Removal and recovery of SO$_2$ and NO in oxy-fuel combustion flue gas by calcium-based slurry

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Abstract. This study investigates the use of calcium-based slurry for simultaneous removal NO and SO$_2$ from oxy-fuel combustion flue gas, and recovery of the sulfur and nitrogen species in resulting solutions. The experiments were performed in a bubbling reactor in a transient mode under the pressure of 20 bar. The various influencing factors including the CaO amount, carrier gas (N$_2$/CO$_2$), and absorption time on the simultaneous NO and SO$_2$ removal process, and the solution products were studied comprehensively. The results show that the NO$_2$ removal efficiency can be improved by the presence of CO$_2$, and the gas phase HNO$_2$ produces in this process. The addition of CaO has positive effects not only on the NO$_2$ removal efficiency but also on the formation of stable HNO$_3$. With the presence of CO$_2$, CaCO$_3$ is formed in a solution initially. With the decrease of pH, CaCO$_3$ is gradually converted to CaSO$_4$, and in particular CaCO$_3$ can be fully avoided through decreasing the pH of an absorption solution to 1.14. At the same time, the formation of unstable S(IV) and NO$_2^-$ can be prevented when the solution pH is lower than 1.37. The nitrogen and sulfur compounds in the absorption solution (at pH 1.14) were further separated by the addition of different amounts of CaO. In particular, 95% of SO$_2^-$ finally can be recovered in the form of CaSO$_4$.4H$_2$O with nitrogen in solution existing as NO$_3^-$ by controlling the Ca/S ratio at 4.70. The effectiveness of calcium-based slurry on the removal and recovery of SO$_2$ and NO is confirmed.

1 Introduction

In order to reduce the greenhouse gas CO$_2$ emission, various pre-combustion, post-combustion (e.g., carbon capture and storage, CCS) and combustion enhanced (e.g., oxy-fuel combustion) technologies have been proposed[1]. Oxy-fuel combustion technology is considered to be one of the most promising ways for carbon capture[2]. This technology not only effectively enriches flue gas with high CO$_2$ concentration[3], but also effectively reduces NO and SO$_2$ emissions per unit mass of fuel[4]. However, the NO and SO$_2$ concentrations are higher in the oxy-fuel combustion flue gas than those in conventional air-combustion flue gas[5]. Therefore, these acid gases (mainly includes NO and SO$_2$) must be removed from CO$_2$ stream considering the safety of transport pipelines and sequestration sites.

Currently, the techniques used in existing power plants to remove SO$_2$ and NO are often independent. The selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) technologies are adopted for NO removal[6], while the wet flue gas desulfurization (WFGD) technology using calcium based solution is adopted for SO$_2$ removal[7]. In the flue gas, NO accounts for more than 90% of the NO[8], and is insoluble in aqueous solution. Thereupon, oxidizing insoluble NO to soluble NO$_2$ before wet scrubbing method is necessary. In this oxidizing process, many oxidation-absorption combined processes have been studied extensively to oxidize NO to NO$_2$ for the purpose of simultaneous removal of NO and SO$_2$, including strong oxidizing agent injection[9], selective catalytic oxidation[10,11], and photo-catalytic oxidation[12].

Apart from conventional technologies for NO and SO$_2$ removal, many new approaches have been proposed specifically for cleaning oxy-fuel combustion flue gases, mainly including two-stage and one-stage methods. Air Products proposed a two-stage scrubbing process with the low pressure (1.5 MPa) and high pressure (3 MPa) stage to remove SO$_2$ and NO separately in the forms of H$_2$SO$_4$ and HNO$_3$[13]. Similarly, Linde also proposed a two-stage method with the first stage (atmospheric pressure) to remove SO$_2$ as CaSO$_4$, and second stage (1.8 MPa) to remove NO as NH$_4$NO$_3$[14]. In addition, Air Liquide proposed using a sodium solution to remove SO$_2$ in the atmospheric caustic scrubber, and using a four-stage compression process (at a final pressure of 2.4 MPa) to remove NO in the condensates in the form of HNO$_3$[15]. Previous methods generally use the two-stage method for
the removal of SO2 and NO separately, and this method increases the infrastructure cost, while using the one-stage method to remove both SO2 and NO is limited. Although the costs for infrastructure and operation for the one stage scrubbing method are significantly reduced, the products are generally mixed in compounds containing sulfur and nitrogen[16], which is detrimental for recovering the sulfur and nitrogen compounds.

Currently, the one-stage method utilizing water solvents to remove both SO2 and NO at a high pressure is extensively studied[17-20]. These studies have reached the following consensus: (1) the liquid products mainly include H2SO4, HNO3, H2SO3, and HNO2 in this process[18]; (2) this process is heavily dependent upon the pH level[19]; (3) the reaction between H2SO4 and H2O2 is critical for the absorption rates of NO and SO2 from the gas to the liquid phase[20]. Moreover, the modeling study mentioned that gas phase HNO2 (HONO) can be produced in this process[20], but it is not identified in the experimental process[21]. Since Platt et al.[22] first measured the HNO2 concentration in the atmosphere by differential absorption spectroscopy (DOAS), the importance of HNO2 in atmospheric chemistry has gradually become known. At the same time, the modeling method can easily obtain the dynamic changes of unstable H2SO4 and H2O2 in solution[23], but these products have not been systematically studied through experiments. Therefore, the quantification of the gas phase HNO2, the liquid phase H2SO4, and HNO2 is critical for the understanding of the simultaneous absorption of SO2 and NO and implementing simultaneous removal technique in the practical applications.

In this work, the one-stage method utilizing calcium-based slurry was adopted to remove NO and SO2 in the oxy-fuel combustion flue gas, and also to recover the sulfur and nitrogen compounds in the forms of CaSO4·2H2O precipitate and NO3-. This approach can potentially reduce the operation cost through the utilization of the low-cost absorbents and the recovery of the end products. The effects of the CaO amount and absorption time on the removal efficiency of SO2 and NO as well as the effectiveness of the recovery of H2SO4 and HNO2 are discussed. In addition, the mechanisms for simultaneous removal, and recovery processes are elucidated.

2 Experimental methods

2.1 Experimental apparatus and method

As shown in Fig.1, the experimental apparatus mainly included a high pressure bubbling reactor, four high pressure mass flow controllers, a light source, an optical lens, an absorption cell, a spectrophotograph and an MRU delta 2000 flue gas analyzer. The high pressure mass flow controllers were used to control the flow rate of the simulated flue gas into the high pressure bubbling reactor, including O2 (purity > 99.999%), N2/CO2 (purity > 99.999%), 1% (NO in N2) and 3% (SO2 in N2). The 316 stainless steel tube was used as the gas transmission line, and the total flow rate of the simulated flue gas was 2 L/min. The simulated flue gas was introduced to the cylinder reactor from top of the reactor to nearly the bottom of the reactor through a 1/8 inch tube to maximize the residence time of gas mixture in the reactor. The volume of the reactor was 1 L with half-filled with absorption solution. The average residence time was obtained by dividing the volume of reactor by the gas flow rate. Under the pressure of 20 bar, the residence time of gas mixture in liquid phase is 300 s. During the contact between gas and liquid, soluble gases in the gas mixture were absorbed into absorption solution. Above the absorption solution, gases containing water vapor flowed upwards to the outlet of the cylinder reactor. The pressure inside the reactor was controlled by the pressure regulator. Following the regulator, the simulated flue gas flowed to the absorption cell, where the NO2 and HNO2 concentrations were measured online by the DOAS. After the absorption cell, the simulated flue gas was partially drawn to the MRU delta 2000 flue gas analyzer for the measurement of the SO2, NO, and O2 concentrations, and the residual flue gas was washed before being vented to atmosphere.

The operation procedures are given as follows. 0.5 L of deionized water with a certain amount of CaO was first introduced into the reactor. The bypass valve was turned on, and then the concentrations of O2, N2/CO2, NO, and SO2 were set to the required concentrations. After 10 minutes stabilization, all the gas bottles were turned off and N2/CO2 gas bottle was left to rinse the gases of NO and SO2 in the system. After that, the bypass valve was turned off, and the N2/CO2 gas was continuously introduced into the reactor to pressurize the reactor to the set pressure, and then the simulated flue gas was continuously introduced into the reactor. In all experiments, the inlet concentrations of O2, N2/CO2, NO, and SO2 were set at 5%, 75%/75%, 1000 ppm, and 2000 ppm, respectively, and the pressure selected was 20 bar. In addition, the pH of the absorption solutions after experiments was determined by a pH meter. The concentrations of SO22- and NO3- in solution were measured by the UV–visible spectrophotometry[24], while the concentrations of S(IV) (i.e., HSO3–, SO32–, and SO2) and NO3 in solution were determined by the acid desorption method. The solid by-products of the absorption solutions were identified by the X-ray diffraction (XRD-6100). Above measurements were sampled after the experiment.

Fig. 1. The schematic diagram of experimental apparatus

2.2 Measurement methods

2.2.1 Measurement of the gas phase NO, NO2,
HNO$_2$, and SO$_2$

The MRU delta 2000 flue gas analyzer was used to measure the SO$_2$ and NO concentrations, whereas the NO$_2$ and HNO$_2$ concentrations were measured online by the DOAS. The absorption characteristics of different gases are different in spectral bands because of the different structures of gas molecules. The measurement of different gases by the DOAS utilized the selective absorption of light from the ultraviolet to near-ultraviolet bands by gases. When a light source with an incident light intensity of $I_0$ passes the measuring medium, and then the emitted light intensity is $I$ due to the radiation absorption of different gases. The Lambert Beer’s law expressed by Eq. (1) describes the relationship between $I$ and $I_0$.

$$\alpha = \frac{\ln\left(\frac{I_0}{I}\right)}{L} = \sum_i c_i \sigma_i$$  \hspace{1cm} (1)

where $\alpha$ is the absorption coefficient; $I_0$ and $I$ are the incident and emitted light intensity, respectively, candela; $\sigma_i$ is the absorption cross section, m$^2$; $L$ is the absorption cell length, 0.35 m; $c_i$ is gas concentration, ppm. NO$_2$ absorbs the lights with the spectral range from 340 nm to 400 nm[25]. The near-ultraviolet absorption peak of HNO$_2$ is 341.8 nm, 354.2 nm, and 368 nm, respectively[26]. The center wavelength of the light source used in the experiment was 355 nm, and the full width at half the maximum light intensity was 15 nm. Therefore, in the spectral range from 340 nm to 370 nm, the least-squares fitting method was adopted for the calculations of the HNO$_2$ and NO$_2$ concentrations. Fig. 2 shows the spectral fitting results for a single-point simultaneous measurement of both the NO$_2$ and HNO$_2$[27]. By comparing the magnitudes of the absorption coefficients for fitting results with these for residuals, the absorption coefficients for NO$_2$ is two magnitudes higher than residuals while the absorption coefficients for HNO$_2$ is the same magnitude with the residuals. Therefore, the measurement for NO$_2$ may be more accurate than the measurement for HNO$_2$.

![Fig. 2. Spectral fitting results for a single-point simultaneous measurement of both NO$_2$ and HNO$_2$.](image)

2.2.2 Measurement of the liquid phase NO$_3^-$, SO$_4^{2-}$, S(IV), and NO$_2^-$

The concentrations of NO$_3^-$ and SO$_4^{2-}$ in solution were measured by UV–visible spectrophotometry, which used the specific wavelength to measure the corresponding substance. Before the measurement, the standard curve for the standard solutions versus the corresponding absorbance was obtained by experiments. The substance concentrations at different absorbance could be regressed from the standard curve. When the light source passes through the solution to be tested, the absorbance of the solution is proportional to the concentration of the substance in the solution. The relationship is expressed by Eq. (2).

$$A = -\lg\left(\frac{I}{I_0}\right) = KLC$$  \hspace{1cm} (2)

where $A$ is the absorbance of the absorption solution; $I$ and $I_0$ are the incident and emitted light intensity, respectively, candela; $K$ is the molar absorption coefficient; $L$ is the length of the cuvette, 50 mm; $C$ is the concentration of the substance, mol/L.

Based on the above principle, the NO$_3^-$ concentration was measured at the specific wavelength of 220 nm. The SO$_4^{2-}$ concentration was measured by the UV-visible-method of barium-chromate (BaCrO$_4$). Under acidic conditions, the reaction between BaCrO$_4$ and SO$_4^{2-}$ forms BaSO$_4$ precipitates and the CrO$_4^{2-}$ ions which have the maximum absorption at 420 nm. After filtering the BaSO$_4$ precipitates, the CrO$_4^{2-}$ concentration could be obtained.
by measuring the absorbance of the solution, so the SO$_4^{2-}$ concentration can be obtained because the CrO$_4^{2-}$ concentration is equal to the SO$_4^{2-}$ concentration.

The S(IV) and NO$_2^-$ concentrations in solution were measured by acid-promoted desorption method. In order to completely convert S(IV) to SO$_2$, a certain amount of HCl (1 ml 2.5 mol/L HCl ) was added to the absorption solution (5 ml), and then the absorption solution was purged with 2 L/min of N$_2$ with the discharged gas measured by the MRU delta 2000 flue gas analyzer for the SO$_2$ concentration. When the SO$_2$ concentration was zero, the N$_2$ purging process was terminated. The total S(IV) concentration in a solution was calculated by integrating the SO$_2$ concentration against time within the desorption period. In order to verify the accuracy of this method, the standard NaHSO$_3$ solutions with four concentrations of 0.0025, 0.005, 0.01, and 0.02 mol/L were measured with relative errors for these measurements being less than 3%.

Similarly, the NO$_2^-$ concentration in solution was also measured by acid-promoted desorption. After adding a certain amount of HCl (1 ml 2.5 mol/L HCl ), NO$_2^-$ was converted to HNO$_2$ which could be desorbed in the forms of NO, NO$_2$, and HNO$_3$. Four standard NaNO$_2$ solutions (0.0025, 0.005, 0.01, and 0.02 mol/L) were used to validate the accuracy of NO$_2^-$ measurement. Overall, the accuracy of acid-promoted desorption method was over 90%.

3 Results and discussion

3.1 Effects of CaO amounts on the simultaneous NO and SO$_2$ removal process

To investigate the influence of CaO amounts on the NO and SO$_2$ removal process, different amounts of CaO (0, 0.285, 0.570, and 0.855 g) were introduced into water to make up a total liquid volume of 0.5 L. The experiments were performed in the presence or absence of CO$_2$ at room temperature. As shown in Figs. 3-A, 3-A', 3-B, and 3-B', the concentrations of NO and NO$_2$ at the outlet of bubble reactor gradually increased with time. Both of them increased significantly initially within 10 min, and then increased slowly after that. The initial 10 min quick increase for both NO and NO$_2$ could be due to the retention time of the bubble reactor before the gas analyzer. The slow increase of NO and NO$_2$ after the quick initial increase may come from the complex chemical reactions between the gas phase NO and NO$_2$ with water. NO is considered oxidized easily under high pressure to form NO$_3$[28]. Through forming high soluble intermediate, the absorption of NO and NO$_2$ into water is greatly enhanced to form HNO$_2$, and HNO$_3$[29]. HNO$_3$ is quite stable in solution, while HNO$_2$ is easily decomposed to form HNO$_2$ and NO at room temperature[30]. The different proportions of HNO$_2$ and HNO$_3$ is strongly dependent on the solution pH[31]. The decomposition of HNO$_2$ to HNO$_3$ and NO was enhanced with the decrease of the liquid pH, which results in the increase of NO in the gas phase. In a similar way, this also results in increasing NO$_2$ in the gas phase due to the re-oxidation of NO to NO$_3$[31].

By comparing with the case in the presence of CaO, it can be seen that the introduction of CaO into water markedly enhanced NO and NO$_2$ absorption. NO and NO$_2$ absorption increased with the increase in the amount of CaO. The reason for this result is that the CaO dissolves into water to increase the alkalinity of the solution, and the alkaline condition leads to slightly higher NO and NO$_2$ absorption efficiencies[32]. Furthermore, the NO$_2$ absorption is further promoted when CO$_2$ is present in the gas phase. This can be explained that in the presence of CO$_2$, the Ca$^{2+}$ preferentially participates in the formation of CaCO$_3$; in the absence of CO$_2$, the Ca$^{2+}$ preferentially participates in the formation of low solubility CaSO$_4$, which is detrimental for the NO$_2$ absorption[33].

Figs. 3-C and 3-C’ show that the outlet of HNO$_2$ concentration increased slightly over time, and the HNO$_2$ concentration was approximately 5 ppm. Both the presence of CO$_2$ and the addition of CaO had little effect on the production of HNO$_2$. SO$_2$ was not observed at the outlet of bubble reactor for all the experiments indicating that all SO$_2$ can be absorbed because of the instantaneous reaction of SO$_2$ with water[30].

![Diagram](https://example.com/diagram.png)
the presence of CO₂, the solution pH initially dropped higher than that in the absence of CO₂, and this is caused more slowly compared with that in the absence of CO₂. However, in the presence of CO₂, the final solution pH increased as well, and this may be caused by the reaction between CaO and H₂O forms alkaline Ca(OH)_2 which increases the alkalinity of solutions. The NO₃⁻ concentration increased with the increase of CaO, and in contrast, the SO₄²⁻ concentrations decreased with the increase of CaO. Overall, the introduction of CaO into water is more favorable for the formation of insoluble CaSO₄ by the reaction between SO₄²⁻ and Ca²⁺. The concentrations of S(IV) and NO₂⁻ decreased with the increase of CaO. This may be due to the formation of insoluble CaSO₄ by the reaction between SO₄²⁻ and Ca²⁺. The concentrations of S(IV) and NO₂⁻ decreased with the increase of CaO. The introduction of CaO into water is more favorable for the formation of stable CaSO₄ precipitates and NO₃⁻.

Fig. 3. The comparison on the gas outlet concentrations of NO ((A) and (A')), NO₂ ((B) and (B')) and HNO₂ ((C) and (C')) in the presence or absence of CO₂ (inlet NO concentration is 1000 ppm, CO₂ and N₂ stand for CO₂ and N₂ atmosphere, respectively)

The dynamic changes of the concentrations of SO₄²⁻, NO₃⁻, S(IV), NO₂⁻, and the solution pH are shown in Fig.4. As shown in Fig.4, CO₂ has a slight effect on the NO₃⁻, S(IV), NO₂⁻ concentrations, and remarkable effect on the SO₄²⁻ concentration, the solution pH. Both the SO₄²⁻ and NO₃⁻ concentrations increased with time, and NO₃⁻ concentrations were quite similar. However, in the presence of CO₂, the SO₄²⁻ concentration was much higher than that in the absence of CO₂, and this is caused by the reaction between SO₄²⁻ and Ca²⁺ to form CaSO₄ precipitate to consume SO₄²⁻[33], while in the presence of CO₂, the Ca²⁺ exists in solution in the form of CaCO₃. In the presence of CO₂, the solution pH initially dropped more slowly compared with that in the absence of CO₂. Because the formed Ca(OH)₂ can be rapidly consumed by HCO₃⁻ to form CaCO₃ in the pressurization process. However, in the presence of CO₂, the final pH (pH = 2.79) (60 min) was much higher than that (pH = 1.92) (60 min) in the absence of CO₂, and this may be caused by the formed CaCO₃, which may work as a buffer in liquid.

Meanwhile, both the S(IV) and NO₂⁻ concentrations first increased, and then decreased dramatically with time because strong acidic conditions accelerate the decomposition of both the S(IV) and NO₂⁻[34], so that their concentrations (60 min) became very low.

Fig. 4. Dynamic changes of the solution pH (A), the concentrations of SO₄²⁻ (A), NO₃⁻ (A), S(IV) (B), and NO₂⁻ (B) with 0.570 g CaO addition into water

The concentrations of SO₄²⁻, NO₃⁻, and the solution pH under different amounts of CaO (0, 0.285, 0.570, and 0.855g) introduced into water for the absorption time of 1 h are shown in Fig.5. From Fig.5, one finds that CaO has a remarkable effect on the NO₃⁻, S(IV), NO₂⁻, SO₄²⁻ concentrations, and the solution pH. With the increase of CaO, the final solution pH increased as well, and this can be interpreted that the reaction between CaO and H₂O forms alkaline Ca(OH)₂ which increases the alkalinity of solutions. The NO₃⁻ concentration increased with the increase of CaO, and in contrast, the SO₄²⁻ concentration decreased with the increase of CaO. This may be due to the formation of insoluble CaSO₄ by the reaction between SO₄²⁻ and Ca²⁺. The concentrations of S(IV) and NO₂⁻ decreased with the increase of CaO. Overall, the introduction of CaO into water is more favorable for the formation of stable CaSO₄ precipitates and NO₃⁻.
combustion flue gas, the formation of CaCO$_3$ cannot be

Therefore, CaCO$_3$ can be converted to CaSO$_4$ if

Fig. 5. The final pH (A), the concentrations of SO$_4^{2-}$ (A), NO$_3^-$ (A), S(IV) (B) and NO$_2^-$ (B) under different additions of CaO into water at an absorption time of 1h

XRD analysis was used to determine the crystal composition of precipitate after gas absorption. Both dried and wet precipitates were analyzed. In the presence of CO$_2$, the only precipitate was CaCO$_3$, whereas in the absence of CO$_2$, the only precipitate was CaSO$_4$·2H$_2$O. In comparison, the most popular WFGD uses CaCO$_3$/CaO to remove SO$_2$ and NO, and the by-product of this process mainly includes CaSO$_4$[35,36]. The comparison indicates that in a high pressure scrubbing process, the generated CaSO$_3$ can be oxidized to CaSO$_4$ by dissolved NO$_2$ and O$_2$ effectively[37,38], and CaSO$_4$ further reacts with H$_2$O to form CaSO$_4$·2H$_2$O[37]. From the aspect of economy, the byproduct CaSO$_4$·2H$_2$O has a higher recycling value than CaCO$_3$. The utilization of by-product CaSO$_4$·2H$_2$O can reduce the operation cost of a scrubber.

Fig. 6. XRD patterns of the precipitate at gas absorption of 1 h with 0.885 g CaO addition into water. (A) CO$_2$ atmosphere; (B) N$_2$ atmosphere

As CO$_2$ is dominate in the gas phase for oxy-fuel combustion flue gas, the formation of CaCO$_3$ cannot be avoided. However, CaCO$_3$ is reactive towards SO$_3$[39,40], and therefore, CaCO$_3$ can be converted to CaSO$_4$ if enough reaction time is provided.

3.2 Effects of absorption time on the simultaneous NO and SO$_2$ removal process

The absorption time was prolonged to avoid the calcium exist in the form of CaCO$_3$. The experiments were carried out under the same amount of CaO (0.855g) in the presence of CO$_2$ with different absorption times including 5, 10, 20, 40, 60, 180, and 240 min. Fig.7 shows the dynamic changes of the concentrations of SO$_4^{2-}$, NO$_3^-$, S(IV), NO$_2^-$, and the solution pH. Based on Fig. 7-A, the solution pH had a slight increase (from pH 4.78 to pH 5.66) within 20 min, and this result may be due to the addition of excessive CaO. In this pH range, the S(IV), NO$_2^-$, and NO$_3^-$ began to form, and in particular, both the S(IV) and NO$_2^-$ concentrations reached the maximum at a pH 5.66. From pH 5.66 to pH 1.37, both the concentrations of S(IV) and NO$_2^-$ sharply decreased to zero, while both the SO$_4^{2-}$ and NO$_3^-$ were increasingly formed with time. In this pH range, following two processes may occur: (1) some S(IV) (mainly includes SO$_3^{2-}$ and HSO$_3^-$) are gradually oxidized into SO$_4^{2-}$ by the dissolved NO$_2$ and O$_2$[41,42]; (2) some S(IV) react with Ca$^{2+}$/CaCO$_3$ to form CaSO$_4$. With the decrease of solution pH, NO$_2^-$ is gradually converted to HNO$_2$, which is more easily decomposed to HNO$_3$ and NO, and this result in the NO$_3^-$ decreasing to zero. From pH 1.37 to pH 1.14, both the SO$_4^{2-}$ and NO$_3^-$ concentrations reached the maximum because the continuous absorption of SO$_2$ and NO$_x$ into water to form the SO$_4^{2-}$ and NO$_3^-$.
NO₂ and O₂[37,38]. The reaction between CaSO₄ and H₂O also takes place in this process. In practical situation, the controllable factor is the pH of the solution. Above results indicate that CaCO₃ can be avoided through decreasing the pH of absorption solution to 1.14.

The ratio of Ca/S plays a significant role in the absorption process. The corresponding pH is 8.94. In the absorption process, SO₄²⁻ decreased sharply with the increase in the ratio of Ca/S. In this process, SO₄²⁻ in the solution was converted to CaSO₄·2H₂O precipitate. It can be expected that the higher Ca/S ratio is more favorable for the conversion of SO₄²⁻ to CaSO₄·2H₂O precipitate, while the NO₃⁻ concentration stays at the same value as the initial concentration. Through controlling the Ca/S ratio at 4.70, the only precipitate was CaSO₄·2H₂O, and there still existed 5% SO₄²⁻ in the solution. Moreover, increasing the Ca/S ratio to 7.05 can promote the conversion of 98% SO₄²⁻ to CaSO₄·2H₂O precipitate, but the precipitates contained CaSO₄·2H₂O and Ca(OH)₂. From the above-mentioned analysis, the optimum ratio of Ca/S is 4.70, and the corresponding pH is 8.94.

Fig. 8. XRD patterns of the precipitates for seven absorption times including 5 min (A), 10 min (A), 20 min (A), 40 min (B), 60 min (B), 180 min (B), and 240 min (B).

3.3 Effects of the ratios of Ca/S on the recovery process

As can be seen from Fig.7-A, the obtained absorption solution still contained a considerable amount of SO₄²⁻ (2.53 × 10⁻² mol/L) and NO₃⁻ (2.43 × 10⁻² mol/L) at the absorption time of 240 min indicating the absorption process cannot effectively separate SO₄²⁻ and NO₃⁻ for further utilization. To further separate SO₄²⁻ and NO₃⁻ in the solutions, a simple approach was to add more CaO into the solution to promote further conversion of SO₄²⁻ to CaSO₄ precipitate. An optimum ratio of Ca/S may exist in this process, SO₄²⁻ (A) and NO₃⁻ (A) and the XRD patterns of the precipitates (B) under different ratios of Ca/S.

3.4 Proposing the mechanism for simultaneous removal and recovery of NO and SO₂

The schematic diagram of the reaction pathway for simultaneous removal, and recovery of NO and SO₂ including the pressurization, absorption, and recovery processes is shown in Fig.10. The solution pH has a significant effect on the products formation. In the pressurization process, CaO firstly reacts with H₂O to form Ca(OH)₂ (R1), and then it is rapidly consumed by HCO₃⁻ to form CaCO₃ precipitate (R2, R3). Compared to the pressurization process, the absorption process is more complicated. With the introduction of the simulated flue gas, NO can be converted into NO₂ by O₂ under high pressure (20 bar) in the gas phase (R4)[20]. NO and NO₂ may also react with water vapor to form the gas phase HNO₃ (R5)[43]. In the liquid phase absorption process, from pH 4.78 to pH 5.66, the NO₂, NO₃⁻ and S(IV) begin to form due to the hydrolysis of SO₂ and NO₂ (R6–R9)[31]. However, some S(IV) (mainly includes SO₃²⁻ and HSO₃⁻) can be oxidized into the SO₄²⁻ by NO₂ and O₂ (R10, R11)[41,42], and some S(IV) react with Ca²⁺/CaCO₃ (R12, R15) to form CaSO₃ which can be oxidized to CaSO₄ by the dissolved NO₂ and O₂ (R16, R17)[37,38], and with the decrease of solution pH, NO₂⁻ is gradually converted to HNO₂ which is more easily decomposed to HNO₃ and NO (R18). From pH 5.66 to pH 1.37, both the NO₃⁻ and S(IV) concentrations decrease to zero, whereas both the NO₂⁻ and SO₄²⁻ increasingly form.
and the formed CaCO₃ is gradually decomposed to form CaSO₄.2H₂O (R12–R14). From pH 1.37 to pH 1.14, the residual formed CaCO₃ can be completely decomposed to form CaSO₄.2H₂O by the formed HNO₃ and H₂SO₄. In this pH range, following two processes occur: (1) the residual formed Ca²⁺ reacts with SO₄²⁻ to CaSO₄ (R19); (2) the formed CaSO₄ reacts with H₂O to form CaSO₄.2H₂O (R20).

In the separation process, the absorption solution (at a pH of 1.14) only contains H₂SO₄ and HNO₃, and CaO was introduced into the obtained absorption solution to further separate H₂SO₄ and HNO₃. When the ratio of Ca/S is 4.70, the solution pH is 8.94, and these reactions only take place in solution to form CaSO₄.2H₂O and Ca²⁺, NO₃⁻ (R19–R22). When the ratio of Ca/S is 7.05, the solution pH is 11.27. As excess CaO is added to the solution, and CaO cannot be fully consumed by H₂SO₄ and HNO₃. Reactions take place in solution to form Ca(OH)₂, CaSO₄.2H₂O, and Ca²⁺, NO₃⁻ (R1, R19–R22).

As high as 95% SO₄²⁻ in the obtained absorption solution can be recovered in the form of CaSO₄.2H₂O by controlling the ratio of Ca/S at 4.70.

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