

## UV/ H<sub>2</sub>O<sub>2</sub> Advanced Oxidation Process for Simultaneous Removal of NO and SO<sub>2</sub>: A Review

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**Abstract:** This study presents a review on advanced oxidation processes (AOPs) for simultaneous removal of NO and SO<sub>2</sub>. AOP, based on using a strong oxidant such as ozone and H<sub>2</sub>O<sub>2</sub>, is able to generate highly reactive intermediates. The pollutant are oxidized and removed by these intermediates. AOP has recently been considered as an effective and attractive technology in flue gas purification.

In this article, first, a brief overview on conventional methods for NO<sub>x</sub> removal is presented. Then, the concepts of AOP are explained and the different AOPs are introduced. Since, H<sub>2</sub>O<sub>2</sub> is widely used as a chemical oxidant in advanced oxidation processes, this article mainly focuses on advanced oxidation with H<sub>2</sub>O<sub>2</sub>. In addition, this study emphasizes on UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process applying UV light for producing active radicals. The concepts, status of progress, and attractive issues for future researches are discussed.

**Keywords:** AOP, UV/H<sub>2</sub>O<sub>2</sub>, Removal of SO<sub>2</sub> and NO, Reactive Absorption.

### 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) and SO<sub>2</sub> are released into the atmosphere during chemical and mineral processes such as coal burning and ceramic production. These gases form acid rain and photochemical smog which seriously harm human health and environment (Hutson, Krzyzyska, Srivastava, 2008; Liu, Y., Zhang, Sheng, Zhang, Zhao, 2010a; Liu, Y. x. , Zhang, 2011; Yue, et al., 2010).

Several types of nitrogen oxides including N<sub>2</sub>O, NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> exist in the environment or are produced by industrial activities. The symbol of NO<sub>x</sub> is usually related to the total content of NO and NO<sub>2</sub>. NO<sub>x</sub> emitted from coal-fired power plants consists of over 90% of NO (Kuroпка, 2011)

NO<sub>x</sub> abatement approaches include pre-combustion (Skalska, Miller, Ledakowicz, 2010), combustion modification, and post-combustion methods (Deshwal, Lee, 2009; Skalska, et al., 2010). These methods are briefly discussed in the following sections. The

most popular post-combustion technology is selective catalytic reduction (SCR) with ammonia in presence of oxygen. Absorption, adsorption and selective non-catalytic reduction (SNCR) are other post-combustion methods (Skalska, et al., 2010).

Removal of SO<sub>2</sub> from flue gases can be achieved by chemical or physical means, using gaseous, liquid or solid substances. The most well-known and successful methods are wet scrubbing with liquid and dry methods with solid substances (Kettner, 1965). However, The least expensive method is the use of a wet scrubber (Haywood, Cooper, 1998). A wet process uses an alkaline solution such as lime/limestone or NaOH solution to absorb SO<sub>2</sub>. Wet scrubbing is the most widely used approach in flue gas desulfurization (FGD) process which usually gives high SO<sub>2</sub> removal efficiencies. However, this process fails to reach high NO<sub>x</sub> removal efficiency because of very low solubility of NO which accounts for more than 90% of NO<sub>x</sub> in the flue gas (Chien, Chu, 2000; Deshwal, Lee, 2009; Hutson, et al., 2008).

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Conventional methods such as wet limestone flue gas desulfurization (WFGD-Ca) and ammonia selective catalytic reduction (SCR-NH<sub>3</sub>) have been developed and applied in large scale for flue gas purification. Nevertheless, none of them can individually achieve simultaneous SO<sub>2</sub> and NO<sub>x</sub> removal. While combining such processes can simultaneously remove SO<sub>2</sub> and NO<sub>x</sub>, large and complex systems and high capital and operating costs limit their utilization (Liu, Y., et al., 2010a; Liu, Y., Zhang, Sheng, Zhang, Zhao, 2010 b, 2010c; Liu, Y. x., Zhang, 2011).

Recently, considerable attention has been paid to simultaneous removal technologies of SO<sub>2</sub> and NO<sub>x</sub> due to economic feasibility, simple equipment, and small space (Liu, Y., Pan, Tang, Wang, 2013).

Recent researches shows that simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> in a single reactor can effectively reduce complexity of systems and the related costs (Liu, Y., Wang, Yin, Pan, Zhang, 2014). Due to the stringent regulations on SO<sub>2</sub> emission reduction, an increase in the number of wet-FGD technologies is expectable. It is likely that, in 2020, almost 60% of the total coal-fired capacity utilizes some type of wet-FGD techniques. With this number of wet processes proposed to be used for SO<sub>2</sub> removal, it is desirable that these technologies could be used for simultaneous removal of pollutants. This makes FGD cost effective because there is no need to install additional costly control equipment such as SCRs. Nitrogen species can be removed simultaneously with SO<sub>2</sub> in existing wet scrubbers. The most important advantage of this method, as compared with SCR, would be a large saving in capital cost (M. Kasper, 1996). However, NO must be oxidized to higher oxidation states (NO<sub>2</sub>, HNO<sub>2</sub> and HNO<sub>3</sub>) which are more easily soluble in water and can be removed by alkaline absorbents (Chien, Chu, 2000; Deshwal, Lee, 2009; Haywood, Cooper, 1998). Thus, finding a suitable way for increasing the absorption of NO in wet flue gas desulfurization equipment can be very effective in making FGD as an attractive process for simultaneous removal of NO and SO<sub>2</sub>. Using some oxidant components which increase NO absorption might serve as the first strategy (Liu, Y., et al., 2014). The most famous NO oxidants are ClO<sub>2</sub> or O<sub>3</sub> which are, however, highly expensive as well as very dangerous for equipment especially in gas phase operations (Chien, Chu, 2000). In recent years, some other complex agents such as Fe<sup>II</sup>EDTA, Fe<sup>II</sup> (CYS)<sub>2</sub> and Co<sup>III</sup> (en)<sub>3</sub> and oxidants such as, KMnO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, NaClO<sub>2</sub>, Fenton and sono-chemical oxidation have been used to improve the absorption rate of NO in

solutions (Adewuyi, Sakyi, 2013; Chien, Chu, 2000; Chu, Chien, Li, 2001; Liu, Y., et al., 2014; Liu, Y., Zhang, Wang, 2012; Owusu, Adewuyi, 2006). However, the use of these chemicals and methods involves high costs and several technical problems. H<sub>2</sub>O<sub>2</sub> is a low cost and environmental-friendly oxidant with oxidation potential of 1.78 V in acidic condition. Its oxidation potential reaches up to 2.8 V in the presence of UV light or catalyst (Zhao, 2014). The results of recently conducted studies show that UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process can be used for simultaneous oxidizing of SO<sub>2</sub> and NO<sub>x</sub> into sulfuric and nitric acid without generating secondary pollution. New researches suggests that if UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process can be used effectively to increase the absorption rate of NO, it may improve the existing wet flue gas desulfurization processes to achieve simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> (Liu, Y., et al., 2014). Depending upon the actual usage ratio of H<sub>2</sub>O<sub>2</sub> to NO<sub>x</sub>, this approach can be economically effective by saving the costs (in comparison to SCR) and weighing out its chemical costs (M. Kasper, 1996).

Applying UV/H<sub>2</sub>O<sub>2</sub> process for simultaneous removal of NO and SO<sub>2</sub> is a new approach which needs further investigation to be comprehensively understood. As such, an in-depth review discussing the main and most recent advances in this field achieved by the experimental studies and kinetic modeling approaches seems in order.

## 2. NO<sub>x</sub> Removal Strategies

NO<sub>x</sub> abatement methods comprise of pre-combustion, combustion modification, and post-combustion. Pre-combustion basically refers to fuel purification for reducing the amount of nitrogen or choosing the fuel with low nitrogen content such as natural gas. However, the main drawback of pre-combustion method is its high cost.

Furthermore, replacement of air in the combustion process by pure oxygen, called oxy-combustion, can also significantly decrease NO<sub>x</sub> formation.

Combustion modification is based on alternation of operational conditions during a combustion process to reduce NO<sub>x</sub> formation. It is evident that the main factors influencing NO<sub>x</sub> formation in a combustion process are combustion temperature, air to fuel ratio, level of air-fuel mixing and combustion products distribution. Hence, the main target of combustion modification is to adjust these factors in order to decrease NO<sub>x</sub> formation. This can be achieved by applying different technologies and methods such as using low

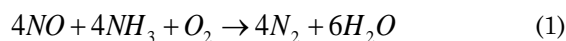
excess air (LEA), low NO<sub>x</sub> burners (LNBs), injection of diluents (in order to reduce flame temperature), and flue gas recirculation (FGR). This should be noted that describing these strategies is beyond of the remits of this review and readers might refer to Skalska et al. (2010) for more details.

According to the Environmental Protection Agency (EPA), the effectiveness of combustion modification technologies depends on the type of combustion system. They can generally achieve a 30-70% NO<sub>x</sub> reduction efficiency (Skalska, et al., 2010).

#### 2.1. Post-combustion methods

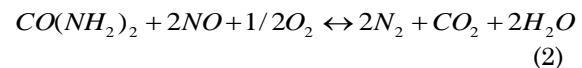
These methods are based on treating the exhaust gases from the combustion processes. In fact, post-combustion controls attempts to physically or chemically remove the existing NO<sub>x</sub> in the flue gas after that the combustion occurs (Haywood, Cooper, 1998). These methods gained a lot of attention because they could provide high NO<sub>x</sub> emission reduction. These methods of NO<sub>x</sub> removal, as noted above, include SCR, SNCR, absorption, and adsorption (Kuroпка, 2011).

Currently, the most commonly used NO<sub>x</sub> control method is SCR by ammonia which can provide up to 85% NO<sub>x</sub> emission reduction (Skalska, et al., 2010). This method is, however, very expensive (Kuroпка, 2011) with the costs ranging from \$140 to \$170 per kW of power production capacity (Haywood, Cooper, 1998). This method requires using catalysts as well as ammonia reacting selectively with nitrogen oxides in the presence of oxygen. The reaction is based on Eq. (1):



Basically, three main groups of catalyst can be distinguished: supported noble metal catalysts, based metal oxide catalysts, and metal ion exchanged zeolite-crystalline silicate. Depending on the catalyst used, the optimal temperature range for the reaction varies usually from 300–800 K. The removal efficiency and effectiveness of a SCR process is affected by many factors such as catalyst type, positioning of the catalyst, and distribution of ammonia. It is extremely important to have perfect distribution of NH<sub>3</sub> to ensure adequate value of NH<sub>3</sub>/NO<sub>x</sub> ratio and limiting NH<sub>3</sub> slip to the exhaust gas. Although SCR is the most popular NO<sub>x</sub> control method, it has its own disadvantages. The use of a catalyst faces this process with other issues such as limited catalyst life, catalyst poisoning by constituents present in flue gas, and catalyst erosion by dust.

SNCR method can be performed with the use of ammonia, aqueous urea (Eq. (2)), or cyanuric acid. A higher temperature (1149-1423) is required in comparison with SCR. SNCR is a simple process and the issues related to the use of catalyst present in SCR are absent here. Thus, the cost related to SNCR are lower than those for SCR. But, the main drawback of SNCR is its low NO<sub>x</sub> removal efficiency which is from 30 to 75 %. More detailed information concerning these strategies can be found in Skalska et al. (2010).



Adsorption methods using conventional adsorbents have not gained attention for nitrogen oxide removal from industrial flue gases. This is mainly due to economic considerations and issues related to regeneration of adsorbent or its utilization. Methods of absorption of nitrogen oxides in acid or alkaline solutions are among the earliest technologies of industrial flue gases treatment (Kuroпка, 2011). But the main drawback of adsorption and adsorption techniques is transferring the NO<sub>x</sub> from flue gas to another medium and thus in many cases generating a waste which has to be treated then (Skalska, et al., 2010). Absorption of nitrogen oxides in acids lead to producing of nitric acid or concentrated nitrogen oxides, thus, there is no side-products. But, the slow mass transfer rate demands big capacities of apparatuses and large space in industrial applications. Furthermore, corrosion problems are also linked to this process. Adsorption methods in alkaline solutions generally have higher efficiency but are more expensive because the products require further treatments. As mentioned before, NO occupies more than 90% of NO<sub>x</sub>. It is poorly soluble in water and has low reactivity with alkaline solutions. To remove the NO from flue gases, it must be oxidized to higher oxidation states, with components which easily release oxygen into the liquid phase and then absorbed by an alkaline solution. Components with strongly oxidizing properties such as sodium hypochlorite, sodium chlorite, calcium hypochlorite, potassium permanganate, potassium dichromate, salts of iron, copper, nickel, cobalt, and hydrogen peroxide are proved to be useful for this purpose (Kuroпка, 2011).

### 3. Advanced Oxidation Processes (AOPs)

Many of the sources that emit NO<sub>x</sub> also emit other gaseous pollutants including SO<sub>2</sub> (Cooper,

Clausen III, Pettey, Collins, Pozo de Fernandez, 2002). NO<sub>x</sub> and SO<sub>2</sub> emission can be controlled by simultaneous use of FGD and denitrification processes, but this combined approach has some disadvantages including system complexity, high initial capital investment, and operating costs. As mentioned before, it seems that simultaneous removal of these two gaseous pollutants in single equipment can effectively reduce the above mentioned problems. Wet flue gas desulfurization (WFGD) is simple process which can achieve high SO<sub>2</sub> removal efficiency. However, because of low solubility of NO, simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> by this process is impossible. In recent years, advanced oxidation processes (AOP) are considered as attractive and effective approaches to improve absorption of NO in WFGDs and making them to be able to achieve simultaneous NO<sub>x</sub> and SO<sub>2</sub> removal (Liu, Y., et al., 2014). An AOP is basically based on production of highly reactive intermediates such as hydroxyl radicals which can be simultaneously oxidized and removed multiple pollutants from flue gas. There are many advanced oxidation process including plasma oxidation, photochemical oxidation, sonochemical oxidation, and Fenton oxidation which are developed for removing various gaseous pollutants, such as SO<sub>2</sub>, NO<sub>x</sub>, trace elements, H<sub>2</sub>S, and volatile organic compounds (VOCs). Among them, UV/H<sub>2</sub>O<sub>2</sub> photochemical oxidation process which produces OH free radicals has gained more attraction. This attraction is because of strong oxidation power of hydroxyl radicals, simple and secure process, low energy consumption, and having no secondary pollution (Liu, Y., et al., 2010 a, 2010 c; Liu, Y. x., Zhang, 2011).

### 3.1. AOP Concepts

In 1987, Glaze et al. defined AOPs as “a near ambient condition water treatment process which involve the generation of sufficient amounts of hydroxyl radicals to effect water purification”. The comprehensive description is that an AOP involves using high energy oxidants that are able to generate highly reactive intermediates. These intermediates react with pollutants and change them to harmless components. Some oxidants such as ozone and H<sub>2</sub>O<sub>2</sub> produce hydroxyl radicals as intermediates.

The hydroxyl radical (OH) is a powerful, non-selective chemical oxidant which acts rapidly with most organic compounds. In the case of organic compounds, based on the nature of them, there are two ways for initial attack of hydroxyl radicals. One is the abstraction of a hydrogen atom, as with alkanes or alcohols.

Another way is when a hydroxyl radical add itself to the contaminant, as in the case of olefins or aromatic compounds.

The methods available for generating hydroxyl radicals can be generally categorized as non-photochemical and photochemical methods. Non-photochemical methods are:

- I. Ozonation at elevated Ph (> 8.5)
- II. Ozone and hydrogen peroxide (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>)
- III. Ozone and catalyst (O<sub>3</sub>/CAT)
- IV. Fenton system (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>)

Additionally, photochemical ones are:

- V. Ozone and ultraviolet light (O<sub>3</sub>/UV)
- VI. Hydrogen peroxide and ultraviolet light(H<sub>2</sub>O<sub>2</sub>/UV)
- VII. Hydrogen peroxide, ozone and ultraviolet light(H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV)
- VIII. Photocatalytic oxidation(UV/TiO<sub>2</sub>)

Hydrogen peroxide is a relatively inexpensive, readily available chemical oxidant. It is produced by electrolysis of ammonium bisulphate or by oxidation of alkyl hydroanthraquinones. The electrolytic process consumes approximately 7.7 kWh per 1 kg of H<sub>2</sub>O<sub>2</sub> produced.

The major operating cost for the ozone oxidation process is the cost of electricity for ozone generation. Ozone can be produced from air or pure oxygen. The energy requirement for ozone synthesis using air as a feed gas ranges from 22 to 33 kWh/kg O<sub>3</sub>. For ozone production from pure oxygen, this energy consumption is in the range of 12 to 18 kWh/kg O<sub>3</sub>, to which the cost of oxygen should be added.

Non-photochemical oxidation approaches do not completely oxidize pollutants. It is found that the oxidation reaction can be completed by supplementing the reaction by UV light (Munter, 2001).

Generally, there are four types of UV wavelengths including UV-A (long wave UV (315-380 nm; 365 nm is the most common), UV-B (medium wave, 280-315 nm; 312 nm is the most common), short wave or UV-C (200-280 nm; 253.7 is the most common), and vacuum or V-UV (spreading in vacuum 100-200 nm; 172 nm is the most common). The Planck equation (Eq. (3)) implies that the energy of a photon is inversely proportional to its wavelength.

$$E = h\nu = h \frac{c}{\lambda} \quad (3)$$

where,  $\epsilon$  is the energy of photons (J),  $\nu$  is the UV frequency (s<sup>-1</sup>),  $h$  is Planck's constant (6.626×10<sup>-34</sup> J·s)



$^{34}J$  s),  $c$  is the speed of light ( $2.998 \times 10^8$  m/s), and  $\lambda$  is the UV wavelength (100-380 nm).

The shorter the UV wavelength, the bigger the energy of the photon. But, the shorter the UV wavelength, the shorter the effective propagation distance (the effective propagation distance corresponds to treatment capacity), too. Therefore, the UV wavelength within the range of 200-300 nm is the most common in photochemical reactions and is the most effective for photolysis of oxidants such as  $H_2O_2$  to produced hydroxyl radicals (Liu, Y., et al., 2010a).

#### 4. UV/ $H_2O_2$ Process for Simultaneous Removal of $SO_2$ and NO

As noted above, AOP, first, is introduced as a water treatment process. Many studies have focused on application of this process in the field water purification. Significantly, UV/ $H_2O_2$  AOP has been widely applied for the degradation and discoloration of organic pollutants in water treatment field over the past 20 years (Canonica, Meunier, Von Gunten, 2008; Hu, et al., 2008; Modirshahla, Behnajady, 2006; Muruganandham, Swaminathan, 2004; Yuan, Hu, Hu, Qu, Yang, 2009). However, recent research studies have shown that this process can also be effective in the field of purifying multiple pollutants from flue gas (Liu, Y. x., Zhang, 2011). As such, a brief review is presented on UV/ $H_2O_2$  application in water treatment field and then the application of this process for gas purification is explained in detail.

The finding of researchers show that injection of hydrogen peroxide into the hot flue gas can be effective to promote the oxidation of NO to more soluble species including  $NO_2$ ,  $HNO_2$ , and  $HNO_3$  which can be easily removed by an conventional wet scrubber (Collins, Cooper, Dietz, Clausen III, Tazi, 2001; Cooper, et al., 2002; Haywood, Cooper, 1998). Using  $H_2O_2$  as an oxidizing agents has long been known. Peroxide is effective because it decomposes to hydroxyl radicals which are extremely reactive (Collins, et al., 2001).

Haywood and Cooper (1998) studied the economic feasibility of using  $H_2O_2$  for removing nitrogen oxides from exhaust gases of coal-fired power plants. They implied that the molar ratio of  $H_2O_2$ :  $NO_x$  is the single largest factor in determining economic feasibility of  $H_2O_2$  injection- wet scrubbing method comparing with a SCR method. At the molar ratio (1.92:1), a laboratory ratio,  $H_2O_2$  injection-wet scrubbing is not economically favorable method. But, in full- scale power plants this molar ratio could be lower than laboratory one. A possible

explanation might be that OH radicals transform into  $H_2O$  and  $O_2$  when they come into contact with a solid surface so that the amount of effective OH radicals becomes lower. A lab scale reactor has very small inner diameter and the ratio of inner surface area to inner gas volume becomes very large comparing with that of in a typical power plants. Thus a full-scale flue gas as far less surface area on which the OH radicals can recombine, as compared to the laboratory tube reactor. Therefore, in an actual coal-fired power plant flue gas duct, the  $H_2O_2$ :  $NO_x$  is lower than that of in lab scale. Based on their finding and cost assumptions, at molar ratio of 1.37:1, the  $H_2O_2$  injection was found to be an economically feasible alternative to the SCR method. The most significant cost operating cost related to SCR are for ammonia use and spent catalyst replacement.

Collins, et al. (2001) also performed pilot-scale evaluation of  $H_2O_2$  injection for  $NO_x$  removal by wet scrubber. Their findings showed that  $H_2O_2$  is very effective at oxidizing NO and conversions above 90% can be achieved and the optimum temperature for the thermally activated peroxide-enhanced oxidation of NO is  $500^\circ C$ . They found that not only the presence of  $SO_2$  in the flue gas did not have a detrimental effect on the peroxide oxidation of  $NO_x$  but also it enhanced  $NO_x$  conversion.  $SO_2$  was oxidized and removed as  $H_2SO_4$  without competing for peroxide. Also, they confirmed that this process has excellent potential one of which is the process can be tailored to any regulatory requirement for  $NO_x$  control simply by adjusting the amount of peroxide used. Collins, et al. (2001) suggested that this process is appropriate for full-scale applications.

In many applications it would very helpful that the oxidation/removal reactions proceed at significantly lower temperature. One solution presented for the first time by Cooper, et al. (2002) was to test UV light as a means to activate the  $H_2O_2$  and initiate the reactions instead of thermal activation. The main objective of their study was to test the ability of ultraviolet light to enhance NO oxidation by hydrogen peroxide at temperatures significantly below  $500^\circ C$ . Numerous experiments were run to evaluate the effect of the UV lamps on the NO and  $H_2O_2$  reactions. Tests were conducted with no lamps on, one lamp on, and two lamps on, at various temperatures, with and without  $SO_2$  and at various initial molar ratios of peroxide to  $NO_x$ . Their results confirmed that UV light can be enhanced the peroxide oxidation of NO to  $NO_2$  and  $HNO_x$  at lower temperatures. The NO conversion increased with number of lamps which NO conversion is described by Eq.

(4). Also the presence of SO<sub>2</sub> had not negative effect on oxidation of NO.

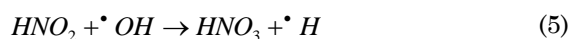
$$NO \text{ conversion} = \frac{NO_{in} - NO_{out}}{NO_{in}} \quad (4)$$

One drawback of their system was that the lamps were difficult to start and tend to overheat in hot flue gases. Therefore, cooling air was required to be flowed through the annular space between each lamp and the quartz sleeve that separated the lamp from the flue gas.

One solution to this problem which has been applied in recent years is the use of UV lamp in a bubble column reactor. This system can be operated at very low temperatures near to ambient temperature without any problem related to aforementioned system. This Wet UV/H<sub>2</sub>O<sub>2</sub> process is studied by some researchers (Liu, Y., Zhang, Sheng, 2011; Liu, Y., et al., 2010a, 2010c; Liu, Y. x., Zhang, 2011). In almost all studies, a jacketed bubble column reactor is used. This reactor operates in semi-batch mode. A simulated flue gas containing NO, SO<sub>2</sub>, N<sub>2</sub> is continuously fed into the reactor through a gas distributor which is located at the bottom of reactor. The flue gas occasionally contains O<sub>2</sub> to investigate the effect of this gas on the removal process. A H<sub>2</sub>O<sub>2</sub> solution is prepared by a 30Wt% H<sub>2</sub>O<sub>2</sub> solution and deionized water and then added into the bubble column reactor. Most studies published in this field considered the effect of parameters such as the UV light intensity, H<sub>2</sub>O<sub>2</sub> initial concentration, liquid layer height, and the gas flow.

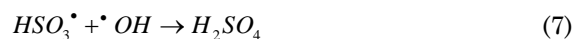
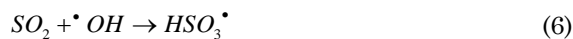
UV/H<sub>2</sub>O<sub>2</sub> oxidation for removal of SO<sub>2</sub> and NO, is in turn a reactive absorption process. The pollutant from flue gas is transferred into the gas-liquid interface, dissolved in liquid, and then consumed by liquid phase through chemical reaction. UV light is used to activate the H<sub>2</sub>O<sub>2</sub> to produce hydroxyl radicals. These are very reactive oxidant which react with gas phase pollutant and transform into the liquid phase products containing sulfuric and nitric acid. Generally, there are three confirmed major reaction pathways for removal of pollutants using UV/H<sub>2</sub>O<sub>2</sub> including excitation removal of UV, oxidation removal of H<sub>2</sub>O<sub>2</sub>, and oxidation removal of OH free radicals. Oxidation removal of OH free radicals plays a leading role and oxidation removal of H<sub>2</sub>O<sub>2</sub> only plays a secondary role (Liu, Y., et al., 2011; Liu, Y. x., Zhang, 2011).

The first step of process is initiation step or producing OH free radicals by H<sub>2</sub>O<sub>2</sub> photochemical degradation based on Eq. (5):



Other steps based on (Liu, Y., et al., 2011; Liu, Y., et al., 2010 b, 2010c; Liu, Y. x., Zhang, 2011) are oxidation of pollutants with OH radicals and or direct oxidation by H<sub>2</sub>O<sub>2</sub>.

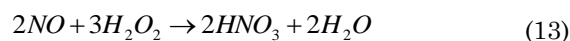
The oxidation pathway for SO<sub>2</sub> via OH radicals is based on following reactions (Eqs. (6) and (7)):



And oxidation of NO with OH radicals goes through Eq. (7) to Eq.(11).



Direct oxidation of SO<sub>2</sub> and NO via H<sub>2</sub>O<sub>2</sub> proceeds according following reactions. Eq. (12) and Eq. (13):



In very high H<sub>2</sub>O<sub>2</sub> contents and UV intensities, the following reactions can occur as side reactions (Liu, Y., et al., 2014; Liu, Y., et al., 2010b, 2010c; Liu, Y. x., Zhang, 2011; Modirshahla, Behnajady, 2006).



Based on the researchers, using UV irradiation, when combined with H<sub>2</sub>O<sub>2</sub>, has a very positive cooperative effect in the removal process. Liu, Y., et al. (2010b) described this effect by a cooperative factor ε which is calculated by the Eq. (18):

$$\varepsilon = \frac{\eta_{UV/H_2O_2}}{\eta_{UV} + \eta_{H_2O_2}} \quad (18)$$

where ε, cooperative factor; η<sub>UV/H<sub>2</sub>O<sub>2</sub></sub> removal efficiency of UV/H<sub>2</sub>O<sub>2</sub>; η<sub>UV</sub>, removal efficiency of UV; and η<sub>H<sub>2</sub>O<sub>2</sub></sub>, removal efficiency of H<sub>2</sub>O<sub>2</sub>. Their results showed that the cooperative factor ε was 6. The cooperative effect between H<sub>2</sub>O<sub>2</sub> and UV is due to producing of very reactive OH free radicals via Eq. (5). These radicals have significant strong oxidation ability for removing of SO<sub>2</sub> and NO and therefore achieving high removal efficiencies.

In almost all of the studies conducted on UV/H<sub>2</sub>O<sub>2</sub> process, the effect of H<sub>2</sub>O<sub>2</sub> concentration is investigated. It is observed that SO<sub>2</sub> removal is nearly complete under different H<sub>2</sub>O<sub>2</sub> concentration. However, the increase of its concentration from 0 to 2 mol/L enhanced NO removal. But, further increase of H<sub>2</sub>O<sub>2</sub> concentration had no significant effect in removal efficiency. H<sub>2</sub>O<sub>2</sub> is key factor of photochemical reaction Eq. (5). The rate of this reaction increases with the H<sub>2</sub>O<sub>2</sub> concentration. On the other hand, H<sub>2</sub>O<sub>2</sub> is a radical scavenger based on Eqs. (14) - (17). Increasing H<sub>2</sub>O<sub>2</sub> concentration causes these side reactions and finally leads to great self-loss of OH free radicals (Liu, Y., et al., 2014; Liu, Y., et al., 2010a, 2010b, 2010c).

In all studies, the SO<sub>2</sub> removal efficiency has been 100% under different UV irradiation intensities. But NO removal increases with UV irradiation intensity. The effect of UV intensity can be described as follow:

When UV irradiation intensity is zero, there is no photochemical reaction and NO removal is performed by direct oxidation and absorption by H<sub>2</sub>O<sub>2</sub> which is a very weaker oxidant rather than OH free radicals. When UV is added, a great amount OH free radicals is produced by photolysis of H<sub>2</sub>O<sub>2</sub>. These radicals are very strong oxidant comparing with H<sub>2</sub>O<sub>2</sub>. Therefore the NO removal increases with adding UV light to the reaction system. Further increase in UV irradiation intensity leads to an increase in photochemical reaction rate based on the Beer-Lambert law (Eq. (19)).

$$I_1 = I_0 \exp(-klc) \quad (19)$$

Where,  $I_1$  is the transmitted light intensity,  $I_0$  is the incident light intensity,  $k$  is the light absorption coefficient,  $l$  is the light path length, and  $c$  is the concentration of the light absorption medium.

This law holds that the photochemical reaction yield (or the photochemical reaction rate) is proportional to the UV irradiation intensity,  $I_0$ . This means that the increase of UV irradiation intensity can increase the energy density of solution per volume to produce more effective photons, and, finally, generate more ·OH free radicals to oxidize and remove NO.

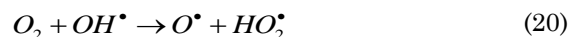
When UV irradiation intensity exceeds a certain value, the increase of UV light intensity results in self-destruction of OH free radicals by colliding with reactor wall (Liu, Y., et al., 2014) or side reactions based on Eqs. (14) - (17) (Liu, Y., et al., 2010a, 2010c).

According to Liu & Zhang (2011) and Liu, Y. et al. (2014) solution temperature had little negative effect on NO removal efficiency and no

effect on SO<sub>2</sub> removal. SO<sub>2</sub> removal was complete in the range of temperatures, while NO removal almost linearly decreases with temperature. The increase in solution temperature leads to an increase in the rate of chemical reaction, while decreases the solubility of NO in H<sub>2</sub>O<sub>2</sub> solution. Finally, this yields in reducing the NO removal efficiency. The latter has a dominant effect so that the removal efficiency finally decreases with the increase of solution temperature. It observed that, as a whole, the solution temperature has small effect on NO removal efficiency. This can be explained based on Arrhenius law which states that activation energies of free radical reactions are very low, and in the case of reaction between free radicals are close to zero. Thus, based on the mentioned law, it can be said that the change of temperature only has a small effect on photochemical reactions.

Liu and Zhang (2011) and Liu, Y. et al. (2010a) investigated the liquid layer heights in ranges from 5.3 to 31.8 cm. The increase of liquid layer height from 5.3 to 15.9 has a great effect on NO removal efficiency. But with further increase to 31.8 cm the NO removal efficiency had only a very slight increase. On the one hand, the increase of liquid layer height resulted in the increase of residence time of pollutants in the reactor so they had adequate time to be oxidized and removed. On the other hand, the reaction between OH radicals and gaseous pollutants (NO) was very fast reaction. Thus, when the reaction time was enough, the removal of NO by UV/H<sub>2</sub>O<sub>2</sub> was mass transfer control process. In this situation, the increase of liquid layer height (residence time) cannot be effective on removal process because this factor has no effect on mass transfer rate.

The effect of presence of O<sub>2</sub> in flue gas is investigated by some researchers and the following side reactions are observed (Liu, Y., et al., 2011; Liu, Y., et al., 2010c):



Oxygen is considered to be a capture intermediate. This gas can consume OH free radicals and produce the oxygen radicals which are strong oxidation agent ( $E_0=2.05$  eV). These radicals transform NO into NO<sub>2</sub> based on Eq.(21). Thus, the presence of appropriate amount of oxygen enhances NO removal efficiency. On the other hand, the oxidation strength of oxygen radicals is smaller than that of OH radicals (2.8 eV). When oxygen consumes OH radicals for producing oxygen radicals, this can reduce the quantity of ·OH free radicals

reacted with the NO. Thus, oxygen had a dual effect on removal efficiency. Liu, Y. et al. (2010c) findings showed that the NO removal efficiency only had a very slight increase when the O<sub>2</sub> content increased from 0% to 6.02% and a very slight decrease with a further increase from 6.02% to 12.45% of O<sub>2</sub> content. As mentioned before, this increase can be explained by producing of oxygen radicals and NO<sub>2</sub> based on Eqs. (20) and (21). But, they mentioned that the decrease is due to much higher solubility of O<sub>2</sub> in H<sub>2</sub>O<sub>2</sub> solution rather than NO. The two-film theory states that when two gases with different solubilities undergo a gas-liquid mass transfer process, the mass transfer situation is favorable for gas with higher solubility. Therefore, when O<sub>2</sub> exceeds from a specified quantity, the competition effect between O<sub>2</sub> and NO in the mass transfer process may be one of the main reasons for the decrease in NO removal efficiency.

Liu, Y., et al. (2014) highlighted the role of oxygen as an effective capture intermediate of OH free radicals. They noted that this can avoid the collision and destruction of OH free radicals with reactor wall or each other, thereby increasing the effective use of OH free radicals. Thus, increasing O<sub>2</sub> concentrations can enhance NO removal efficiency.

The effect of NO concentration was also studied by some researchers (Liu, Y., et al., 2013; Liu, Y., et al., 2014; Liu, Y., et al., 2010c). According to these researchers, the increase of NO concentration in ranges of 200-1000 ppm leads to an increase in removal efficiency from 80 to 60%. They described that the increase of NO concentration increases the amount of NO per unit time which is to be treated in reactor and therefore causes a decrease in the ratio of OH free radicals to NO. But it should be noted that Liu, Y., et al. (2014) paid attention to the increase of the gas-liquid mass transfer driving force of NO due to increasing in its concentration and implied that this can lead to an increase in removal efficiency. However, the effect of former is predominant, and as a whole, the removal efficiency decreases with the increase of NO concentration. Based on Liu, Y., et al. (2013) the effect of the increase in mass transfer driving force is predominant and the NO absorption increases with NO concentration. Liu, Y., et al. (2010c) asserted that this decrease also can be contributed to the exponential decrease in the transmitted light intensity based on Beer-Lambert law (Eq. (19)). This results in a great decrease in effective utilization of UV energy, and finally inhibiting the removal of NO.

A few studies considered the effect of pH on the UV/H<sub>2</sub>O<sub>2</sub> process for simultaneous removal of

SO<sub>2</sub> and NO. For example, Liu, Y. x. & Zhang (2011) investigated the effect of increasing initial solution pH on NO and SO<sub>2</sub> removal efficiencies. Their results revealed that the SO<sub>2</sub> removal was complete under the different pH values. While the NO removal efficiency increases with the increase of solution initial pH. They reported the effect of pH factor was related to several side reactions which result in formation of HO<sub>2</sub>. These species is very effective scavenger of OH free radicals, and it can consume these radicals, finally decreasing the effective utilization rate of OH free radicals. Furthermore, the HO<sub>2</sub> can also enhance self-decomposition of H<sub>2</sub>O<sub>2</sub> to produce H<sub>2</sub>O and O<sub>2</sub>, and consequently reduce the effective utilization rate of H<sub>2</sub>O<sub>2</sub>. Also, it is reported that H<sub>2</sub>O<sub>2</sub> solution has stronger oxidation ability at lower solution pH. So, the increase of solution initial pH can decrease the oxidation ability of H<sub>2</sub>O<sub>2</sub>. On the other hand, with the increase of solution initial pH, OH can cause an acid-base neutralization reaction. The consumption and neutralization of H<sup>+</sup>, which is produced by reactions 8,10,11,12, via this OH finally results in the increase of the gas-liquid reaction absorption rate. Therefore, the increase of pH value has simultaneous negative and positive effects. However, they confirmed that the positive effects were predominant in their study.

Liu, Y., et al. (2010a) described the effect of pH factor from another point of view. They examined the inherent changes of pH value through removal reaction. Nitric acid solution is the main final product from the wet scrubbing of NO with UV/H<sub>2</sub>O<sub>2</sub>. Hence, as the removal reaction progresses, the solution pH will continuously decrease. This continuous change in pH value has simultaneous negative and positive effects. In alkaline media (at upper pH values) because the formation of HO<sub>2</sub> and more oxidation ability of H<sub>2</sub>O<sub>2</sub> (as described by Liu, Y. x. & Zhang (2011)) a continuous decrease in solution pH will be beneficial for the removal of NO and use of H<sub>2</sub>O<sub>2</sub>. On the other hand, with continuous decrease of pH, a large amount of H<sup>+</sup> produced by Eqs. 8,10,11,12 will inhibit the shift of these absorption reactions to the right for the removal of NO, and finally decrease the gas-liquid mass transfer absorption rate.

Liu and Zhang (2011) believed that these two studies confirmed each other. Because of formation of a large amount of H<sup>+</sup> by Eqs. 8,10,11,12 and continuous decrease reaction in solution pH, the increase in initial solution pH can be beneficial for the removal process. As demonstrated by Liu and Zhang (2011) the consumption and neutralization of H<sup>+</sup> via OH



shifts these absorption reactions to the right, and finally increases of the gas-liquid reaction absorption rate.

The effect of presence of SO<sub>2</sub> on removal process has been discussed by (Liu, Y., et al., 2013; Liu, Y., et al., 2014; Liu, Y., et al., 2011; Liu, Y., et al., 2010c). According to these researchers, the NO removal efficiency decreases with an increase in SO<sub>2</sub> initial concentrations. SO<sub>2</sub> can consume a lot of OH free radicals and H<sub>2</sub>O<sub>2</sub> and thereby reducing the available amount of OH free radicals and H<sub>2</sub>O<sub>2</sub> reacted with the NO. However, SO<sub>2</sub> is still removed completely under different initial concentrations of this gas. This is because SO<sub>2</sub> has far larger solubility in H<sub>2</sub>O<sub>2</sub> solution than that of NO. Therefore, the mass transfer is more favorable to the transfer of SO<sub>2</sub> and more quickly enters into the liquid phase reaction zone to react with OH free radicals and H<sub>2</sub>O<sub>2</sub>. Liu, Y., et al. (2010c) considered the hydrolysis reaction of SO<sub>2</sub>. It can be seen that the absorption rate of SO<sub>2</sub>, compared with that of NO, can also be increased by the hydrolysis reactions of SO<sub>2</sub>. Therefore, under all conditions, especially the high concentrations of SO<sub>2</sub>, it is possible that SO<sub>2</sub> has a complete removal.

Liu, Y., et al. (2010a) and Liu, Y., et al. (2010c) and Liu, Y., et al. (2014) studied the different gas flows and discussed the effect this factor on NO removal efficiency. Their results showed that NO removal efficiency significantly decreased with an increase in gas flow rate. On the one hand, an increase in the gas flow enhanced the gas-liquid mass-transfer process and then improved the mass-transfer absorption rate. On the other hand, increasing the gas flow increased the treating amount of NO through the reactor per unit time and reduced the relative molar ratio of absorbent to NO. The latter may play a leading role; therefore, NO removal efficiency decreased with the increase of the gas flow.

Based on author's information, there are few studies related to the kinetic model of NO removal from SO<sub>2</sub>-containing simulated flue gas. Liu et al. (2011) presented a kinetic model for the simultaneous removal NO and SO<sub>2</sub> by UV/H<sub>2</sub>O<sub>2</sub> process without considering the effect of mass transfer process. They implied that the rate of consumption of NO by chemical reaction is described by Eq. (22):

$$r_{NO} = -\frac{d[NO]}{dt} = r_{OH^\bullet} + r_{H_2O_2} + r_{O^\bullet} \quad (22)$$

where  $r_{NO}$ , the total reaction rate of NO removal by the wet UV/H<sub>2</sub>O<sub>2</sub> AOP;  $r_{OH^\bullet}$ , the oxidative removal rate of NO by OH free radicals;  $r_{H_2O_2}$ , the oxidative removal rate of NO

by H<sub>2</sub>O<sub>2</sub>;  $r_{O^\bullet}$ , the oxidative removal rate of NO by O free radicals (when oxygen is present in flue gas).

The first and the latter term in Eq. (22) can be described based on Eqs. (23) and (24), respectively:

$$r_{OH^\bullet} = (k_8 + k_9)[OH^\bullet][NO] \quad (23)$$

$$r_{O^\bullet} = k_{21}[O^\bullet][NO] \quad (24)$$

They suggested that the absorption process of NO in H<sub>2</sub>O<sub>2</sub> solution was a two-order reaction, which was a first-order reaction for H<sub>2</sub>O<sub>2</sub> and NO, respectively. Thus the rate of oxidative removal rate of NO by H<sub>2</sub>O<sub>2</sub> in Eq.(22) can be written as Eq.(25):

$$r_{H_2O_2} = k_{12}[H_2O_2][NO] \quad (25)$$

Based on Eqs. (23) to (25) the total rate of consumption of NO by chemical reaction can be expressed by Eq. (26):

$$r_{NO} = -\frac{d[NO]}{dt} \quad (26)$$

$$= ((k_8 + k_9)[OH^\bullet] + k_{21}[O^\bullet] + k_{12}[H_2O_2])[NO]$$

The intermediates species of HNO<sub>2</sub> and NO<sub>2</sub> have very low concentrations. Also all of the OH, the O and the HSO<sub>3</sub> free radicals usually have very low concentrations because of their very short lifetime. So based on steady-state approximation, the rate of consumption of these species can be considered to be zero. By applying this consumption and after simplifications, the total rate of NO consumption can be described by a pseudo-first order kinetic which can be written as Eqs. (27) and (28). The reader referred to this researchers for more detail about how the equations can be simplified to the Eqs. (27) and (28).

$$r_{NO} = -\frac{d[NO]}{dt} = k_{obs}[NO] \quad (27)$$

$$\ln\left(\frac{[NO]}{[NO]_0}\right) = -k_{obs}t + A_i \Rightarrow y_i = (1 - \eta_{NO,i})$$

$$= \exp(-k_{obs}t + A_i) \quad (28)$$

where,  $k_{obs}$  is term based on  $k_8$ ,  $k_9$ ,  $k_{12}$ ,  $k_{21}$  and initial concentrations of H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, NO, SO<sub>2</sub> and UV irradiation intensity ( $[h\nu]_0$ ).  $A_i$  is a constant corresponded to NO removal efficiencies,  $\eta_{NO,i}$ , under different conditions. They discussed the effect of parameters such as H<sub>2</sub>O<sub>2</sub> initial concentrations, UV lamp power, NO initial concentrations and reaction temperature on values of  $y_i$  and  $A_i$ .

Liu et al. (2013) investigated the mass transfer-reaction kinetics of NO absorption from flue gas by using UV/H<sub>2</sub>O<sub>2</sub>/NaOH process based on two-film theory. They also claimed

that the absorption process of NO from flue gas by using this process was a pseudo-first-order fast reaction with respect to NO. Based on their study, an absorption rate equation can be presented according to Eq. (29) which involves the mass transfer and chemical reaction parameters.

$$N_{NO} = p_{NO,G} \left( \frac{1}{k_{NO,G}} + \frac{1}{H_{NO,L} (k_{ov,1} D_{NO,L})^{1/2}} \right)^{-1} \quad (29)$$

where  $N_{NO}$  is the absorption rate of NO, mol/m<sup>2</sup>s;  $k_{NO,G}$  is the gas phase mass transfer coefficient, mol/sm<sup>2</sup>Pa;  $p_{NO,G}$  is the NO partial pressure in bulk of gas phase, Pa,  $k_{ov,1}$  is the pseudo-first reaction rate constant with respect to NO, s<sup>-1</sup>.  $H_{NO,L}$  is the solubility coefficient of NO in liquid phase, mol/ (L Pa) and  $D_{NO,L}$  is the liquid phase diffusion coefficients of NO. They reported that their kinetic model has an acceptable values of maximal average errors and the calculated kinetic values are in good agreement with experimental data.

#### 4. Conclusion

UV/H<sub>2</sub>O<sub>2</sub> process has been subject of many studies in the air pollution control field in recent years. Table 1 presents the information related to the technologies for SO<sub>2</sub> and NO<sub>x</sub> removal, their advantages and disadvantages. The data given in Table 1 present a brief overview of what has been performed on the topic. It should be noted that this comparison is not flawless as each technique has its own benefits and drawbacks. Selection of a suitable process depends on many factors such as source of pollutant, flue gas temperature, limit of emission, and particularly for NO<sub>x</sub> the composition of this pollutant is also important. As mentioned in previous sections, most studies on UV/H<sub>2</sub>O<sub>2</sub> process for simultaneous

removal of NO and SO<sub>2</sub> have been taken consideration since 2010. This confirmed that this new technology provides several venues for further research. There are some problems that should be coped with ranging from experimental study to mathematical modeling. The change in pH value through the reaction progress is an important issue which is almost understudied. The general effect of this factor on NO removal process is a complex combination of positive and negative effects. To author's knowledge, there is no precise study on the effect pH value on removal process and reaction kinetic. Since the removal of NO and SO<sub>2</sub> by UV/H<sub>2</sub>O<sub>2</sub> is a gas-liquid absorption process with chemical reaction, the gas removal is conducted by cooperative effect of chemical reaction and mass transfer process. Future research in the field can investigate parameters affecting mass transfer, and the effect of mass transfer rate through the existing phases on overall reaction rate and reaction kinetic. So far, there is little information about the reaction mechanisms and kinetics, specifically in conditions in which the mass transfer effect should be considered. The investigation of mass transfer-reaction kinetics of simultaneous absorption of NO and SO<sub>2</sub> is a new and attractive issue. Additionally, the determination of mass transfer coefficient and the factors affecting this coefficient are other interesting venues for further studies. Therefore, more precise studies in this filed are needed to comprehensive understanding and developing of the process.

In modeling filed, there is no comprehensive mathematical model considering all aspects of the process including mass transfer, reaction kinetics, and absorption enhancement by chemical reaction.

**Table 1.** Comparison between some most Common Technologies for SO<sub>2</sub> and NO<sub>x</sub> Removal

Removal Technique	Pollutant	Removal Efficiency (%)	Advantage	Disadvantage
SCR	NO <sub>x</sub>	80-90	NO need to NO <sub>x</sub> transform to another medium	Catalyst poisoning, especially with SO <sub>2</sub> -laden flue gas which is important component of technology cost, high installation cost
SNCR	NO <sub>x</sub>	30-75	Simple process, no need to catalyst, lower operating and installation costs in comparison to SCR,	Low removal efficiency, with its low effectiveness it should be combined by other technologies like combustion modification techniques
Wet-FGD	SO <sub>2</sub> /NO <sub>x</sub>	Up to 90 for SO <sub>2</sub>	Low cost, controlling acid gas and particulate materials at the same time	Not possibility to remove NO
UV/H <sub>2</sub> O <sub>2</sub>	SO <sub>2</sub> /NO <sub>x</sub>	Complete SO <sub>2</sub> removal, up to 80% for NO	Simultaneous removal of NO and SO <sub>2</sub> , no secondary pollution, simple process	Higher chemical cost comparison to SCR depending on H <sub>2</sub> O <sub>2</sub> /NO <sub>x</sub> ratio

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