



Experimental aspects of combined NO_x and SO₂ removal from flue-gas mixture in an integrated wet scrubber-electrochemical cell system

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ABSTRACT

The objective of this work was to study the effect of some operating conditions on the simultaneous removal of NO_x and SO₂ from simulated NO–SO₂–air flue-gas mixtures in a scrubber column. The gaseous components were absorbed into 6 M HNO₃ electrolyte in the scrubber in a counter-current mode, and were oxidatively removed by the Ag(II) mediator oxidant electrochemically generated in an electrochemical cell set-up. The integration of the electrochemical cell with the scrubber set-up ensured continuous regeneration of the Ag(II) mediator and its repeated reuse for NO_x and SO₂ removal purpose, thereby avoiding: (1) the usage of chemicals continuously for oxidation and (2) the production of secondary waste. The influences of packing material (raschig glass rings, raschig poly(vinylidene) fluoride rings, Jaeger tri-pack perfluoroalkoxy spheres), feed concentrations of NO and SO₂ (100–400 ppm NO and 100–400 ppm SO₂), superficial gas velocity (0.061–0.61 m s⁻¹) and liquid velocity (0.012–0.048 m s⁻¹) were investigated. The raschig glass rings with high surface area provided highest NO removal efficiency. NO and NO_x showed decreasing abatement at higher feed concentrations. The removal of nitrogen components was faster and also greater, when SO₂ co-existed in the feed. Whereas the gas flow rate decreased the removal efficiency, the liquid flow rate increased it for NO and NO_x. The flow rate effects were analyzed in terms of gas/liquid residence time and superficial liquid velocity/superficial gas velocity ratio. SO₂ removal was total under all conditions.

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1. Introduction

The simultaneous removal of NO_x and SO₂ is an emerging process for flue gas cleaning. Flue gas treatment for NO_x and SO₂ removal has been stimulated by the increasing importance of control of pollution by these gases. Their removal is mostly realized by treatment for individual gas emission (Yang et al., 1998; Rodenhause, 1999; Sarkar et al., 2007; Colle et al., 2008). To control NO_x emission, advanced flue gas treatment technologies, broadly classified as dry and wet techniques, are adopted (Yang et al., 1998). The dry techniques are further classified as selective catalytic reduction (SCR) by NH₃ at 300–500 °C, selective noncatalytic reduction, adsorption and electron beam irradiation. The wet techniques use scrubber columns in which the flue-gas mixture is subjected to liquid wash to remove particulate and the gaseous NO_x pollutants. Similarly, for SO₂, wet flue gas desulfurization (WFGD) using alkaline solutions (of sodium, calcium and magnesium compounds) as absorbents are the most widely used process that can remove it efficiently (Colle et al., 2008). Attempts to achieve simultaneous removal of NO_x and SO₂ by conventional

methods indicated that the SCR processes are very difficult to apply to pollution sources containing SO_x, because of catalyst poisoning by SO₂. Similarly, the WFGD treatment could not remove NO_x because of low solubility in aqueous solution of NO, which accounts for 90–95% of the NO_x in a typical flue gas stream. A great deal of extensive work in order to overcome these problems so as to achieve the removal of both NO_x and SO₂ gases simultaneously in a single operation led to the recognition that absorption techniques (chemical scrubbing), using aqueous solutions containing an oxidizing agent to convert insoluble NO to soluble NO₂ or to form a complex, which could then be removed, are more promising and convenient with higher removal efficiencies, and also economically attractive.

In wet scrubbing treatment, gases are continuously scrubbed in the column, whereas the aqueous phase is circulated batch wise in counter-current or co-current mode. It involves absorption of the gaseous reactants into the liquid phase promoted by rapid, irreversible chemical reaction provided by the oxidizers in solution phase. The gas absorption in to the scrubbing solution is further facilitated by materials of high surface area (high pore size or void fraction) packed in the column to provide large gas/liquid interfacial area for larger mass transfer. Thus, several scrubber columns of different types have been developed to accomplish the combined removal of NO_x and SO₂ from combustion flue gases utilizing

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strong oxidizing catalysts, like peracids (Littlejohn and Chang, 1990), metal chelates (Harriott et al., 1993; Xu and Chang, 2007), chloric acid (Kaczur, 1996), $\text{KMnO}_4/\text{NaOH}$ (Chu et al., 2001), hexaminecobalt(II)/iodide (Long et al., 2005), ClO_2 (Jin et al., 2006), NaClO_2 , etc., with NaClO_2 being the most frequently studied: under alkaline conditions (Sada et al., 1978; Yang and Shaw, 1998; Chien and Chu, 2000), buffered conditions (Adewuyi et al., 1999), and in acidic medium (Chien et al., 2003).

Although this approach using chemical oxidants has been showing good results for many years, there are certain drawbacks in the wet scrubbing systems utilizing various chemicals. One problem concerns the fact that the scrubbing processes require continuous usage of large amounts of expensive oxidizing agents. In addition, it also presents special disposal problems because of the high concentration of the spent scrubbing solution. In recent years, a great deal of attention has been devoted to electrochemical methods as a potential option (Chen, 2004; Panizza and Cerisola, 2007) which could avoid the problems that the chemical scrubbers represent in their application. A promising electrochemical technique suitable for the removal of NO_x and SO_2 from industrial flue gas is the mediated electrochemical oxidation (MEO) process. The MEO is a United Nations Environmental Programme (GEF, 2003) identified process for the ambient temperature destruction of toxic organic pollutants and waste streams including persistent organic pollutants and dioxins. It consists of utilizing metal ion based redox systems, like Ag(II)/Ag(I) , Co(III)/Co(II) , Ce(IV)/Ce(III) , Mn(III)/Mn(II) , generated in an electrochemical cell and supplied to a scrubber column in a closed loop for complete mineralization of organic pollutants to CO_2 and H_2O in a shorter duration of time (Galla et al., 2000; Pillai et al., 2009). The MEO based treatment has also been extended for flue gas abatement (Arousseau et al., 1994, 1996; Hoffmann et al., 1997; Bringmann et al., 1997). Lapicque and his co-workers have done pioneering work in this area, and they used electrogenerated Ce(IV) in sulfuric acid for wet scrubbing of NO_x (Arousseau et al., 1994) and SO_2 (Arousseau et al., 1996) from single component-containing flue gas, and also for simultaneous removal of NO_x and SO_2 from a mixture (Hoffmann et al., 1997). Electrogenerated Ce(IV) was found to have good catalytic effect to give a complete removal of SO_2 and below 45% removal efficiency of NO_x gases (Hoffmann et al., 1997). In a study related to NO and NO_2 off-gases emanated from the cathode compartment of an electrochemical cell due to nitric acid reduction, Bringmann et al. (1997) used electrogenerated Co(III) and Mn(III) in sulfuric acid medium for NO_x to HNO_3 conversion with conversion efficiencies of 36% and 97%, respectively, at 20 °C. In a recent study (Raju et al., 2008), we reported some preliminary work on the application of Ag(II)/Ag(I) in 6 M HNO_3 -based MEO system for combined removal of NO_x and SO_2 from a flue-gas mixture in two laboratory-made packed scrubber columns. The scrubber-I was integrated with an electrochemical cell for mediator generation and oxidation of flue gas components, and the outlet gas from scrubber-I was subsequently admitted into scrubber-II for further continuous washings by 3 M HNO_3 for the removal of remaining NO_2 . Electrogenerated Ag(II) in the integrated scrubber-I-electrochemical cell set-up was found to produce total removal of not only SO_2 but also NO , showing highly promising performance compared to the other redox ion, e.g. Co(III) , Ce(IV) and Mn(III) , reflecting its higher oxidizing capability due to higher redox potential $E^0 = 1.98 \text{ V}$ (NHE).

In this study, the effect of some of the process parameters, which have a direct bearing on the functioning of the scrubber column and, in turn, on the simultaneous removal of NO_x and SO_2 from the flue gas by sequential absorption and oxidation of both NO_x and SO_2 in a single reactor, was studied. These include: packing material, feed concentration, superficial gas velocity (U_{SG}) and liquid velocity (U_{SL}), contact time, U_{SG}/U_{SL} ratio. An aqueous solu-

tion of 6 M HNO_3 containing 0.1 M Ag(I)NO_3 was used as the scrubbing solution. The second-stage scrubber column was not used in the present work. The results of the present study allowed us to derive useful information on the efficiency of the integrated wet scrubber-electrochemical reactor set-up and the effect of each individual parameter in achieving highest removal for NO , NO_2 and SO_2 components from a simulated flue-gas mixture.

2. Experimental details

2.1. Materials

Gas cylinders of NO (concentration 99.5%) and SO_2 (concentration 0.998%) supplied by Inter Gas, Korea were used. Mesh-type Pt-coated-Ti (Pt/Ti) and Ti electrodes (10 cm × 14 cm × 0.2 cm with 0.8 roughness factor) were purchased from Wesco, Korea. Nafion 324 membrane was from Dupont, USA. Silver(I) nitrate (99.8%) from Junsei Chemical Co. Ltd., Japan, nitric acid (60%) from Sam Chun Chemicals, Korea, and sulphuric acid (95%) from DC Chemicals Co. Ltd., Korea were used as-received. All the solutions were made using water purified by reverse osmosis (Human Power III plus, Korea).

2.2. Apparatus and process

The experimental set-up consisting of a wet scrubber coupled with an electrochemical cell is shown in Fig. 1. The scrubber related units include a scrubber column made of glass sitting on a 7 L PVC liquid storage tank and a pump (Pan World Co., Ltd., Taiwan) for solution circulation. The scrubber column was of 1.2 m length and 0.05 m inner diameter, and packed to a height of 0.8 m with packing material. The simulated flue gas-air mixtures were supplied by high pressure cylinders of NO and SO_2 gases and air blown by an air-compressor (model: AC-B15PA2, Kyungwon Airboy Co. Ltd., Korea). The gaseous mixtures of required NO and SO_2 composition were obtained by controlled mixing of air, NO and SO_2 using mass flow controllers (MFC, model: 1179A13CS1BK-S, MKS Co. Ltd., USA) and the homogenized gas mixture was introduced at the bottom of the scrubber. The U_{SG} ranged from 0.061 to 0.61 m s^{-1} (volume gas flow rate Q_G from 0.3 to 3.0 $\text{m}^3 \text{ h}^{-1}$). Around 3 L of scrubbing solution of 6 M nitric acid containing silver(II)/(I) redox ions was pumped and distributed on the top of the bed by means of a conical tube. The U_{SL} varied from 0.012 to 0.048 m s^{-1} (volume liquid flow rate Q_L from 0.06 to 0.24 $\text{m}^3 \text{ h}^{-1}$).

The electrochemical cell used in this study was of plate-and-frame type narrow gap divided flow cell configuration (Fig. 1). It consisted of a mesh type Pt/Ti anode and a mesh type Ti cathode, each with effective geometrical area of 112 cm^2 , separated by a Nafion 324 membrane. The inter-electrode gap was maintained at 5 mm with the help of two Vitron rubber gaskets (thickness = 2 mm). The electrode assembly set-up was tightly clamped to Ti end plates of thickness 5 mm with the help of a series of Teflon plates (thickness = 5 mm) and rubber gaskets. Provisions were made with separate channel media by which the anolyte and catholyte solutions flowed across the respective electrodes. The 3 L solution of silver(I) nitrate in 6 M nitric acid from the 7 L PVC liquid storage tank and a 1.0 L of 3 M sulphuric acid taken in a separate catholyte glass tank were continuously circulated through the anode and cathode compartments of the electrochemical cell at 2 L min^{-1} constant flow rate with the help of magnetic pumps (Pan World Co., Ltd., Taiwan). A locally made constant current source from Korea Switching Instrument was used to generate Ag(II) redox mediators by electrolysis at a constant current of 10 A.

All the measurements were performed using a constant concentration of Ag(I) at 0.1 M. Before commencing the gas removal

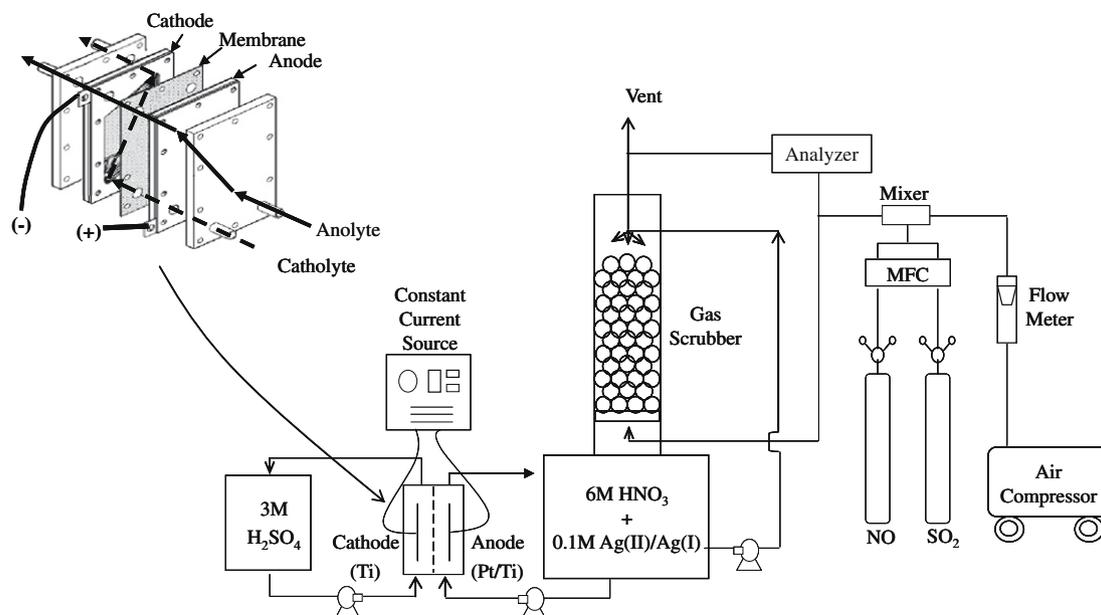


Fig. 1. Experimental set-up.

experiments, the electrochemical cell was run until 15% of Ag(II) conversion from the oxidation of 0.1 M Ag(I) was achieved, and only then the solution was allowed in to the scrubber with gas-air mixture simultaneously passed in a counter-current mode. While referring the silver ion concentration in the scrubber solution, the initially taken Ag(I) concentration, i.e., 0.1 M, will be mentioned in the entire text that follows.

An NO & SO₂-Fuji ZSU gas analyzer was used to measure the concentration of NO and SO₂, while NO₂ concentration was measured by an NO₂-Teledyne Model No. 9110 gas analyzer. From the inlet and outlet concentration of NO, NO₂ and SO₂ the gas removal efficiencies were calculated.

All the processes were conducted at 25 °C and atmospheric pressure conditions.

3. Results and discussion

3.1. Studies with different packing materials

Initially the effect of the packing material on the removal efficiency of NO gas was studied in order to choose the most efficient material with higher removal efficiency. Three different packing materials were used in the present work. The raschig glass rings were 10 mm dia, 10 mm height and 2 mm thickness with a void factor of 0.70 and packing geometric area 460 m² m⁻³, which takes the surface offered by the packing itself and the column wall in to account. The raschig poly(vinylidene) fluoride (PVDF) rings (dia = 25 mm, height = 25 mm, thickness = 2.5 mm, void factor = 0.78, and packing geometric area = 235 m² m⁻³) and the Jaeger tri-pack perfluoroalkoxy (PFA) spheres (dia = 25 mm, void factor = 0.90, packing geometric area = 279 m² m⁻³) were the other two packing materials.

Fig. 2 shows the NO concentration profile, and its removal efficiency, measured at the gas outlet of the scrubber as a function of the removal time for the scrubber column packed with the three packing materials. The results correspond to NO removal from a 400 ppm NO-air mixture with the gas and liquid (6 M HNO₃ containing 0.1 M Ag(I)) passed at constant U_{SC} and U_{SL} at 0.061 m s⁻¹ and 0.048 m s⁻¹, respectively. It is clear that the NO concentration in the outlet solution decreased rapidly with time reaching low concentration less than 50 ppm within 120 s for all the three pack-

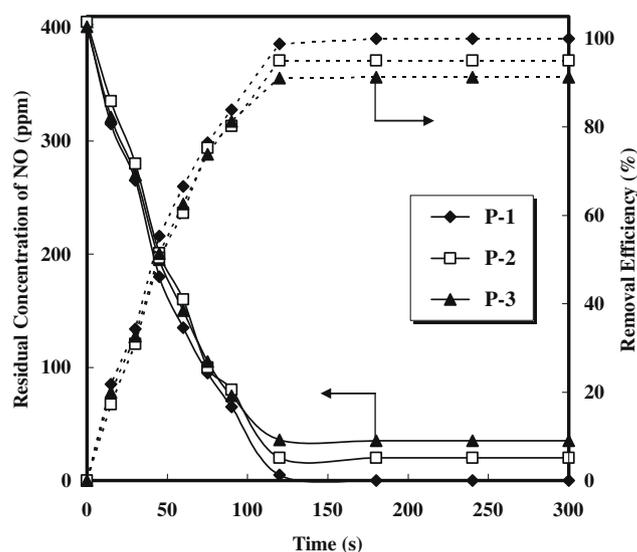


Fig. 2. Changes in residual NO concentration and its removal efficiency as a function of removal time for different packing materials: (P-1) Raschig glass rings; (P-2) Raschig PVDF rings; (P-3) Tri-pack spheres. Experimental conditions: $U_{SC} = 0.061$ m s⁻¹; $U_{SL} = 0.048$ m s⁻¹; feed = 400 ppm NO-air; Ag(I) concentration in cell = 0.1 M; $T = 25$ °C.

ing materials. Interestingly, of all the three materials, raschig glass ring was more effective with the removal degree reaching as high as 100% compared to others, namely raschig PVDF ring (95%) and tri-pack PFA sphere (91%). The better performance of raschig glass ring might be attributed to its higher geometric specific area by providing intimate contact between the gas and absorbing liquid for greater NO gas absorption in to the scrubbing solution for its enhanced oxidation by Ag(II) ions in solution phase. Based on this observation, raschig glass rings were used for all the further work.

3.2. Studies on removal from single component-air mixture

3.2.1. Removal of NO and NO_x from NO-air mixture

In these studies, NO-air mixtures containing different concentrations of NO in the range 100–400 ppm were used as feed with

fixed concentration of 0.1 M Ag(I) in the electrochemical cell. The other experimental parameters were maintained constant as $U_{SC} = 0.12 \text{ m s}^{-1}$ and $U_{SL} = 0.048 \text{ m s}^{-1}$. Fig. 3a illustrates the residual concentration of NO remaining in the gas outlet of the scrubber column, packed with raschig glass rings, for four different initial feed concentrations of NO. The NO removal efficiency was also included in the same graph for a better understanding. It may be noted that NO concentration was reduced to almost zero for lower NO concentrations 200 and 100 ppm, with removal efficiency reaching 100% in a short span of 100 s. Thereafter it was sustained for an extended time as long as 120 min. With increase in feed concentration the removal started decreasing. For example, it was 98% and 94% for 300 and 400 ppm feed NO.

Fig. 3b shows similar plots concerning residual concentration and removal efficiency for the NO_x gas removal from the four NO-air feed mixtures studied above. Note that the concentration of NO_x gas in a given NO-air mixture corresponds to the total NO and NO_2 concentration present in the system. It must be mentioned that the initial gas analysis in the NO-air mixture always showed the presence of some quantities of NO_2 around 10–15% of the initial NO concentration possibly due to air oxidation of NO. Thus, the removal efficiency for the NO_x gas was calculated from the total NO and NO_2 gas concentrations in the feed and in the gas outlet of the scrubber column.

Unlike NO (Fig. 3a), which showed complete removal for low NO feed concentrations 100 and 200 ppm, NO_x was not completely

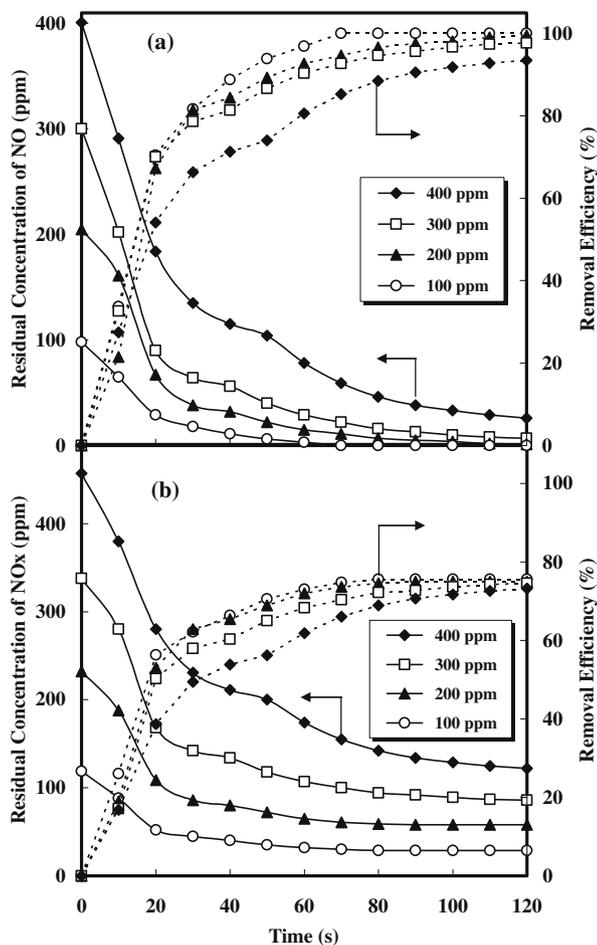


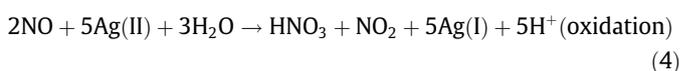
Fig. 3. (a) Changes in residual NO concentration and its removal efficiency as a function of removal time for inlet NO-air mixtures of different NO gas concentration. (b) Changes in residual NO_x concentration and its removal efficiency as a function of removal time for inlet NO-air mixtures of different NO gas concentration. Experimental conditions: $U_{SC} = 0.12 \text{ m s}^{-1}$; $U_{SL} = 0.048 \text{ m s}^{-1}$; Ag(I) concentration in cell = 0.1 M; $T = 25 \text{ }^\circ\text{C}$.

removed from these low feed mixtures even when reaction time was prolonged up to 120 min. There remained always some net quantity of NO_x in the treated gas, the value being higher for higher initial feed mixtures. The maximum removal was only 76% and 75% for 100 and 200 ppm, respectively, at the end of 120 s. Since NO_x is a mixture of NO and NO_2 , realizing that NO gas was effectively removed by Ag(II) system within 100 s, at least for low NO feeds (Fig. 3a), the majority of NO_x in the treated gas (Fig. 3b) should correspond to NO_2 component, which would have not been easily removed by Ag(II)/Ag(I) redox system in the scrubbing solution.

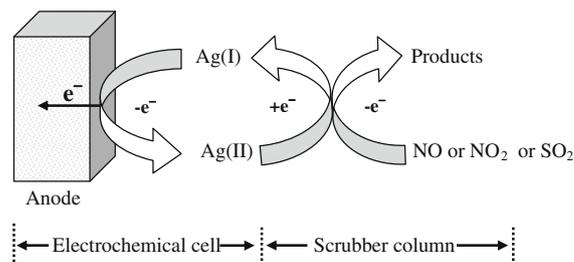
The absorption/oxidation reactions associated are described by the following reactions: NO_x gases in presence of air are well known to establish several complex equilibria (Aurousseau et al., 1994; Bringmann et al., 1997).



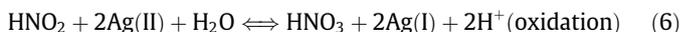
The oxidation of NO and NO_2 in the scrubber solution by Ag(II) ions may occur as (Eqs. (4) and (5)):



The mechanism of MEO (Bard and Faulkner, 1980), which represents regeneration of mediator ions (Ag(II) ions in the present case) in an external electrochemical cell and their supply to the scrubber column by a closed loop to bring about reactions (4) and (5), can be represented schematically as follows:



HNO_2 generated in reaction (3) may also be oxidized in to HNO_3 by Ag(II) in an equilibrium reaction, as suggested for Ce(IV) (Aurousseau et al., 1994), with the overall stoichiometry:



The absorption of NO_2 in to aqueous nitric acid in the scrubber column may occur as



The better NO removal shown in Fig. 3a is a direct indication that NO oxidation to NO_2 by Ag(II) (Eq. (4)) was facile. On the contrary, the limited performance in NO_x removal (Fig. 3b) reveals that the reaction kinetics of NO_2 oxidation by Ag(II) (Eq. (5)) was slower; not all the NO_2 quantity was oxidized, and a sizeable amount of it remained at the solid/liquid interfacial area. Note that NO_2 is soluble in aqueous HNO_3 (Eq. (7)). Nevertheless, the scrubber outlet gas always showed NO_2 , although small, indicating a poor absorption of NO_2 in to the scrubbing solution. This could be attributed to the fact that the excess NO_2 gas might have exceeded the gas solubility limit at the experimental temperature and pressure, and thus was not completely absorbed in to the scrubbing solution.

3.2.2. Removal of SO₂ from SO₂-air mixture

A series of runs were performed to study the removal of SO₂ by wet scrubbing method at different SO₂-air mixtures containing SO₂ concentration viz 100, 200, 300 and 400 ppm, using 0.1 M Ag(I) redox ion in 6 M HNO₃ scrubbing solution, at fixed $U_{SC} = 0.12 \text{ m s}^{-1}$ and $U_{SL} = 0.048 \text{ m s}^{-1}$. Fig. 4 shows the outlet SO₂ concentration and its removal efficiency as a function of removal time. It can be clearly seen that SO₂ concentration in the outlet gas stream fell sharply, and within 40 s the entire SO₂ was removed completely even when SO₂ concentration was high ca. 400 ppm.

The direct oxidation of SO₂ by transition metals, and oxidation of SO₂ by the oxygen contained in air catalyzed by transition metals have been studied by several authors, and depending on sulfuric acid concentration, the formation of sulfate and dithionate ions have been proposed as reaction products (Aurousseau et al., 1996). Similar reactions for SO₂ oxidation in the present case of Ag(II)/Ag(I) redox system forming highly water soluble forms may be expected (Eqs. (8)–(10)):

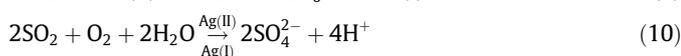
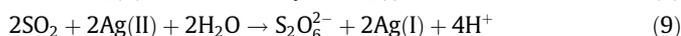
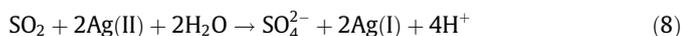


Fig. 4 for SO₂ system, compared to Fig. 3a for NO and Fig. 3b for NO_x, clearly illustrates that the Ag(II) redox mediator although effectively removed SO₂ and NO with 100% efficiency for low feed concentrations 100 and 200 ppm, the SO₂ gas was removed more quickly and easily compared to NO. Also, Ag(II) was found to be 100% effective even for high concentrations of SO₂ ca. 400 ppm, unlike for the NO system. It could be suggested from all these results that the SO₂ oxidation by mediation by Ag(II) (Eqs. 8, 9), and the aerial oxidation catalyzed by silver ions (Eq. (10)) were rapid enough for a complete SO₂ conversion to water soluble sulfur forms. It will be shown later from residence time studies (Section 3.4) that SO₂ gas possessed good gas-liquid mass transfer under all the experimental conditions adopted in the present study.

3.3. Simultaneous removal of NO, NO₂ and SO₂ from NO-SO₂-air mixture and the influence of inlet gas concentration

Fig. 5 shows the residual concentrations of NO, NO₂ and SO₂ remaining in the scrubber gas outlet after their removal by

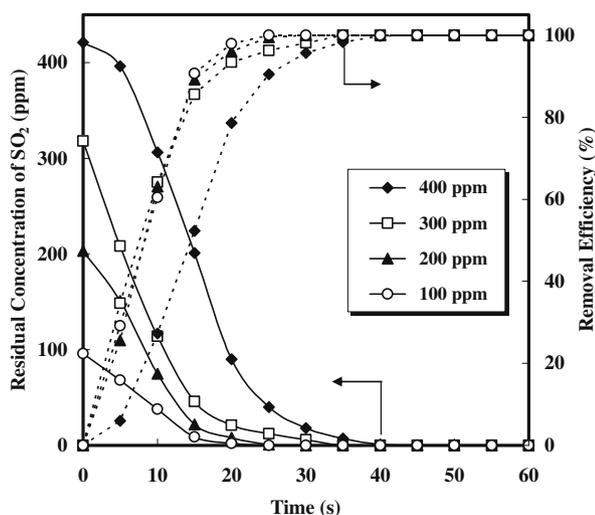


Fig. 4. Changes in residual SO₂ concentration and its removal efficiency as a function of removal time for inlet SO₂-air mixtures of different SO₂ gas concentration. Experimental conditions: $U_{SC} = 0.12 \text{ m s}^{-1}$; $U_{SL} = 0.048 \text{ m s}^{-1}$; Ag(I) concentration in cell = 0.1 M; $T = 25^\circ \text{C}$.

Ag(II)/Ag(I) redox system from NO-SO₂-air mixtures of different feed concentrations ca. 100 ppm NO-100 ppm SO₂-air (Fig. 5a), 200 ppm NO-200 ppm SO₂-air (Fig. 5b), 300 ppm NO-300 ppm SO₂-air (Fig. 5c) and 400 ppm NO-400 ppm SO₂-air (Fig. 5d). All these measurements were carried-out at a fixed 0.1 M Ag(I) in the cell in 6 M HNO₃ with $U_{SC} = 0.12 \text{ m s}^{-1}$ and $U_{SL} = 0.048 \text{ m s}^{-1}$.

Considering 200 ppm NO-200 ppm SO₂-air (Fig. 5b) as an example, it is clear that the Ag(II) in scrubber solution removed both NO and SO₂ quite effectively approaching 100% cleaning efficiency, as it did for individual gases. The NO₂ is, as expected, was around 20 ppm initially. As the NO oxidation to NO₂ reaction progressed (Eq. (4)), excess NO₂ being unable to dissolve in aqueous scrubbing solution, for the reasons discussed already in Section 3.2.1, more NO₂ was detected in the outlet gas at around 37 ppm.

At high feed concentrations 300 ppm (Fig. 5c) and 400 ppm (Fig. 5d), complete 100% removal was observed only for SO₂. NO was removed by 99% and 96%, respectively. Correspondingly, more NO₂ quantity was found in treated gas for these systems.

At this point it is interesting to realize the effect of each component ca. SO₂ or NO on the absorption and removal of the other component. One can notice that NO removal became faster in the presence of SO₂: at input SO₂ concentration of 400 ppm, NO concentration was reduced from 400 to 16 ppm within 40 s (Fig. 5d), whereas in the absence of SO₂, 400 ppm NO was removed much slowly to 115 ppm during the same period (Fig. 3a) (under similar experimental conditions: $U_{SC} = 0.12 \text{ m s}^{-1}$; $U_{SL} = 0.048 \text{ m s}^{-1}$; [Ag(I)] = 0.1 M). Also, note that the removal efficiency of NO was 94% (Fig. 3a) and that of NO_x was 73% (Fig. 3b) in the absence of SO₂ input for 400 ppm NO-air mixture. But, at input SO₂ concentration of 400 ppm, the removal of NO and NO_x was increased (Fig. 5d): marginally from 94% to 96% for NO, and considerably from 73% to 81% for NO_x. Such an enhancement in NO_x removal in presence of SO₂ was observed by Jin et al. (2006) with ClO₂ oxidant, and it has been attributed to increased NO₂ absorption promoted by S(IV) species, originally suggested by Shen and Rochelle (1998). However, note that opposite effects were reported too. Adding SO₂ decreased the absorption of NO, when a phosphate-buffered NaClO₂ (Adewuyi et al., 1999) or KMnO₄/NaOH (Chu et al., 2001) was used as the chemical oxidant for combined NO_x-SO₂ removal, indicating some specific inhibiting chemical interaction by these oxidants.

Note that the SO₂ removal was 100% whether NO was present or not, indicating that there was no effect by NO_x on SO₂ removal efficiency/mechanism. Similar results were reported for several chemical oxidants e.g. lime slurry containing ferrous EDTA (Harriott et al., 1993), aqueous NaClO₂ (Yang et al., 1998), phosphate-buffered NaClO₂ (Adewuyi et al., 1999), and KMnO₄/NaOH at 50 °C (Chu et al., 2001).

Simultaneous removal experiments were also carried out from different NO and SO₂ mixing modes as feed, in addition to the above equal concentration of NO and SO₂-mode. These included: (i) constant NO at 400 ppm with varying SO₂ concentration in the range 100–400 ppm, and (ii) constant SO₂ at 400 ppm with varying NO concentration in the range 100–400 ppm. In all the cases, results (not shown) similar to those in Fig. 5 were observed: SO₂ improved removal of NO and NO_x, and SO₂ removal remained at 100% unaffected by NO_x.

3.4. Effect of gas velocity on simultaneous NO, NO_x and SO₂ removal efficiency from the mixture

Fig. 6a shows the changes in the removal efficiency of NO, NO_x and SO₂ with the increase of gas superficial velocity for a constant $U_{SL} = 0.048 \text{ m s}^{-1}$, and [Ag(I)] = 0.1 M. U_{SC} was varied in the range 0.061–0.61 m s⁻¹, and the results in Fig. 6a correspond to a 400 ppm NO-400 ppm SO₂-air feed mixture. It can be observed

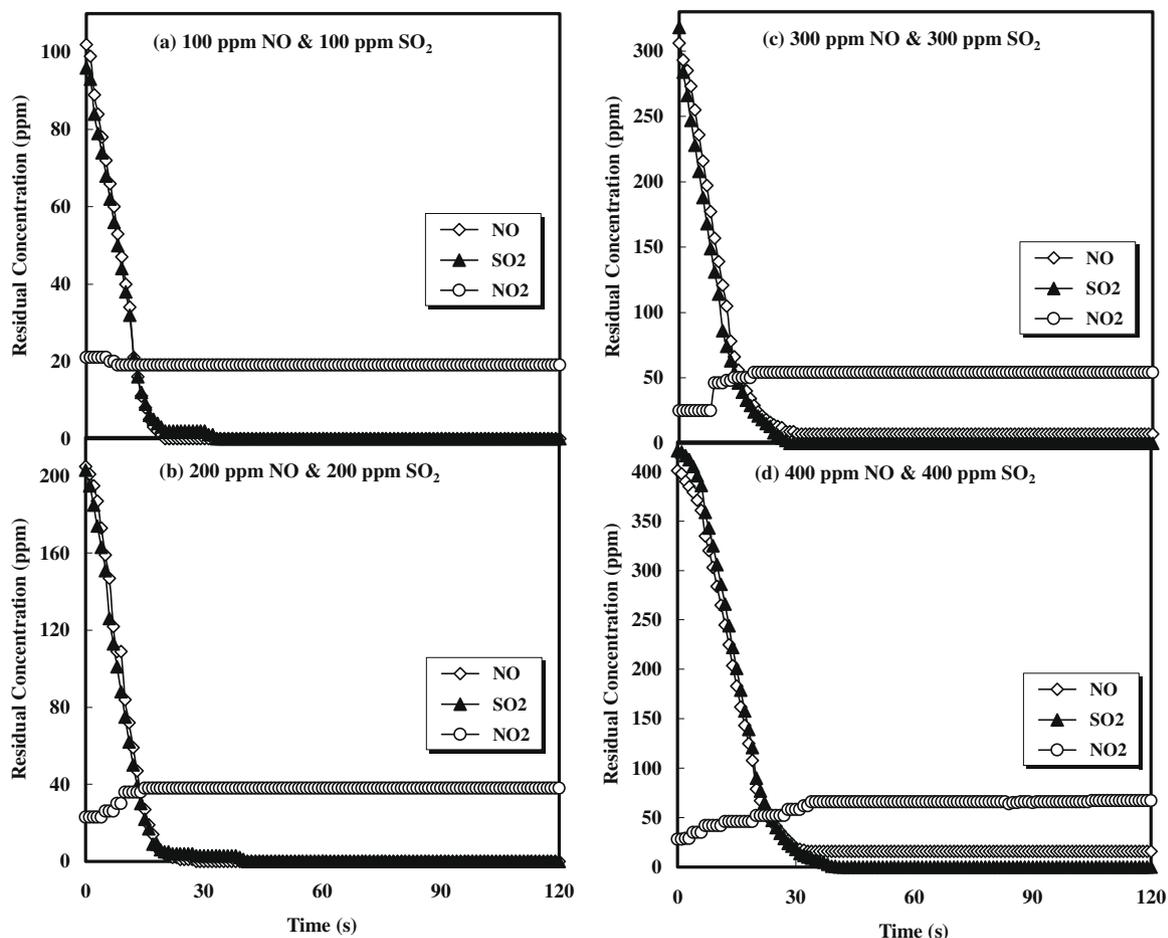


Fig. 5. Changes in residual NO, NO₂ and SO₂ concentrations during their simultaneous removal from NO–SO₂–air mixture of different compositions (ppm NO: ppm SO₂): (a) 100:100; (b) 200:200; (c) 300:300; (d) 400:400. Experimental conditions: $U_{SC} = 0.12 \text{ m s}^{-1}$; $U_{SL} = 0.048 \text{ m s}^{-1}$; Ag(I) concentration in cell = 0.1 M; $T = 25 \text{ }^\circ\text{C}$.

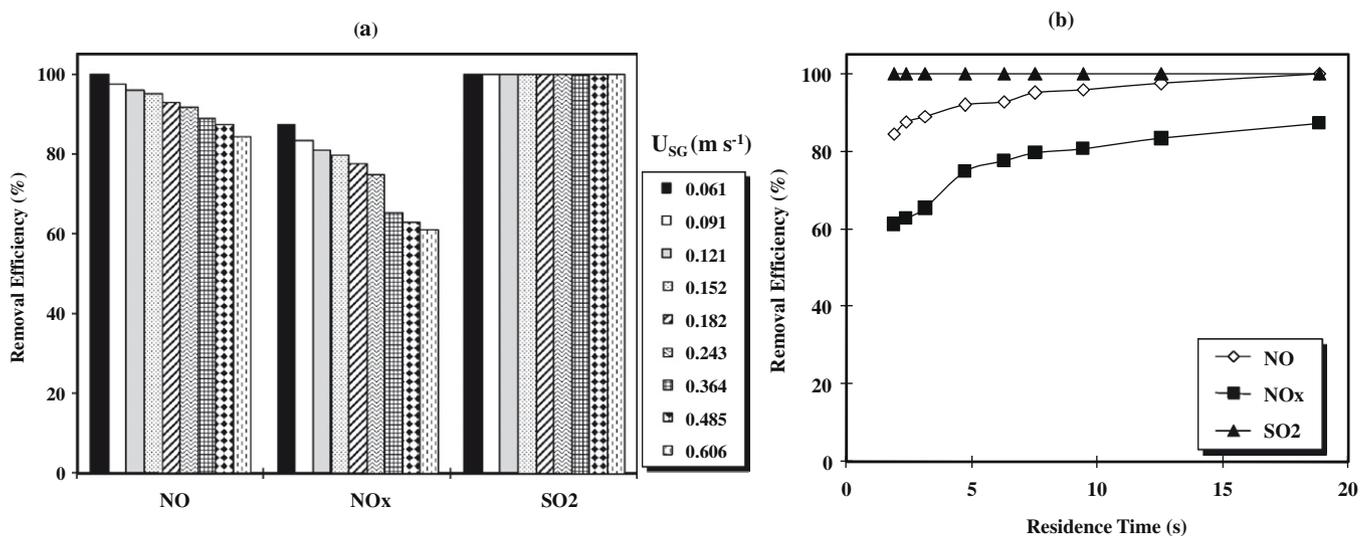


Fig. 6. (a) Influence of superficial gas velocity (in the range $0.061\text{--}0.61 \text{ m s}^{-1}$) on NO, NO_x and SO₂ removal efficiency during their simultaneous removal from NO–SO₂–air mixture. (b) NO, NO_x and SO₂ removal efficiency as a function of residence time. Experimental conditions: $U_{SL} = 0.048 \text{ m s}^{-1}$; Ag(I) concentration in cell = 0.1 M; feed = 400 ppm NO–400 ppm SO₂–air mixture; $T = 25 \text{ }^\circ\text{C}$.

that the removal of both NO and NO_x decreased with increase in U_{SC} ; NO_x showing greater effect. This was quite expected since at high gas flow rate, as there was more NO and NO_x to be oxidized, the Ag(II) concentration in the scrubbing solution could decrease resulting in poor performance. In addition to this, one could realize

that at higher gas flow rates the gas phase would be allowed to remain in contact with the scrubbing solution with Ag(II) oxidant only for a shorter residence time, which could also add-up in lowering the removal efficiency of the flue gas treated in the packed column.

In order to check for this effect, the gas side residence time with constant scrubbing liquid flow rate was calculated as the ratio of effective reactor volume (in m^3) to the gas velocity (in $\text{m}^3 \text{h}^{-1}$). The residence times were found to be 18.9 to 1.9 s for the Q_G in the range from 0.3 to $3.0 \text{ m}^3 \text{h}^{-1}$, for the reactor volume = $1.571 \times 10^{-3} \text{ m}^3$ (1.571 L) at the given $Q_L = 0.24 \text{ m}^3 \text{h}^{-1}$ used in the above work. The removal efficiency as a function of residence time is shown in Fig. 6b. It is quite obvious that at higher residence time 18 s and above, NO removal efficiency was highest around 100%; but, it gradually declined as the residence time became smaller attaining a value of 85% at the 1.9 s residence time (a net decrease of 15%: from 100% to 85%). This decrease was even more rapid for NO_x (a net decrease of 26%: from 87% to 61%). This could mean that the time necessary to their transfer from the gas phase to the liquid phase was not enough, and this absorption was the rate limiting in the overall removal process, more stronger for NO_2 compared to NO.

Considering SO_2 gas, Fig. 6a shows that it was completely removed from the gas mixture for all runs. Fig. 6b shows that its removal was always 100% even when the gas residence time was shorter ca. 1.9 s. This clearly indicates that the SO_2 gas absorption in to the scrubbing solution was rapid enough that the time necessary to its transfer from the gas phase to the liquid phase must have been much smaller than even 1.9 s covered in this study. Matching this good gas–liquid mass transfer, the reactions in the liquid phase (Eqs. (8)–(10)) were also driven faster for the total removal of SO_2 (100% removal efficiency) under all conditions studied.

The results of Fig. 6a and b once again prove that the SO_2 removal from the NO– SO_2 mixture occurred independent of NO_x with no interference what so ever.

3.5. Effect of liquid velocity on NO, NO_x and SO_2 removal efficiency from the mixture

A series of measurements on the simultaneous removal of NO, NO_x and SO_2 from 400 ppm NO–400 ppm SO_2 –air mixture were made at different superficial liquid velocities in the range 0.012 – 0.048 m s^{-1} , maintaining the other experimental parameters constant as $U_{SG} = 0.12 \text{ m s}^{-1}$, and $[\text{Ag(I)}] = 0.1 \text{ M}$. The results are shown in Fig. 7a. It can be seen that higher the liquid flow rate the better the NO and NO_x removal. Note that an increase in liquid flow rate

could provide scrubbing solution more often regenerated, and in this way the concentration of Ag(II) ions would be higher with improved oxidation of NO and NO_x .

As far as SO_2 is concerned, its removal efficiency of 100% at the slowest liquid flow rate stayed unaffected even at higher flow rates. The data in Fig. 7a shows that as soon as U_{SL} reached 0.048 m s^{-1} , the NO removal became greater than 96% for a middle gas flow rate ca. 0.12 m s^{-1} . On the other hand, the NO removal efficiency data for different gas flow rates in the previous plot, Fig. 6b (in terms of residence time), at a specific liquid flow rate of 0.048 m s^{-1} indicated that there was much scope to attain higher removal efficiency by working at higher residence times that is, slower gas flow rates. Thus, a correct matching of liquid flow rate with gas flow rate must exist for an adequate gas absorption into scrubbing solution at the solid/liquid interfacial area provided by the packing material and subsequent oxidation by Ag(II) in solution. Information on this behavior was obtained by considering the liquid to gas flow rate ratio (L/G) and its effect on gas removal.

Fig. 7b is a typical plot of percentage removal of NO, NO_x and SO_2 versus U_{SL}/U_{SG} for the data of Fig. 7a. It can be seen from the figure that the percentage removal of NO and NO_x increased with the increase in U_{SL}/U_{SG} ratio. It can also be seen from the figure that high removals, almost 96% for NO and around 81% for NO_x , were attained at a U_{SL}/U_{SG} ratio of 0.4. With this ratio greater than 0.4, still higher efficiencies could be achieved. This result could be attributed to higher L/G ratios increasing the gas–liquid contacting surface area and mass transfer (Bandyopadhyay and Biswas, 2006). Thus, the results show that good efficiency for the removal of NO and NO_x could be expected for L/G ratio above 0.4. However, the selection of a correct L/G ratio is fundamental to the functioning of a packed column, because the L/G ratio is not only stipulated for high efficiency, but also for sufficient liquid flow to keep the packing wet, since inappropriate supply of liquid can result in dry portion at the packed bed and cessation of gas absorption, and also to avoid flooding etc. A complete consideration of these factors is essential for a proper scrubber operation.

Finally, it must be mentioned that the effects of U_{SG} and U_{SL} on gas removal efficiency in terms of residence time (Fig. 6b) and L/G ratio (Fig. 7b) clearly indicate the importance of mass transfer parameters ca. interfacial area, volumetric liquid side mass transfer coefficient and volumetric gas side mass transfer coefficient. Work towards a quantitative evaluation of these parameters for the

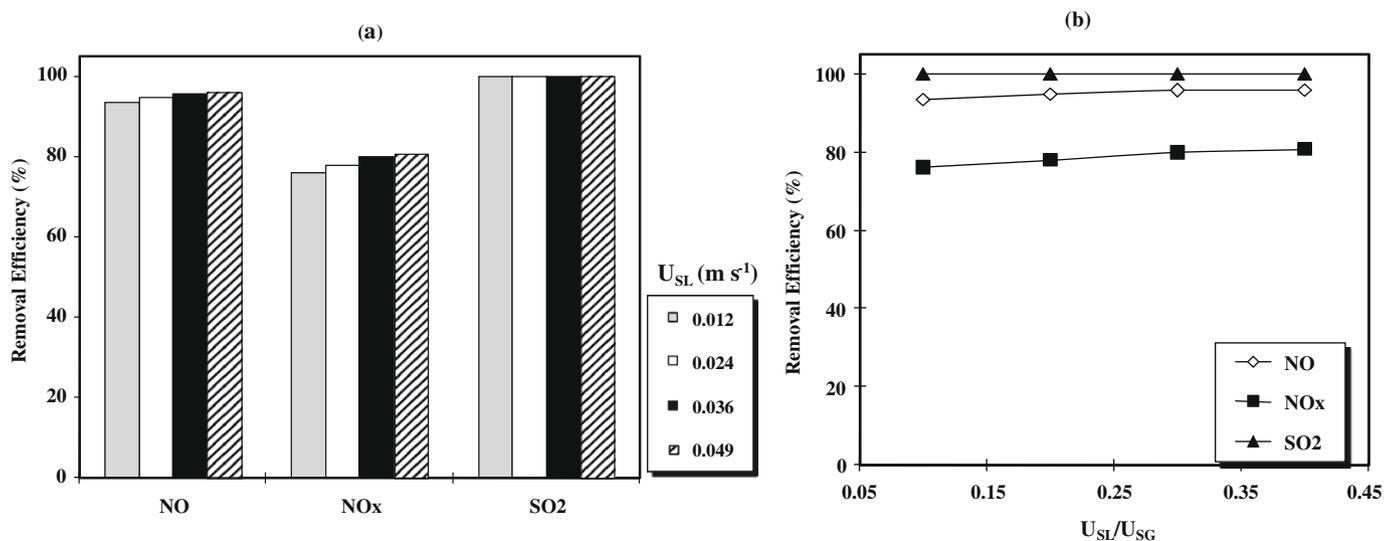


Fig. 7. (a) Influence of superficial liquid velocity (in the range 0.012 – 0.048 m s^{-1}) on NO, NO_x and SO_2 removal efficiency during their simultaneous removal from NO– SO_2 –air mixture. (b) NO, NO_x and SO_2 removal efficiency as a function of U_{SL}/U_{SG} ratio. Experimental conditions: $U_{SG} = 0.12 \text{ m s}^{-1}$; $[\text{Ag(I)}]$ concentration in cell = 0.1 M ; feed = 400 ppm NO–400 ppm SO_2 –air mixture; $T = 25 \text{ }^\circ\text{C}$.

scrubber designed for flue gas removal is under progress following the suggested methods (Sanchez et al., 2007; Couvert et al., 2008). Comprehensive details on these parameters and their evolution with gas and liquid superficial velocities will be dealt with separately.

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