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Removal of NO\textsubscript{x} and SO\textsubscript{2} in the Coal-fired Flue Gas Using the Low-speed Rotating Packed Bed Pilot Reactor with Peroxymonosulfate activated by Fe(II) and Heating.

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Abstract

An advanced oxidation processes (AOPs) involving the combined Fe(II) ions and heating activation of peroxymonosulfate (PMS) in low-speed rotating packed bed pilot reactor (LRPB) for NO$_x$ and SO$_2$ removal in coal-fired flue gas was proposed. The major influencing factors, radical species, reaction products and mechanism, mass transfer process and kinetic of NO$_x$ and SO$_2$ simultaneous removal were investigated. The results indicated that NO removal efficiency reached at 70% or more, while the SO$_2$ and NO$_2$ were almost completely removed. As the temperature increased, the NO removal efficiency was increased, and the intensity of $\cdot$SO$_4^-$, $\cdot$OH and $\cdot$O$_2$ radicals via PMS activated and $\cdot$NO from radical-radical reaction were enhanced through the electron spin-resonance spectroscopy (ESR) test. Increased liquid flow led to higher NO removal efficiency and increased gas flow played the opposite role. Increased rotational speed caused the NO removal efficiency to be enhanced, and then decreased. Furthermore, the mass transfer coefficient obtained in this LRPB was significantly higher than that of the conventional bubbling reaction. Finally, NO removal processes in the PMS/Fe(II)/LRPB systems was accompanied by fast pseudo-first-order reactions, and was considered to be a fast reaction completed in the liquid film base on liquid-phase reaction utilization efficiency. The intermediate experiment is to further study the main parameters that influence chemical reactions in devices of a certain scale and to solve problems that cannot be solved or discovered in the laboratory.
1. Introduction:

Emission of NO\textsubscript{x} (mainly NO~90%, NO\textsubscript{2}~10%) and SO\textsubscript{2} during coal, fossil fuels and solid waste combustion cause serious damage to the environment (haze, acid rain and eutrophication) and human health (cardiovascular and respiratory diseases).\textsuperscript{1-4} Generally, SO\textsubscript{2} has been effectively controlled using wet flue gas desulfurization (WFGD) process, however, there is no effective measure to control the emission of NO\textsubscript{x} due to the inferior solubility.\textsuperscript{5} Although selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) denitrification technologies have achieved large-scale commercial applications in the field of coal-fired power plants, it cannot be widely used especially small and medium-sized industrial furnaces and boilers due to certain drawbacks such as huge economic burden, large occupying area and hazardous chemical treatment, etc.\textsuperscript{6-8} Therefore, the contamination of NO\textsubscript{x} in air environment has become a great concern in recent years. And considerable researchers in this filed have been attracted to exploring more effective and innovative simultaneous removal of SO\textsubscript{2} and NO\textsubscript{x} technologies, therefore, the liquid oxidants are found can significantly enhance the NO solubility in liquids thereby increasing the removal efficiency of gaseous...
pollutants.\textsuperscript{9-13} Currently, the liquid oxidants commonly employed are peroxymonosulfate (PMS), \(\text{KMnO}_4\), persulfate (PS), \(\text{H}_2\text{O}_2\) and sodium chlorite (NaClO\(_2\)) etc.\textsuperscript{14-18} Among these oxidation absorbents, PMS seems to be more attractive. PMS is a cost-effective and environmentally friendly oxidant base on some excellent properties such as strong oxidative, non-selective behavior, relatively stability at room temperature and lower energy input.\textsuperscript{19-23} In general, heating, UV or transition metal ions can effectively activate PMS to create \(\text{SO}_4^{2-}\), \(\cdot\text{OH}\) and \(\text{O}_2\) radicals.\textsuperscript{24,25} During the past years it has been found that the three kinds of radicals display the strong oxidation-reduction potential which will enhance the oxidation performance thereby ultimately elevate contaminants decontamination efficiency.\textsuperscript{26,27} Furthermore, various research groups have studied the reaction of NO with liquid strong oxidant using different reactor configurations and experimental conditions. Those studies indicated that the absorption rate was strongly affected by mass transfer limitation of oxidation system due to the high reaction rate in these traditional reactors, such as stirred cell and bubble column.\textsuperscript{12,23} As mentioned above, the performance of PMS activated by heating and Fe(II) ions investigated by our group is generally restricted by the mass transfer rate especially for the inferior solubility NO. To overcome this obstacle, we have designed a rotating packed bed with PMS/Fe(II) oxidation system to boost the mass transfer efficiency, thereby enhancing NO removal efficiency. The rotating packed bed is a type of high-efficiency mass transfer equipment, because when the fluid flows through the filler it is smashed into rich ultrafine droplets by the strong shear forces, this increases the interface area of the reaction, resulting in a massive improvement in mass transfer, reaction and micro-mixing between the gas-liquid phase.\textsuperscript{28,29} Simultaneously, it has stable operation, small equipment, low energy consumption and investment, which has shown their unique advantages in waste gas absorption treatment.\textsuperscript{30-32} Since
the higher rotating speed may broken the liquid seal, this will result in the flue gas might through reactor without reaction or a reaction in reduced contact time, resulting in reduced NO removal efficiency and high energy consumption, so the low speed rotating packed bad is designed and used.

To the best of our knowledge, this article should be considered an innovative and effective study integrating low-speed rotating packed bad pilot reactor, strong oxidizer, catalysis and high temperature to systematically investigate the NO absorption removal process in coal-fired flue gas. The objectives of the study are to (1) calculate mass transfer coefficient of NO removal in the PMS/Fe(II)/LRPB system; (2) evaluate the mass transfer performance of the LRPB with traditional bubble reactor; (3) investigate the NO removal efficiency in the PMS/Fe(II)/LRPB system at the different reaction conditions; (4) study the absorption kinetics of NO removal, in term of the reaction order and liquid-phase reaction utilization efficiency.

2. Materials and methods.

![Fig.1. Schematic design of the low-speed rotating packed bed pilot reactor used for removing NO from coal-fired flue gas.](image-url)

2.1. Procedure and apparatus.

The experimental setup for NO removal was schematically shown in Fig. 1. The apparatus was mainly composed of a flue gas supply system, a gas-liquid reaction system, a measurement system and an exhaust gas treatment system.

The flue gas for experiment was coal-fired flue gas from the small boiler. The main gas composition were NO, NO$_2$, SO$_2$, CO and CO$_2$, and the concentrations of those were measured by the inlet and outlet flue gas analyzer. The flue gas flow rate was 0.112-0.255 m$^3$/s, and the concentrations and flows were regulated by the flow velocity meter. The key part of reactor was a vertical rotating packed bed with a height of 1.0 m, an inner diameter of 0.9 m, which was packed the filler. The filler used in this work was a stainless steel wire mesh having a diameter of 0.2 mm and was wound around in the rotor of the LRPB. The pilot reactor with the low rotating speed varying from 500 to 1000r/min, and the rotating speed was measured using a Dc motor speed measuring instrument. The rotor was installed throughout the reactor and connected to the motor.

The PMS/Fe(II) solution with the molar ratio 1:1 was introduced via the pump from the solution storage tank and injected into the inner side of the packed bed from a liquid distributor. Then, the liquid stream traveled radially in the packed bed and was smashed into rich ultrafine droplets by the strong shear forces due to centrifugal force, then, exited from the lateral export, and flowed back to solution storage tank. Simultaneously, the coal-fired flue gas flowed into the LRPB pilot reactor as well. The gas stream flowed inward from the outside of the packed bed by the pressure driving force, and reacted with the PMS/Fe(II) oxidation liquid, then, was discharged through the gas outlet. Oxidation liquid for
experiments was carried out in the 22-80°C range, and temperature setting was maintained by the heater until the temperature reached desired level and stabilizing.

The exit gas from the reactor passed through a solid dryer prior to analysis to remove moisture. The data was recorded when the flue gas after the reaction flowed through the flue gas analyzer of outlet. Exhaust gas could be further processed by the exhaust gas absorber. The pH probe was used for pH measurement.

2.2. Analytical method.

The flue gas analyzers (ZR-3710D) are used to measure the inlet and outlet concentrations of gas. The ion chromatography (IC, CIC-300) is used to measure NO$_3^-$, NO$_2^-$ and SO$_4^{2-}$ in PMS/Fe(II)/LRPB system. The pH meter (SIN-pH120) is used to measure the initial and final pH value. The SO$_4^{2-}$, 'OH, $^1$O$_2$ and 'NO radicals are detected by the electron spin-resonance spectroscopy (Bruker ESP-A300) combining with the spin trap of 5,5-Dimethyl-1-pyrrolidine N-Oxide (DMPO), 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and imidazole nitrooxide (IN), respectively.

3 Results and discussion.

3.1 Mass transfer coefficient of gas in solution.

In order to quantitatively characterize the mass transfer process of NO removal in the PMS/Fe(II)/LRPB system, the gas–liquid mass transfer coefficient which is evaluated as the basis of the kinetics for investigation. The NO gas absorbed and oxidation by the PMS liquid undergoes a moderately fast pseudo-first-order reaction process (the hypothesis will be proved in the back). Therefore the classical Danckwerts absorption system method can be employed to derive the mass transfer coefficients in the gas phase and liquid phase through the conversion the CO$_2$ system to NO system are as follows (1) - (3).
\[ k_{NO,G} = k_{CO_2,G} \left( \frac{D_{NO \cdot N_2}}{D_{CO_2 \cdot N_2}} \right)^m \]  
(1)

\[ k_{NO,L} = k_{CO_2,L} \left( \frac{D_{NO \cdot H_2O}}{D_{CO_2 \cdot H_2O}} \right)^m \]  
(2)

\[ a_{CO_2} = a_{NO} \]  
(3)

Where, \( k_{NO,G} \) and \( k_{NO,L} \) are the gas phase and liquid phase mass transfer coefficients of NO respectively, (m/s); \( k_{CO_2,G} \) and \( k_{CO_2,L} \) are the gas phase and liquid phase mass transfer coefficients of CO\(_2\) respectively, (m/s); \( D_{NO \cdot N_2} \) and \( D_{NO \cdot H_2O} \) are the diffusion coefficients in N\(_2\) gas and water of NO respectively, (m\(^2\)/s); \( D_{CO_2 \cdot N_2} \) and \( D_{CO_2 \cdot H_2O} \) are the diffusion coefficients in N\(_2\) and water of CO\(_2\) respectively, (m\(^2\)/s); in general \( m = 0.5 \sim 1.0 \), Sada et al think \( m = 2/3 \), take 2.3 in this paper;\(^{36,37}\)

\( a_{CO_2} \) and \( a_{NO} \) are the specific interfacial areas of CO\(_2\) and NO, respectively, m\(^{-1}\).

\[ D_{AB} = 0.00266 \frac{T^{1.5}}{P^0.5} \left( \frac{\rho_{AB} \mu_{AB}}{\eta_{AB}} \right) \]  
(4)

Where, \( M_A \) and \( M_B \) stand for the molecular weights, \( M_{AB} = \frac{2}{\frac{M_A}{\rho_A} + \frac{M_B}{\rho_B}} \), g/mol. T is the temperature in Kelvin, K; P is the pressure (atm); \( \sigma_{AB} \) stands for the characteristic length, \( \sigma_{CO_2} = 3.941 \), \( \sigma_{NO} = 3.492 \), \( \sigma_{N_2} = 3.798 \);\(^{38}\) and \( \Omega \) stands for the collision integral which can be calculated by the Eqs. (S1)-(S3) in the SI.

\[ D_{CO_2 \cdot H_2O} \] \( \text{and} \) \( D_{NO \cdot H_2O} \) can be estimated by the following Eq. (5);\(^{33-35}\)

\[ D_{gas \cdot H_2O} = 7.4 \times 10^{-12} \frac{T^{(x_{H_2O} - 1)} \rho_{H_2O}^{X_{H_2O}}}{\nu_{H_2O} \rho_{H_2O}} \]  
(5)

Here, \( V_{NO} \) and \( V_{CO_2} \) stand for the molar volume of NO and CO\(_2\), which are 23.6 and 34, respectively, cm\(^3\)/mol; \( X \) stands for the association factor, \( x_{H_2O} = 2.6 \), other non-association factors \( x = 1 \); \( \nu_{H_2O} \) stands for the kinetic Newtonian viscosities of water, Pa \( \cdot \) s.

In a conventional reactor, as a bubbler reactor, the liquid phase mass transfer coefficient of the NO removal reaction reported in the literature was approximately \( 10^{-5} \sim 10^{-4} \) m/s, such as Liu et al
In this research, the liquid phase mass transfer coefficient of the denitrification process with the LRPB pilot reactor measured was $8.612 \times 10^{-3}$ m/s (Table 1).

Base on this result, we could conclude that compared to the conventional bubbler reactor, the supermass transfer coefficient of the liquid phase in the LRPB was increased by about one order of magnitude, which indicated that the LRPB showed a very obvious strengthening effect on the absorption process. According to the previous study, at 343 K, the apparent rate constant of the NO removal reaction with the PMS solution was around $10^3$~$10^4$ s$^{-1}$, which was much larger than the mass transfer rate $8.612 \times 10^{-3}$ m/s by comparison. Therefore, it was stated that the mass transfer process was a key parameter in controlling the NO removal process in the PMS/Fe(II) oxidation system, and the NO removal efficiency could increase with increasing of the mass transfer coefficient.

According to the previous comparison results, the LRPB of this research could improve the performance of mass transfer process. Thus we used the PMS/Fe(II)/LRPB oxidation system to further optimize the process of removing NO in the coal-fired exhaust gas, thereby improved the NO removal efficiency.

### 3.2 Influence of temperature.

### 3.2.1 Effect of temperature on removal Efficiency.

Fig. 2 revealed the effect of PMS liquid temperature on NO removal efficiency. With the increasing temperature from 22 ℃ to 80 ℃, the NO removal efficiency had a remarkable advance from 23.2% to 78.6%, and the peak was found to occur at the temperature around 70 ℃, then a tendency to stabilize appears on 70 ℃ to 80 ℃. Compared with NO, NO$_2$ and SO$_2$ were almost completely removed at all reaction temperatures because of their very high solubility and relatively high reactivity in solution. In addition, high temperature could reduce reaction free energy and increase the activity of Fe(II) ions to...
promote the progress of the catalytic reaction, accelerating the generation of free radicals to achieve an
effect of increasing the NO removal efficiency. The main reaction pathways were listed as follows
(Eqs.(6)-(18)). \(^{10,23,39}\)

\begin{align}
\text{(6)} & & \text{Fe}^{2+} + \text{HSO}_3^- \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{OH}^- \\
\text{(7)} & & \text{NO} + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{NO}_2 + \text{H}^+ \\
\text{(8)} & & \text{NO} + \cdot \text{OH} \rightarrow \text{NO}_2 + \cdot \text{H}^+ \\
\text{(9)} & & 2\text{NO} + 3\text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + 2\text{NO}_3^- + 2\text{SO}_4^{2-} + 4\text{H}^+ \\
\text{(10)} & & \cdot \text{O}_2 + 2\text{NO} \rightarrow 2\text{NO}_2 \\
\text{(11)} & & \text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \cdot \text{H}^+ \\
\text{(12)} & & \text{HSO}_3^- \leftrightarrow \text{SO}_3^{2-} + \cdot \text{H}^+ \\
\text{(13)} & & \text{SO}_3^{2-} + \cdot \text{OH} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH}^- \\
\text{(14)} & & \text{SO}_3^{2-} + 2\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HSO}_4^- + \text{SO}_4^{2-} \\
\text{(15)} & & \text{SO}_3^{2-} + \text{HSO}_5^- \rightarrow 2\text{SO}_4^{2-} + \cdot \text{H}^+ \\
\text{(16)} & & 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\cdot \text{H}^+ + 2\text{NO}_3^- + \text{NO} \\
\text{(17)} & & \text{NO}_2 + \cdot \text{OH} \rightarrow \cdot \text{H}^+ + \text{NO}_3^- \\
\text{(18)} & & \text{NO}_2 + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{HSO}_4^- \\
\end{align}

However, the removal efficiency of NO slightly reduced with the temperature increased from 70 to 80 °C. According to our previous studies, if the liquid temperature was higher than 65 °C, PMS would be liable to decompose and release oxygen and potassium sulfate. This occasion hindered the production of free radicals, resulting in a decrease in the removal efficiency of target pollutants. Base on the kinetics, when the temperature was from 22 to 80°C, the liquid phase mass transfer coefficient that played a positive role in the NO removal increased significantly (as shown in Table 1).
This was because the diffusion coefficient was proportional to the temperature, and inversely proportional to the viscosity. Both increasing the temperature and decreasing the viscosity of the ionic liquid would promote the increase of the diffusion coefficient $D_{NO,L}$ of NO in the solution base on the Eq. (5), accompany by the increase of $K_{NO,L}$. Moreover, the temperature elevated was beneficial to the diffusion process of NO in the PMS/Fe(II) system, and the resistance of the gas-liquid mass transfer process was reduced through $D_{NO,L}$ increased. In the end, the liquid phase mass transfer coefficient $K_{NO,L}$ increased with temperature elevated, which resulted an increasing in the NO removal efficiency.

Base on the thermodynamics, the NO solubility in the absorption liquid decreased with increasing temperature; meanwhile, the NO absorption reaction was an exothermic reaction, and increasing the temperature caused the chemical equilibrium to move toward the reverse reaction. These were not conducive to the NO removal.\textsuperscript{40} It could be seen from the experimental results that the effect on the thermodynamics was more obvious after the temperature was raised to 80 °C, thus the NO removal efficiency did not rise further but tends to be constant in Fig. 2.

**Fig.2.** Effect of temperature on NO\textsubscript{x} and SO\textsubscript{2} removal in the coal-fired flue gas using the PMS/Fe(II)/LRPB system. Conditions: pH = 3.0; $C_{PMS} = 10$ mmol/L; $Q_G = 0.17$~$0.18$ m\textsuperscript{3}/s; $Q_L$
= 1.9~2.0 L/s and RCF =322 g.

Table 1. The mass transfer coefficients of NO in gas and liquid phase at the different parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( k_{NO,L} \times 10^3 )</th>
<th>( k_{NO,G} \times 10^4 )</th>
<th>( a_{NO} )</th>
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<td></td>
<td>m/s</td>
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<tr>
<td>0.255</td>
<td>10.219</td>
<td>18.435</td>
<td>3404.89</td>
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3.2.2. Intensity of free radicals changes with temperature.

From the obtained data, it was seen that increasing temperature had a significant positive influence on NO removal, another reason was temperature increasing could active PMS solution to dissolve more \( \text{SO}_4^{2-} \), 'OH and \( \text{O}_2 \) radicals (Eqs. 19 and 20).\(^{23}\) The \( \text{SO}_4^{2-} \) and 'OH radicals intensity increased twice, and radical \( \text{O}_2 \) intensity increased by about five times from the ESR spectra in Fig. 3.

\[ \text{HSO}_5^- + \text{heat} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} \]  
(19)

\[ \text{HSO}_5^- + \text{SO}_3^{2-} \rightarrow \text{HSO}_4^- + \text{SO}_4^{2-} + \cdot \text{O}_2 \]  
(20)

According to our previous research, electron transfer occurred between NO and free radicals in PMS/Fe(II) oxidation system to generate nitric oxide radical ('NO), then it reacted with molecular oxygen dissolved in solution instantaneously to form \( \cdot \text{NO}_2 \) radical via a radical-radical reaction,
accompanied by generation of nitrate ions $\text{NO}_3^-$ and nitrite $\text{NO}_2^-$ via the reaction of $\bullet\text{NO}_2$ and $\text{H}_2\text{O}$ (Eqs. (21)-(23)).

\begin{align*}
\text{NO} + \text{SO}_4^{2-} \rightarrow & \bullet\text{NO} + \text{SO}_4^{2-} & (21) \\
2\bullet\text{NO}_2 \rightleftharpoons & \text{N}_2\text{O}_4 \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+ & (23)
\end{align*}

As shown in Fig. 4, it was desirable that the peaks of the $\bullet\text{NO}$ radicals were detected by the ESR test in the PMS/Fe(II)/LRPB system at the room temperature 22 °C and 70 °C with spin probe imidazole nitroxide (IN) selected as the spin probe to capture $\bullet\text{NO}$ radicals. The iconic nine peaks of the $\bullet\text{NO}$ radical were clearly detected base on NO in the liquid in an unsaturated state, and the hyperfine splitting constants were the $a_N=0.42$ mT and $g=0.94$ mT at the 22 °C, with the $a_N=0.4$ mT and $g=0.9$ mT at the 70 °C respectively, which agreed with the previous literature parameters the $a_N=0.44$ mT and $g=0.98$ Mt. The typical nine peaks of $\bullet\text{NO}$ in ESR spectrum and two sets of data provided a powerful evidence for a formation of an imidazole -$\bullet\text{NO}$ compound. This indicated that there was $\bullet\text{NO}$ radical production during the reaction process at the different temperature. Meanwhile, the signal intensity of $\bullet\text{NO}$ radicals at 70 °C was twice that of $\bullet\text{NO}$ at 22 °C, which strongly demonstrated increase temperature not only promoted the mass production of $\text{SO}_4^{2-}$, $\cdot\text{OH}$ and $\cdot\text{O}_2$ radicals, but also promoted the output of $\bullet\text{NO}$ radicals that had the higher activity than NO gas to react with the radicals. Thus increased temperature was more conducive to the reaction between $\bullet\text{NO}$ and free radicals, which fundamentally strengthened the removal reaction of NO. This was one of the reasons why the NO removal efficiency increased with temperature as well.
Fig. 3. ESR spectra of $\cdot$SO$_4^-$, $\cdot$OH and $^1$O$_2$ free radicals trapping by DMPO and TEMPO are shown in the PMS/Fe(II)/LRPB system at the room temperature 22 °C and 70 °C, respectively (solid quadrilateral represents the DMPO - $\cdot$SO$_4^-$, hollow quadrangle represents the DMPO - $\cdot$OH, and circle represents the TEMPO - $^1$O$_2$).

Fig. 4. ESR spectra of $\cdot$NO radical trapping by IN shown in the PMS/Fe(II)/LRPB system (a) at the 22 °C (b) at the 70 °C temperature.

3.3 Influence of rotating speed.
Since the centrifugal force is not only a function of the rotational speed but also a function of the centrifugal radius, that is, the longer the centrifugal radius, the greater the centrifugal force generated. Therefore, it is not scientific enough to express centrifugal force only at the rotational speed. In recent years, it has been reasonable to use relative centrifugal force (RCF). The gravitational acceleration equation for rotating equipment is converted to equation (24):

\[ g = \omega^2 r \]

\[ RCF = 0.00001118 \times r \times N^2 \] (24)

Where, RCF represents the relative centrifugal force, \( g \) (\( g=9.8 \text{m/s}^2 \)); \( N \) represents the rotational speed in revolutions per minute, rpm; \( r \) represents the centrifugal radius, ie the distance from the bottom end of the centrifuge tube to the axis, cm.

In order to maintain an excellent low-speed environment, controlled the rotational speed at 500 to 1000 rpm for the experiment, which ensured that the low-speed level generated in the LRPB reactor was 125.8 g to 503.1 g. As shown in Fig. 5, the highest removal efficiency was 78.6% under the low-speed level of 322 g with a gas flow rate of 0.17-0.18 \( \text{m}^3/\text{s} \). It was noted that the preferable the low-speed level of the highest NO removal efficiency was around 322 g. When the rotation speed exceeded 322 g, the NO removal rate started to decline, indicating that the positive effect of the rotational speed on NO removal efficiency began to decrease as well. This observation was close to that investigated by Pei et al.\(^{42}\) Direct support was available for the conclusions that, the high rotating speeds would accelerate the formation of smaller droplets and thinner films, which resulting in an increase of the gas–liquid mass transfer rate, accompanied by a continuous rising state in the NO removal efficiency. Afterwards, due to the excessive rotating speed, the liquid seal might be broken such that the flue gas flew through the LRPB without reaction or a reaction in reduced contact time,
which caused the reduction of NO removal efficiency.\textsuperscript{42-44} In addition, NO\textsubscript{2} and SO\textsubscript{2} achieved a removal rate of 95% and complete removal, respectively.

On the other hand, from the perspective of mass transfer process, the varying NO removal efficiency was analyzed under various velocity of rotation. The mass transfer resistance decreased with the increase of the rotating speed, which could accelerate the mass transfer process. And with the increase of rotating speed, the liquid phase shocked on the surface of the filler into lots of finer droplets and the liquid droplets surface was updated faster, which increase gas-liquid contact area to promote the mass transfer process. The above reasons might increase NO removal efficiency.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Effect of low-speed on NO\textsubscript{x} and SO\textsubscript{2} removal in the coal-fired flue gas using the PMS/Fe(II)/LRPB system. Conditions: pH = 3.0; C\textsubscript{PMS} = 10 mmol/L; Q\textsubscript{G} = 170~180 m\textsuperscript{3}/s; Q\textsubscript{L} = 1.9~2.0 L/s and Temperature\textsuperscript{o} = 70 °C.}
\end{figure}

\subsection*{3.4 Influence of liquid flow.}

As shown in Fig. 6, obviously, the NO removal efficiency had a steady rise with the increase of PMS liquid flow. The process of NO\textsubscript{2} achieved a higher removal efficiency and SO\textsubscript{2} was complete
removal. As the liquid flow rate increased, the gas-liquid flow ratio became smaller causing an increase
in the oxidizing liquid to which the unit volume of gas was distributed, which was equivalent to adding
the oxidizing power of liquid, thereby promoting the removal of NO.\textsuperscript{40,44} In addition, when the liquid
flow rate increased, the sturdiness of the liquid film was enhanced, resulting in a decrease in mass
transfer resistance of liquid phase and promoting the NO absorption process.

Furthermore, since the enhancement of liquid phase mass transfer coefficient $K_{NO,L}$ was
accompanied with the mass transfer process promoted, so the NO removal efficiency increased. This
phenomenon shall be ascribed to increasing liquid flow resulted from the thinning boundary layer,
which reduced the mass transfer resistance on the liquid side, and promoted the gas-liquid mass
transfer, thereby benefiting for the increase of $K_{NO,L}$ to elevate NO removal efficiency.\textsuperscript{40,42,45}

Subsequently, as the enhancement of chemical reactions, mass transfer step might gradually start to
play a momentous role as well. Therefore, as the liquid flow further increase, the growth of NO
removal efficiency gradually flattened.\textsuperscript{46}

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**Fig. 6.** Effect of liquid flow on NO\textsubscript{x} and SO\textsubscript{2} removal in the coal-fired flue gas using the
319 PMS/Fe(II)/LRPB system. Conditions: pH = 3.0; C_{PMS} = 10 mmol/L; Q_{G} = 0.17~0.18 m³/s; RCF
320 =322 g and Temperature=70 ℃.

321 3.5. Influence of gas flow.

322 As could be seen from the Fig. 7, the NO removal emerged a significantly downward trend with the
323 increase of gas flow from 0.112 m³/s to 0.255 m³/s. This could be explained by an increase in the gas
324 flow rate was equivalent to a decrease in the liquid oxidant, reducing the oxidizing power of liquid, and
325 shortening the gas-liquid contact time. With the increase of gas flow, the liquid phase mass transfer
326 coefficient $K_{NOL}$ slightly increased due to the surface of liquid droplets and films constantly updated
327 (Table. 1), however, which was not sufficient to counteract the effect of increased gas flow on the NO
328 removal. The NO removal in the PMS solution was a process of liquid phase mass transfer control, and
329 $K_{NOL}$ played a dominant role in the entire mass transfer process. Therefore, increasing the gas flow had
330 a very little effect on the $K_{NOL}$, which not enough to influence the general trend of NO removal. On
331 the contrary, there was no significant reduction in the removal efficiency of NO₂, and SO₂ could still
332 be completely removed.

333 \[\text{Fig. 7. Effect of gas flow on NO}_x\text{ and SO}_2\text{ removal in the coal-fired flue gas using the}\]
PMS/Fe(II)/LRPB system. Conditions: $\text{pH} = 3.0$; $C_{\text{PMS}} = 10 \text{ mmol/L}$; Temperature = $70 ^\circ \text{C}$; $Q_L$ = 1.9~2.0 L/s and RCF = 322 g.

3.6. The kinetics of NO removal in the PMS/Fe(II)/LRPB system.

3.6.1. The reaction order.

In order to further strengthen the NO removal process, the effect of PMS concentration on NO removal was investigated and the kinetics of absorption reaction was studied. These investigat results would provide more systematic and comprehensive technical parameters for amplification industrial experiments.

The overall reaction equation between PMS and NO can be described by Eq. (25):

$$\text{HSO}_5^- + \text{NO} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{NO}_3^- + 3\text{H}^+$$  \hspace{1cm} (25)

Base on the Eq. (25), the NO removal chemical reaction rate equation can be expressed as follows:

$$r_{\text{NO}} = k_{m,n} C_{\text{NO},i} C_{\text{PMS}}$$  \hspace{1cm} (26)

Where, $k_{m,n}$ is the reaction rate constant, $s^{-1}$ or $M^{-1}$ s$^{-1}$; $C_{\text{NO},i}$ is interface concentration of NO, mol/L; $m$ and $n$ are the partial reaction order for NO and PMS, respectively; H$_2$O as a solvent, its concentration is generally considered to be a constant, so it is not within the scope of investigation in this study.$^{23,47}$ Establish a mass transfer rate equation based on the double membrane theory:

$$N_{\text{NO}} = k_{\text{NO},L} (C_{\text{NO},L} - C_{\text{NO},i})$$  \hspace{1cm} (27)

Where, $N_{\text{NO}}$ is the mass transfer rate of NO, mol/(m$^2$s); $C_{\text{NO},L}$ is the concentration of NO in liquid phase, mol/L.

According to the mass transfer rate equation (27) and Henry's law, the expression of $C_{\text{NO},i}$ can be derived as:

$$C_{\text{NO},i} = H_{\text{NO},L} (\frac{N_{\text{NO}}}{k_{\text{NO},L}})$$  \hspace{1cm} (28)
Where, $H_{NO,L}$ solubility coefficient of NO in liquid phase can be calculated by the Henry’s law,

$$H_{NO,L} = \frac{N_{NO}}{k_{NO}} \text{ mol/(L·Pa)};$$

is the gas partial pressure of NO in gas phase body, Pa; Based on the order analysis method, as the $P_{NO,G}$ can be omitted and deleted approximatively. So $N_{NO}k_{NO,G}$ can be approximated as $10^{-2} \sim 10^{-5}$ \( \ll P_{NO,G} \). The Eq. (28) can be simplified to Eq. (29):

$$C_{NO,i} = H_{NO,L} P_{NO,G}$$

To determine the m and n value, the absorption rate of NO in PMS solution can be described as follows on account of double membrane theoretical and reaction rate equation (30):

$$N_{NO,L} = \left(\frac{2k_{m,n,D_{NO,L}}C_{PMS}^{n/2}}{m+1}\right)^{1/2}$$

By making the logarithm on both sides of Eq (30), the relationship between ln $N_{NO,L}$ and ln $C_{NO,I}$ can be obtained.

$$\ln N_{NO,L} = \frac{1}{2} \ln \left(\frac{2k_{m,n,D_{NO,L}}C_{PMS}^{n/2}}{m+1}\right) + \frac{m+1}{2} \ln(C_{NO,I})$$

Based on the data of NO and PMS concentration versus NO removal efficiency and the Eqs. 30 and 31, ln $N_{NO,L}$ and ln $C_{NO,I}$ were fitted to a straight line with the good correlation coefficients of 0.987 and 0.971, respectively (Fig. 8 (a)). Two fitted line slopes ($m_{NO/350}+1$) / 2 = 0.939 and ($m_{NO/500}+1$) / 2 = 1.092. This was, $m_{NO/350}$=0.8781=1.0 and $m_{NO/500}$=1.184=1.0. Therefore, NO removal process in the PMS/Fe(II)/LRPB system could be regarded as a pseudo first-order reaction under the import NO concentration 350 mg/m$^3$ and 500 mg/m$^3$, respectively.

The value of N could be determined according to $m=1$, through converting Eq.(31) to Eq.(32), and fitting $\ln \frac{N_{NO,L}}{C_{NO,I}}$ and $\ln C_{PMS}$.

$$\ln \frac{N_{NO,L}}{C_{NO,I}} = \frac{1}{2} \ln \left(k_{m,n,D_{NO,L}}\right) + \frac{n}{2} \ln(C_{PMS})$$

As shown in Fig. 8 (b), ln $N_{NO,L}/C_{NO,I}$ and ln $C_{PMS}$ are fitted to a straight line with the good correlation coefficients of 0.980 and 0.977, respectively. Two fitted line slopes were $n_{NO/350}/2 = 0.91$ and $n_{NO/500}/2 = 0.92$. Therefore, NO removal process in the PMS/Fe(II)/LRPB system could be regarded as a pseudo first-order reaction.
and $n_{NO/350} = 1.82$ with $n_{NO/500} = 1.08$ and $n_{NO/500} = 2.16$. Therefore, according to the reaction order of the PMS, it could be considered that the NO absorbing reaction in the PMS/Fe(II)/LRPB system was pseudo-1.82-order reaction under the import NO concentration 350 mg/m$^3$, and the reaction of absorbing NO in the PMS/Fe(II)/LRPB system was pseudo-2.16-order reaction under the import NO concentration 500 mg/m$^3$, respectively.

![Logarithmic fit of $N_{NO,L}$ and $C_{NO,l}$](image)

**Fig. 8.** (a) Logarithmic fit of $N_{NO,L}$ and $C_{NO,l}$ (b) Logarithmic fit of $\frac{N_{NO,L}}{C_{NO,l}}$ and $C_{PMS}$, under the import NO concentration 350 mg/m$^3$ and 500 mg/m$^3$, respectively.

### 3.6.2. Liquid-phase reaction utilization efficiency.

Further study of gas-liquid reaction kinetics on the basis of liquid-phase utilization efficiency, and measurement of liquid-phase utilization efficiency can be estimated by means of the following Eq. (33).

$$\eta = \frac{\frac{\sqrt{M(\alpha - 1)} + \theta M}{\alpha M[(\alpha - 1)\sqrt{M} + 1]}}{\frac{\sqrt{M(\alpha - 1)} + \theta M}{\alpha M[(\alpha - 1)\sqrt{M} + 1]] (33)}}$$

where, $\alpha$ is the ratio of liquid to liquid film thickness, $m$; $M$, the dimensionless number (Hatta number), indicates the ratio of the reaction rate to the mass transfer rate in the liquid phase.
According to our and previous studies, the NO removal reaction with PMS solution has a fast reaction,\textsuperscript{23,41} so M was much larger than 1, ie \( \theta \sqrt{M} \) tend to 1. Eq. (33) could be simplified to Eq. (34)

\[
\eta = \frac{1}{\alpha M}.
\]

(34)

Since \( \alpha \) stands for the ratio of liquid to liquid film thickness and is much greater than 1 (in general, \( \alpha \) was between 10-10\textsuperscript{4} and M value is much larger than 1. Hence \( \eta \) is a very small value, closes to 0, which further indicates that NO removal reaction using the innovative PMS/Fe(II)/LRPB system can be regarded the reaction process is completed in the liquid film, and the average reaction concentration of liquid phase approaches to 0.

4. conclusions.

In this study, using of the AOPs in the PMS/Fe(II)/LRPB system for multi-pollutants (NO, NO\textsubscript{2} and SO\textsubscript{2}) reductions in coal-fired flue gas obtained the well removal effect. The results indicated that the NO reached a removal efficiency of 70% or more, while the SO\textsubscript{2} and NO\textsubscript{2} were almost completely removed and were hardly affected by other parameters varying. Both increased temperature and liquid flow led to increased the conversions of NO in the PMS/Fe(II)/LRPB system. The increased rotational speed caused the NO removal efficiency to be enhanced, when the super-gravity level reached to 322 g, the removal efficiency obtained the maximum value, and then a slight drop occur. Nevertheless, increased gas flow led to lower NO removal efficiency. Furthermore, the mass transfer coefficient obtained according to the classical Danckwerts absorption system method was significantly higher than that of the conventional bubbling reaction, indicating that NO removal reaction had the better mass transfer process in the PMS/Fe(II)/LRPB system. Finally, NO removal processes in the investigated PMS/Fe(II)/LRPB oxidation systems was accompanied by the pseudo-first-order reactions, and was considered to be a fast reaction with the reaction process completed in the liquid film base on
liquid-phase reaction utilization efficiency. In summary, this research conducted a pilot study on the reaction mechanism, gas-liquid mass transfer and kinetics in the absorption process of NO and PMS activated by Fe(II)/heating in low-speed rotating environment. On this basis, the reaction parameters were optimized, which was to provide theoretical basis and support for industrial application.

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Supporting Material

Calculation methods, equations of physical and mass transfer parameters were added in the supporting material.

Reference:


2245–2256.


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