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SO_x and NO_x absorption based removal into acidic conditions for the flue gas treatment in oxy-fuel combustion

Isabelle Liémans^{a*}, Bruno Alban^b, Jean-Pierre Tranier^b, Diane Thomas^a

^aChemical Engineering Department, Faculty of Engineering, University of Mons, 20 Place du Parc, 7000 Mons, Belgium

^bPhysical Separation of Gases Group, Air Liquide CRCD Research Center, 1 Chemin de la Porte des Loges, 78354 Jouy-en-Josas, France

Abstract

In order to reduce simultaneously nitrogen and sulfur oxides contained in oxyfuel exhaust gases (composed mostly of carbon dioxide), an original absorption technique is proposed consisting in the scrubbing with aqueous acidic solutions containing hydrogen peroxide to oxidize NO_x and SO₂ in HNO₃ and H₂SO₄, forming a mixture which can be reused or separated. Individual and combined effects of acids and H₂O₂ concentrations in the liquid phase were here observed on the NO_x and SO_x absorption efficiencies. Absorption tests were achieved at 20°C and atmospheric pressure in a cables-bundle contactor; a range of partial pressures (600-2000 ppm SO₂, 5000 ppm NO_x) and liquid phase concentrations (0-4 mol/l for each acid, 0-1 mol/l for H₂O₂) was investigated.

While the presence of acids, especially H₂SO₄, has a negative effect on SO₂ absorption rates, more acid conditions were found to promote the global NO_x absorption. Comparatively to the use of classical alkaline conditions leading to slightly higher SO_x and NO_x absorption efficiencies, acid solutions allow to avoid the undesired absorption of CO₂ and the extra-consumption of the reactant.

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1. Introduction

Coal plays a vital role in electricity generation worldwide. Coal-fired power plants currently produce 41% of global electricity and this percentage is higher in some countries. Nevertheless, a new constraint seems to emerge from the quantity of CO₂ released into atmosphere by coal power plants because of its major contribution to the climate change by the greenhouse effect. Carbon Capture and Storage (CCS) is one of the most promising ways to decrease atmospheric emissions of CO₂ without stopping coal power plants. This technology allows conciliating a durable economic development and the control of the pollution level. Three main technologies can be applied to capture carbon dioxide emissions: pre-combustion, post-combustion and oxy-combustion processes.

* Corresponding author. Tel.: +32(0)65-374406; fax: +32(0)65-374407.

E-mail address: isabelle.liemans@umons.ac.be

The oxy-combustion processes, using relatively pure oxygen (from 95 to 100% vol.), have the major advantage to increase the concentration of CO₂ in the flue gas and thus to facilitate the post-treatment of the gas in order to capture the CO₂ (when dried, up to ~95%), due to the absence of nitrogen into the burner even if a small residual part still exists because of the air flow inside the furnaces (often operating at a pressure slightly under atmospheric pressure). The flue gas is mainly composed of carbon dioxide, water, air gases (i.e. oxygen, nitrogen, argon...) and a wide range of impurities depending on the complexity of the raw material burned into the furnace : acid gases (called NO_x for NO, NO₂, N₂O₄, ... and SO_x for SO₂ and SO₃...), metals (Hg, Fe...), dust and other (arsenic...).

The oxy-burners are placed inside a boiler which is the heart of the whole process. It produces steam and electricity from the steam. Other essential equipments are:

- an Air Separation Unit ASU to produce the pure oxygen,
- a post-treatment of the flue gas Compression & Purification Unit (CPU) for final purification of the CO₂ stream, producing a quite pure CO₂ flow with a good efficiency.

An example of a CPU has been drawn in the following figure.

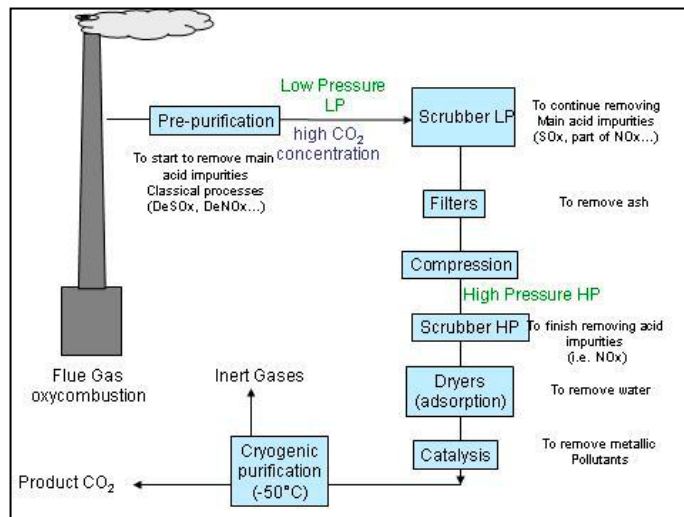


Figure 1 - An example of CO₂ CPU process based on the oxycombustion

Usually, the purification process is composed of different unit operations which can ensure the dust removal (an electrostatic precipitator e.g.) and the purification (acid gas removal system, essentially the SO_x removal like a Flue Gas Desulfurization e.g.).

Despite the fact that absorption processes usually have very good performances at high pressure, the scrubbing will be preferably used at a low pressure because of the major interest in removing the SO_x at the beginning of the CPU. Indeed, if SO_x are not removed from the flue gas, very strong acids (sulfuric acid) can be formed everywhere in the CPU process, especially inside compressors, corroding irremediably materials. NO_x can also be partially captured.

After the compression step in the CPU nevertheless, the use of a HP scrubber can present a certain interest to remove largely the residual NO_x before coming inside the final cryogenic part because NO_x are essentially composed of NO at the output of the furnace due to the thermodynamic equilibrium at operating conditions. No unit can unfortunately remove a large part of NO from the flue gas while NO₂ can be easily absorbed in a wide range of liquids, especially in an alkaline solution. NO can be advantageously converted into NO₂ in presence of oxygen, especially at higher pressure and therefore a HP scrubber disposed at the end of the CPU could remove a large part of the NO_x which have been converted in NO₂ in the upstream unit.

The required high purity of CO₂, the maximization of the global recovery of the CO₂ and the minimization of the global cost are a direct consequence of trade-off and optimization of each part of the whole process. Nevertheless, the high concentration of CO₂ inside the flue gas will disturb the purification by absorption in alkaline solutions (usually used for FGD), the main problems being:

- An over-consumption of alkaline reactants due to the high partial pressure of CO₂ in the flue gas,

- The production of a lot of complex by-products. Actually CO_2 , NO_x and SO_x will produce nitrites, sulfites, nitrates, carbonates and sulfates whose valorization is very difficult, and the liquid waste generated will thus need a treatment,
- Some alkaline liquids used to wash the flue gas present solubility problems (Ca, Na, K, with an increasing solubility) for the management of the scrubber. It is particularly true when increasing the pressure.

An alternative to these alkaline scrubbers could be the acid scrubbers: on the one hand, the acidity of the washing solution can limit largely the CO_2 transfer from the gas to the liquid phase and, on the other hand, SO_x and NO_x are absorbed and transformed into unstable (nitrites) and stable molecules (nitric and sulfuric acids) which are valuable as by-products. The addition to the liquid phase of an oxidant such as hydrogen peroxide results in the formation of sulfuric and nitric acids only.

The aims of this paper are to characterize the effects of HNO_3 and H_2SO_4 concentrations in the scrubbing solution on the absorption performances of SO_2 and NO_x , respectively, in presence of H_2O_2 , from qualitative (absorption-reaction mechanisms) and quantitative (determination of design parameters) points of view.

2. SO_2 and NO_x absorption mechanisms in presence of H_2O_2

Absorption mechanisms of SO_2 into $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ solutions [1] and of NO_x into $\text{HNO}_3 + \text{H}_2\text{O}_2$ solutions [2] have been separately but extensively studied prior to this study, and are represented in Fig.2.

Absorption of SO_2 into water is not of great industrial interest. Though the reaction with water is instantaneous, it is not irreversible, limited by the equilibrium [3].



When sulfur dioxide is absorbed in a solution containing hydrogen peroxide, it results in the formation of sulfuric acid in the liquid phase.



This reaction with H_2O_2 is irreversible and occurs at a finite speed. Increasing the H_2O_2 concentration in the liquid phase enhances the oxidation reaction kinetics rate resulting in higher SO_2 absorption rates. However the presence of H_2SO_4 in the liquid solution (H_2SO_4 will be concentrated with the recycle of the scrubbing solution in the industrial absorption system) is unfavorable to the SO_2 removal [1].

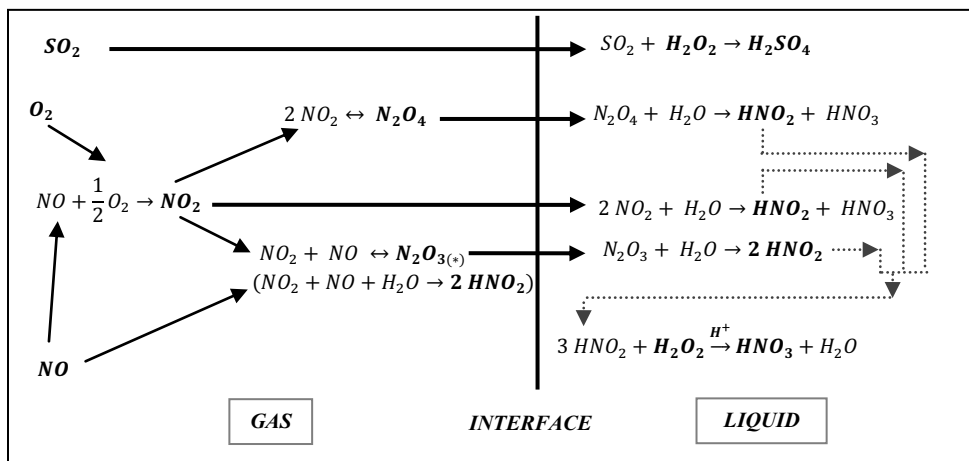


Figure 2 - Absorption mechanisms of SO_2 and NO_x into H_2O_2 containing solutions

The nitric oxides of interest in this study are NO , NO_2 , N_2O_3 and N_2O_4 . The amounts of these species in the gas phase are dependent, following the reaction mechanism described in Fig.2. The quite complex mechanism of absorption of these nitrogen oxides into water results in the formation of nitric and nitrous acids [4], the latter being decomposed with an undesirable release of NO to the gas phase according to the reaction:



The addition of hydrogen peroxide in the liquid phase prevents the decomposition of HNO_2 by oxidation into HNO_3 , but also enhances substantially the mass transfer rate of the nitrous acid formed in the gas phase:



It was shown [2][5] that nitric acid promotes the oxidation reaction (4) (auto-catalytic effect), improving the absorption rates for gaseous mixtures containing trivalent NO_x species.

Two important differences between the present study and the previous ones are that:

- simultaneous NO_x and SO_x absorptions in mixed acid solutions are studied,
- the gas phase is composed mainly of CO_2 which could react in the liquid phase.

3. Experimental set-up and procedure

The absorption tests were achieved by means of a laboratory installation depicted in Fig.3.a. The main part of the experimental set-up is the gas-liquid contactor: a ring-shaped column made of a vertical glass tube in the axis of which stands a polypropylene rod supporting 6 twisted polypropylene cables, constituting the packing. The dimensions of the contactor are given in Fig.3.c. This special contactor is well suited for kinetic studies as its specific surface was well characterized in our previous studies and is quite insensitive to the liquid flow rate and viscosity [6].

The carrier gas (CO_2) is humidified preliminary to the addition of solute gases and a complement of nitrogen. The gas enters the gas-liquid contactor at the bottom, flowing upwards, while the scrubbing solution is fed to the top of the column with a gear pump, flowing downwards (Fig.3.b.). The liquid is distributed around each cable through individual holes drilled in the bottom of the distribution chamber and a steady flow is set up around the yarns. The liquid and gas feed temperature is controlled by means of a thermostatic bath.

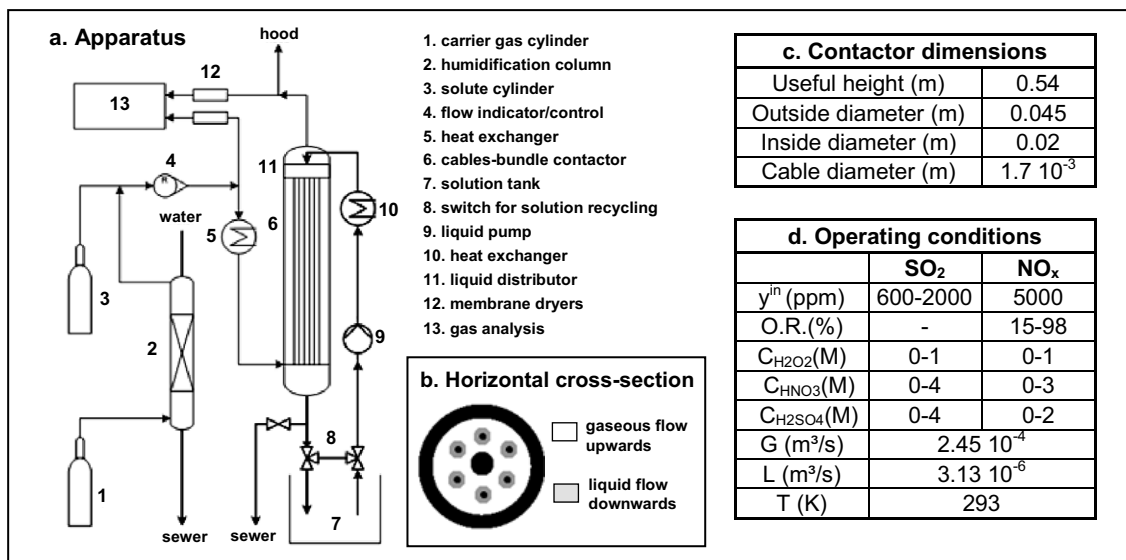


Figure 3 - a. Experimental apparatus b. Horizontal cross-section of the contactor c. Contactor dimensions d. Operating conditions of the absorption experiments

Gas composition is analyzed continuously, simultaneously at the input and the output, through membrane dryers followed by a two-channel U.V. analyzer for SO_2 , and a chemiluminescence analyzer for NO and total NO_x , allowing the calculation of the SO_2 and NO_x absorption rates $A_i = (y_i^{\text{in}} - y_i^{\text{out}}) / y_i^{\text{in}}$ and the NO_x oxidation ratio $\text{O.R.} = (y_{\text{NO}_x}^{\text{in}} - y_{\text{NO}}^{\text{in}}) / y_{\text{NO}_x}^{\text{in}}$, characterizing the inlet gas composition. A two-channel I.R. analyzer gives the CO_2 concentration in the gas.

The liquid phase analysis is performed by means of a total acidity titration and a conductimetric titration of SO_4^{2-} with BaCl_2 in order to analyze separately sulfuric and nitric acids, and an iodometric titration method in presence of KI gives the H_2O_2 concentration.

All experiments reported in this paper were carried out at atmospheric pressure and a temperature of $20 \pm 0.3^\circ\text{C}$. Operating conditions are summarized in Fig.3.d. The gas flow was maintained at $0.85 \text{ m}^3/\text{h}$ resulting in a superficial velocity of 0.2 m/s and the liquid flow rate was fixed at 185 ml/min ($33.3 \text{ ml/min/cable}$, which is the nominal value for an industrial cables-bundle scrubber).

4. Results and discussion

4.a Comparison of SO_x and NO_x absorption efficiencies

As far as the absorption tests are concerned, the absorption rate depending on the contactor and the operating conditions which are fixed in all the experiments, it can easily be used for performances comparisons between the different liquid solutions. All the following charts present relative SO_x and NO_x absorption rates, for which absorption performances into NaOH solutions (maximal performances) are used as reference ($A=1$). Indeed, both the reactions between SO_2 and NaOH [7] and the reaction between HNO_2 and NaOH [8] are instantaneous. For the sake of comparison, absorption rates into water are also illustrated on the charts, but present relatively moderate values due to the reasons explained previously in part 3.

Absorption tests of SO_2 into sulfuric-nitric acid solutions of various concentrations and containing hydrogen peroxide were achieved continuously for different SO_2 inlet concentrations between 600 and 2000 ppm. As carbon dioxide is used as carrier gas (simulating oxyfuel exhaust gases), a comparison of the performances reached with CO_2 and nitrogen can be observed on Fig.4.a, showing that absorption rates in N_2 are slightly higher, but this difference is very small and can be explained by the lower diffusivity of SO_2 into CO_2 ($D_{\text{SO}_2\text{-CO}_2}=0,099 \text{ cm}^2/\text{s}$, $D_{\text{SO}_2\text{-N}_2}=0,129 \text{ cm}^2/\text{s}$).

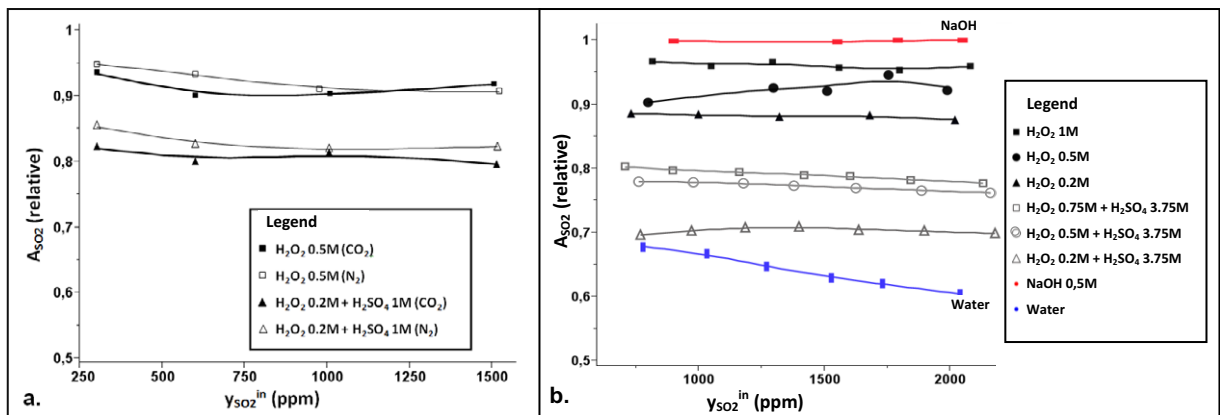


Figure 4 - a. Difference between carbon dioxide and nitrogen as carrier gas.

b. Effect of H_2O_2 concentration on SO_2 absorption rate in water and H_2SO_4 solutions.

Due to the chemical reaction between SO_2 and H_2O_2 (2), the enhancement effect on SO_2 absorption increases with the hydrogen peroxide concentration in the scrubbing solution, as shown in Fig.4.b, but remains always lower than with a NaOH solution, resulting from the fact that the rate of reaction with H_2O_2 remains finite. SO_2 absorption rates in oxido-acidic solutions and NaOH are independent of the inlet partial pressure of SO_2 because of an excess of oxidizing or neutralizing agent.

The presence of sulfuric acid has a negative effect on SO_2 absorption rates, as can be seen on Fig.4.b and Fig.5. A higher H_2O_2 concentration is required in order to achieve similar absorption rates than in the absence of H_2SO_4 . For a given peroxide concentration, Fig.5 clearly shows that the presence of nitric acid slightly decreases absorption performances even at higher concentrations, while the negative effect of H_2SO_4 concentration is much more obvious.

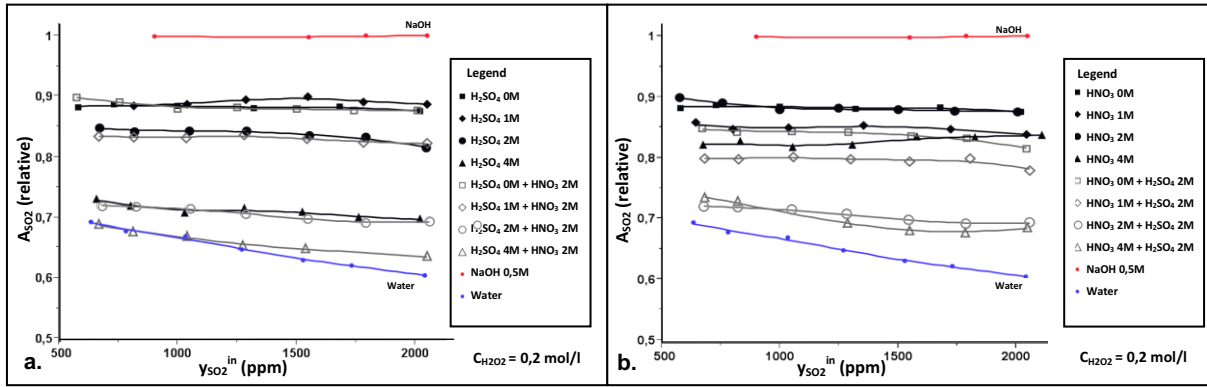


Figure 5 - a. Effect of sulfuric acid concentration on SO₂ absorption rate in solutions containing H₂O₂ without and with nitric acid.
 b. Effect of nitric acid concentration on SO₂ absorption rate in solutions containing H₂O₂ without and with sulfuric acid.

Absorption tests of NO_x into sulfuric-nitric acid solutions of different concentrations and containing hydrogen peroxide were achieved continuously for 5000 ppm NO_x inlet and various oxidation ratios in the range 15-98%. It was shown that the hydrogen peroxide concentration has no effect on NO_x absorption rates [2], as long as the concentration reaches the minimum to respect stoichiometry and, as confirmed on Fig.6.a, an increase in nitric acid concentration results in higher NO_x absorption rates, especially at medium O.R., where trivalent NO_x species are in higher concentration. Sulfuric acid leads to a similar effect as nitric acid at equal H₃O⁺ content, as shown in Fig.6.b, revealing that only acidity is the catalyst of the oxidation reaction by H₂O₂ (4).

Finally, no significant CO₂ absorption was observed during absorption tests in oxydo-acidic conditions, in comparison with absorption into NaOH solutions (Fig.7.a). Fig. 7.b shows that the existing reaction of CO₂ with OH⁻ consumes the reactant, lowering consequently SO₂ absorption rates. Oxido-acidic solutions could then be advantageously used for oxyfuel exhaust gases desulfurization and denitrification, avoiding the extra-consumption of the reactant.

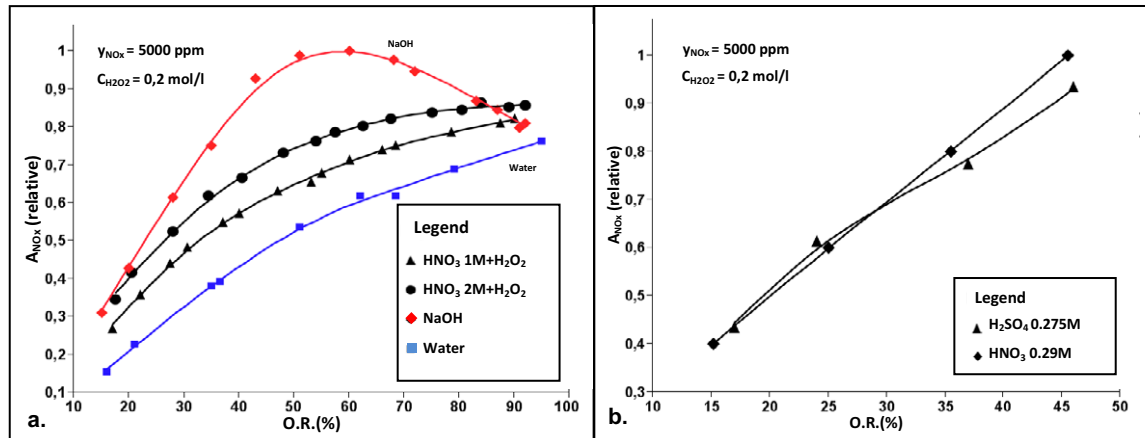


Figure 6 - a. Effect of nitric acid concentration on NO_x absorption rates in solutions containing H₂O₂.
 b. Effect of sulfuric acid on NO_x absorption rate in comparison with nitric acid.

4.b Determination of design parameters

A mathematical model was developed to simulate SO₂ absorption, with chemical reaction, into HNO₃-H₂SO₄ solutions containing H₂O₂, based on the two-film theory. The kinetics of reaction (2) is considered of global second order according to:

$$r = k_2 C_{SO_2} C_{H_2O_2} \tag{5}$$

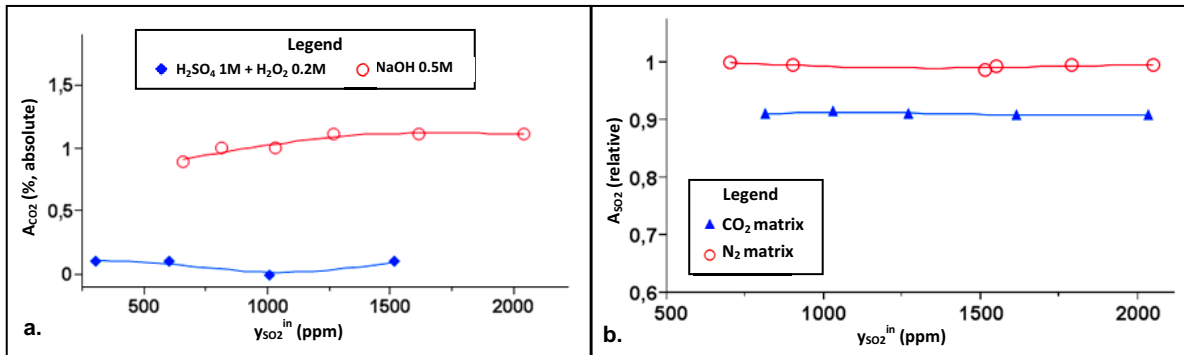


Figure 7 - a. Comparison of CO₂ absorption rates into oxido-acidic solutions and sodium hydroxide solutions.
 b. Effect of a CO₂ gaseous matrix on SO₂ absorption efficiencies into sodium hydroxide solutions

In the case of a fast irreversible reaction, the absorption flux R_{SO_2} (kmol/m² s) can be written as:

$$R_{SO_2} = k_G(p_{SO_2} - p_{SO_2}^i) = Ek_L C_{SO_2}^i \tag{6}$$

where

- $p_{SO_2}^i$ (Pa) and $C_{SO_2}^i$ (kmol/m³) are the SO₂ partial gas pressure and liquid concentration at the interface,
- k_G (kmol/m² s Pa) and k_L (m/s) are the gas and liquid film mass transfer coefficients,
- E (-) is the enhancement factor, function of Hatta number Ha (-):

$$Ha = \frac{\sqrt{k_2 D_{SO_2} C_{H_2O_2}}}{k_L} \tag{7}$$

with D_{SO_2} (m²/s) the liquid diffusivity of SO₂ in the solution.

When H₂O₂ concentration is much higher than SO₂ interfacial concentration $C_{SO_2}^i$, the reaction can be considered of pseudo-first order, and for large Ha numbers $E \approx Ha$.

Equation (6) combined with relation (7) and Henry equilibrium relation at the gas-liquid interface ($p_{SO_2}^i = H_{SO_2} \cdot C_{SO_2}^i$) gives the following expression for the mass transfer rate:

$$R_{SO_2} \approx Ha k_L \left(\frac{p_{SO_2}^i}{H_{SO_2}} \right) = \frac{\sqrt{k_2 D_{SO_2}}}{H_{SO_2}} \sqrt{C_{H_2O_2} p_{SO_2}^i} \tag{8}$$

In this relation appears a factor, regrouping the kinetic constant, diffusivity and solubility, which was called Global Parameter of Absorption of SO₂ (GPA_{SO2}). Since it is not dependent on hydrodynamic conditions [1], it can be used for the design of absorption towers. From its definition, GPA varies with liquid phase concentrations and temperature.

With the mathematical model associated to the discretization of the column, the simulation element by element allows the computation of GPA. A polynomial regression was made out of the values as a function of nitric and sulfuric acids concentrations. Fig.8.a presents precisely the combined effect of increasing sulfuric and nitric acid concentrations on the decreasing GPA value. The regression was also used for the simulation giving the SO₂ partial pressure at the output of the column: comparison between simulated and experimental values is very satisfying, as it can be seen in Fig.8.b.

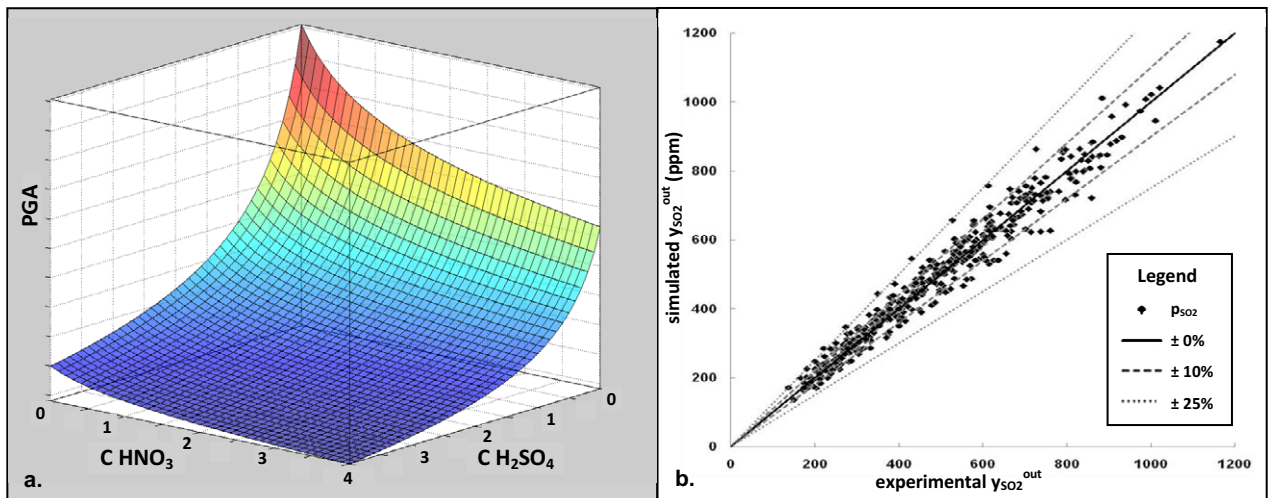


Figure 8 – a. Evolution of GPA with HNO₃ and H₂SO₄ concentrations.

b. Comparison between experimental SO₂ output partial pressures and simulated values using modeling and GPA_{SO₂}

Similar developments should be soon achieved for NO_x species. In that specific case, three GPA values have to be determined simultaneously: GPA_{NO₂}, GPA_{N₂O₃*} (N₂O₃* regrouping the two trivalent species N₂O₃ and HNO₂) and GPA_{N₂O₄}. These can be deduced from absorption tests achieved with a largely varying NO_x composition, namely the oxidation ratio.

5. Conclusion

In order to reduce simultaneously nitrogen and sulfur oxides contained in oxyfuel exhaust gases (composed mostly of carbon dioxide), an original absorption technique is proposed consisting in a scrubbing process with aqueous acidic solutions containing hydrogen peroxide in order to oxidize irreversibly NO_x and SO₂ in HNO₃ and H₂SO₄. In comparison with alkaline reactants, this technique presents the advantage of no extra-consumption of the reactant H₂O₂ as the CO₂ present in the gas phase is only slightly absorbed.

Absorption tests have been performed in a cables-bundle contactor, operating at 293 K and 1 atm, for SO₂ concentrations up to 2000 ppm, with mixed aqueous solutions containing sulfuric and nitric acids with hydrogen peroxide. It was found that, in oxido-acidic solutions, a rise in H₂SO₄ concentration involves a decrease in SO₂ absorption efficiencies, while HNO₃ has only a slight negative effect on performances. Similar experiments have been achieved with nitrogen oxides, showing that NO_x absorption rates are enhanced by both acids, especially for higher proportions of trivalent NO_x in the gas.

Global parameters of absorption (GPA, function of concentrations and temperature) have been deduced for SO₂, allowing an easier scale-up of this technique.

In a next future the simultaneous presence of SO₂ and NO_x will be investigated in mixed acids solutions in order to reveal if combined specific interactions occur. The temperature effect on NO_x and SO₂ absorption efficiencies has also to be taken up soon.

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