

OXIDATIVE AQUEOUS SCRUBBING FOR SIMULTANEOUS NO_x/SO₂ REMOVAL

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ABSTRACT

An aqueous scrubbing system containing strong oxidants was studied for the removal of nitric oxides and sulfur dioxide from gas streams. Up to 95% NO_x removal was obtained using a packed bed scrubber. The corresponding SO₂ removals were 100%. Experiments were also conducted in a bubble column, a spray chamber, and an ejector venturi scrubber in order to obtain engineering data for scale-up and process design. A novel UV/Vis photodiode array (PDA) method was developed for real-time monitoring of oxychlorine compounds in the scrubbing solutions. As a consequence of the data obtained with the PDA system, a much better understanding of the chemistry of the scrubbing system has led to a simpler mass transfer model than is available in the literature. Absorption rates are reported in terms of overall reaction rates for a spray chamber scrubber and of height of transfer units for a packed bed scrubber. Further processing of the spent scrubbing solution for salable byproducts is under investigation. With an on-site generation cell, the operating cost of the oxidative aqueous scrubbing for NO_x removal is estimated to be one tenth of that of a selective catalytic reduction unit. A review of current literature shows the capability of this scrubbing system for removing heavy metals, phenolic tastes and odors from gas streams as well.

INTRODUCTION

Commercially applied control technologies have typically involved combustion modification techniques for NO_x and wet scrubbing for SO₂. Recently, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) for NO_x control have achieved commercial status for some applications. To understand existing utility plant issues, it is important to focus on Title I of the Clean Air Act Amendments (CAAA) of 1990, which is charged with the task of reducing NO_x emissions to clean up severe ground-level ozone problems, commonly known as smog. As directed by Title I, existing utility plants are required to install reasonable available control technology (RACT). According to industry sources, Phase I (1995) RACT requirements will be low-NO_x burners, enhanced overfire air systems, combustion modifications, and other in-furnace techniques (35-50% NO_x reduction). Meanwhile, it is generally accepted that Phase II (1999) RACT requirements will lead to the application of SCR, SNCR or wet scrubbing which has 70-85% NO_x reduction (1).

Advanced flue gas treatment technologies to control both NO_x and SO₂ emissions continue to be active areas of research and development in the United States and abroad. Most of the ongoing development programs address an approach of extending the capability of the catalyst in the SCR system for SO₂ reduction (2). Hence, a flue gas desulfurization (FGD) process that promotes NO_x removal merely by using chemical additives could have a significant impact on control strategies.

For wet scrubbing processes, when the concentration of nitric oxide (NO) is less than 50 ppm, it is desirable to provide a fast chemical reaction to achieve reasonable rates of absorption. Extensive investigation has been undertaken on the chemistry and the performance of additives in wet scrubbing, such as ozone, hydrogen peroxide, potassium permanganate, sodium sulfite, Fe-EDTA, and oxychlorine compounds (ClO_x). Currently, the last three processes are being actively pursued.

The SOXAL process is a regenerable Na₂SO₃ scrubbing system coupled with urea/methanol injection in the boiler. The goal is 90% for NO_x and SO₂ removal. Urea reduces 50%-70% of the NO to N₂, and methanol oxidizes the remaining NO to NO₂, which is then removed in the Na₂SO₃ scrubber. A 3-MW

pilot program was completed in July 1993 by Allied-Signal, Inc. at the Niagara Mohawk Power Corp.'s Dunkirk station. Removals of 98% SO₂ and 70% NO_x were reported. However, high oxidation of the Na₂SO₃ solution to Na₂SO₄ occurred during the simultaneous NO_x/SO₂ scrubbing mode (2).

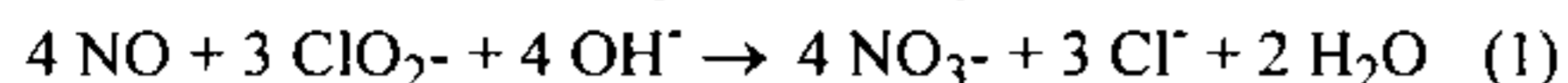
Among the scrubbing systems for NO_x/SO₂ removal, the Fe-EDTA enhanced FGD system is the most evolved. Ferrous ethylene-diamine-tetraacetate (Fe-EDTA) is added to the FGD scrubbing solution to promote NO_x removal. Tests at Argonne National Laboratory achieved NO_x removals of 60% when SO₂ removals were at 90%. Pilot scale tests of the technology were conducted during 1991 by the Dravo Lime Co., with support from the U.S. Department of Energy (DOE). NO_x removals of up to 60% were obtained using a packed bed scrubber. The corresponding SO₂ removals were 100%. Dravo conducted an economic analysis, assuming 50% NO_x reduction by low-NO_x burners, 50% reduction from Fe-EDTA, the operating costs were \$646-\$830/ton NO_x removal.

Two Japanese patents claimed the use of chlorine dioxide for NO oxidation (3, 4). The process was used to remove NO from flue gas. 300 m³/hr and 70,000 m³/hr of flue gas containing 100 ppm NO were used to investigate oxidation with chlorine dioxide. In both cases, the NO conversion was about 90%. Stroemblad of Sweden (5) reported that a modified FGD system with NaClO₂ yielded 75% NO_x removal along with more than 90% SO₂ removal. Hitachi Zosen Corp. of Japan (6) received a Japanese patent for simultaneous removal of mercury and NO_x. A flue gas containing 0.837 mg/m³ Hg and 54 ppm NO_x was scrubbed with an aqueous solution containing Ca(ClO)₂ and CaClO₂, resulting in removal of 95% Hg and 80% NO_x. Chlorine injection for the removal of NO from gas streams was patented by Dow Company (7). The removal was found to be highly dependent upon the Cl₂/NO ratio, the temperature and pH. More than 90% removal is achievable. A U.S. patent was awarded to Vicard of France (8) who claimed that with HBr and Br salts as intermediate agents, NO can be reduced to N₂ using SO₂ in the flue gas. This oxidation-reduction system can occur only in the presence of NaClO₂ in the scrubbing solution.

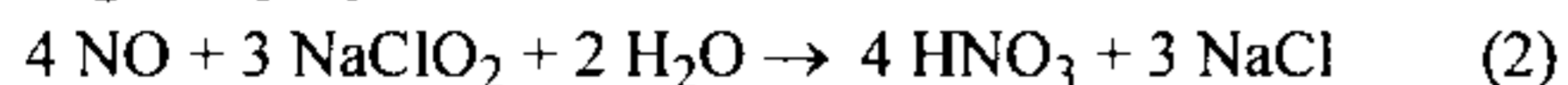
THEORY

The Chemistry

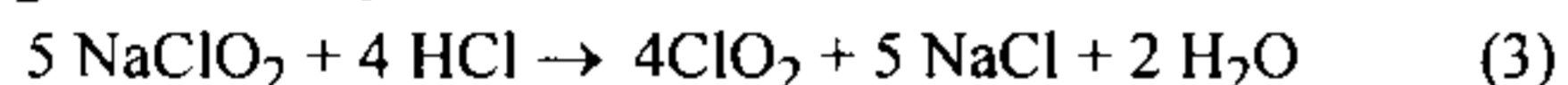
Sada (9) proposed that oxidation of NO with NaClO₂ in the presence of NaOH can be represented by:



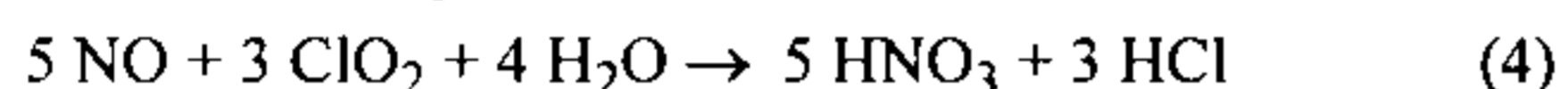
We found that the absorption rate in terms of height of transfer units (HTU) increases with high pH (10). Apparently, NaOH in the scrubbing solution inhibits NO oxidation. Therefore, most of the scrubbing experiments were conducted with a neutral or slightly acid solution. The overall reaction of NO with NaClO₂ was proposed as:



In acidic aqueous scrubbing, ClO₂ was found to be the active ingredient for NO oxidation. The greenish ClO₂ was identified and quantified using a LC/PDA system. During the scrubbing, ClO₂ is formed by acid activation:



and then followed by the reaction of NO with ClO₂



For a combined NO_x/SO₂ scrubbing, HNO₃, H₂SO₄ and NaCl are the only products in the spent scrubbing solution.

Oxidation and Absorption in a Packed Bed

Consider a packed bed with the following characteristics. The cross section is Ω and the differential volume in height dZ is ΩdZ . If the change in molar flow rate F is neglected, the amount absorbed in section dZ is $-Fdy$, which equals the absorption rate times the differential volume:

$$-Fdy = K_y a (y - y^*) \Omega dZ \quad (5)$$

This equation is rearranged for integration, grouping the constant factors F , Ω , and $K_y a$ with dZ .

$$\frac{K_y a \Omega}{F} \int_0^{Z_T} dZ = \frac{K_y a \Omega Z_T}{F} = \int_b^a \frac{dy}{y - y^*} \quad (6)$$

The equation for column height can be written as follows:

$$Z_T = \left[\frac{F}{K_y a \Omega} \right] \int_b^a \frac{dy}{y - y^*} \quad (7)$$

The integral in Eq. 7 represents the change in vapor concentration divided by the average driving force and is called the number of transfer units (NTU) or N_{oy} . The other part of Eq. 7 has the unit of length and is called the height of transfer unit (HTU) or H_{oy} .

Reaction in the liquid phase reduces the equilibrium partial pressure of the solute over the solution, which greatly increases the driving force for mass transfer. If the reaction is essentially irreversible at absorption conditions, the equilibrium partial pressure is zero, and N_{oy} can be calculated just from the change in gas composition. For $y^* = 0$,

$$N_{oy} = \int_b^a \frac{dy}{y} = \ln \left(\frac{y_a}{y_b} \right) \quad (8)$$

A large part of the research described in this paper is directed at obtaining the H_{oy} for NO absorption with NaClO₂ oxidation in a packed bed. Other parts of this research are designed to evaluate the effects of key parameters such as temperature, concentration, pH, on NO absorption using H_{oy} as an index.

EXPERIMENTS

Apparatus

The experiments were conducted in a laboratory-scale scrubber reactor system shown in Fig. 1. The scrubbing equipment consists of a flue gas blending system, four interchangeable types of scrubbers, and a continuous analytical train. The blending system was capable of producing a wide variety of synthetic flue gases by mixing pure or high concentration gases from high pressure cylinders. The gaseous mixture was then passed through another rotameter and fed to the scrubber where the gas-liquid reaction occurs. The composition of the inlet and effluent flue gases were measured by the analytical train as a function of run time.

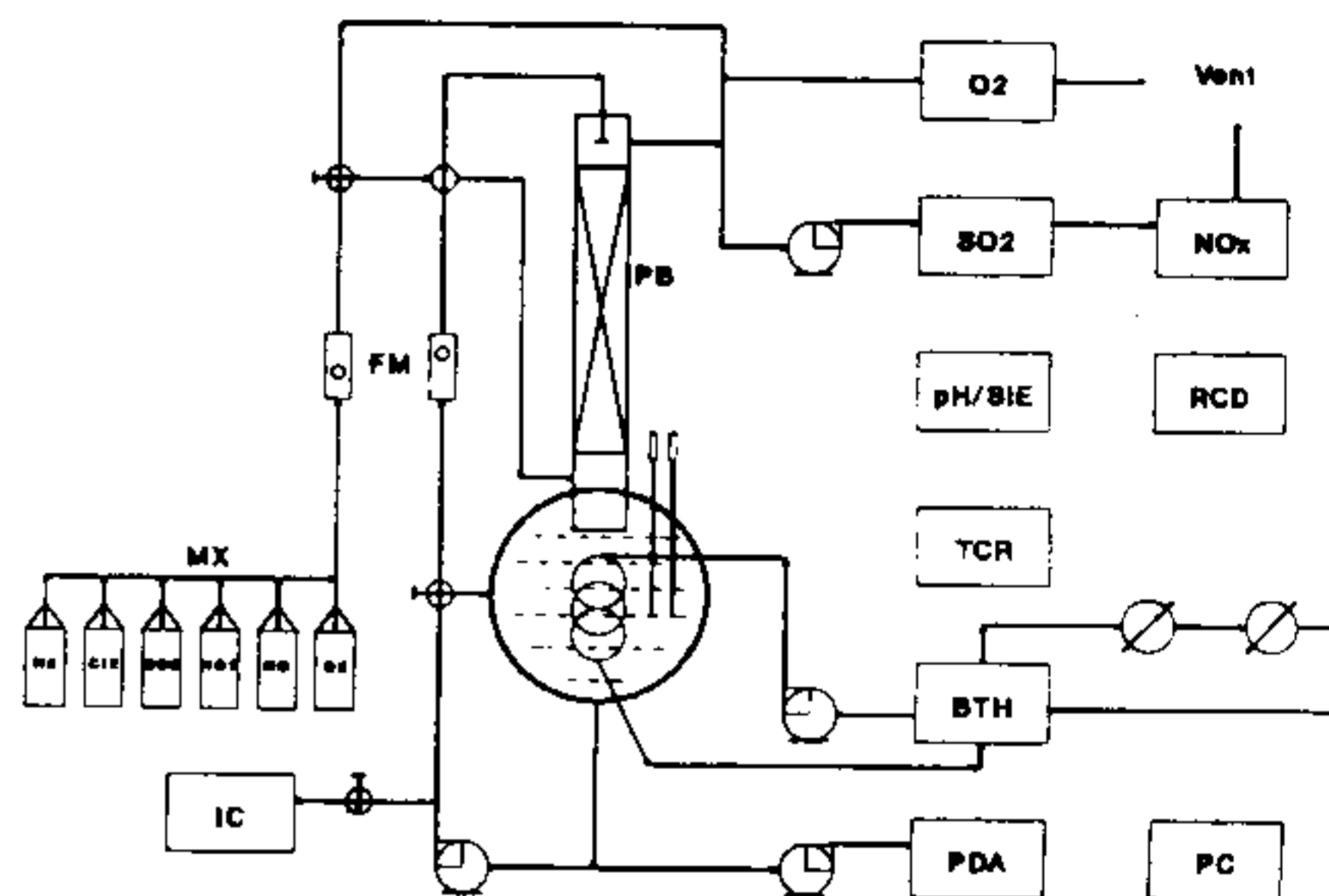


Fig. 1. Schematic diagram of NO_x scrubbing system.

Analysis

During scrubbing experiments, the gas phase samples were measured by the on-line analytical train containing NO_x analyzer, SO₂ analyzer and O₂ analyzer. The depletion of reactants and formation of intermediates were monitored continuously with a modified Waters LC/PDA system developed in our laboratory. Liquid samples were taken from the scrubber after the NO breakthrough. Ionic concentrations of Cl⁻, NO₃⁻, and/or SO₄²⁻ were determined both qualitatively and quantitatively using Waters ion chromatography method # A-102. Figure 2 shows a chromatogram of a standard solution.

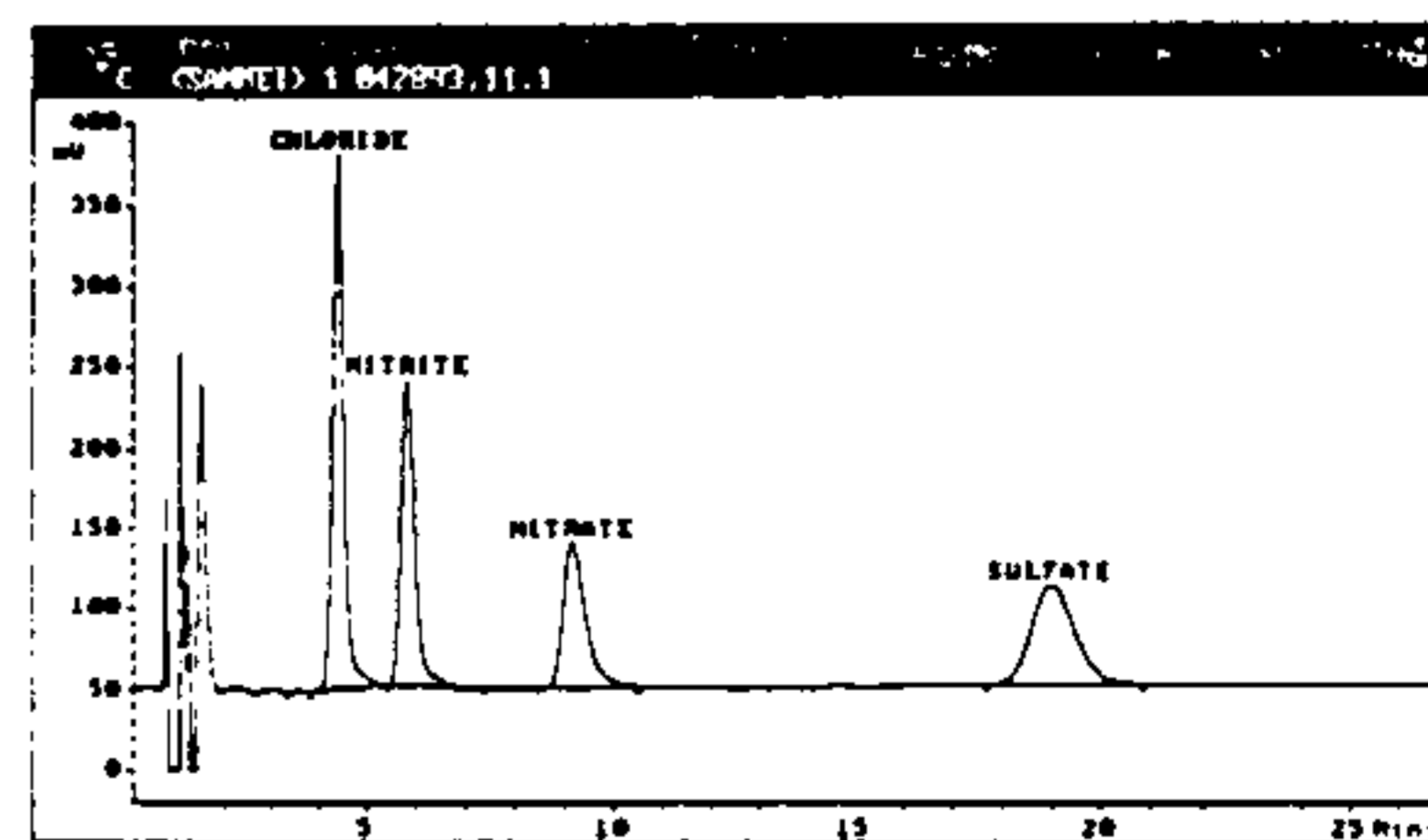


Fig. 2. The chromatogram of standard aqueous solution of Cl⁻, NO₃⁻, and SO₄²⁻.

The Waters preparatory liquid chromatography (prep. LC) with no separation column and equipped with a UV/Visible range photodiode array detector was used to obtain all spectra in this research (11). A NEC AT PC with Waters PDA 990 Data Acquisition System was employed to collect and treat all analytical data. Samples were diluted and buffered by the eluent

pumping system of the prep. LC and were pumped into the flow cell where light could pass through the solution and reach the photodiode array detector reflecting from a flatfoot holographic grating. There are a variety of slit widths available ranging from 0.05 mm to 0.25 mm.; the width of the slit used in this research was 0.25 mm. The Waters PDA consists of 512 photodiodes, each with a dynamic range from ultraviolet to near infrared, 190 nm to 800 nm.

An appropriate concentration of sodium chlorite in aqueous solution was prepared to obtain an absorbance of about 2 absorbance units (AU) at a wavelength of 260 nm. Programmed pumping was used to dilute the inlet sample of 330 ppmw Cl by 1/10, 2/10, and so on, of the original concentration with deionized water. The spectrum of aqueous sodium chlorite as a function of concentration is shown in Fig. 3. According to the stoichiometric equation for the formation of chlorine dioxide from sodium chlorite, hypochlorous acid was titrated with aqueous sodium chlorite in an ice bath to produce an appropriate concentration of chlorine dioxide with absorbance of about 2 AU at a wavelength of 358 nm. A UV/Vis spectrum for ClO_2 was obtained, as shown in Fig. 4; this spectrum, which was not independently confirmed, is in agreement with the data in literature (12). Calibration curves for both ClO_2^- and ClO_2 have multiple coefficients of determination; R^2 better than 0.998.

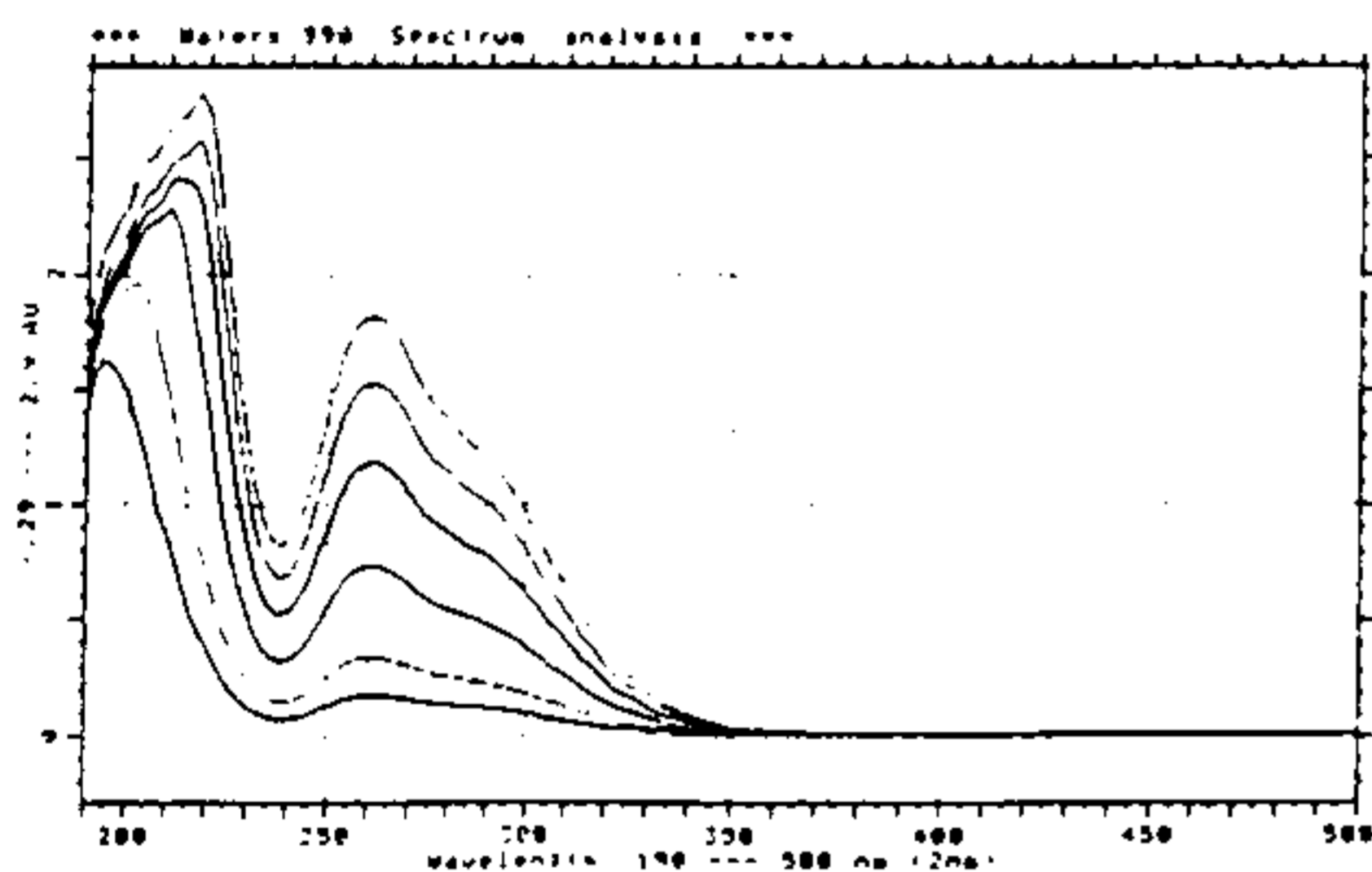


Fig. 3. The UV/Vis spectrum of NaClO_2 as a function of wavelength and concentrations.

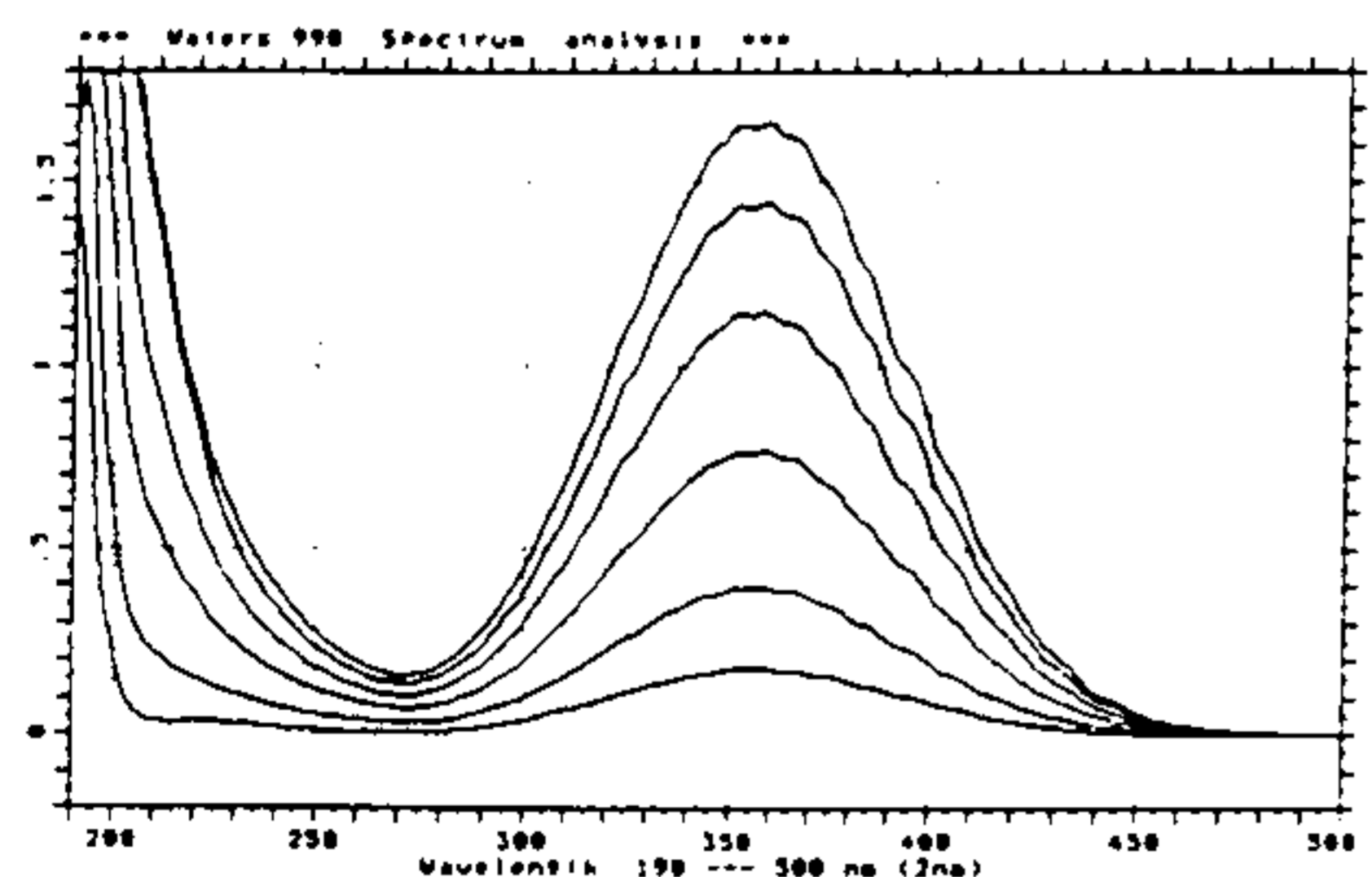


Fig. 4. The UV/Vis spectrum of ClO_2 as a function of wavelength and concentrations.

RESULTS AND DISCUSSION

pH Effects

The pH effects on NO removal in NaClO_2 aqueous scrubbing are shown in Fig. 5. Low concentrations of NaOH, provided there is sufficient NaClO_2 , do not inhibit the NO removal effec-

tiveness. High concentrations of NaOH appear to inhibit the NO oxidation and absorption. The upper limit of NaOH concentration necessary to completely absorb NO in NaClO_2 aqueous solution depends on the concentration of NaClO_2 . NO is absorbed quantitatively in 0.008 molar NaClO_2 aqueous solution when the concentration of NaOH is equal to, or less than, 0.001 molar. The upper limit of NaOH in 0.08 molar NaClO_2 aqueous solution is 0.1 molar. The inhibiting effect is due to the high pH rather than specifically to the NaOH.

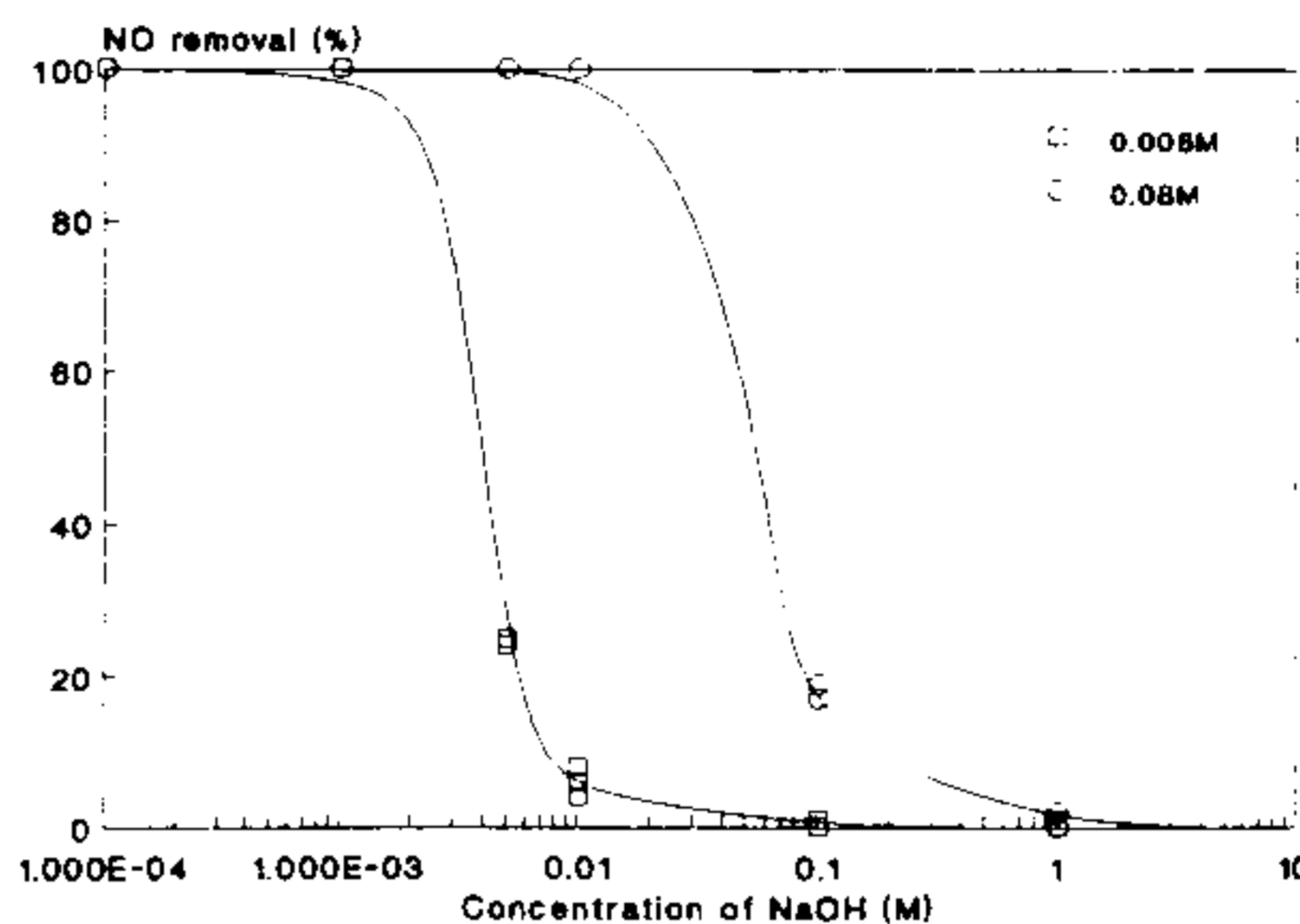


Fig. 5. Effect of pH on NO absorption in NaClO_2 aqueous scrubbing.

Utilization

Utilization is defined as the amount of NO removed by one unit of NaClO_2 . Experimental data in Fig. 6 is presented as molar ratio of NO and NaClO_2 . According to the Eq. (2) in the previous section, more than 100% of utilization can be obtained under some conditions. The experiment was conducted in a bubble column scrubber. Figure 6 shows that without pH control, the higher the concentration of NaClO_2 , the lower the utilization. A scrubbing solution with a higher concentration of NaClO_2 ends up with higher HNO_3 concentration and lower pH. Equation (3) indicates the formation of Cl^- . When converting NaClO_2 to Cl^- , its capacity of NO removal decreases. With equal molar quantities of NO/ SO_2 in the flue gas, the SO_2 reduces the utilization for NO removal to a half. Because of its higher solubility, SO_2 is dominating in the competition with NO for NaClO_2 consumption.

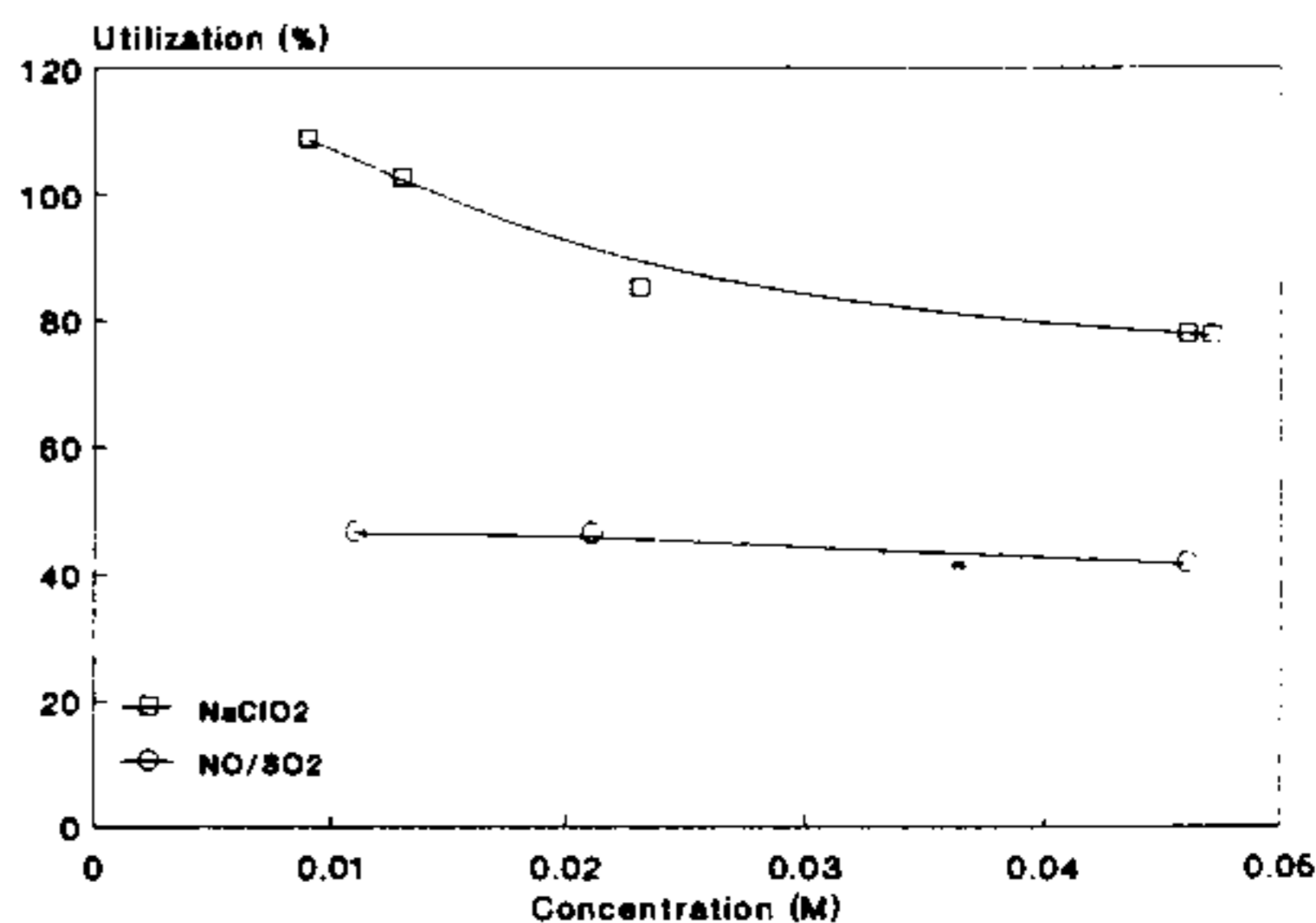


Fig. 6. The utilization of NaClO_2 for NO and SO_2 removal.

Material Balance

Parameters in this study were NO, SO₂, NaClO₂, NO₃⁻, SO₄²⁻, and Cl⁻. NO was calculated from the breakthrough time, and concentration change from the NO_x analyzer. Ions concentrations were determined quantitatively using a Waters ion chromatography system with UV and conductivity detectors. Experiments were conducted at room temperature with flue gases of 1000 ppm NO in N₂ and 2000 ppm NO and 1000 ppm SO₂ in N₂. Figures 7 and 8 are the material balance of nitrogen and chlorine elements. The material balance of sulfur was not performed due to the ambiguousness of its breakthrough time. The lower Cl⁻ recovery from uncontrolled scrubbing is explained by Eq. (3). Under low pH, ClO₂ is produced in the solution. A portion of ClO₂ can be stripped out from the liquid, which is also consistent with our previous statement that the higher the concentration of NaClO₂ the lower the utilization.

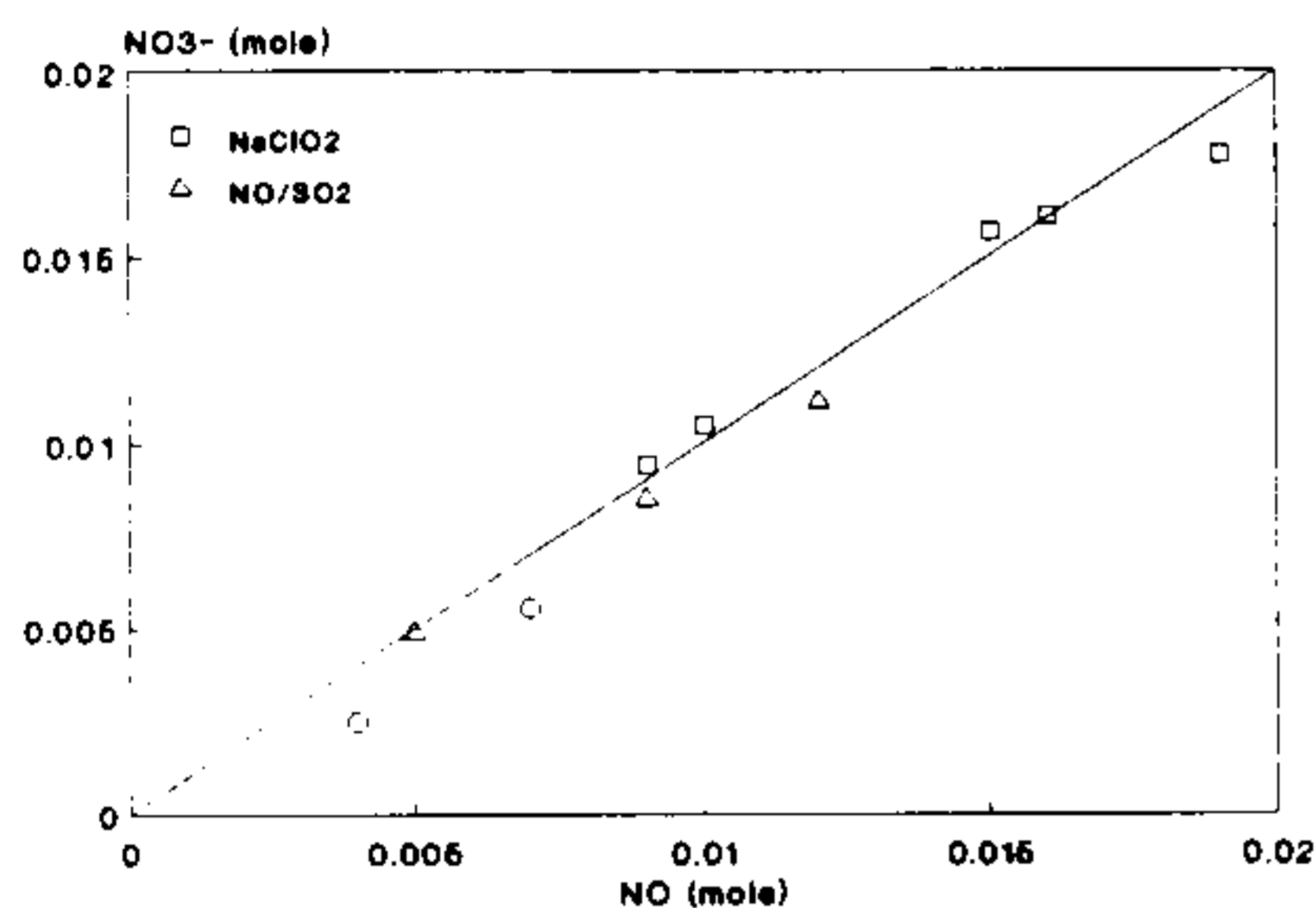


Fig. 7. Nitrogen balance of NaClO₂ aqueous scrubbing for NO and SO₂ removal.

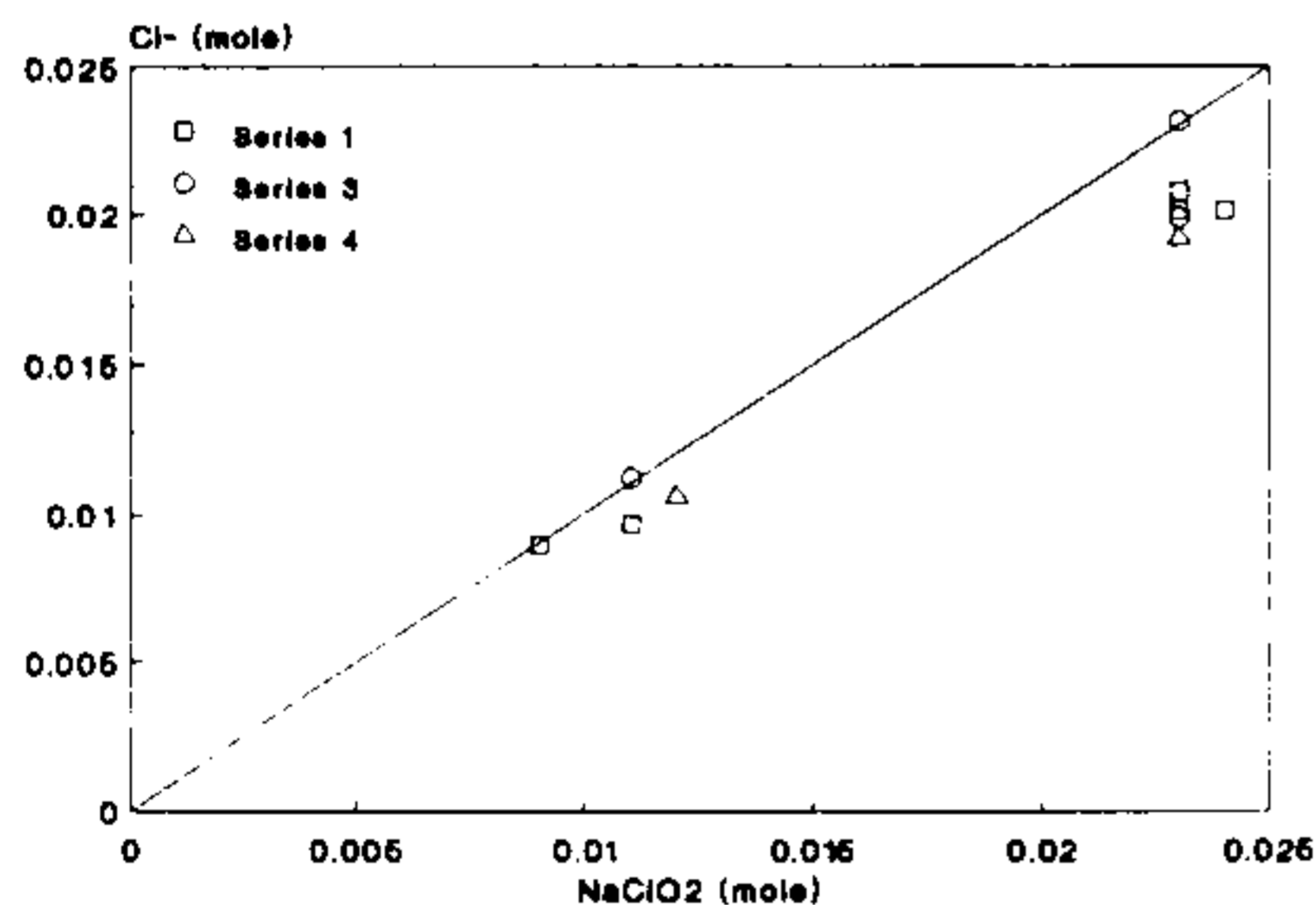


Fig. 8. Chlorine balance of NaClO₂ aqueous scrubbing for NO and SO₂ removal.

Oxidation in a Spray Chamber

Equal molar quantities of NO and NO₂ in gas stream can be removed quantitatively by NaOH aqueous scrubbing (12). A spray chamber scrubber was studied as a prescrubber to convert 50% of incoming NO into NO₂. The outlet flue gas is then introduced into a NaOH aqueous scrubber where both NO and NO₂, and SO₂, if any, can be removed simultaneously. Parameters in this system can be categorized into physical and chemical parameters. The effect of physical parameters on interfacial area, indicated in the literature (14), are accepted as the same effects on NO removal. Experiments

were focused on the effects of chemical parameters on NO oxidation. Figure 9 shows the agreement between experimental values and the model calculation. The oxidation rate of NO with a NaClO₂ aqueous solution in a spray chamber scrubber was found to be zero order in NO concentration and 1.2 order with respect to NaClO₂ concentration.

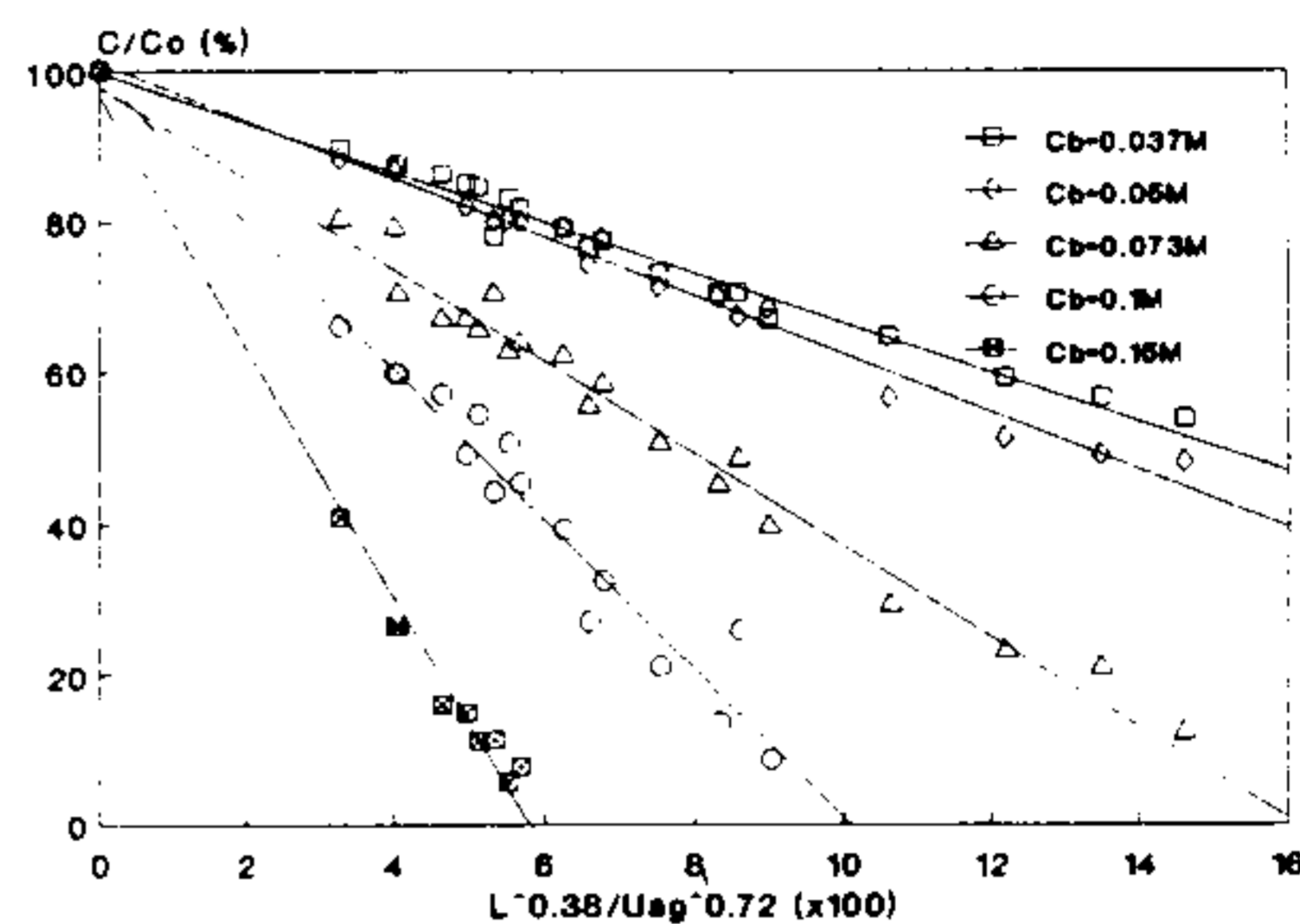


Fig. 9. A comparison between the model and the experimental data used in the correlation with zero order in NO.

Oxidation and Absorption in a Packed Bed

Consider a single run at pH 10, in which 300 ppm NO in N₂ was injected into the scrubber. With 300 ppm SO₂ present, more than 80% NO goes through the packed bed unreacted, and no NO₂ is detected. Without an SO₂ injection, 38% NO₂ and no NO were detected in the effluent. The HTU for NO oxidation, for NO absorption with oxidation, for NO₂ absorption, and for NO₂ absorption with oxidation were therefore defined as follows. HTU calculated from NO injection and NO breakthrough is the HTU for NO oxidation. HTU calculated from NO injection and NO_x breakthrough is the HTU for NO absorption with oxidation. HTU calculated from NO₂ injection and NO₂ breakthrough without an oxidizing agent in the scrubbing solution is the HTU for NO₂ absorption. HTU calculated from NO₂ injection and NO₂ breakthrough with an oxidizing agent in the scrubbing solution is the HTU for NO₂ absorption with oxidation. Figure 10 shows that up to 300 lb/hr ft², HTU for NO oxidation is less than 0.5 ft. HTUs for NO and NO₂ absorption with oxidation are identical, between 1 to 3.5 ft. Absorption of low concentration NO₂ is slow. The SO₂ present in the flue gas actually enhances the reaction of NO and NaClO₂ solution under acid conditions. Figure 11 shows the different effects of SO₂ on NO absorption in acidic and alkaline solutions. In an acidic case, HTU for NO oxidation is always very small compared to that for absorption. In the first few centimeters of a packed bed, all NO has been oxidized to NO₂. The rest of the bed is needed to carry out the absorption of NO₂ with NaClO₂ oxidation.

CONCLUSION

The LC/PDA system has been successfully developed for dissolved chlorite ions (ClO₂⁻) and chlorine dioxide (ClO₂) monitoring. ClO₂⁻ can be quantified by its absorbance at 258 nm, and ClO₂ at 358 nm.

NaOH inhibits the oxidation of NO but enhances the utilization of NaClO₂ for NO removal to more than 100%.

NO and SO₂ can be quantitatively oxidized by NaClO₂ in aqueous solution. During scrubbing, NO is oxidized to NO₃⁻, SO₂ to SO₄²⁻, and ClO₂⁻ is converted to Cl⁻.

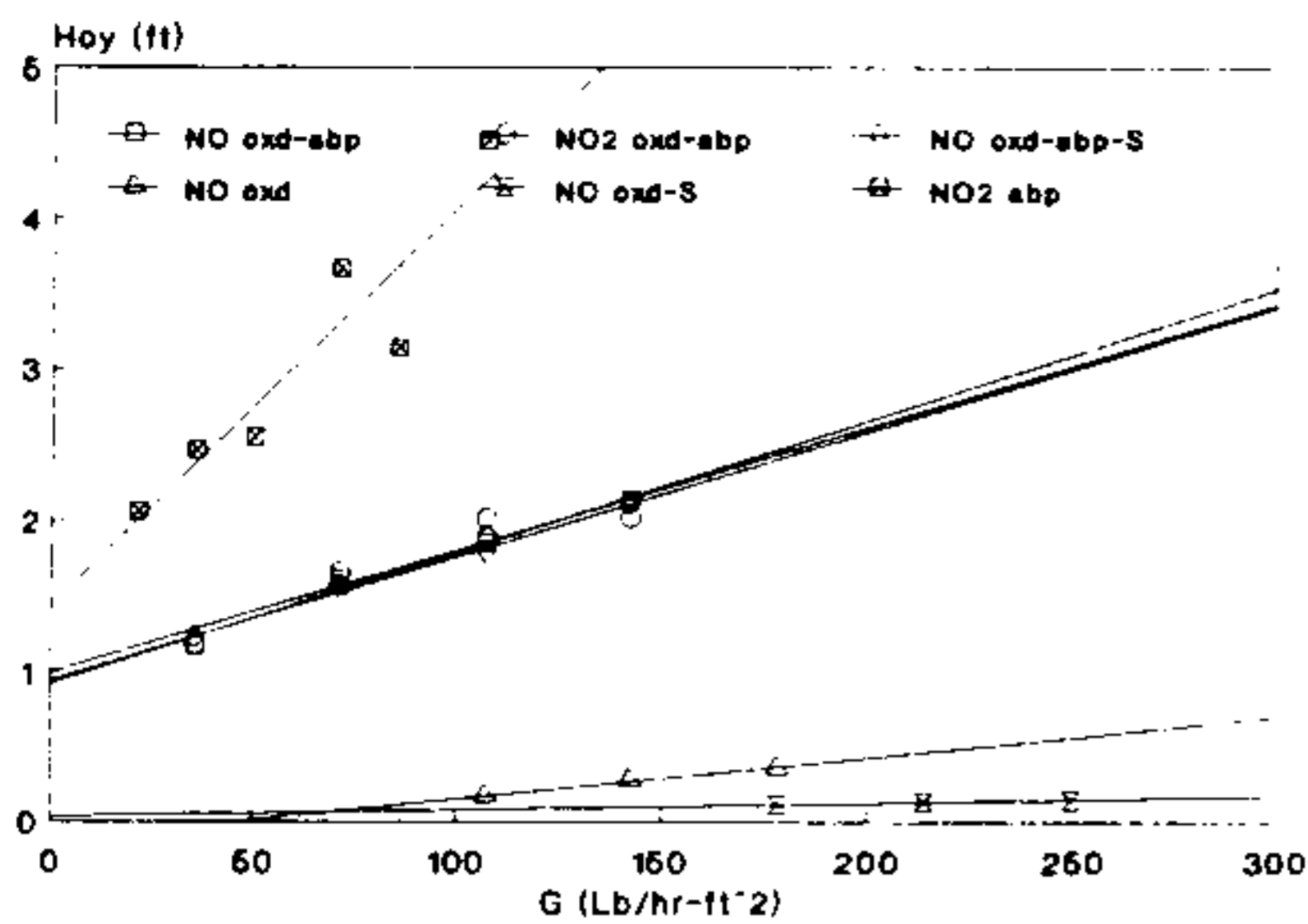


Fig. 10. HTUs for NO_x aqueous scrubbing at pH 4.1.

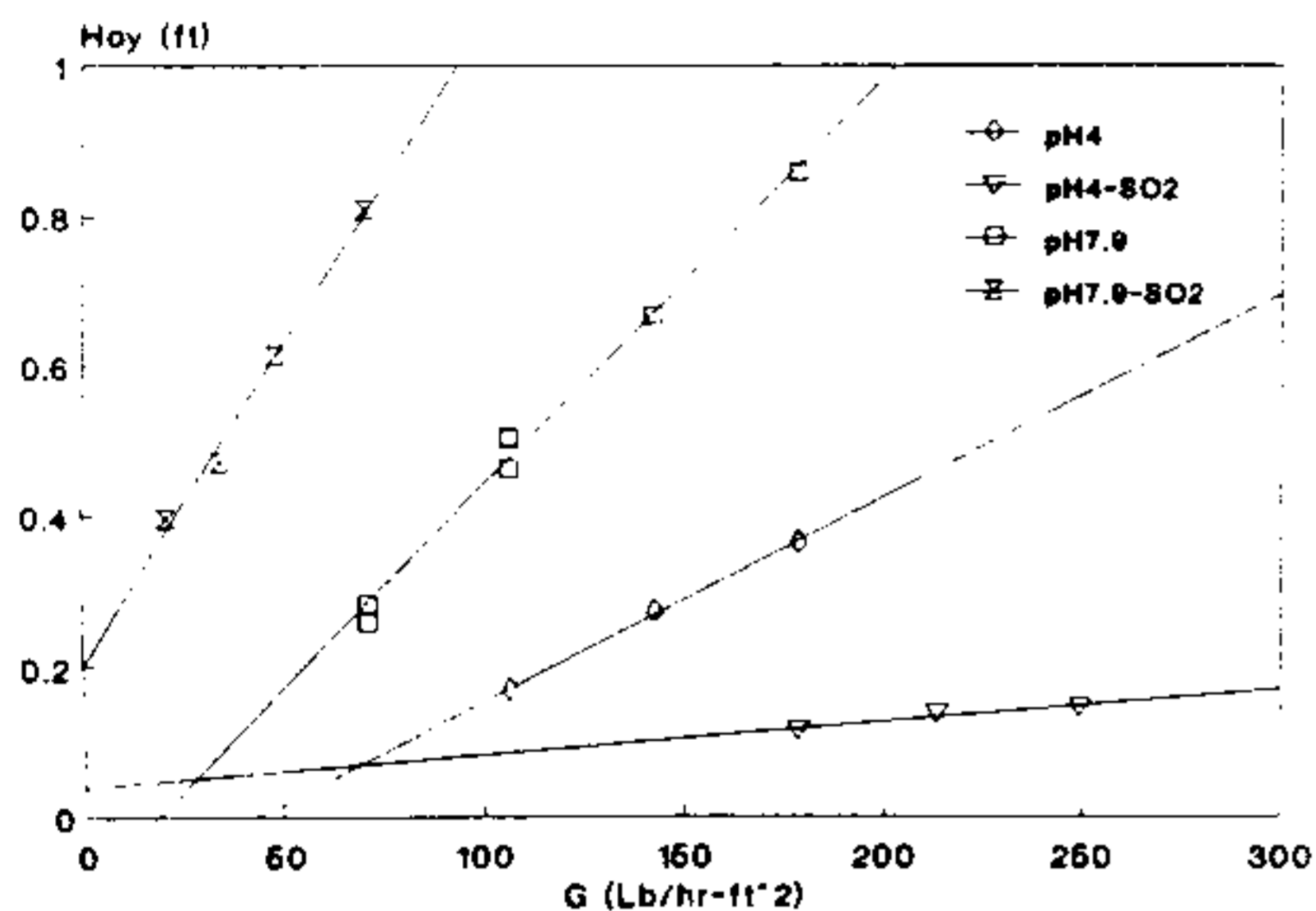


Fig. 11. A comparison of the effect of SO_2 on HTU for NO oxidation in NaClO_2 alkaline and acidic scrubbing.

The existence of SO_2 increases the reaction rate of NO to NO_2 in acid solution but decreases it in alkaline solution.

A low pressure drop spray chamber scrubber can be used as a prescrubber to convert 50% of NO to NO_2 . The mixture of equal molar NO/ NO_2 flue can then be absorbed into an alkaline solution without an oxidizing agent.

HTUs for NO oxidation, for NO oxidation and absorption, for NO_2 absorption and NO_2 absorption with oxidation are linear functions to gas phase mass velocity in the range of 30 to 250 lb/hr-ft^2 .

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