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EFFECT OF NITRIC AND SULFURIC ACIDS ON NO_X AND SO_X ABSORPTION INTO OXIDO-ACIDIC SOLUTIONS

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Abstract
SO_2 and NO_x efficiencies were studied at 293 K and 1 atm, in a cable contactor, up to partial pressures of 2000 ppm, in mixed aqueous solutions containing sulfuric and nitric acids, as products of the wet oxidative removal of SO_x and NO_x, and hydrogen peroxide, as oxidizing agent. The carrier gas was essentially carbon dioxide (90% vol). The CO_2 absorption in oxido-acidic conditions was found to be negligible.
The SO_2 absorption rate was determined for various SO_2 partial pressures and different concentrations of H_2SO_4 and HNO_3 (0-4M) and hydrogen peroxide (0.05-1M) in the scrubbing liquid. It was found that the SO_2 absorption rate increases sharply with the hydrogen peroxide concentration and decreases as the H_2SO_4 concentration increases. This influence of sulfuric acid is preponderant and, in presence of both nitric and sulfuric acids, only a slight influence of HNO_3 is noticed, modifying the properties of the scrubbing liquid but likely involving a negligible effect on the kinetic of the reaction between SO_2 and H_2O_2.
Similar experiments have been carried out with NO_x as gas solutes, for different oxidation ratios, showing that an acid medium enhances the NO_x absorption rates.

Keywords: absorption, SO_2, NO_x, hydrogen peroxide, mixed acids

1. Introduction

In combustion processes, especially with coal as combustible and air as oxidant, non negligible amounts of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are produced, source of air pollution involving acid rains and corrosion problems in the industrial installations. In desulfurization and denitrification processes, most of the techniques are designed to remove SO_x or NO_x separately. Dry, semi-dry or wet alkaline desulfurization processes[1,2] do not remove NO_x in an efficient way; SCR[3,4] or SNCR denitrification processes are quite inefficient for SO_x abatement, which acts moreover as a poison in the system. In industrial flue gases however these two compounds are very often present together, in variable concentrations up to 5000 ppm, depending on the combustible composition and on combusting conditions. An efficient simultaneous removal of SO_x and NO_x is thus attractive. As alkaline solutions produce liquid effluents containing nitrites, nitrates, sulfites and sulfates, a downstream waste treatment process is required. An absorption technique that has been proposed[5,6] and extensively studied[7,8] as well for desulfurization as for denitrification purposes uses hydrogen peroxide in the scrubbing liquid to oxidize SO_2 and NO_x in sulfuric and nitric acids respectively, acids that can be reused or valorized. Moreover, hydrogen peroxide is a very clean compound from an environmental point of view, adding only water and oxygen to the system and thus generating no additional pollution problems. The aim of this paper is to characterize the effect of HNO_3 and H_2SO_4 concentrations in the scrubbing solution on the absorption performances of SO_2 and NO_x respectively. The following steps of this study will be focused on the comprehension of absorption-reaction mechanisms and on the determination of the best operating conditions of the industrial process of simultaneous absorption and, in a final step, to determine design parameters.

2. Absorption mechanisms of SO_2 and NO_x in presence of H_2O_2

Previous studies were achieved on separate absorption process of SO_2 into H_2SO_4+H_2O_2 solutions[7] and of NO_x into HNO_3+H_2O_2 solutions[8]. When SO_2 is absorbed in solutions containing hydrogen peroxide, the absorption-reaction mechanism results in the formation of sulfuric acid which concentrates if the liquid solution is recycled in the process. The reaction of SO_2 with H_2O_2 occurs irreversibly, at a finite speed, producing sulfuric acid according to:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \quad (1)$$

Hydrogen peroxide is efficient even at low concentrations, and increasing its concentration in the liquid phase results in higher SO_2 absorption rates, enhancing the oxidation reaction. However the presence of H_2SO_4 in the absorbent (while recycling the solution for instance) is unfavorable to the SO_2 removal.

The nitrogen oxides of interest in liquid and gas phases are NO, NO_2, N_2O_3, N_2O_4 and, in presence of water, HNO_2 and HNO_3. The amounts of these species in the gas phase are not independent, following the next equations (3)-(7). The presence of water and oxygen in the gas phase is taken into account in equations (3),(6),(7):

$$2\,NO + O_2 \rightarrow 2\,NO_2 \quad (2)$$
$$NO + NO_2 \leftrightarrow N_2O_3 \quad (3)$$
$$2\,NO_2 \leftrightarrow N_2O_4 \quad (4)$$
$$N_2O_3(NO + NO_2) + H_2O \rightarrow 2\,HNO_2 \quad (5)$$

The quite complex mechanism of absorption of these nitrogen oxides into water[9] is represented by equations (6)-(8). The hydrolyses of NO_2, N_2O_3 and N_2O_4 generate HNO_3 and HNO_2 in the liquid phase:

$$N_2O_4(2\,NO_2) + H_2O \rightarrow HNO_2 + HNO_3 \quad (6)$$
$$N_2O_3 + H_2O \rightarrow 2\,HNO_2 \quad (7)$$

A part of the nitrous acid formed in liquid phase is decomposed with the undesirable release of NO., as nitrogen monoxide has a very low solubility into water:

$$3\,HNO_2 \leftrightarrow HNO_3 + H_2O + 2\,NO \quad (8)$$

The presence of an oxidizing agent in the liquid phase appears to be dual: on the one hand to stabilize the dissolved NO_x or HNO_2 formed in liquid phase by oxidation in form of HNO_3, on the other hand, to enhance the mass transfer rate of HNO_2 from the gas phase. These two roles are dependent on the following reaction:

$$HNO_2 + H_2O_2 \xrightarrow{H^+} HNO_3 + H_2O \quad (9)$$

Furthermore, it was shown that, when NO_x are absorbed in hydrogen peroxide solutions, the nitric acid formed enhances the NO_x absorption for gaseous mixtures containing trivalent NO_x species (N_2O_3 and HNO_2) due to an autocatalysis of the oxidation reaction (9)[10,11]. It was previously proved that the absorption phenomenon of the species NO_2, N_2O_3 and N_2O_4 is controlled by hydrolysis, and there is no enhancement of the transfer rates with H_2O_2 for these compounds.

3. Experimental set-up and procedure

The experimental equipment is illustrated in Figure 1. It includes a cables-bundle laboratory scrubber which is well suited for kinetic studies as its specific surface is quite insensitive to the liquid flow rate and viscosity[12].

The absorption reactor is a ring-shaped column made of a vertical glass tube in the axis of which stands a polypropylene rod which supports 6 twisted polypropylene cables of 1.7 mm diameter, constituting the packing. Outside and inside diameters of the annulus are equal to 0.045 and 0.02 m, respectively and the useful height of this micro-contactor is 0.54 m.

The prepared scrubbing solution is fed to a top distributing chamber with a peristaltic pump, the liquid being distributed around each cable through individual holes drilled in the bottom of the chamber. A steady flow having the shape of cylindrical films is set up around the yarns (Fig.2b). Gas and liquid phases come into contact counter-currently in the scrubber. The liquid and gas feed temperature is controlled by means of a thermostatic bath. The liquid phase analysis is performed by a classical titration of total acidity with a sodium hydroxide solution and an iodometric method for H_2O_2, using a $Na_2S_2O_3$ solution in presence of KI. In order to analyze separately the two acids (HNO_3 and H_2SO_4), a conductimetric titration method was set up for the determination of SO_4^{2-} ions concentration.

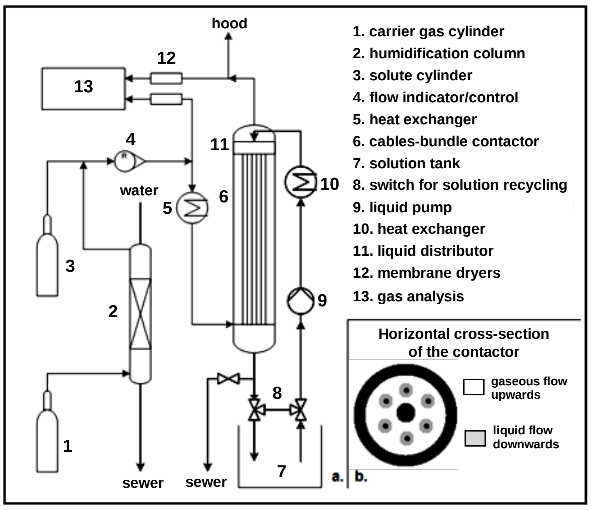

Figure 1. a. Experimental apparatus. b. Horizontal cross-section of the contactor

The carrier gas, entering axially at the bottom and flowing out up to the top of the column, is humidified in a saturator, in which SO_2 (or NO_x) is added to obtain the desired concentration. The gas flow rates are metered by rotameters. Sampling of gas simultaneously at the input and the output of the column is performed continuously through membrane dryers followed by a two-channel U.V. analyzer for SO_2, allowing to calculate the fraction of SO_2 absorbed $A_{SO2}=(y_{SO2}^{in}-y_{SO2}^{out})/y_{SO2}^{in}$ or a chemiluminescence analyzer for NO and total NO_x, allowing the calculation of the absorption rate of NO_x: $A_{NOx}=(y_{NOx}^{in}-y_{NOx}^{out})/y_{NOx}^{in}$ and the oxidation ratio O.R.:$(y_{NOx}^{in}-y_{NO}^{in})/y_{NOx}^{in}$, characterizing the inlet gas composition.

All experiments reported here were carried out at atmospheric pressure and a temperature of 20±0.3 °C with a carrier gas containing 90%vol. of carbon dioxide and nitrogen ±10%. The gas flow rate was maintained at 0.85 m³/h resulting in a superficial velocity of 0.2 m/s and the liquid flow rate was fixed at 185 ml/min (33.3 ml/min/cable which is the nominal value for an industrial cable scrubber) (Table 1).

Table 1. Operating conditions

	y^{in} (ppm)	O.R. (%)	C_{H2O2} (M)	C_{HNO3} (M)	C_{H2SO4} (M)	G (m³/s)	L (m³/s)	T (K)
SO_2	600-2000	-	0-1	0-4	0-4	$2.45\ 10^{-4}$	$3.13\ 10^{-6}$	293
NO_x	5000	15-98	0-1	0-3	0-2			

4. Results and discussion

As a preliminary, mass balances were checked for the case of SO_2 absorption into aqueous solutions of H_2O_2 by measuring the quantities of absorbed SO_2 (equivalent to H_2SO_4 produced) and consumed H_2O_2. Moreover, as far as the absorption test results are concerned, since the absorption rate depends on the contactor and operating conditions, it can be easily used for performances comparisons of the different scrubbing solutions. Concentrations of nitric acid, sulfuric acid and hydrogen peroxide respectively represented in figures by x,y and z in mol/l.
In all oxido-acidic conditions applied in our absorption tests it was found that CO_2 absorption rates can be considered as negligible.

4.1. Effect of H_2O_2, H_2SO_4 and HNO_3 on SO_2 absorption

Absorption tests of SO_2 into water and sulfuric-nitric acid solutions of different concentrations containing hydrogen peroxide were achieved continuously for various SO_2 inlet concentrations varying from 600 to 2000 ppm (Table 1). For the sake of comparison, SO_2 absorption tests were also performed with water and 0.5M sodium hydroxide solutions.

As it can be seen in Figure 2.a., fractions removed with water are relatively moderate. Indeed, the reaction of SO_2 with water, though instantaneous, is limited by the equilibrium[13]:

$$SO_2 + 2\,H_2O \leftrightarrow H_3O^+ + HSO_3^- \qquad (10)$$

Absorption of SO_2 into water is not of great interest for a desulfurization process, except maybe because it is very easy and cheap to operate.

If the liquid solution contains acids in addition of water[14], for instance, to simulate a process recycling the solution, these absorption rates drop drastically to very low values. When the oxidizing agent H_2O_2 is added to the acidic solution, quite higher SO_2 efficiencies are clearly observed.

As shown in Figure 2.b., maximum absorption rates are observed for sodium hydroxide solutions. Actually the reaction of SO_2 with NaOH[2]:

$$SO_2 + 2\,NaOH \rightarrow Na_2SO_3 + H_2O \qquad (11)$$

known as a proton transfer reaction is irreversible and instantaneous[1]. The charts here above present relative absorption rates, for which absorption rates into NaOH solutions are used as reference (A=1).

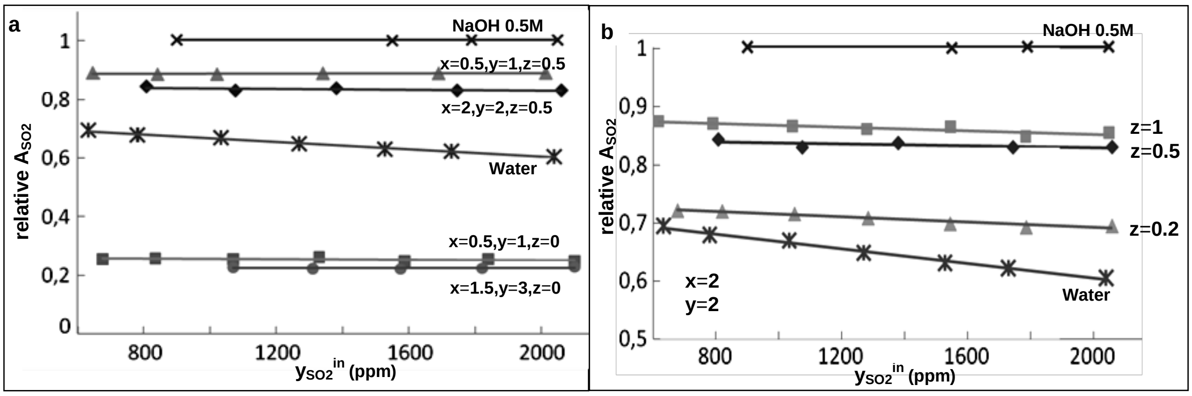

Figure 2. Effect of hydrogen peroxide in acidic solutions on SO_2 absorption performances (a), effect of H_2O_2 concentration (b).

It appears quite clearly in Figure 2 that in aqueous H_2SO_4-HNO_3-H_2O_2 mixtures the enhancement effect of the mass transfer, due to the chemical reaction of SO_2 with H_2O_2, increases with the liquid phase content in peroxide, but remains always lower than for a sodium hydroxide solution, which implies that the rate of reaction with H_2O_2 remains finite. The absorption rate is independent of the partial pressure of SO_2 in the inlet gas for NaOH or sufficiently high H_2O_2 content, actually in presence of an excess of neutralizing or oxidizing agent.

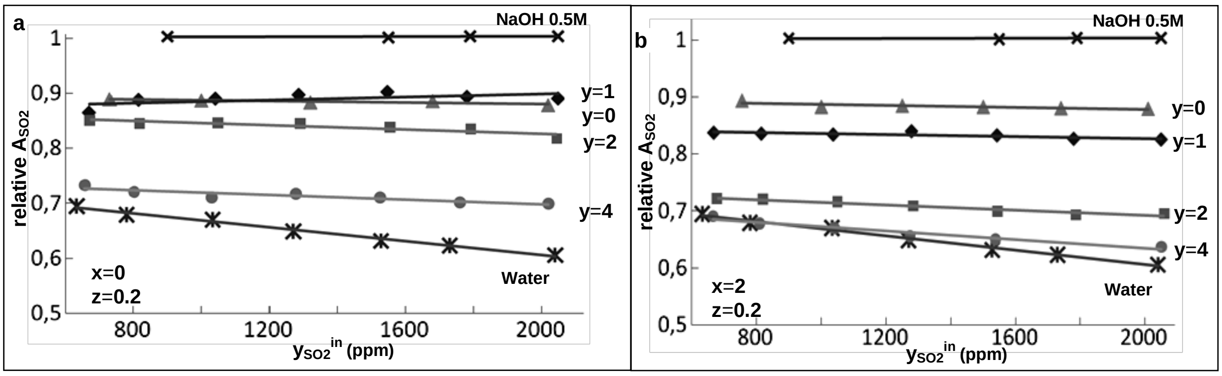

Figure 3. Effect of sulfuric acid concentration on SO_2 absorption performances in solutions containing hydrogen peroxide without (a) and with (b) nitric acid.

The presence of sulfuric acid always leads to a negative effect on SO_2 absorption rates, as can be seen on Figure 3 when increasing H_2SO_4 for a given H_2O_2 content in the liquid phase. The presence of nitric acid does not seem to affect appreciably the result. On the other hand, if a rise in the nitric acid concentration decreases the SO_2 absorption performances, it is negligible compared to the effect of sulfuric acid, as shown on Figure 4 as a down shift of the group of curves, for concentrations of both acids up to 2M. At higher nitric acid concentrations (4M on Figure 4.b), a noticeable decrease of A_{SO2} can be observed.

The negative effect of sulfuric acid on global absorption process is well known[7]. But, concerning the nitric influence, since it has only a slight effect at low concentrations (up to 2M), the decrease in absorption rates at higher concentrations could probably be explained by a lower pH or lower SO_2 diffusivity or solubility in the liquid phase, making the solute transfer more difficult. However, no kinetic effect can clearly be pointed out. The presence of nitric acid in the absorption solution, even if a small negative effect has been shown, is not a real disadvantage for the absorption performances since the negative influence of H_2SO_4 is predominant and its formation, in a SO_2 oxidative absorption process, is unavoidable.

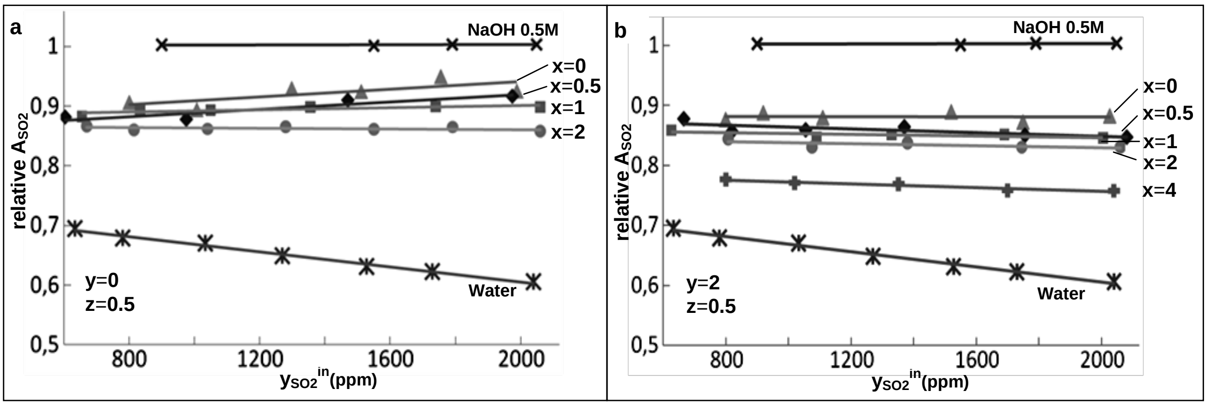

Figure 4. Effect of nitric acid concentration on SO_2 absorption performances in solutions containing hydrogen peroxide without (a) and with (b) sulfuric acid.

4.2. Effect of H_2O_2, HNO_3 and H_2SO_4 on NO_x absorption

Compared to experimental SO_2 absorption study, fewer experiments were achieved for NO_x study at this step of our study, leading however to interesting conclusions. Absorption of NO_x into water rises with the oxidation ratio $((y_{NOx}^{in}-y_{NO}^{in})/y_{NOx}^{in})$. Actually, at low O.R. values, NO_x are mainly composed of NO, the far least soluble compound. The proportion of more soluble species rises with the oxidation ratio, inducing a better removal. The addition of hydrogen peroxide into water results in the same absorption rates, but when nitric acid is present in the oxidizing solution, a rise in the performances can be observed (Figure 5.a) as the concentration of HNO_3 rises, especially at intermediate O.R. (maximum NO_x trivalent forms).

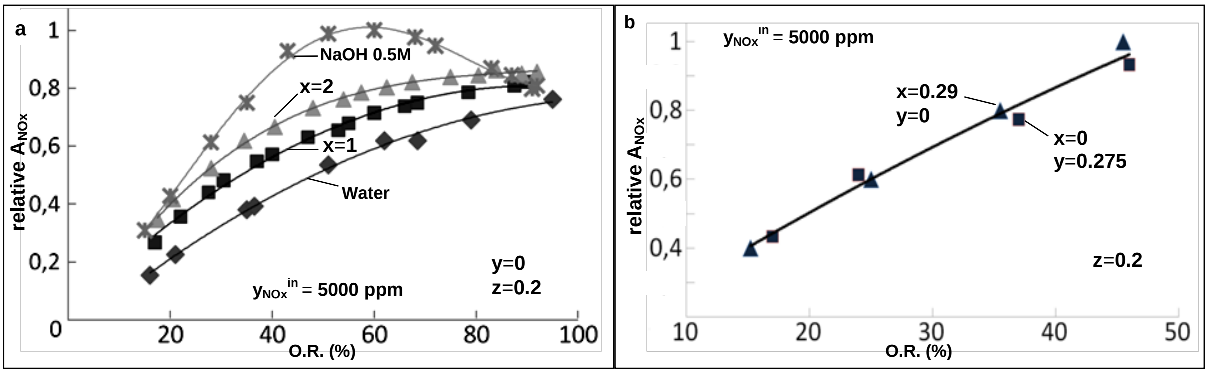

Figure 5. Influence of nitric acid concentration (a) and sulfuric acid concentration (in comparison with HNO_3) (b) on NO_x absorption performances in solutions containing hydrogen peroxide 0.2M

Figure 5.b illustrates quite similar absorption rates obtained with a HNO_3 solution (0.29M), and a H_2SO_4 solution (0.275M) and presenting equal H_3O^+ concentration (M), and both containing H_2O_2 (0.2M). This clearly means that the enhancement is caused by the H_3O^+ ions in the solution, whatever the H_3O^+ source. It can be concluded that the presence of sulfuric acid in the absorption solution together with nitric acid appears therefore as an advantage for the nitrogen oxides absorption.

5. Conclusions

Absorption performances of dilute gaseous SO_2 were studied in a cable contactor at 293 K and 1 atm, up to concentrations of 2000 ppm, with mixed aqueous solutions containing sulfuric and nitric acids and hydrogen peroxide. The absorption rate was determined for various SO_2 partial pressures and different concentrations of H_2SO_4 and HNO_3 (0-4M) and hydrogen peroxide (0.05-1M) in the scrubbing liquid. It was found that the SO_2 absorption rate increases with the hydrogen peroxide concentration and decreases as the H_2SO_4 concentration increases. While sulfuric acid concentration has an unfavorable effect on SO_2 absorption, HNO_3 does not seem to have a kinetic effect on the oxidation reaction (1). Its concentration somehow modifies the pH and physicochemical properties of the liquid solution, and thus the transfer properties, altering the absorption performances, but the influence of H_2SO_4 remains predominant.

Similar experiments have been carried out with NO_x as gas solute, for different gas compositions and 5000 ppm, confirming that both sulfuric and nitric acids enhance the absorption rates for trivalent NO_x species.

Simultaneous absorption of SO_2 and NO_x into H_2O_2 solutions, producing both sulfuric and nitric acids, shouldn't pose a problem in SO_2 and NO_x removal performances.

The next step of this study will be the determination of the interaction effects in simultaneous SO_2 and NO_x absorption in mixed solutions HNO_3+H_2SO_4+H_2O_2. It aims finally at developing a modeling of the absorption process for simultaneous reduction of SO_2 and NO_x with H_2O_2 as oxidant in liquid phase, and formation of nitric and sulfuric acids as by-products.

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