_2$ removal ranged from 20% to 100%. Increasing the $SO_2$ concentration increased NO removal, although the NO removal leveled out at 40% in spite of increasing the $SO_2$ concentration. Increasing the

$H_2O_2$ feed rate increased NO removal only when it also increased $SO_2$ removal. Once 100% $SO_2$ removal had been achieved, increasing the $H_2O_2$ feed rate had no effect on NO removal. The presence of NO had no effect on $SO_2$ removal. Performic acid solutions did not appear to be any better than hydrogen peroxide solutions for NO and $SO_2$ removal in a spraying system, except when only NO was present. The stoichiometries for removal were in the range of (peroxy compound added)/(NO + $SO_2$ removed) = 5 to 10. The fraction of peroxy compound added that did not react was not determined. Use of peracids in a spraying system does not appear to be particularly promising, primarily because of the difficulty in removing $NO_2$ and the carboxylic acid vapor. A compound such as ammonia would need to be co-added to neutralized sulfuric acid and possibly remove some of the $NO_2$. Treatment of the gas leaving the spraying system would be required for the system to be effective.

The stoichiometry of NO removed by peracids was also checked in the wet scrubbing system. From equations 4 and 5, the stoichiometry for moles of peracid consumed to moles of NO converted to $NO_3^-$ should be 1.5 to 1. This was checked by determining the total peroxide concentration in a scrubbing solution before use by colorimetry, then measuring the amount of NO removed by the solution when 2.5% NO in $N_2$ was flowed through it for several hours at 60°C. The final peroxide concentration was determined and corrected for the peroxide found in the cold trap downstream of the scrubber. These measurements gave a stoichiometry of about 1.8 to 1 for peracid lost to NO removed. The somewhat larger value of peroxide consumption than expected from the equations is presumably due to decomposition of the peracid.

The rate of decomposition of the peracids was studied using colorimetry to determine total peroxide concentrations of PFA and PPA solutions at 20°C and 50°C as a function of time. PFA solutions at pHs of about 0 and 1.5 and PPA solutions at pHs of 2, 4 and 6 were used. The rate constants for decomposition were derived from the measurements, using the expression $dx/dt = -kx$, where $x$ is the concentration of the peracid. The values of k are listed below.

| | pH | k (20°C), $sec^{-1}$ | k (50°C), $sec^{-1}$ |
|---|---|---|---|
| performic acid | 0 | $0.7 \times 10^{-6}$ | $15.6 \times 10^{-6}$ |
| | 1.5 | $3.4 \times 10^{-6}$ | fast |
| perpropionic acid | 2 | $0.8 \times 10^{-6}$ | $2.0 \times 10^{-6}$ |
| | 4 | $1.2 \times 10^{-6}$ | $4.4 \times 10^{-6}$ |
| | 6 | $0.8 \times 10^{-6}$ | $5.8 \times 10^{-6}$ |

There is some uncertainty in the values of the rate constant that are below $2 \times 10^{-6}$ $sec^{-1}$, so there may not be much change with pH in the 20°C decomposition rate for PPA. The decomposition rate for PAA appears to be intermediate between that of PFA and PPA. Swern (1949) states that PPA is somewhat more stable than PAA. The increase of the decomposition rate with pH suggests that the peracid anions formed by reaction 6 are less stable than their respective acids. There are a number of stabilizers, such as sodium pyrophosphate (Greenspan, 1946), that inhibit the decomposition of peracids. Use of these compounds could improve the peroxide to NO stoichiometry in the removal process.

To determine the best pH for operation of a scrubber, one needs to compare the influence of pH on NO removal efficiency and on decomposition rate. For the dissociation of nitrous acid and dissolved $SO_2$,

$$HNO_2 \quad <==> \quad H^+ \; + \; NO_2^-$$

$$SO_2(aq) \quad <==> \quad H^+ \; + \; HSO_3^-$$

the $pK_a$s are both well below 4. Since the fully protonated compounds can release significant amounts of $NO_2$ and $SO_2$ into the gas phase, it would be advantageous to maintain a pH of 4 or higher in the scrubbing solution. Use of a stabilizing agent could minimize problems with decomposition occurring at high pH conditions.. Doing a similar comparison of the temperature dependences of NO removal efficiency and decomposition rate for PPA, it appears that scrubber operation at higher temperatures (50 - 60°C) is advantageous. A negative aspect of higher temperature operation is the increased volatility of the peracid and $H_2O_2$. The most suitable design for a scrubber utilizing a peracid solution for removal of $SO_2$ and $NO_x$ is likely to be a two stage system. The first stage would contact the flue gas with the peracid solution and the second stage would recover the volatilized peracid and $H_2O_2$ and capture any $NO_2$ not collected by the first stage. The nitrate and sulfate ions produced by the scrubbing process would need to be removed from the scrubbing solution periodically. $H_2O_2$ would need to be added to replace that consumed in the formation of the peracid and in reaction with $SO_2$.

## Acknowledgement

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## Figure Captions

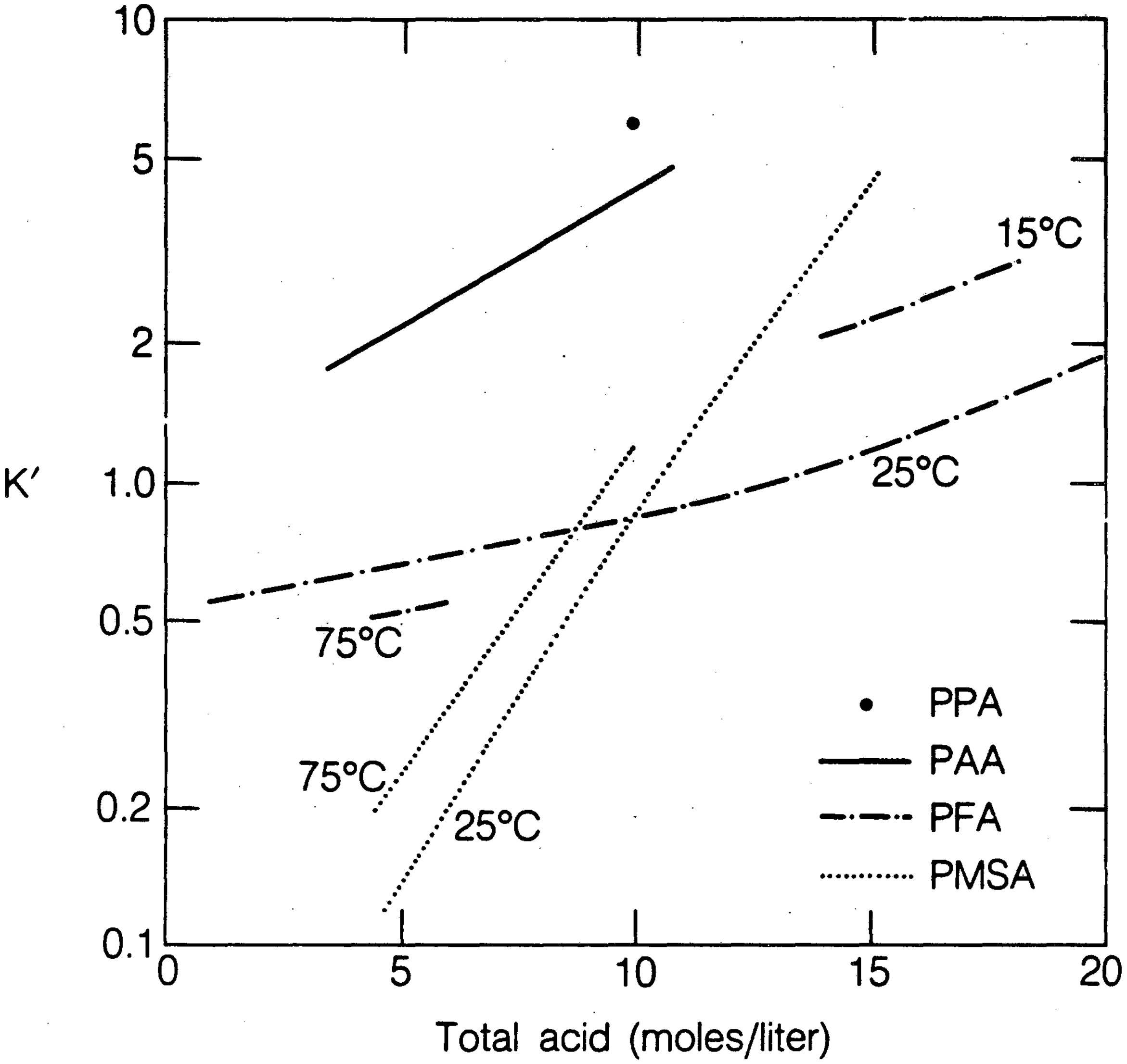
Figure 1. Equilibrium quotients for PFA, PAA, PPA and PMSA as a function of total acid concentration.

Figure 2. Wet scrubber system used to test peracid solutions.

Figure 3. Temperature dependence of NO removal by PFA, PAA, PPA and PMSA.

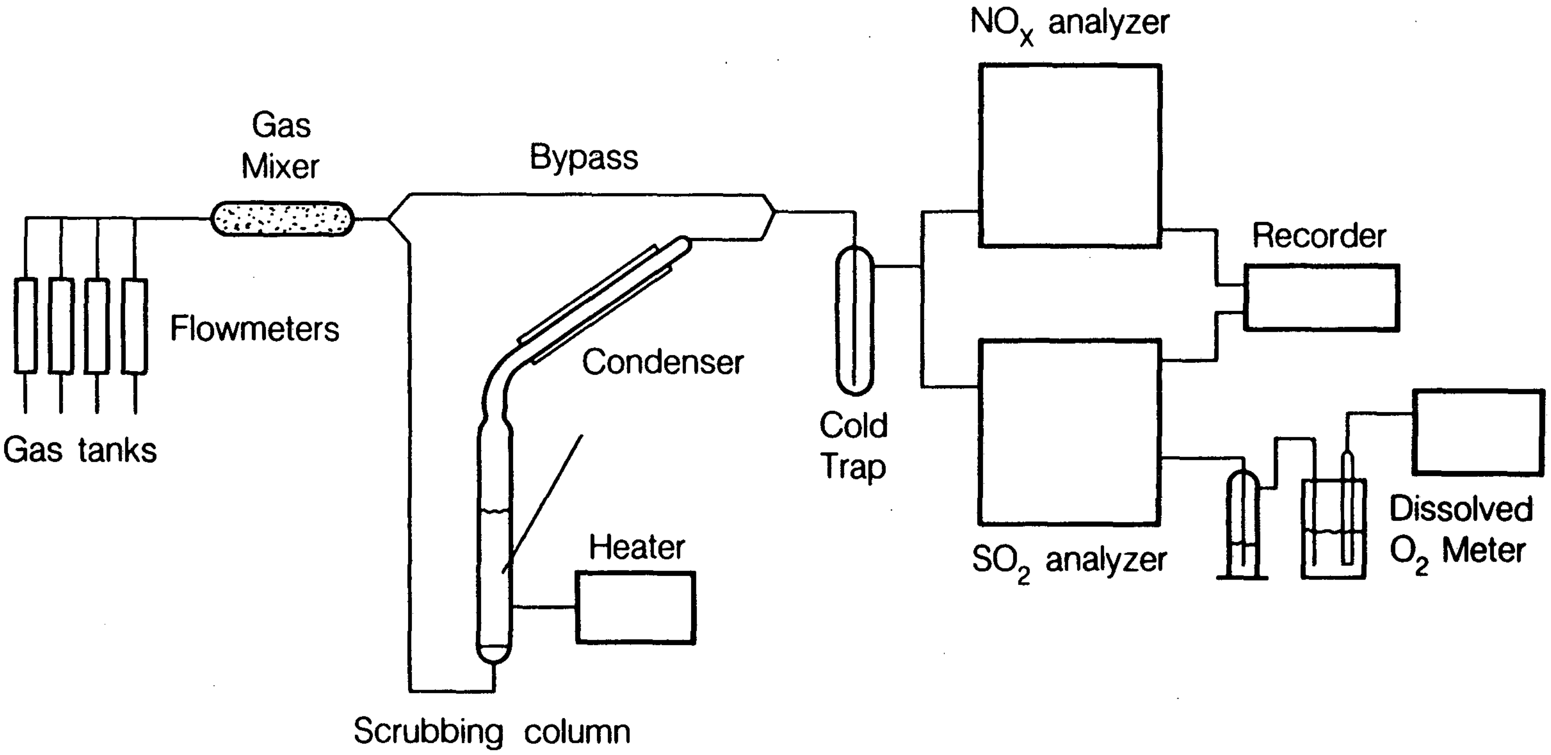
Figure 4. Effect of pH on NO removal by a PPA solution.

Figure 5. Effect of concentration on NO removal by PPA at 60°C.



XBL 891-6120

Fig. 1



XBL 884-8864

Fig. 2

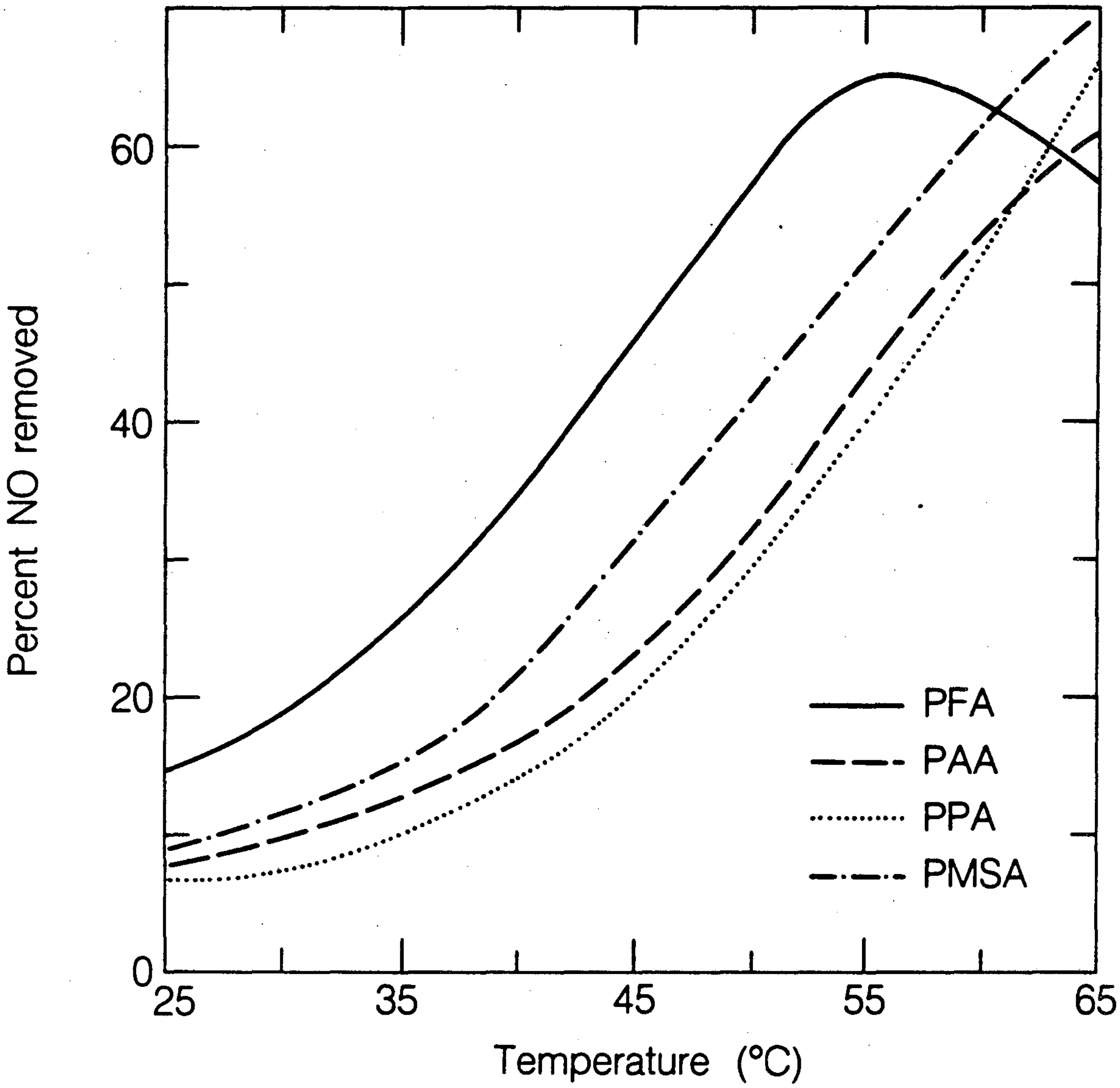


Fig. 3

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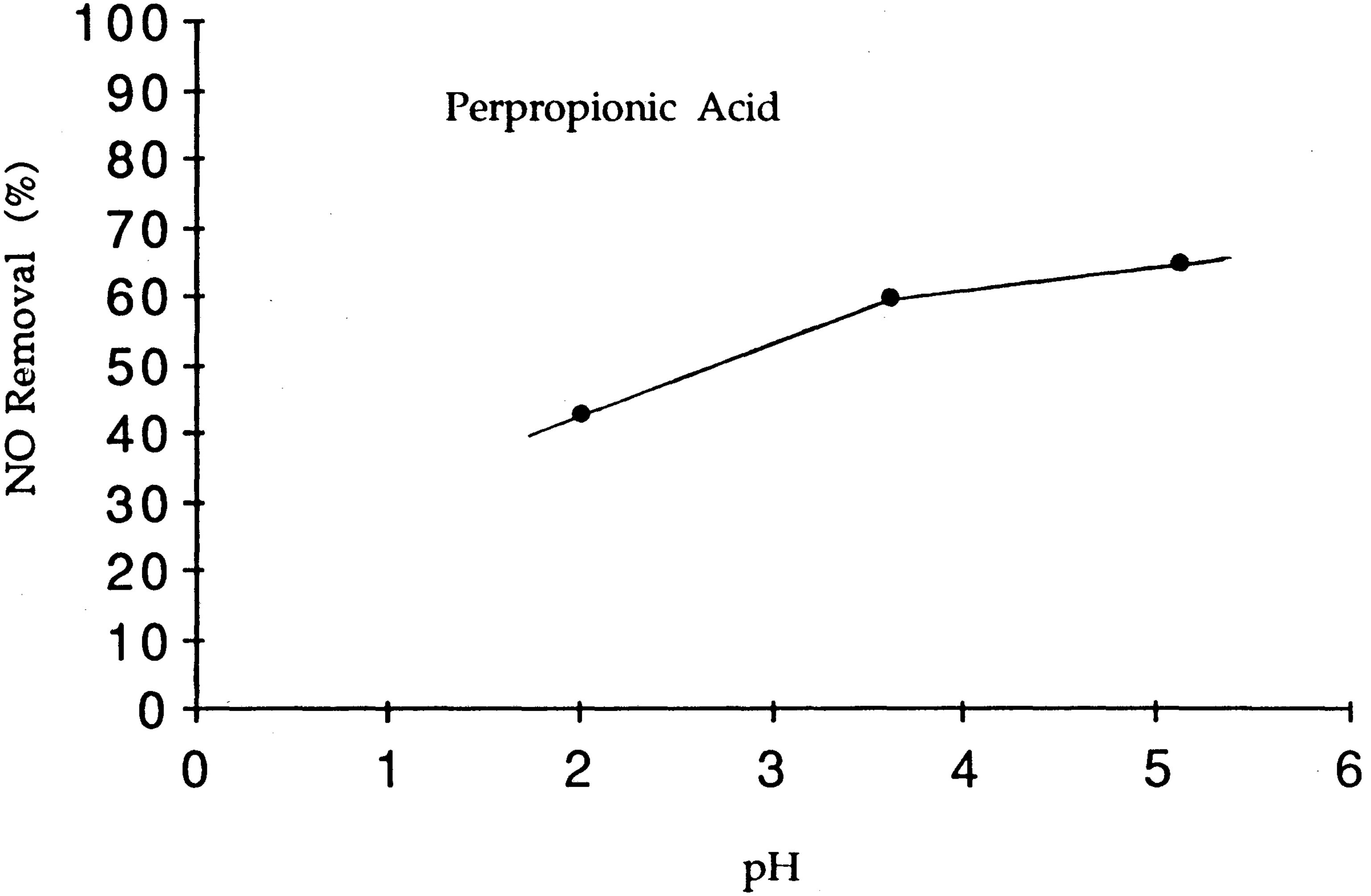

XBL 891-298

Fig. 4

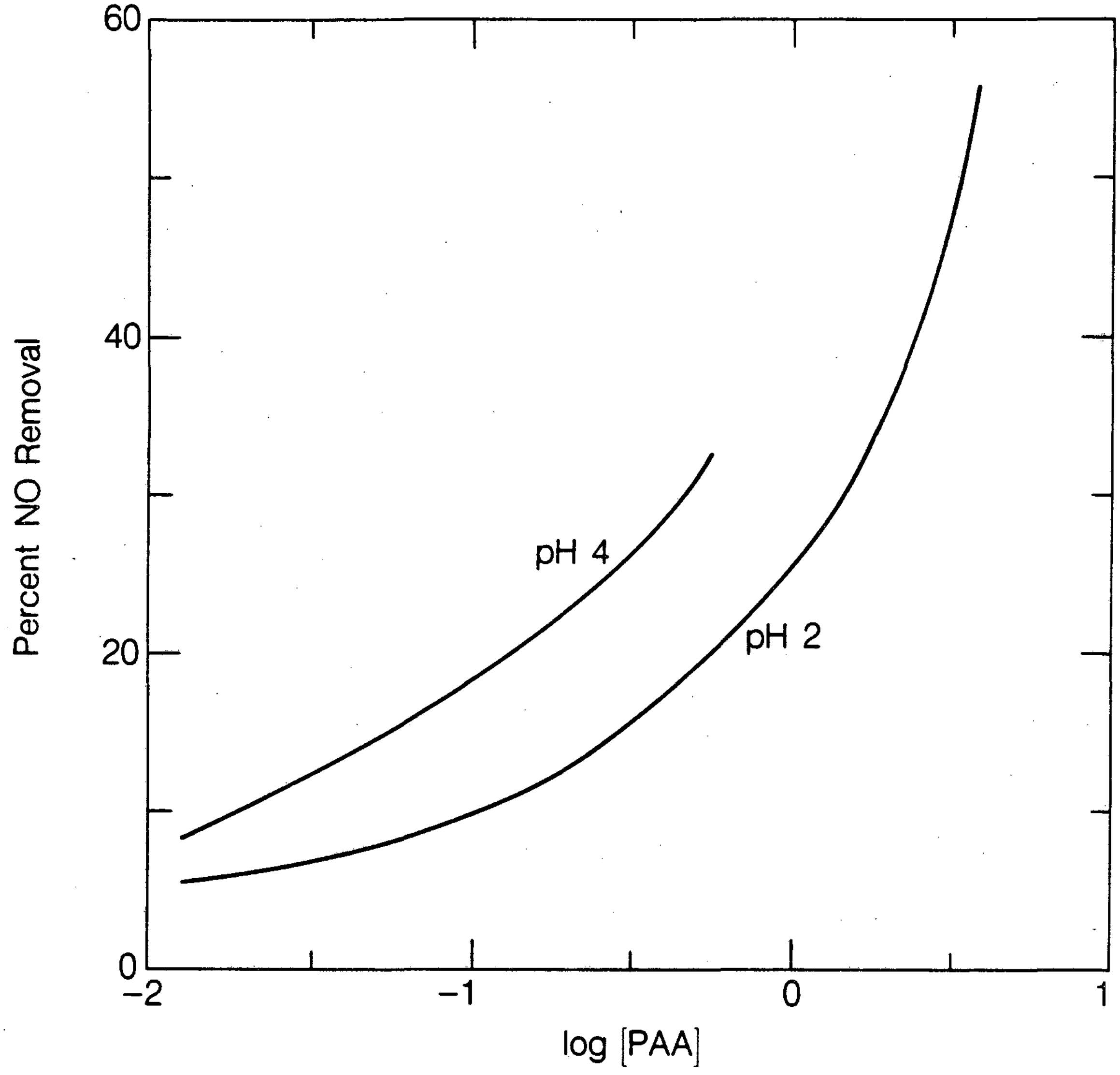

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Fig. 5

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