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Preparation and Characterization of a New Desulfurizer and Its Performance on Removal of SO$_2$

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Abstract

Sulfur dioxide is one of the major pollutants resulting from fuel combustion. In this study, CaO and attapulgite were utilized as raw material for synthesizing CaO/attapulgite (CaO/ATP) desulfurizer. The physicochemical characteristics of CaO/ATP desulfurizer were evaluated by various techniques such as XRD, SEM, FT-IR. The performance of samples was studied in dynamic conditions. Major factors affecting on desulfurization such as weight ratio of CaO to total, types of modifiers, roasting time and temperature were investigated. The desulfurization agent synthesized under optimal synthesis conditions with CaO content of 30 wt% and NaOH modifier, and the desulfurization roasting time of 2 hours and roasting temperature of 600°C, exhibit sulfur tolerance of 10.15 wt%. This desulfurizer with excellent absorbency and catalysis of desulfurization, economical and environment-friendly, could be especially useful in industrial applications.

Keywords

Attapulgite; CaO; Desulfurization; SO$_2$; Adsorption

1. Introduction

Sulfur dioxide (SO$_2$) emission from coal-fired power plants and refinery operations is one of the most important pollution among other pollutants. Discharge of SO$_2$ from various sources can easily create air pollution and cause harmful effects on living things and the environment. For instance, it causes acid rain affecting negatively on plant and animals (Aytar, 2011; Cao, 1996; Chen, 2003).

It is noted that the dry processes are generally advantageous over the wet systems in terms of secondary treatment of wastes produced during wet methods. So because of their simplicity and relatively low cost, dry sorption technologies are applied more than the wet methods. Application of calcium-based sorbents, spray dry flue gas desulfurization, metal oxides sorption and activated carbon or coke processes are the main dry sorption processes used for SO$_2$ and NO$_x$ removal (Chen, 2003).

Lime/gyp method is a conventional dry desulfurizing method, which uses CaO or Ca(OH)$_2$ as desulfurizers.

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The lime/gyp method is considered to be more effective and cheaper than other desulfurizing methods, such as activate carbon adsorption and Claus recycle, etc. But the calcium-based desulfurizer has a big problem: It is easy to scaling during the process of desulfurization, because $CaSO_4$, whose molar volume is three times as much as CaO, is generated, and the micro pore of desulfurizer would be soon jammed by $CaSO_4$, which prevent the reaction and decreased SO_2 removal efficiency (Chen, 2004; Frost, 1998; Görkem, 2006; Hernández-Maldonado, 2005).

In the field of dry and regenerable sorbents, considerable attention has been devoted to activated carbon or activated coke due to their large adsorption capacity of SO_2 at near room temperatures (Li, 2007; Li, 2008). Much work has also been done on metal oxides such as CuO, Fe_2O_3, MnO, CaO, Co_3O_4, ZnO and CeO_2 for H_2S or SO_2 capture at higher temperatures (Lin, 1998). Despite that the metal oxides alone exhibit high sulfur sorption capacity, their performance and life time are adversely affected by problems such as sintering, evaporation, and mechanical disintegrations. To overcome these problems, Al_2O_3 and natural zeolites were added to metal oxides or their mixtures as structure stabilizer (Liu, 2011; Ma, 2003; Pan, 2005). Jianrong Ma *et al.* (Cao, 1996) investigated a novel regenerable Fe/activated coke (AC) desulfurizer prepared by impregnation of $Fe(NO_3)_3$ on an activated coke. Experiment results showed that at 200°C the SO_2 adsorption capacity of the Fe/AC was higher than that of AC or Fe_2O_3.

Attapulgite (or palygorskite-as it often called) is a crystalline hydrated magnesium aluminum silicate with unique three-dimensional structure and has a fibrous morphology. Attapulgite has the structural formula $Si_8O_{20}Mg_5(Al)(OH)_2(H_2O)_4·4H_2O$. The distinguishing feature of its structure is that the Si-O tetrahedral form long strips, each an amphibole unit wide, on alternate sides of the oxygen sheet in a manner which confers a regular corrugated Si-O structure. The formulas are written as such to indicate the two types of water present; magnesium coordinated water and adsorbed water. The structure of the mineral results in zeolite-like channels, which are approximately 3.7×6.0 and 5.6×11.0Å wide, respectively. These channels may be filled with water or organic molecules. The water is partly arranged in these channels and water molecules are also bound to the magnesium cations of the Mg(Al, Fe) brucite-like ribbon edges that border the channels running along the length of the crystals. Specific surface areas of about 200m²/g may, therefore, result form fine particle size rather than significant contributions from internal channel surface (Perderiset, 1988; Shen, 2012; Wang, 2005). Because of its structural morphology, attapulgite has received considerable attention with regard to the adsorption of organics on the clay surface and to their use as support for catalysts (Wang, 2011; Wieckowska, 1995; Yan, 2002).

In this study, CaO and attapulgite were utilized as raw material for synthesizing CaO/attapulgite (CaO/ATP) desulfurizer. Major factors affecting on desulfurization such as weight ratio of CaO to total, types of modifiers, roasting time and temperature were investigated.

2. Experimental

2.1. Material and Equipment

Attapulgite clay came from Linze County, Gansu Province, China (60-mash sieve, specific surface area 110 ~ 150 m²/g), with ATP content of 31% ~ 57%, illite and kaolinite content of 18% ~ 23%, quartz and feldspar content of 15% ~ 25%, dolomite and montmorillonite content of trace. Its chemical components (%) are as follows: SiO_2, 57.61; Al_2O_3, 14.06; MgO, 1.10; CaO, 5.26; Fe_2O_3, 4.96; K_2O, 2.57; Na_2O, 1.41; Ti, 0.3873; Mn, 0.0603; P, 0.0585; Sr, 0.0451; Ba, 0.0424; Zr, 0.0197; V, 0.0093; Cr, 0.0071; Zn, 0.0067; La, 0.0041; Ni, 0.0032; Cu, 0.0030; Y, 0.0024; Pb, 0.0015; Th, 0.0014; Nb, 0.0013; Co, 0.0010. The other reagents supplied by their manufacturers was all analytical pure.

2.2. Preparation Method of the Desulfurizer

CaO, ATP and some water were mixed and well-distributed at a certain ratio. The mixture was aged for a day, shaped, and dried in the oven at the temperature of 105°C. The samples were roasted in the high temperature oven at 600°C for 2 hours, then cooled. The CaO/ATP desulfurizer samples were obtained.

2.3. Characterization and Analysis

SEM was utilized to determine the crystal morphology and chemical element composition. Measurements were made on a JSM-5500 SEM instrument using a digital imaging process. FT-IR was used to confirm the chemical groups in the prepared CaO/ATP desulfurizer. Measurements were made on a Nicolet AVTAR 360 FT-IR spectrometer after samples were mixed with 300 mg of spectroscopic grade KBr and ground in an agate mortar. The

crystalline form of the samples was identified by a Panalytical X'Pert PRO XRD instrument (Cu Ka radiation), operating at 40 kV and 30 mA. Surface area, pore volume, and pore size distribution were obtained on a ASAP2010 BET apparatus.

2.4. Determining the Properties of the CaO/ATP Desulfurizer

The ability of desulphurization of CaO/ATP desulfurizer was determined by the experiment equipment showed in **Figure 1**. The experimental conditions can be seen in **Table 1**. SO_2 gas went through the little desulfurizing tower continuously and was absorbed and transferred by CaO/ATP desulfurizer. SO_2 concentration both at the inlet and at the outlet were determined ever few minutes until the desulfurizer was fully penetrated (SO_2 concentration at the inlet equals to that at the outlet). Then the desulfurization efficiency curves (penetrating curves) were obtained and the sulfur tolerance (S) was calculated by following formula:

$$S = \frac{G_a - G_b}{G_b} \times 100\% \tag{1}$$

G_a—the weight of the desulphurizer after desulphurization;
G_b—the weight of the desulphurizer before desulphurization.

3. Results and Discussion

3.1. Characterization of the Synthesized Samples

The phase structures of samples were investigated by XRD, and the obtained results are shown in **Figure 2** and **Figure 3**. XRD patterns of the samples prepared with different CaO content are contrasted with those of ATP. Samples CaO/ATP with different CaO content showed the characteristic peaks (26.8˚, 29.9˚, 39.6˚, 43.3˚, 47.6˚,
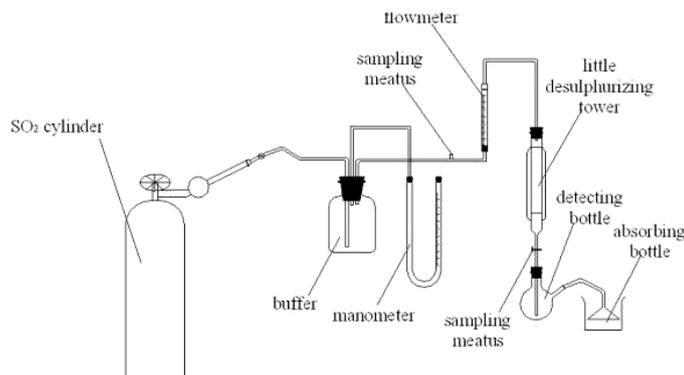

Figure 1. Experimental equipment.

Table 1. Characteristics of experimental conditions.

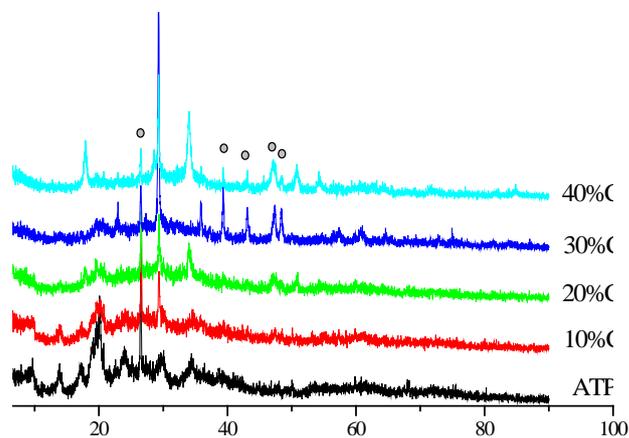| Gas	SO_2
Temperature	20˚C
Pressure	Normal
Desulfurizer	CaO/ATP
Column length (m)	0.20
Column diameter (m)	0.02
Particle diameter (m)	0.003
Total porosity	0.34
Apparent density (kg/m^3)	398.089
BET surface area (m^2/g)	206.9

Figure 2. XRD patterns of ATP and CaO/ATP samples with different CaO content (○—CaO).
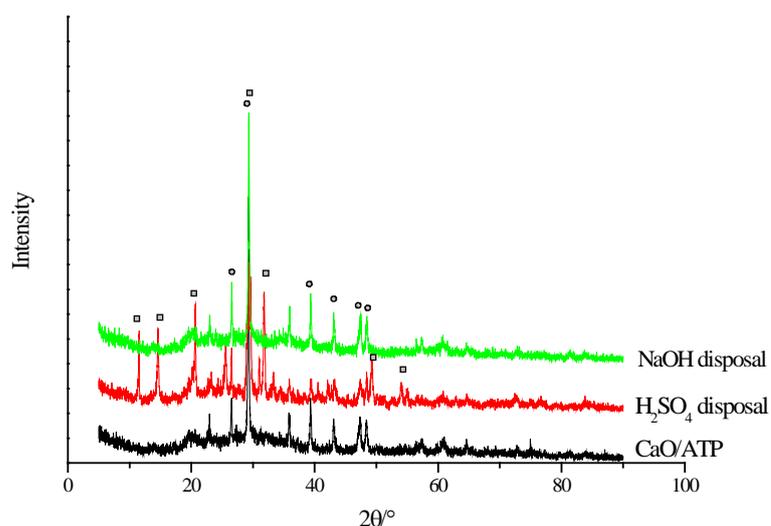

Figure 3. XRD patterns of CaO/ATP samples with different modifier (□—CaSO$_4$, ○—CaO).

48.4˚) of cubic spinel structure known from bulk CaO phase. The intensity of some characteristic peaks of CaO of CaO/ATP sample became stronger along with CaO content increasing.

Figure 3 showed XRD patterns of CaO/ATP samples were disposed by H$_2$SO$_4$, NaOH respectively. From **Figure 3** we can see that the samples which were disposed by NaOH did not change remarkably compared with the samples which were not disposed. The main reaction of that is ion exchange. But when H$_2$SO$_4$ was used as modifier, CaO reacted with H$_2$SO$_4$ and generated CaSO$_4$.

SEM micrographs were collected to illustrate the morphologies of ATP, CaO/ATP, modified samples by MgCl$_2$, H$_2$SO$_4$ or NaOH, as depicted in **Figure 4**. Rod-shaped particles with lengths of 500 ~ 700 nm and widths of 100 ~ 150 nm are visible (**Figure 2(a)**). After the introduction of CaO species into ATP, rod-shaped crystal still can be seen, but the surface area decreased (**Figure 2(b)**). Morphological observations of CaO/ATP modified by NaOH is shown in **Figure 2(c)**, which we cannot see the rod-shaped particles because NaOH destroyed three-dimensional space structure of ATP (Zhang, 2005), the surface area increased instead. While the sample modified by H$_2$SO$_4$, which can be seen in **Figure 2(d)**, its surface presented a chaotic condition.

The FT-IR results of CaO/ATP (different roasting temperature) can be seen in **Figure 5**. The strong wide absorption bands appeared at 3440 cm^{-1} associated with the surface hydroxyl groups. The weak sharp absorption
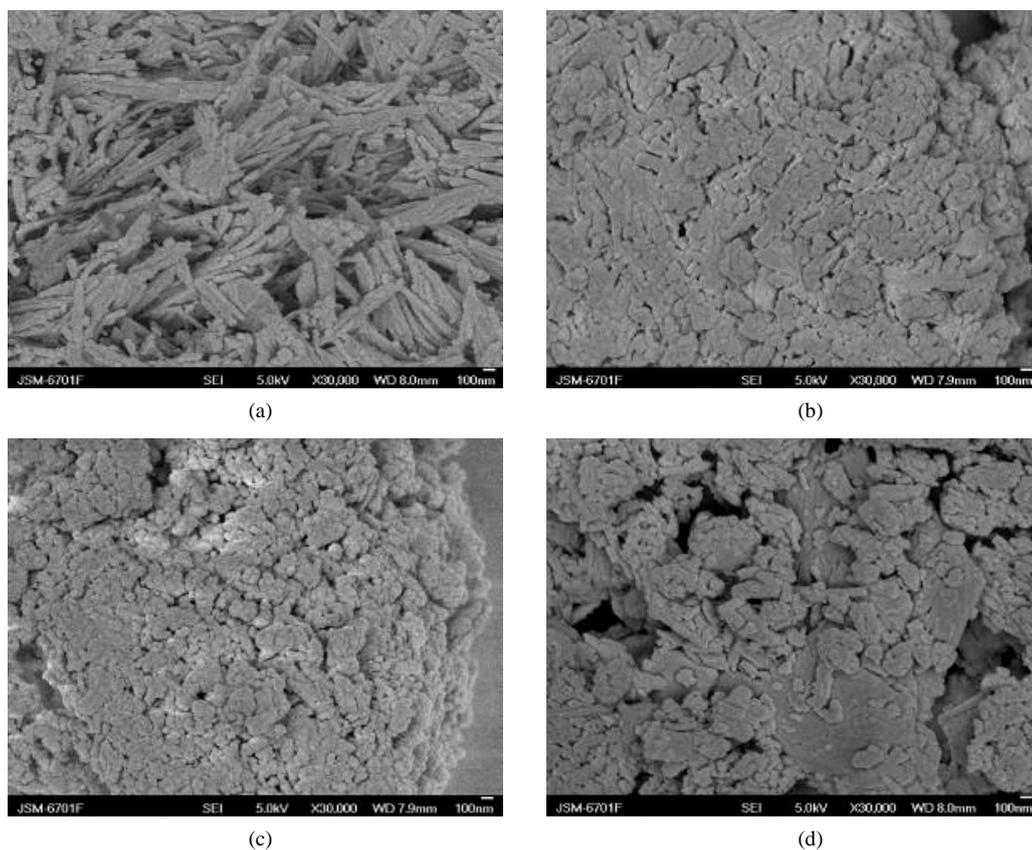
Figure 4. SEM micrographs of ATP, CaO/ATP, CaO/ATP modified samples by H_2SO_4 or NaOH. (a) ATP; (b) CaO/ATP; (c) CaO/ATP modified by NaOH; (d) CaO/ATP modified by H_2SO_4.
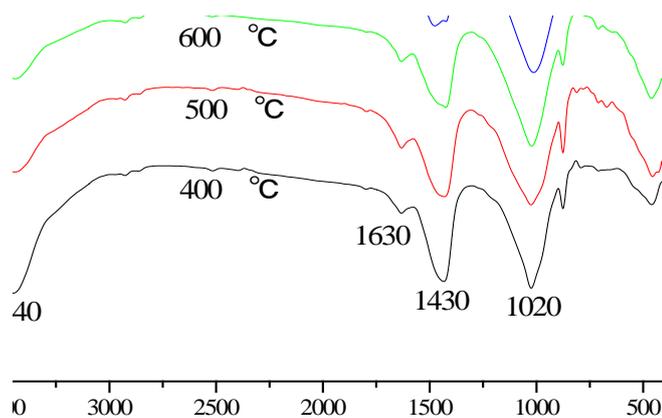

Figure 5. FT-IR results of CaO/ATP (different roasting temperature).

bands at 1630 cm^{-1} is flexural vibrations of water H-O-H. The strong wide absorption bands at 1020 cm^{-1} is dissymmetry stretching vibrations of Si-O-Si, and the absorption bands at 777 cm^{-1} and 476 cm^{-1} are symmetry stretching and flexural vibrations of Si-O. The strong wide absorption bands appeared at 3440 cm^{-1} became weak when increasing roasting temperature from 400°C to 700°C, for zeolitic water, crystal water and constitution water of ATP crystal will decrease when temperature increase. Crystal structure changed at high temperature. Over 600°C, zeolitic duct was destroyed, and zeolitic water disappeared.

3.2. SO$_2$ Desulfurizing Experiment by CaO/ATP Desulfurizer

Except ATP, CaO was another main component of the desulfurizer. Its content would influent sulfate efficiency. The results were presented in **Figure 6** and **Figure 7**. The SO$_2$ removal efficiency represents the ratio of SO$_2$ concentration at the inlet subtracting that at the outlet to that of inlet feed. Thus, the efficiency curves also indicate the penetrating curves. With increasing content of CaO, the penetrating time and sulfur tolerance were gradually increased. It was because CaO was basic oxide, which could react with acidic gas SO$_2$ quickly. In fact, the desulurizer has two effects on SO$_2$, ATP adsorbed SO$_2$ and CaO transferred it to sulfate. The higher CaO content was, the more SO$_2$ was transferred. Meanwhile, CaO content could not be too high, that would cause mechanical intensity of the desulfurizer decreased. As a result, CaO content should be about 30 wt%, the effect of desulfurization of the samples was better.

ATP is often modified by acid, such as sulfur acid and hydrochloric acid. When acid was dissociated in aqueous solution, H$^+$ was produced and exchanged with K$^+$, Na$^+$, Ca^{2+} of ATP to enlarge pore volume of that. In this study, H$_2$SO$_4$ and NaOH were used for CaO/ATP modifying, and the result can be seen in **Figure 8**. Because ATP was corporated with CaO, H$_2$SO$_4$ reacted with CaO and generated CaSO$_4$, which blocked the micropore and reduced its activities. The samples modified by NaOH had higher surface area so that the higher sulfur tolerance can be obtained.

Roasting temperature and time will influence the sulfur tolerance, as we saw from **Figure 9** and **Figure 10**. At
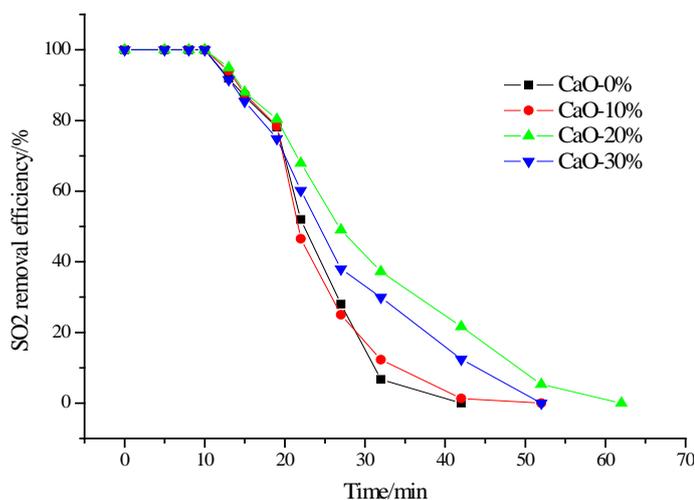
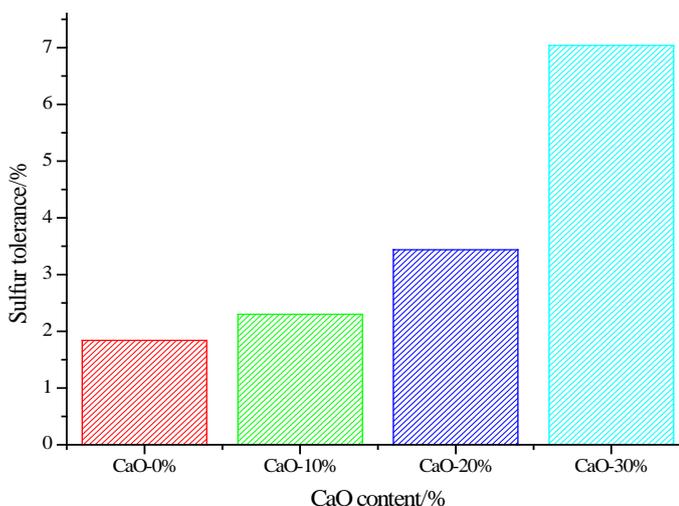**Figure 6.** Influences of CaO content on SO$_2$ removal efficiency.

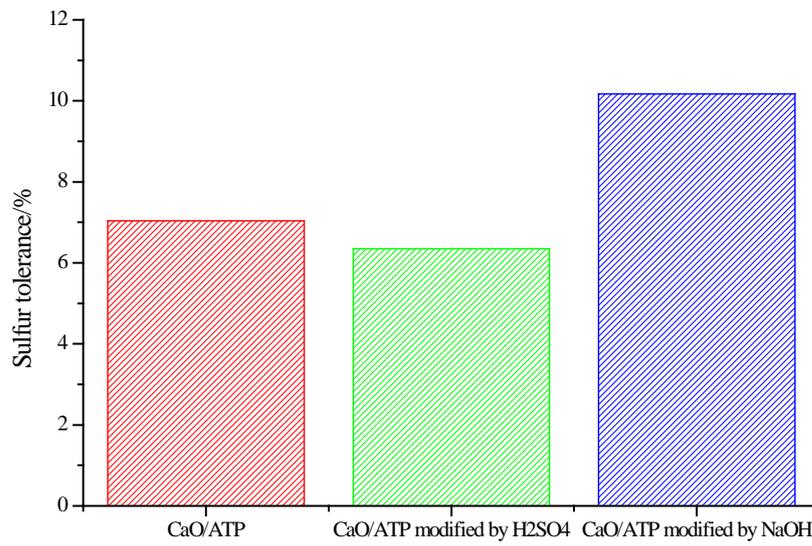**Figure 7.** Influences of CaO content on sulfur tolerance.

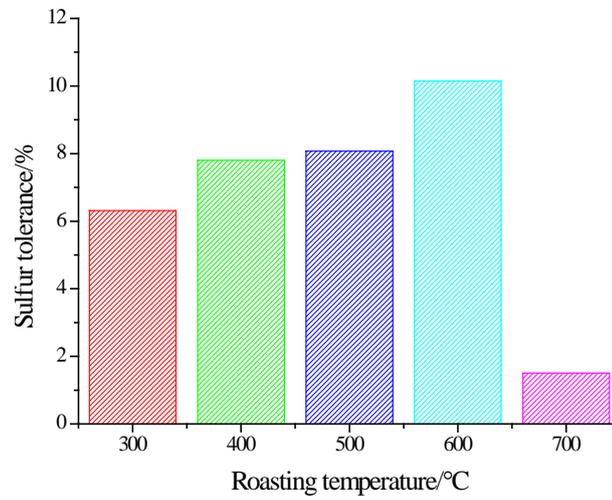**Figure 8.** Influences of modifier on sulfur tolerance.

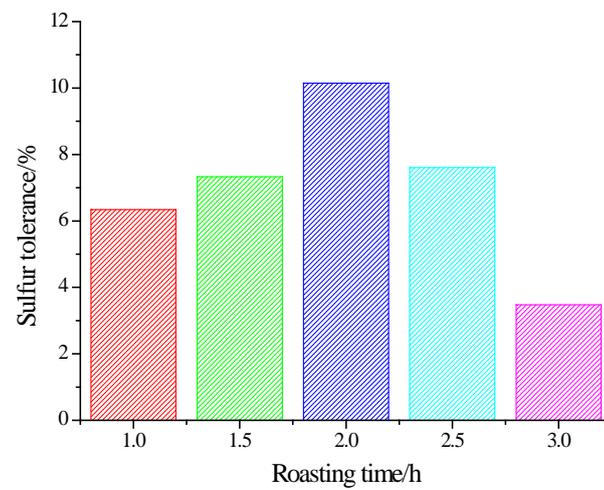**Figure 9.** Influences of roasting temperature on sulfur tolerance.

Figure 10. Influences of roasting time on sulfur tolerance.

600˚C and roasting sample 2 hours, highest sulfur tolerance (10.15%) was achieved. It is known from **Figure 5** that duct was destroyed when roasting over 600˚C, which will make the surface area of samples decrease. Roasting time will also influence the sulfur tolerance. The CaO/ATP samples were roasted to clot gradually. When roasted over 2 hours, the pore canal of samples would collapse because of losing water excessively.

4. Conclusion

A new CaO/attapulgite desulfurization agent was synthesized by mixing of CaO and attapulgite directly. The optimum synthesizing and operating conditions were as follows: weight ratio of CaO to attapulgite, 3:7; types of modifiers, NaOH (1 mol/L); roasting temperature and time, 600˚C and 2 hours; weight ratio of water to CaO/ATP desufurizer, 20 - 30 wt%. The desufurizer synthesized and operated under optimal synthesis conditions exhibited sulfur tolerance of 10.15 wt%.

This new approach showed promising in utilizing natural resource of Gansu, China, such as attapulgite in the production of desulfurization agent, which could significantly reduce the production cost and make the technique quite environmental friendly.

Acknowledgements

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