The Removal of Hydrogen Sulfide by Phosphate Ore Slurry

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Summary：In the present study, the reaction process of H_2S removal by calcined phosphate ore slurry was investigated by XRD and kinetics analysis. It was found that the absorption amount of H_2S was 69.47 mg in 200 min, and 70.09% of the absorption caused by calcium oxide, indicating that the reaction was mainly the action of calcium oxide. Furthermore, it is showed that Fe_2O_3 played an important role in the removal process. Fe(III) can be dissolved form the phosphate ore, and became an efficiently catalytic oxidant. H_2S can be catalytically oxidized by Fe(III)/Fe(II) system. It was indicated that about 30% removal of H_2S was caused by Fe(III). By the model analysis, the leaching reaction was belonged to the diffusion chemical reaction mixing control model. And the activation energy of the reaction was 17.224 kJ/mol obtained from the Arrhenius equation, which further proved that the reaction belonged to the mixed control model.

Keywords：Phosphate ore slurry; Hydrogen sulfide; Catalytic oxidation.

Introduction

Hydrogen sulfide (H_2S) is a typical toxic gas, which exits in natural gas, biogas petroleum, and other waste gas. It has a characteristic smell of rotten eggs [1-3]. H_2S is also produced in association with some industrial processes, such as gas streams from yellow phosphorus tail gas, natural gas processing, petroleum refining, paper and pulp manufacturing, and solid waste processing plants [4, 5]. Because of the significant economic and environmental repercussions for the H_2S separation and purification, lots of researchers developed many kinds of methods for the H_2S pollution control, including chemical oxidation, biological treatment, adsorption, etc [6-10]. Claus process is the most ancient removal methods of H_2S, which uses SO_2 to oxide H_2S, and the by-product is sulfur, while the sulfur conversion rate can be 94% ~ 98%, but there is a risk of secondary pollution by SO_2 and H_2S [11].

In our earlier study for the removal of H_2S [12], a kind of natural mineral, phosphate ore, had been developed as a new absorbent instead of traditional absorbent. Due to the Ca-based chemical composition, the phosphate ore showed an excellent performance on the removal of H_2S. However, the reaction mechanism was still not clear. Thus, in this study, the reaction mechanism has been further analyzed to investigate the role of reaction between H_2S and phosphate ore.

Experimental

In the present study, the raw samples of phosphate ore were obtained from Kunyang Phosphate Mine in Yunnan Province, China. To clean out the floatation [13, 14] on the particle surface, the samples were washed by distilled water twice. After calcination at 800~1000℃ for about 2h, the samples were crushed, ground, and then sieved to 200 mesh (about 74μm). Chemical analysis of the phosphate ore was carried out by standard gravimetric, volumetric and spectrometric methods, and the results are shown in Table-1.

The schematic experimental set-up is shown in Fig. 1. The simulated H_2S flue gas was prepared by the static air bag method. The mixed gas of H_2S, O_2 and N_2 were controlled by the flow-meter to make a required concentration. The well-prepared uniform mixture was called H_2S(in). In a cylinder-shaped glass reactor, H_2S(in) was reacted with suspended phosphate ore slurry. Furthermore, a homoeothermic water bath of magnetic stirrer was used to control the reaction temperature and agitation rate. Finally, the concentration of H_2S come out of the reactor (H_2S(out)) was detected by the multi-functional flue gas analyzer (RBRJ2KN, Germany). XRD was applied to identify the mineralogical constituents of the raw, calcined and reacted phosphate ore samples. The conditions of H_2S removal experiments were set as below: temperature was 20℃, gas flow rate was 300 ml/min, H_2S concentration was 1,500 mg/m^3, agitation rate was 1,000 r/min and oxygen content was 0.5%.

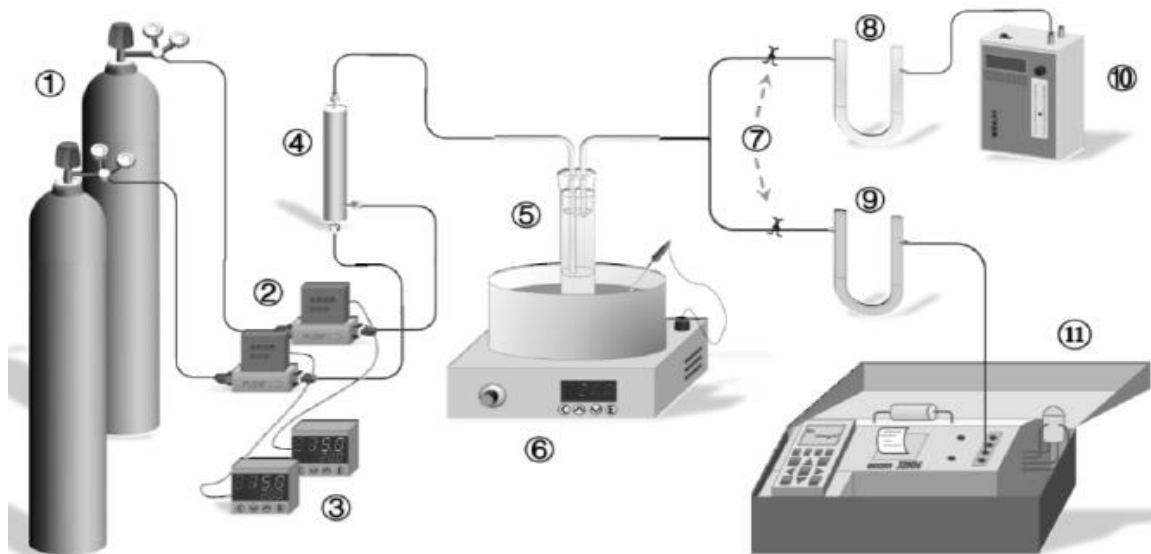*To whom all correspondence should be addressed.

Fig 1:   The schematic diagram of the experimental apparatus.

     1. gas cylinder 2.mass flow meter 3.digital display instrument 4.gas mixer 5.reactor

     6. homoeothermic water bath of magnetic stirrer 7. clip 8.tail gas absorption 9.u-shaped gas drying tube 10. atmosphere sampling instrument 11. flue gas analyzer

Table-1:   Phosphate ore composition before and after calcinations (%).

Components	Al_2O_3	$Ca_5(PO_4)_3F$	SiO_2	Fe_2O_3	$MgCO_3$	$CaCO_3$	Others
Raw ore	0.77	66.60	1.91	0.56	12.67	11.83	5.66
Components	Al_2O_3	$Ca_5(PO_4)_3F$	SiO_2	Fe_2O_3	MgO	CaO	Others
Calcinated ore	0.83	73.56	1.82	0.60	6.32	6.39	10.48
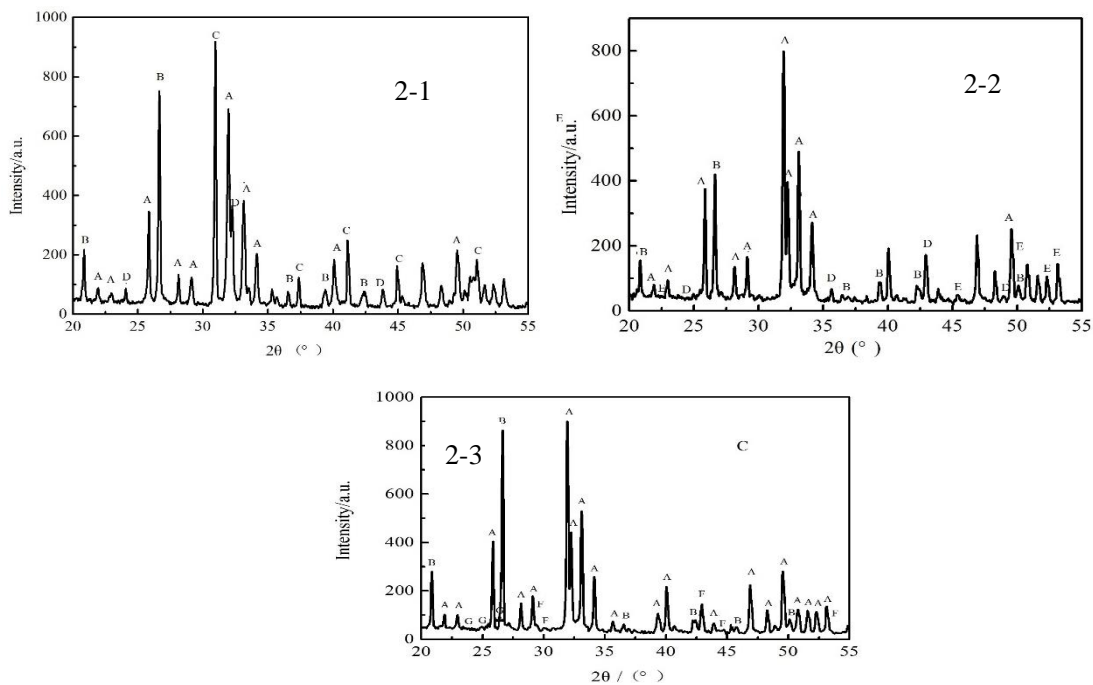
A-$Ca_5(PO_4)_3F$, B-SiO_2, C-$CaMg(CO_3)_2$, D-Fe_2O_3, E-$Ca_5(PO_4)_3(OH)$, F-Fe_3O_4, G-sulfur

Fig. 2:   XRD spectra: 2-1 Raw ore, 2-2 Calcined for 60 min at 900℃ and 2-3 After reaction with H_2S for 120 min.

Results and Discussion

XRD analysis

XRD determination was used to investigate the change in chemical composition or structure occurred in samples mentioned above. It is obtained from Fig. 3 that the main minerals of the raw samples were calcite, fluorapatite and carbonate-fluorapatite. After calcination, the main minerals became to calcium oxide and fluorapatite, which agreed with Table-1. Thus, the removal of H_2S by calcined phosphate ore was mainly due to the calcium oxide, the reaction process was presented as follows [17]:
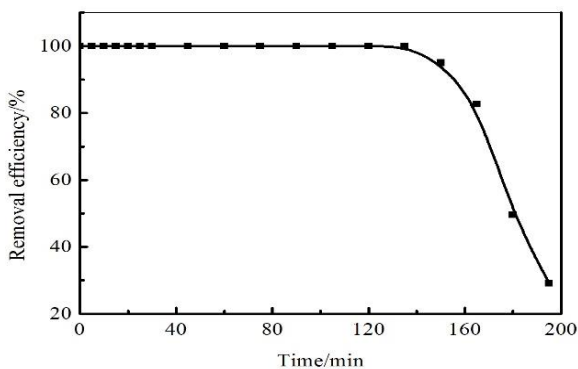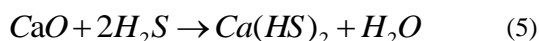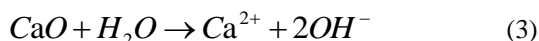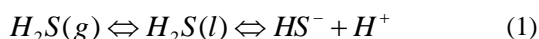
$$H_2S(g) \Leftrightarrow H_2S(l) \Leftrightarrow HS^- + H^+ \tag{1}$$

$$HS^- \Leftrightarrow S^{2-} + H^+ \tag{2}$$

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \tag{3}$$

$$H^+ + OH^- \rightarrow H_2O \tag{4}$$

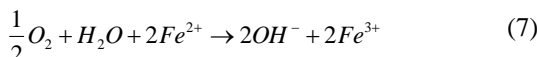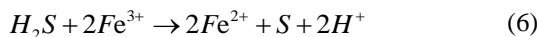$$CaO + 2H_2S \rightarrow Ca(HS)_2 + H_2O \tag{5}$$

Fig. 3:   The removal rate of H_2S with the change of the reaction time.

The XRD results also showed that the main minerals of the reacted samples were fluorapatite, silica, ferroferric oxide and sulfur (Fig. 3-3). The calcium oxide disappeared after reaction is due to the calcium absorption of hydrogen sulfide in the process of reaction after dissolved in the liquid phase [18]. A redox reaction of H_2S occurred by the detection of sulfur, which was not included in the equation (1)-(5).
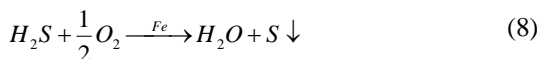
The role of Fe_2O_3 in the ore

It was not only the redox reaction of H_2S, but also can be obtained from Fig. 3 that the H_2S absorb capacity of phosphate ore was 69.47mg within 200 min. Through the analysis of the components before and after reaction, the consumed mass of calcium oxide was 40.1 mg, and the mass converted to H_2S was 48.69 mg by equation (5). Therefore, the removal percentage of H_2S by calcium oxide was 70.09%.

By a further investigation, it was found that Fe_2O_3 could be the key point of the H_2S removal process [19]. As the results showed above, iron oxide changed to ferroferric oxide after reaction. Fe(Ⅲ) is an effective oxidant, and often used in the liquid-phase catalytic oxidation reaction[20,21]. Based on the following equation (6)~(8), it can be conclude that Fe_2O_3 played an important role in the removal of H_2S by phosphate ore slurry.

$$H_2S + 2Fe^{3+} \rightarrow 2Fe^{2+} + S + 2H^+ \tag{6}$$

$$\frac{1}{2}O_2 + H_2O + 2Fe^{2+} \rightarrow 2OH^- + 2Fe^{3+} \tag{7}$$

Overall reaction:

$$H_2S + \frac{1}{2}O_2 \xrightarrow{Fe} H_2O + S \downarrow \tag{8}$$

Kinetics analysis of the reaction process

From the view point of many researchers, the leaching performance of calcium from the ore could be attributed to the gas-liquid-solid reaction process, and the kinetic model varies with the control steps [10,22]. If the reaction interface was controlled by a chemical reaction, the relationship between the calcium leaching rate and the reaction time should be in accordance with equation (9).

$$1 - (1 - X)^{1/3} = kt \tag{9}$$

If the reaction was diffusion-controlled, the relationship between calcium leaching rate and time should be consistent with equation (10).

$$1 - \frac{2}{3}X - (1 - X)^{2/3} = kt \tag{10}$$

Table-2:   Correlation coefficients (R2) of three kinetic models at different leaching temperature.

T/°C	$1-(1-X)^{1/3}=kt$		$1-\frac{2}{3}X-(1-X)^{2/3}=kt$		$\frac{1}{3}\ln(1-X)+\left[(1-X)^{(-1/3)}-1\right]=kt$	
	b	R^2	b	R^2	b	R^2
20	0.0399	0.8217	0.0028	0.9462	0.0011	0.9555
30	0.0486	0.7801	0.0047	0.9225	0.0024	0.9524
40	0.044	0.838	0.0029	0.912	0.0003	0.9288
50	0.0433	0.8671	0.0023	0.9217	0.0007	0.9477
60	0.0405	0.9146	0.0009	0.9582	-0.0003	0.9868

Li proposed a dynamic model (equation (10)) suitable for diffusion-chemical reaction mixing control based on a thorough study of the characteristics of manganese leaching rate with particle size during leaching, where k is the chemical reaction rate and X is the manganese leaching rate [23].

$$\frac{1}{3}\ln(1-X)+\left[(1-X)^{(-1/3)}-1\right]=kt \qquad (11)$$

The relationship between the leaching rate of manganese and the reaction time at different temperatures was well studied and fitted according to the three models mentioned above. The resulting constant term *k* and the linear fit ratio were shown in Table-2. The linear fitting rate of the diffusion control and chemical reaction control models was low, while the linear fit rate of the mixed control model was above 0.92, indicating that the reaction in the present study was a mixed control process. According to the equation (11), the linear relationship between different temperatures can be calculated and presented in Fig. 4, and the *k* values at different temperatures were shown in Table-3.
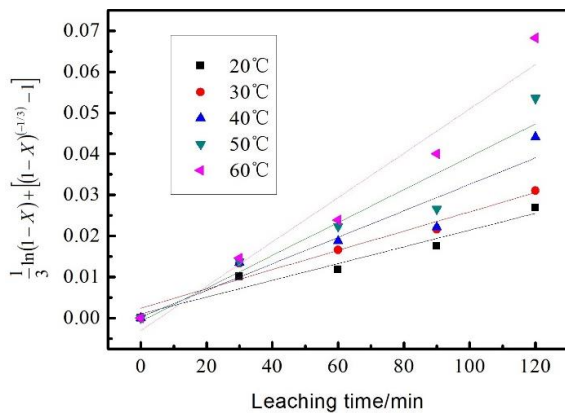
Table-3:   Value of *k* under different temperature.

T/°C	20	30	40	50	60
10000*k	2	3	3	4	5

For most chemical reactions, the relationship between the reaction rate and temperature can be expressed by the Arrhenius equation (12) [24]. The activation energy can be obtained graphically. Take the natural logarithm of the Arrhenius equation (13), and then the activation energy of the reaction can be obtained by equation (14).

$$k = A_0 \times e^{-\frac{E_a}{RT}} \qquad (12)$$

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A_0 \qquad (13)$$

$$E_a = -k \times R \qquad (14)$$

In this study, the reaction rate k at different temperatures and the corresponding lnk value was calculated by equation (14). Then the relationship between 1/T and lnk was shown in Fig. 5. Finally, the reaction activation energy was calculated to be 17.224 kJ/mol. It was found that the activation energy was 12-42 kJ/mol when the chemical reaction process was mixed control model [24]. Then, the leaching reaction in this study was further proved belonged to the diffusion-chemical reaction mixed control process.
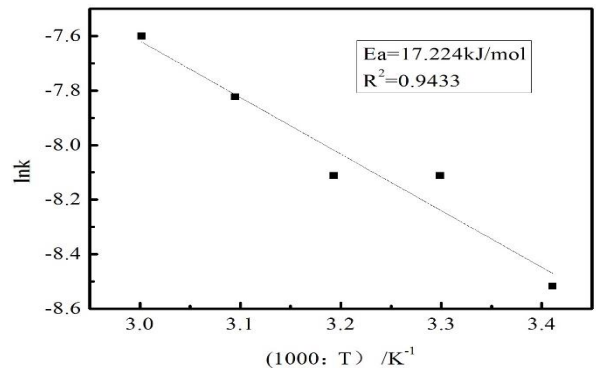

Fig. 4:   Relationship between $\frac{1}{3}\ln(1-X)+\left[(1-X)^{(-1/3)}-1\right]$ and time.

Fig. 5:   Relationship between ln*k* and 1/*T*.

Conclusion

In summary, the process of H_2S removal by calcined phosphate ore slurry was investigated by XRD and kinetics analysis. The total amount of H_2S absorbed by the ore in 200 min was 69.47 mg. Through the analysis of the components before and after the mineral reaction, the mass of calcium oxide consumed in the reaction was 40.1 mg, and the mass converted to H_2S was 48.69 mg, and the ratio of total hydrogen sulfide absorption was 70.09%, indicating that the reaction was mainly the action of calcium oxide. Furthermore, Fe_2O_3 played an important role in the removal process because $Fe(III)$ was an effective oxidant, which could cause the other about 30% removal of H_2S.

Through model analysis, the leaching reaction belonged to the diffusion chemical reaction mixing control model. The rate constants were calculated by the relationship between the model equations and time at different temperatures. The activation energy of the reaction was 17.224 kJ/mol obtained from the Arrhenius equation, which further proved that the reaction belonged to the mixed control model.

Acknowledgements

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