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Enhanced absorption process of NO_2 in $CaSO_3$ slurry by the addition of $MgSO_4$

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ABSTRACT

In this study, $CaSO_3$, the by-product of flue gas desulfurization (FGD) process, was used as an absorbent for NO_2 absorption. As the $CaSO_3$ content exceeded 0.1 mol L^{-1}, the absorption efficiency of NO_2 could reach more than 70%. Three types of additives, $MgSO_4$, Na_2SO_4 and $MgCl_2$, were also investigated for the enhancement of NO_2 absorption, and it was found that $MgSO_4$ was the most effective. When $MgSO_4$ was added, the NO_2 absorption efficiency could increase significantly from 70.8% to 86.0%, and the oxidation rate of $CaSO_3$ became around 10 times higher than that of additive free condition. Furthermore, the addition of $MgSO_4$ would also lead to the raise in the ratio of NO_2^- to the total NO_2 absorption products. All these aspects could be ascribed to the increment of the capacity of dissolved sulfite species (CDSS) which resulted from the combined effects of SO_4^{2-} and Mg^{2+}. Firstly, SO_4^{2-} would react with Ca^{2+} and promote the dissolution of $CaSO_3$, resulting in the increase of CDSS. And then the neutral $MgSO_3^0$ ion pair would form in the absorbent slurry, which could play the same role as dissociated SO_3^{2-} in the NO_2 absorption.

1. Introduction

The emission of NO*x* remains one of the major environmental concerns because they are associated with acid deposition, photochemical smog and ozone depletion. Wet scrubbing process promises to be less expensive than other techniques for NO*x* removal, such as selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) and combustion modification [1]. However, the main component (85–95%) of NO*x* in flue gases is NO, which is of low solubility and reactivity. Thus, it is necessary to oxidize NO to NO_2 before scrubbing [2]. Consequently, many oxidation–absorption combined processes have been studied extensively [2–4].

A variety of methods have been developed for NO oxidation, including strong oxidizing agent injection (e.g., ozone, hydrogen peroxide and chlorine dioxide) [2,5–7], selective catalytic oxidation [8,9], photocatalytic oxidation [3,10,11], and so on. As for the subsequent absorption process, many absorbents (such as water, acid solutions, basic solutions and reducing agents) have been investigated [12–16]. Among them, reducing absorbents including Na_2SO_3 and Na_2S seem to be most effective and have garnered extensive attentions. However, large extra consumption of these reducing absorbents usually occurs inevitably due to the presence of oxygen in flue gas [2,16–18]. Considering their high prices, the operation costs would be too high for practical use. It is still necessary to seek a more cost-effective absorbent for NO_2 absorption.

In the traditional wet calcium-based flue gas desulfurization (FGD) processes, another kind of sulfite, $CaSO_3$, is produced in a considerable amount. $CaSO_3$ might be a suitable NO_2 absorbent potentially, since SO_3^{2-} is also dissociated in its slurry. At the same time, NO_2 could promote the oxidation of $CaSO_3$, thereby reducing the volume of the hold tank of FGD absorption tower [16]. In this case, NO_2 absorption and $CaSO_3$ oxidation will be complementary to each other and then desulfurization and denitrification processes will be combined reasonably.

Unfortunately, the low solubility of $CaSO_3$ will limit the NO_2 absorption efficiency. Therefore it is meaningful to promote the dissolution of $CaSO_3$. $MgSO_4$ has been used as an effective additive in wet FGD process, since it can promote the sulfite dissolution significantly and improve the mass transfer of limestone slurries [19,20]. Similarly, the addition of $MgSO_4$ in $CaSO_3$ slurry may also enhance the NO_2 absorption.

To the best of our knowledge, absorption of NO_2 in $CaSO_3$ slurry has not yet been studied directly in the literatures. In this study, the performance of $CaSO_3$ slurry for NO_2 absorption in a packed column was investigated. Here, $MgSO_4$ was employed as an additive to enhance the absorption process. Its effects on the NO_2 absorption efficiency, $CaSO_3$ oxidation and absorption product composition were discussed.

2. Experimental

The schematic diagram of experimental setup is shown in Fig. 1. It consisted of a laboratory-scale packed column, a gas supply system, a solution recycle system and an analytical system. All the

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Nomenclature

CDSS	the capacity of dissolved sulfite species ($\mathrm{mmol\,L^{-1}}$)
OR	the mole ratio of NO_2 to total NO*x*
($SO_3{}^{2-}$)	concentration of sulfite ion ($\mathrm{mol\,L^{-1}}$)
($SO_4{}^{2-}$)	concentration of sulfate ion ($\mathrm{mol\,L^{-1}}$)
$K_{sp,CaSO_3}$	the solubility product of $CaSO_3$ ($3.1\times10^{-7}\,\mathrm{mol^2\,L^{-2}}$, 25 °C)
$K_{sp,CaSO_4}$	the solubility product of $CaSO_4$ ($2.3\times10^{-5}\,\mathrm{mol^2\,L^{-2}}$, 25 °C)

absorption experiments were conducted in a continuous countercurrent manner and under isothermal conditions. The inside diameter and the height of the glass packed column were 35 and 480 mm, respectively. Glass-spring packings of 3.5 mm × 15 mm were placed randomly inside the glass column. The N_2, NO, NO_2 and O_2 gas streams mixed in the mixing bottle were introduced into the bottom of the column. The absorption slurry stored in the circulation tank was pumped up to the top of the packed column by a peristaltic circulating pump (Baoding Longer Precision Pump Co. Ltd., BT01-100). During each experiment, the inlet gas flow rate and the liquid flow rate were kept unchanged. The temperature in the column was controlled at 25 °C by a jacket. The basic operating conditions for all the experiments are shown in Table 1.

A chemiluminescence NO–NO_2–NO*x* analyzer (Thermo Environmental Instruments 42i-HL) was used to analyze the concentrations of NO*x* (NO and NO_2) in gas phase. The concentration of dissolved sulfite species in the slurry was determined by iodometric titration. After the absorption of NO_2 for 100 min, the slurry was withdrawn from circulation tank and divided into two parts: one was used to measure the sulfite oxidation rate also by iodometric method, and the other part was filtered. The concentrations of nitrite and nitrate in the filtrate were determined by an ion chromatograph (Dionex DX-80), and the filter cake was dried at 105 °C for 4 h in an oven (in N_2 atmosphere) and then analyzed by X-ray diffractometer (Rigaku D/MAX-RA).

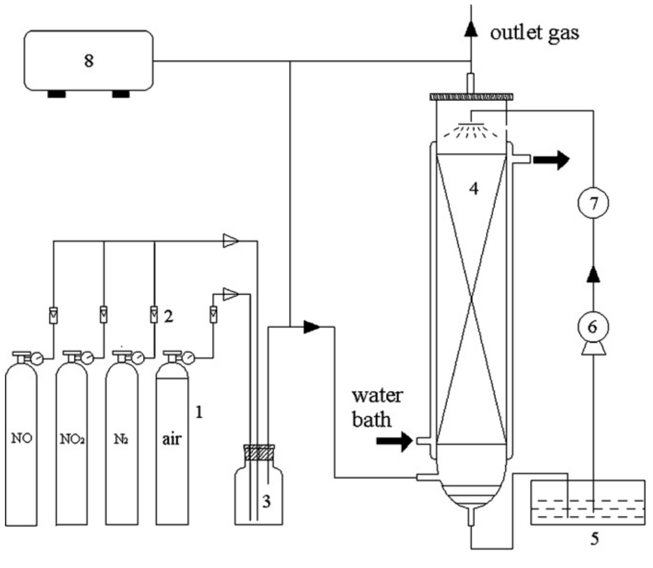

Fig. 1. Schematic diagram of the experimental setup.

Table 1
Operating conditions maintained in this work.

Property	Value
Working temperature	25 °C
pH value of liquid	8
Inlet gas flow rate	$5\,\mathrm{L\,min^{-1}}$
Liquid flow rate	$5\,\mathrm{L\,h^{-1}}$
Residence time of gas	4 s
Residence time of liquid	30 s
O_2 concentration	3%
Inlet concentration of NO*x*	600 ppm
Total pressure	100 ± 1 kPa

3. Results and discussion

3.1. Performance of $CaSO_3$ for NO_2 absorption

The performances of $CaSO_3$ slurry for the NO*x* absorption compared with that of water and aqueous Na_2SO_3 solution are shown in Fig. 2. All the experiments were carried out under the same conditions except for the absorbents, and the contents of $CaSO_3$ and Na_2SO_3 were both $0.1\,\mathrm{mol\,L^{-1}}$. The OR was defined as the mole ratio of NO_2 to total NO*x*. From Fig. 2, it could be seen that the absorption efficiency of NO*x* increased with OR for all these absorbents, because NO_2 is much more soluble and reactive than NO both in water and sulfite solutions, which was in agreement with the conclusion drawn by Takeuchi et al. [13]. The overall reaction between NO_2 and $SO_3{}^{2-}$ could be described as [14]:

$$2NO_2 + SO_3{}^{2-} + H_2O \rightarrow 2NO_2{}^- + SO_4{}^{2-} + 2H^+ \tag{1}$$

and the hydrolysis of NO_2 could be represented by

$$2NO_2 + H_2O \rightarrow NO_2{}^- + NO_3{}^- + 2H^+ \tag{2}$$

NO_2 would be absorbed via reactions (1) and (2) parallelly in sulfite solution. As suggested by Fig. 2, $CaSO_3$ slurry was a promising absorbent and an absorption efficiency of NO*x* above 70% was obtained when OR = 1. It was much more effective than water, with which the highest efficiency was below 50%. Thus the sulfite species in $CaSO_3$ slurry could contribute to the absorption improvement. However, $CaSO_3$ slurry was less effective than Na_2SO_3 solution, and the latter could absorb NO_2 nearly completely when OR = 1. This could be ascribed to the difference in their solubilities, for Na_2SO_3 was much more soluble than $CaSO_3$. Since NO_2 was the predominant species in NO*x* being absorbed, all the following experiments were carried out with OR = 1.

The effect of $CaSO_3$ content on NO_2 absorption was also investigated, and the experimental results and fitting curve are shown

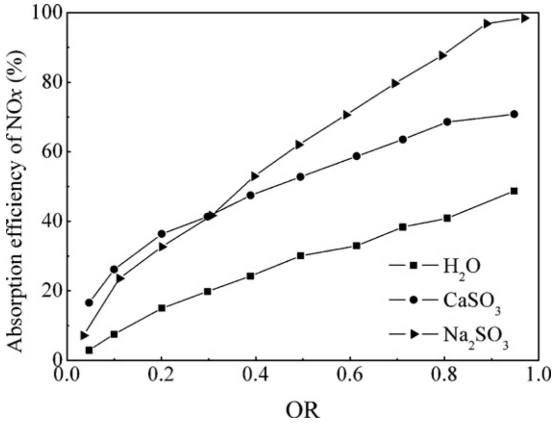

Fig. 2. Performances of different absorbents for NO*x* absorption. Experimental conditions: inlet concentration of NO*x* = 600 ppm; contents of Na_2SO_3 and $CaSO_3 = 0.1\,\mathrm{mol\,L^{-1}}$; pH values of Na_2SO_3 and $CaSO_3$ = 8.

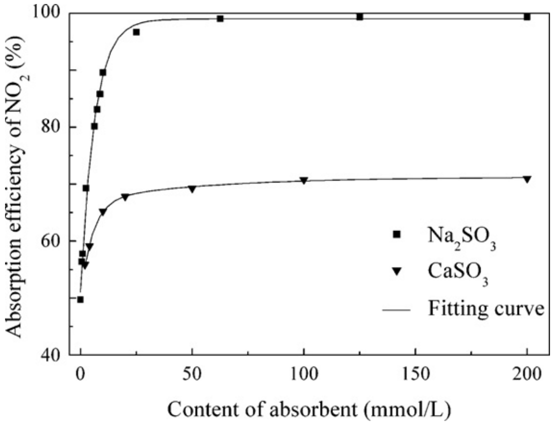

Fig. 3. The effect of absorbent content on the NO_2 absorption. Experimental conditions: inlet concentration of NO_2 = 600 ppm (OR = 1); pH value of liquid = 8.

in Fig. 3. It could be seen that the absorption efficiency increased gradually from 55.9% to 70.8% as the $CaSO_3$ content increased from 2 mmol L^{-1} to 0.1 mol L^{-1}. According to the solubility constant given by Bronikowska et al. [21], the concentration of dissolved $SO_3{}^{2-}$ in $CaSO_3$ slurry was about 0.56 mmol L^{-1}, which could not change significantly with $CaSO_3$ content. Therefore, the efficiency promotion could not be ascribed to the increase of $SO_3{}^{2-}$ concentration. According to the research of Uchida et al. [22], gas absorption rate in a slurry containing fine particles of absorbent was considerably higher than the rate in a saturated solution without solid component, and the absorption rate would increase with solid content within a certain range. Since there were many absorbent particles suspending in the $CaSO_3$ slurry, their participation in the absorption process could explain the promotion of NO_2 absorption reasonably. As shown in Fig. 3, when the $CaSO_3$ content exceeded 0.1 mol L^{-1}, the efficiency would not change obviously further. Accordingly, it might be feasible to use the FGD slurry to remove NO_2 and SO_2 simultaneously, since calcium-based FGD slurry contains some amount of $CaSO_3$. However, the absorption efficiency would still be limited by its low solubility, so it was still necessary to make efforts to enhance the absorption process.

It was reported by Takeuchi et al. [13] that the reaction between NO_2 and $SO_3{}^{2-}$ was first order with respect to $SO_3{}^{2-}$, so its concentration might play an important role in the absorption process. Therefore, the effect of Na_2SO_3 concentration on NO_2 absorption was also studied. The experimental results and fitting curve are shown in Fig. 3. It was indicated that the effect of the Na_2SO_3 concentration on NO_2 absorption was much more significant than that of $CaSO_3$. As its concentration increased to 30 mmol L^{-1}, the NO_2 absorption increased sharply to nearly 100%, which was similar to the experimental results in the literature [3]. Thus the promotion of the dissolved $SO_3{}^{2-}$ in $CaSO_3$ slurry might be useful to accelerate the NO_2 absorption.

3.2. *Effect of $MgSO_4$ on the absorption of NO_2*

In the following experiments, $MgSO_4$ was employed as an additive into 0.1 mol L^{-1} $CaSO_3$ slurry. Its effect on the NO_2 absorption was investigated and compared with that of Na_2SO_4 and $MgCl_2$, as shown in Fig. 4. The experimental results indicated that all the three additives could enhance the NO_2 absorption, and the efficiency increased with their concentrations. When the concentrations of $MgSO_4$, Na_2SO_4 and $MgCl_2$ increased from 0 to 0.6 mol L^{-1}, the NO_2 absorption efficiencies were enhanced from 70.8% to 86.0%, 80.0% and 78.0%, respectively. From the results shown in Fig. 4, it could be concluded that $MgSO_4$ was the most efficient one among the three additives employed.

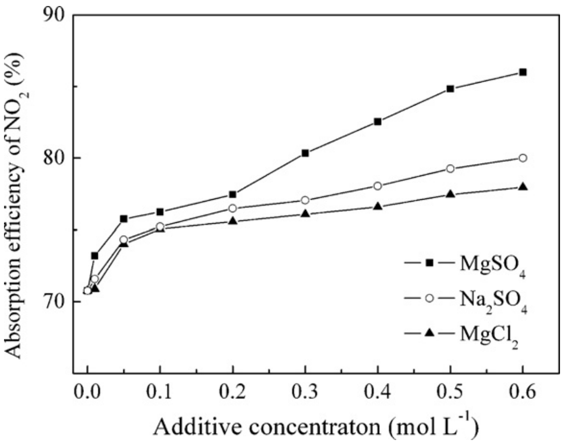

Fig. 4. The effect of additive concentration on the absorption of NO_2. Experimental conditions: inlet concentration of NO_2 = 600 ppm (OR = 1); $CaSO_3$ content = 0.1 mol L^{-1}; pH value of liquid = 8.

In Fig. 5, iodometric titrations of the supernatants separated from $CaSO_3$ slurries with or without additives are compared. The titration value represented the capacity of dissolved sulfite species, which was denoted by CDSS hereinafter. The results showed that all the additives promoted the CDSS of $CaSO_3$ slurry significantly, and that CDSS increased with the additive concentrations. $MgSO_4$ also appeared to be the most effective in CDSS promotion. The CDSS of $CaSO_3$ slurry without additive was determined to be only 0.49 mmol L^{-1}. With 0.6 mol L^{-1} $MgCl_2$ and Na_2SO_4 added, the CDSS was promoted to 4.80 and 5.75 mmol L^{-1}, respectively. While 0.6 mol L^{-1} $MgSO_4$ was used, the CDSS increased remarkably to 9.69 mmol L^{-1}.

$SO_3{}^{2-}$ ion is one of the major reducing components of CDSS in $CaSO_3$ slurry. As stated above, the dissociated $SO_3{}^{2-}$ concentration was very low in the $CaSO_3$ slurry without promoting agent. When $SO_4{}^{2-}$ was present, it could promote the concentration of dissociated $SO_3{}^{2-}$ according to the following equations:

$$CaSO_3 \leftrightarrow Ca^{2+} + SO_3{}^{2-} \tag{3}$$

$$Ca^{2+} + SO_4{}^{2} \leftrightarrow CaSO_4 \tag{4}$$

The relationship between the concentrations of $SO_3{}^{2-}$ and $SO_4{}^{2-}$ could be obtained from the solubility products of $CaSO_3$ and $CaSO_4$ [19]:

$$(SO_3^{2-}) = (SO_4^{2-}) \cdot \frac{K_{sp,CaSO_3}}{K_{sp,CaSO_4}} \tag{5}$$

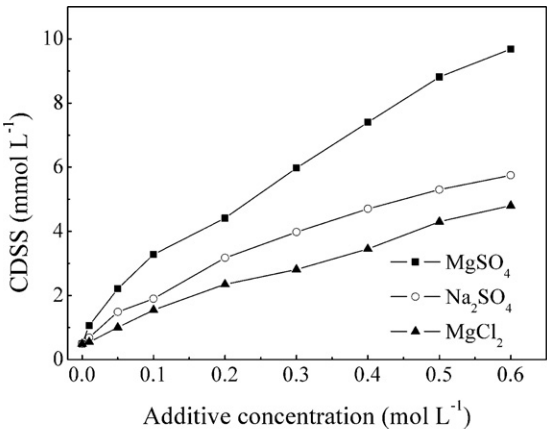

Fig. 5. The relationship between additive concentration and CDSS. Experimental conditions: $CaSO_3$ content = 0.1 mol L^{-1}; pH value of liquid = 8.

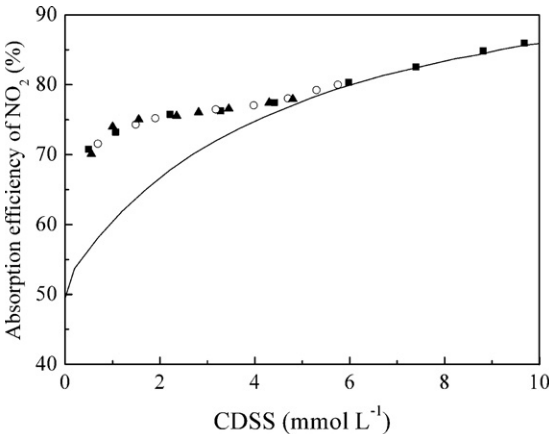

Fig. 6. The effect of CDSS on the absorption of NO_2. CDSS with the addition of $MgSO_4$ (■), Na_2SO_4 (○) and $MgCl_2$ (▲). Fitting curve of Na_2SO_3 solution system (–).

The more SO_4^{2-} was added, the more CDSS could be produced. This could explain the effect of Na_2SO_4 reasonably and was in agreement with the corresponding titration results.

When Mg^{2+} was present in a sulfite system, the formation of another soluble sulfite species, neutral $MgSO_3^0$ ion pair, has been confirmed in the literatures [19,23]. Therefore, as $MgCl_2$ was added to the $CaSO_3$ slurry, the promotion of CDSS could be ascribed to the formation of $MgSO_3^0$. The effect of $MgCl_2$ on the CDSS could be described as:

$$SO_3^{2-} + Mg^{2+} \rightarrow MgSO_3^0 \qquad (6)$$

For $MgSO_4$ additive, both SO_4^{2-} and Mg^{2+} could contribute to the promotion of CDSS based on Eqs. (4) and (6), therefore it became the most effective among the three additives employed. $MgSO_4$ has also been used as an additive in wet FGD process, and it was proved to be effective [19,20]. $MgSO_3^0$ contributed to the improvement of SO_2 removal because it could act as an alkali in FGD system like SO_3^{2-}. Since the effects of additives on CDSS and NO_2 absorption in this study showed the similar trend, it could be presumed that $MgSO_3^0$ might also act as an effective reducing agent in NO_2 absorption like SO_3^{2-}.

The relationship between the CDSS and the NO_2 absorption in $CaSO_3$ slurry system (symbols) is shown in Fig. 6, and the fitting curve representing the effect of SO_3^{2-} concentration on NO_2 absorption in Na_2SO_3 solution system (extracted from Fig. 3) is also presented for comparison. For $CaSO_3$ slurry system, it could be seen that the CDSS appeared to be the only factor that affected the absorption efficiency, regardless of the additives used. This result indicated that all the sulfite species constituting CDSS played the same role in NO_2 absorption. When CDSS was below 5 mmol L^{-1}, there was an obvious deviation between the slurry system and solution system, but the deviation became smaller gradually with the increase of CDSS. As the CDSS exceeded 5 mmol L^{-1}, a good agreement was obtained. Taking into account the effect of $CaSO_3$ content on NO_2 absorption as stated above, the deviation could be attributed to the effect of absorbent particles suspending in slurry. Under a low CDSS, the suspending particles played an important role and promoted the absorption obviously. As the CDSS increasing, its effect on NO_2 absorption enhanced gradually and then predominated over the impact of suspending particles. Since the experimental results for slurry system agreed well with the fitting curve as CDSS was above 5 mmol L^{-1}, it could be concluded that the CDSS acted like SO_3^{2-} in NO_2 absorption. And then it could be further confirmed that $MgSO_3^0$ was also an effective reducing absorbent and played the same role as SO_3^{2-} in NO_2 absorption through the reaction as follows:

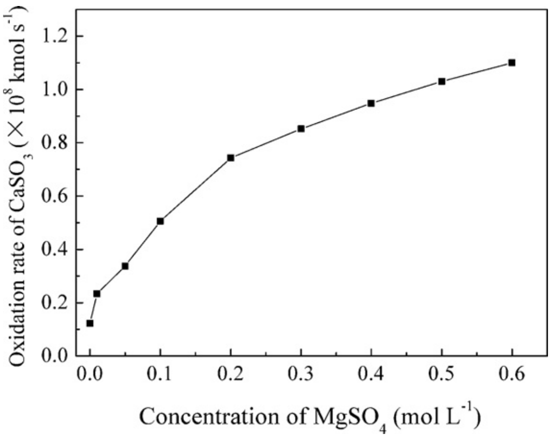

Fig. 7. The effect of $MgSO_4$ on the oxidation of $CaSO_3$. Experimental conditions: inlet concentration of NO_2 = 600 ppm (OR = 1); $CaSO_3$ content = 0.1 mol L^{-1}; pH value of liquid = 8.

$$2NO_2 + MgSO_3^0 + H_2O \rightarrow 2NO_2^- + SO_4^{2-} + 2H^+ + Mg^{2+} \qquad (7)$$

3.3. Effect of $MgSO_4$ on the oxidation of $CaSO_3$

It has been reported that the absorption of NO_2 into sulfite solution initiated a series of free radical reactions involving oxygen species [17], so sulfite would be oxidized by both NO_2 and O_2 in the process. Shen et al. [16] employed Na_2SO_3 solution as the NO_2 absorbent, and found that the oxidation rate of Na_2SO_3 increased with its own concentration and the rate of NO_2 absorption. It has already been proved that the addition of $MgSO_4$ could promote the CDSS of $CaSO_3$ slurry and enhanced the absorption of NO_2 significantly, so it should also accelerate the oxidation of $CaSO_3$. The effect of $MgSO_4$ on the $CaSO_3$ oxidation was investigated and the experimental results are shown in Fig. 7. It was indicated that the addition of $MgSO_4$ accelerated the $CaSO_3$ oxidation considerably as expected. The more $MgSO_4$ was added, the higher the oxidation rate of $CaSO_3$ was. The XRD results (Fig. 8) also confirmed this conclusion. From Fig. 8, there was no significant difference between the fresh sample and the post-absorbed slurry without $MgSO_4$, in which only $CaSO_3$ phase was detected. In contrast, the peaks attributed to $CaSO_4{\cdot}2H_2O$ and $CaSO_4{\cdot}0.67H_2O$ could be obviously observed in the sample with 0.6 mol L^{-1} $MgSO_4$, which directly

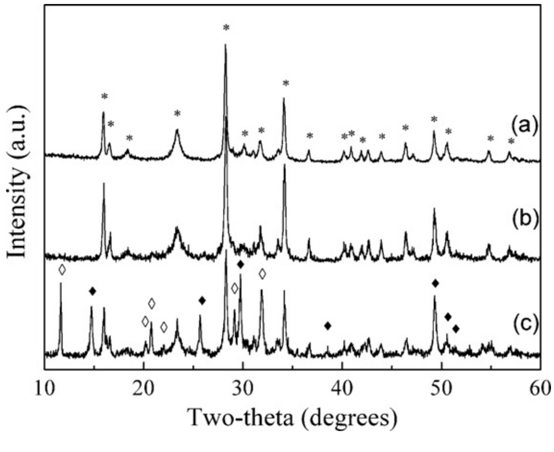

Fig. 8. XRD patterns of $CaSO_3$ unoxidized and partially oxidized in absorption process: (a) unoxidized; (b) partially oxidized without additive; (c) partially oxidized with additive of 0.6 mol L^{-1} $MgSO_4$: $CaSO_3{\cdot}0.5H_2O$ (*), $CaSO_4{\cdot}2H_2O$ (◊) and $CaSO_4{\cdot}0.67H_2O$ (♦).

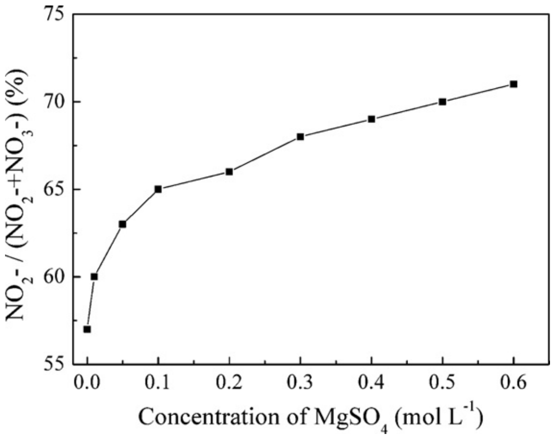

Fig. 9. The effect of $MgSO_4$ on the liquid phase composition. Experimental conditions: inlet concentration of NO_2 = 600 ppm (OR = 1); $CaSO_3$ content = 0.1 mol L^{-1}; pH value of liquid = 8.

demonstrated the enhancement of $CaSO_3$ oxidation by the addition of $MgSO_4$. This would have a beneficial effect on forced oxidation of FGD slurry, resulting in the reduction of operation cost.

3.4. *Effect of $MgSO_4$ on the liquid phase composition*

When NO_2 was absorbed in $CaSO_3$ slurry with or without $MgSO_4$, the liquid phase products were determined by ion chromatography. It was found that nitrite NO_2^- and nitrate NO_3^- were the two main products of NO_2 absorption, which was in accordance with the indications of Eqs. (1) and (2). But the liquid phase composition varied obviously with the amount of $MgSO_4$ added. As shown in Fig. 9, the ratio of NO_2^- to (NO_2^- + NO_3^-) increased significantly from 57% to 71% with the addition of $MgSO_4$ from 0 to 0.6 mol L^{-1}. According to the abovementioned equations (Eqs. (1) and (2)), the reaction of NO_2 with SO_3^{2-} produces only NO_2^- and the hydrolysis of NO_2 produces both NO_2^- and NO_3^- equimolarly. Thus the higher ratio of NO_2^- to the total NO_2 absorption products [NO_2^-/(NO_2^- + NO_3^-)] in the liquid phase indicated more contribution of sulfite species to NO_2 absorption (Eqs. (1) and (7)). This result further confirmed the role of CDSS in NO_2 absorption when $MgSO_4$ was used as the additive.

4. Conclusions

The performances of $CaSO_3$ slurry in NO_2 absorption in a laboratory-scale packed column were investigated. It was found that NO_2 absorption efficiency above 70% could be obtained as the $CaSO_3$ content exceeded 0.1 mol L^{-1}. $MgSO_4$ was employed as an additive to promote the capacity of dissolved sulfite species (CDSS) and absorption efficiency, which appeared to be more effective than the other two additives, Na_2SO_4 and $MgCl_2$. When 0.6 mol L^{-1} $MgSO_4$ was added, the CDSS was promoted considerably from 0.49 to 9.69 mmol L^{-1}, and the efficiency increased significantly from 70.8% to 86.0%. Both SO_4^{2-} and Mg^{2+} contributed to the CDSS promotion. And a neutral $MgSO_3^0$ ion pair was formed in the process, which was confirmed to play the same role in the NO_2 absorption as dissociated SO_3^{2-}. At the same time, the addition of $MgSO_4$ would accelerate the $CaSO_3$ oxidation significantly and influence the liquid phase composition. The experimental results provide a possibility for achieving desulfurization and denitrification by wet FGD process simultaneously.

Acknowledgements

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