

Hydrogen sulfide removal by copper sulfate circulation method

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Abstract—Although copper sulfate (CuSO_4) as a valuable desulfurizer is commonly used in the laboratory, it is not applied in industry due to its high cost and lack of practical regeneration method. In this study, a method for regeneration of the absorption product copper sulfide (CuS) under mild conditions is put forward. In the presence of sodium chloride (NaCl), CuSO_4 could be regenerated smoothly in acid solution and be recycled for the absorption of hydrogen sulfide (H_2S). Specifically, under the conditions of 0.30 mol/L chloride ion (Cl^-), 1.8% acidity at 323 K, for 5.5 h, the regeneration efficiency will be higher than 99%. Moreover, extensive experimental studies showed that the addition of Cl^- would not observably influence the absorption efficiency of H_2S . These results reveal the potential for developing a novel, efficient and low-cost desulfurization technology.

Keywords: Hydrogen Sulfide, Copper Sulfate, Regeneration, Oxygen Oxidation

INTRODUCTION

Hydrogen sulfide (H_2S) is a colorless, combustible and poisonous gas with an offensive stench which smells like rotten eggs. It can be detected by humans at a volumetric level of 0.21 ppb [1]. When H_2S concentration exceeds 30 ppm, it will affect the human nervous and respiratory systems. Inhalation of even a low amount of H_2S will be lethal. From the perspectives of health and safety, it is very important to remove H_2S from gas streams before vented. In consideration of the corrosion to equipment during transportation and distribution, as well as the prevention of catalyst poisoning, it is also necessary to remove H_2S from the gas streams prior to use.

Therefore, it is imperative to find an efficient sulfur removal technology, which has been extensively attempted over centuries. In general, the desulfurization methods can be divided into chemical, physical and biochemical systems [2]. Among chemical methods, direct conversion and chemical solvent methods are applied worldwide. The early industrial use of Fe(III) as a regenerable oxidant for gas stream hydro-desulfurization appeared around the 1830s with the introduction of ferric oxide (Fe_2O_3) as a replacement for calcium hydroxide [Ca(OH)_2]-based desulfurization processes [3]. In the 1930s, a creative method using alcohol amine to remove H_2S appeared and which is still the primary process for natural gas sweetening [4]. The most commonly used amines are methyldiethanolamine (MDEA), monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGE) and diisopropanolamine (DIPA) [5]. Besides amine process, chelated iron is also a mature technology used in small-scale desulfurization. The introduction of chelated iron processes can be traced to the early 1960s

[6], but its industrial operation did not succeed until small capacity systems were commissioned in the 1970s [7]. Due to the generation of degradation product, operation could only be sustained by continuous addition of considerable quantities of costly ethylene diaminetetraacetic acid (EDTA) and hydroxyethyl-EDTA (HEDTA) [8,9]. In addition, biotechnological process [10,11], catalytic process [12-15] and adsorption using activated carbons [16,17] or carbon nanotubes [18] as an absorbent are used to remove H_2S .

For a gas that contains both H_2S and carbon dioxide (CO_2), it is better to get rid of them separately to collect pure CO_2 . Though DIPA and MDEA were found to be highly selective for H_2S in natural gas, 10% of CO_2 would be absorbed. The chelated iron methods are 100% selective for H_2S , but the capacity of desulfurization is limited by the H_2S concentration in complex gas stream [9], which is a crucial disadvantage for practical use. Therefore, developing a mild, cheap and efficient desulfurization technology with high selectivity and high capacity in industry is still desirable.

Selective H_2S removal can be accomplished by a process based on the precipitation reaction of H_2S with metal ions in an aqueous solution. Since copper sulfide (CuS) has an extremely low solubility product, CuSO_4 solution has an excellent desulfurization performance [19]. The process will be the most attractive when selective removal of H_2S is required, as will be the case in most gases containing a high level of CO_2 . However, it is difficult to reuse CuS due to the lack of regeneration methods for free cupric ion (Cu^{2+}) from CuS , which impeded its industrial application. Thus, developing an efficient protocol for the circulation regeneration of CuSO_4 from CuS will be the most attractive in an industrial process. A tentative method is to collect the CuS precipitate, roast it at 1,073 K, and then add acid to dissolve the product CuO [20]. Obviously, this method is not suitable for industrial application because of the operational complex of the procedure.

Herein, we report a novel and efficient method for the regeneration of CuSO_4 from CuS in an acid solution using air as the green

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oxidant in the presence of sodium chloride (NaCl). In this system, highly selective absorption of H_2S is realized and the absorption ratio of H_2S obtains nearly 100% at room temperature and atmospheric pressure. Notably, only through continuous regeneration of CuSO_4 from CuS , the cost of desulfurizer is significantly reduced. In addition, using air as the cheap oxidant represents an added advantage of the method for commercial applications. The results are beneficial to the further study of treatment techniques to remove H_2S by circulation method under mild conditions with almost no waste. This study might be paving the way for industrial applications of highly selective and low-cost H_2S removal through circle regeneration of CuSO_4 .

THEORY

Upon the absorption of H_2S into an aqueous bivalent metal sulfide solution, the following reactions will occur. First, H_2S will be transported from the gas phase and dissolve physically in the liquid phase, and then, it dissociates in two steps as shown in Eqs. (2) and (3) [19].



If the soluble product of the metal sulfide is exceeded, the sulfide ion and the metal ions will subsequently precipitate [19]. In this paper, the metal ion is Cu^{2+} , so the precipitation is CuS .



In the solution, CuS can be oxidized into copper hydroxide ($\text{Cu}(\text{OH})_2$) by air as shown in Eq. (5), and the reaction will be different under the acidic condition, because of the formation of free Cu^{2+} as shown in Eq. (6).

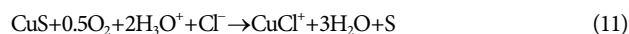


The oxidation of CuS in acid solution is reversible, and the formation of a tight passivation sulfur layer will lead to the incomplete oxidation of CuS . It was found that chloride ion (Cl^-) could speed up the oxidation of CuS in an acid solution, by reviewing the literature about metallurgy [21-27]. When low concentration of chloride is added, the oxidation rate of CuS will be speeded up. Despite some detailed studies that have been carried out in hydrometallurgical fields, reasons for the beneficial role of low chloride concentration in sulfide oxidation in sulfate systems still remain unknown. The general view is that during atmospheric oxidation in the presence of NaCl in H_2SO_4 , a porous and somewhat crystalline sulfur layer is formed on the sulfide surface [28,29], so that the oxidation would proceed smoothly.

When Cl^- and Cu^{2+} occur within the same aqueous system, the composition of the resulting solution is governed by the following equilibria [30]:



Herreros et al. found that the predominant species are Cu^{2+} and CuCl^+ in the $\text{Cu}^{2+}/\text{Cl}^-$ system [31]. Based on their results, the overall reaction involving the formation of CuCl^+ in acid solutions at low pH is shown in Eq. (11) [32].



MATERIALS AND METHODS

1. Experimental Methods

1-1. Absorbent Process of H_2S

Experiments were performed in lab-scale as shown in Fig. 1.

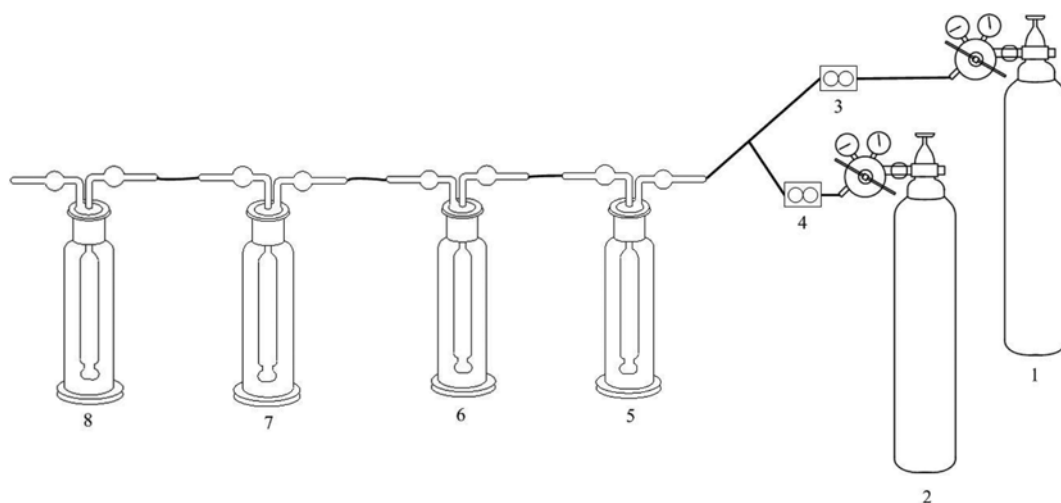


Fig. 1. Experimental set-up.

1, 2. Cylinder

3, 4. Flow meter

5, 7. Surge flask

6, 8. H_2S absorption flask

The setup consisted of four gas bottles and two gas cylinders, one filled with H_2S (H_2S bottle was bought from Beijing Huake specialty gases Co. The purity is 99.99%), and the other is N_2 (N_2 bottle was bought from Fuzhou Xinhang gases Co. The purity is over 99.99%). In the surge flask, H_2S was mixed with N_2 to compose the desired gas flow. The No. 5 and 7 bottles are for buffering gas and the other two bottles are filled with aqueous CuSO_4 to absorb H_2S . No. 6 flask will absorb the most H_2S , and the other absorption-flask is arranged for preventing the residual H_2S diffusion into the air. The absorptivity of H_2S by CuSO_4 solutions with varying amounts of H_2SO_4 was calculated by comparing the concentrations of CuSO_4 in the first absorption flask before and after absorption.

1-2. Regeneration Tests

The regeneration tests were in a 250 mL cylindrical glass reactor containing 100 mL of solution, and the air was sprayed at the reactor's bottom at a flow rate of 100 L/h by an aerator to oxidize the precipitate.

2. Analytical Methods

In the absorption test, No. 7 and 8 flasks were not used and the concentration of outlet H_2S was detected by HD-5 pump suction type gas detector (Gas detector was bought from Nanjing Huideng electronics co., Ltd.) and its measuring range was from 0 to 100 ppm.

The concentration of CuSO_4 solution was measured by an ultra violet-visible (UV-VIS) spectrophotometer (UV1101) at 807 nm. Standard solutions (concentrations of solutions with or without addition of Cl^- range from 0.00 to 0.10 mol/L) were prepared for drawing some calibration curves with the UV-VIS workstation.

RESULTS AND DISCUSSION

1. Effects of CuSO_4 Concentration in Aqueous Solutions on Absorption Efficiency

An absorption test was carried out at 293 K in 100 mL 0.05 mol/L CuSO_4 solutions without H_2SO_4 or NaCl. The mixed gas flow was 50 L/h and the H_2S volume concentration was kept at 2%. The results are shown in Fig. 2. Before 300s, the outlet H_2S concentration remains 0 and then starts to increase quickly. According to Söhnel and Garsides, if highly insoluble precipitates (as is the case for CuS) are formed in a process, the precipitation (nucleation) may

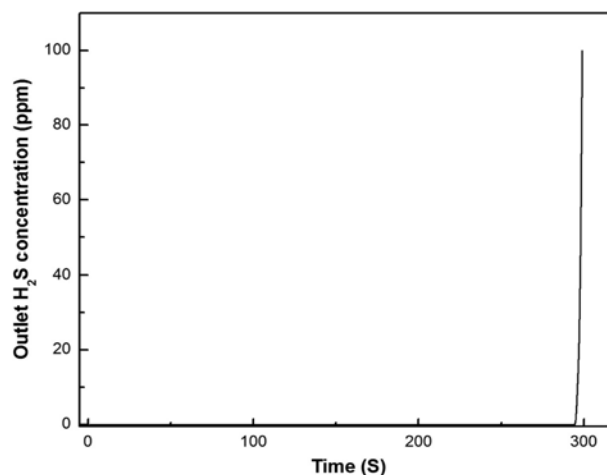


Fig. 2. The absorption of H_2S in a CuSO_4 solution. CuSO_4 : 0.05 mol/L, 100 mL, H_2S : 20 mL/min, N_2 : 1 L/min, 298 K.

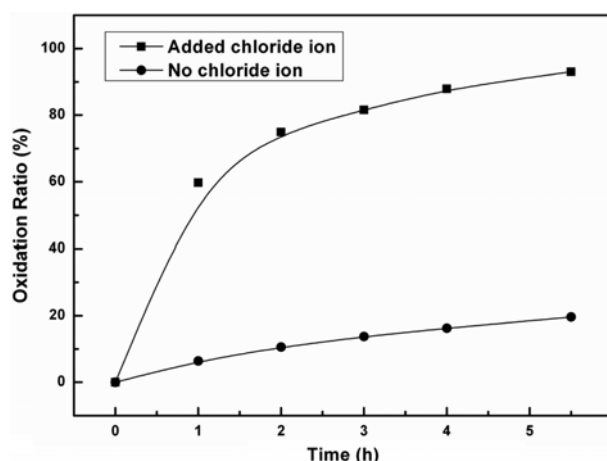


Fig. 3. Comparison of regeneration ratio of copper sulfide solution with or without addition of chloride ion. CuS : 6.6×10^{-3} mol, 98% H_2SO_4 : 1.81 wt%, air flow rate: 100 L/h, 303 K.

be considered to be instantaneous with respect to mass transfer [33]. For H_2S absorption accompanied by an instantaneous irreversible reaction in a CuSO_4 solution, the absorption rate is deter-

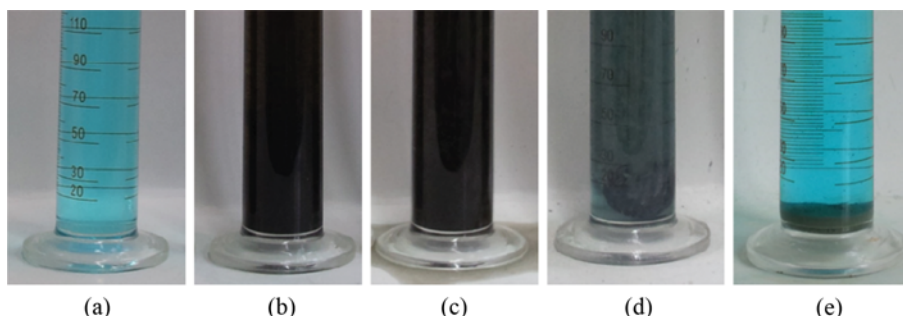


Fig. 4. Color variations of solution in adsorption and regeneration procedure. CuS : 6.6×10^{-3} mol, 98% H_2SO_4 : 1.81 wt%, NaCl: 0.30 mol/L, air flow rate: 100 L/h, 303 K. (a) Original solution for adsorption test. (b) Solution after adsorption test. (c) Solution after oxidation for 0.5 h. (d) Solution after oxidation for 2 h. (e) Solution after oxidation for 5.5 h.

mined by the mass transfer on both sides of the gas-liquid interface, or even by gas phase mass transfer. The absorption efficiency of H_2S would keep at 100% until the CuSO_4 concentration dropped below a very low level of 4–10 mmol/L [34]. Because of this, CuSO_4 has the potential to be a reliable industrial desulfurizer as long as there is a low concentration of copper ions in the solution.

3. Regeneration Procedure

A comparison of regeneration tests was carried out in CuSO_4 solution containing 6.6×10^{-3} mol CuS, 1.81 wt% H_2SO_4 in two reactors at 303 K. One solution had been added with 0.3 mol/L NaCl and the other one had not. Air was bubbled at the reactor's bottom at a flow rate of 100 L/h by an aerator. The copper regeneration rate is depicted as a function of oxidation ratio in Fig. 3. The color variations of solution are shown in Fig. 4.

As is shown, the regeneration rates of CuS in the two solutions were quite different; the one added NaCl was much quicker. After 5.5 h, the faster one achieved an oxidation rate of 93% compared with the other one, which was less than 20%.

According to the literature, NaCl could accelerate the oxidation, probably owing to the formation of a porous and somewhat crystalline sulfur layer. Without Cl^- , a tight passivated sulfur layer would form on the sulfide surface, which would block the active surface and slow down the reaction [21–27].

To verify the formation of the porous and somewhat crystalline sulfur layer, unoxidized CuS precipitates and the obtained precipitates after oxidation of CuS (in the presence of Cl^-) by air were all tested by X-ray diffraction (Ultima IV) and SEM (SIGMA). The analysis of X-ray diffraction demonstrated elemental sulfur was produced when 90% of CuS precipitates were oxidized by air, as shown in Fig. 5. But solid sulfur is difficult to recognize through the observation of SEM (Fig. 6). These results, in agreement with the report of literature [28,29], suggest that the reaction product may be a somewhat crystalline sulfur layer in the presence of Cl^- .

4. Effects of Cl^- Concentration on Absorption and Regeneration

Although NaCl has positive effect on the regeneration procedure of Cu^{2+} , we still wondered if it would reduce the absorption of H_2S . Therefore, an absorption test was conducted in aqueous CuSO_4 solution (100 mL, 0.05 mol/L) containing 0.30 mol/L NaCl without addition of H_2SO_4 . The absorption efficiency of H_2S is shown in Fig. 7(a). In conclusion, the addition of NaCl into the aqueous CuSO_4 solution will not influence the absorption efficiency of H_2S ,

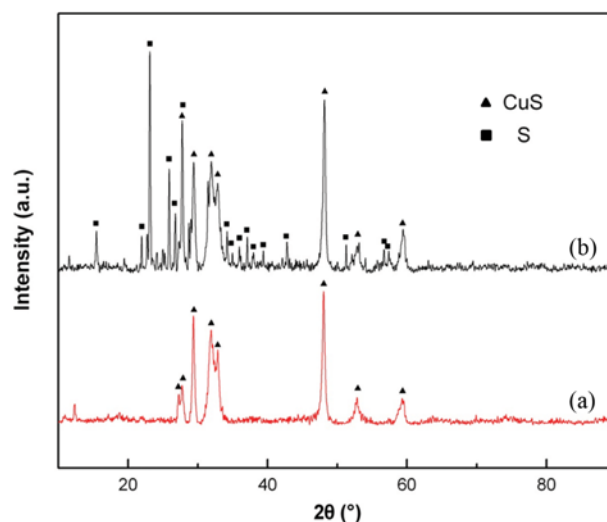


Fig. 5. XRD patterns of the precipitates. (a) Unoxidized CuS precipitates. (b) Precipitates that 90% of CuS was oxidized.

because Cl^- will not participate in the absorption reaction. But Cl^- concentration has a huge impact on the regeneration of Cu^{2+} (Fig. 7(b)). Those regeneration tests were performed in solutions containing 6.6×10^{-3} mol CuS, 5.23 wt% H_2SO_4 and varying amounts of NaCl at 293 K. The oxidation rate of CuS enhanced gradually with the increase of Cl^- concentration in our experimental scope. Within an hour, less than 20% of CuS was oxidized in the solution added with 0.10 mol/L Cl^- , while up to 60% of CuS was oxidized in the solution added with the highest concentration 0.30 mol/L. These results indicate that high Cl^- concentration is conducive to speeding up the regeneration. Though the mechanism of how low chloride addition promotes the CuS oxidation is still not clear. The reason may be, in the experimental range, more Cl^- will lead to the formation of a more porous and somewhat crystalline sulfur layer, so that the oxidation rate is quicker.

5. Influence of Acidity on Absorption and Regeneration Efficiency

Note, from Eq. (6), that the oxidation of copper should be carried out in acid solution, so a series of absorption tests were performed in CuSO_4 solutions (constant concentration of 0.05 mol/L, no NaCl). The solutions contained varying amounts of H_2SO_4 and

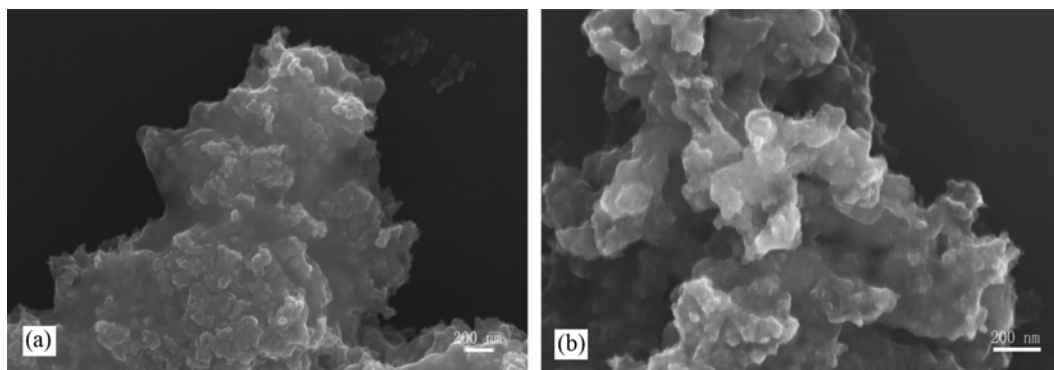


Fig. 6. SEM images of CuS precipitates' surface. (a) Unoxidized CuS precipitates. (b) Precipitates that 90% of CuS was oxidized.

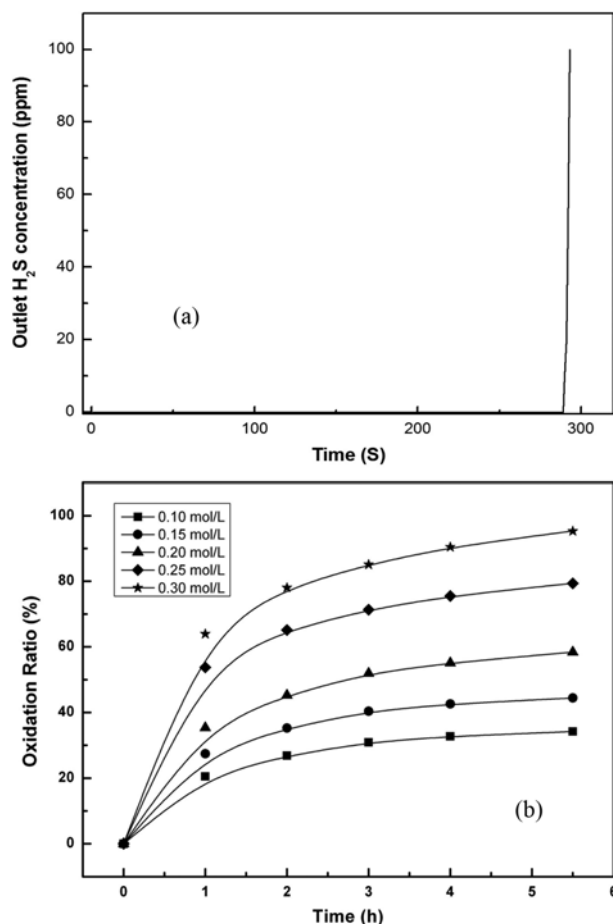


Fig. 7. Effects of Cl-concentration on (a) absorption of H₂S and (b) regeneration of CuS. (a) CuSO₄: 100 mL, 0.05 mol/L, NaCl: 0.30 mol/L, H₂S: 20 mL/min, N₂: 1 L/min, 293 K. (b) CuS: 6.6 × 10⁻³ mol, 98% H₂SO₄: 5.23 wt%, air flow rate: 100 L/h, 293 K.

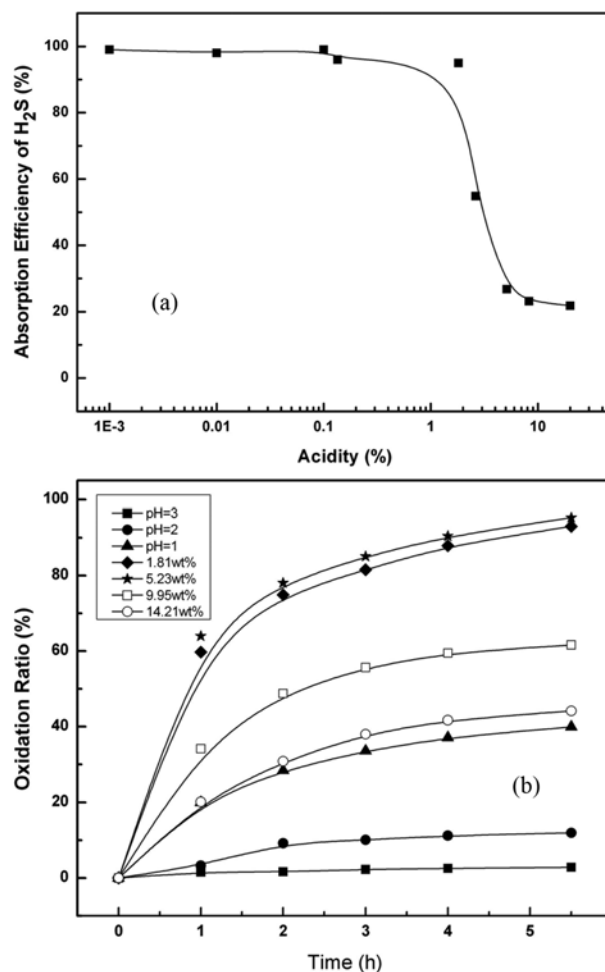


Fig. 8. Effects of acidity on (a) absorption of H₂S and (b) regeneration of CuS. (a) CuSO₄: 100 mL, 0.05 mol/L, H₂S: 20 mL/min, N₂: 1 L/min, 293 K. (b) CuS: 6.6 × 10⁻³ mol, NaCl: 0.30 mol/L, air flow rate: 100 L/h, 293 K.

the acidity ranged from 0.001% to 20%. The absorptivity of CuSO₄ solutions was calculated by comparing the concentrations of CuSO₄ in the first absorption flask before and after absorption. The duration time of inlet gas was 200 s. The results are shown in Fig. 8. Less than 1.8% acidity, the absorption efficiency was higher than 95%, but it would fall rapidly as the acidity rose. When the acidity exceeded 5%, the absorption efficiency of H₂S was only 20% and the rate was unfavorable for practical application.

The reason may be H₂S will dissociate in two steps in the liquid phase, and both of them will produce hydrogen ion as shown in Eqs. (2) and (3). The first and second dissociation constant are defined as Eqs. (12) and (13).

$$K_{a1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} \quad (12)$$

$$K_{a2} = \frac{[\text{S}^{2-}][\text{H}_3\text{O}^+]}{[\text{HS}^-]} \quad (13)$$

At the same temperature, the dissociation constant was certain. For the first step, if the amount of H₂S [L] that transported from the gas phase is constant, with the H⁺ concentration in aqueous solu-

tion gradually increasing, the amount of HS⁻ decreases. Second step is similar, so that the final dissociation product S²⁻ is less. Considering the above analysis, high H⁺ concentration will influence the dissociation of H₂S molecules to decrease the absorption.

The regeneration efficiency would be satisfactory when acidity was 1.81% or 5.23%. The regeneration tests were carried out in solutions containing 6.6 × 10⁻³ mol CuS, 0.30 mol/L NaCl and varying amounts of H₂SO₄. After 5.5 h, the regeneration efficiency at those conditions exceeded 90%. In consideration of both absorption efficiency and regeneration efficiency, the acidity should be controlled at 1.8%, namely, 100 mL of solution was added with 1 mL of 98% H₂SO₄.

6. Effects of Reaction Temperature on Regeneration Efficiency

A series of regeneration tests were carried out several times in solutions containing 6.6 × 10⁻³ mol CuS, 0.30 mol/L NaCl and 1.81 wt% H₂SO₄ at different temperatures, and the results are shown in Fig. 9. Clearly, high temperature does not necessarily lead to high regeneration efficiency. At the above conditions, 323 K was the best temperature for the regeneration tests. This is because the increase of the oxidation rate with increasing temperature may have been

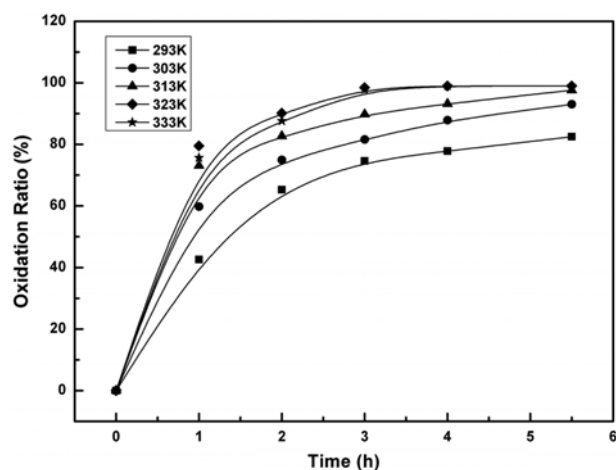


Fig. 9. Effects of reaction temperature on regeneration efficiency of CuS. CuS: 6.6×10^{-3} mol, 98% H_2SO_4 : 1.81 wt%, NaCl: 0.30 mol/L, Air flow rate: 100 L/h.

offset by the decreased dissolved oxygen content as the temperature exceeded 333 K. Though the reaction rate was slower at other temperatures, the final regeneration efficiency also exceeded 97% after some hours.

7. Precipitate

The regeneration efficiency could not be 100%, probably because some precipitates could not be oxidized. It was unmistakable from Eq. (6) that the elemental sulfur would be produced. As mentioned previously, in the presence of NaCl, a porous and somewhat crystalline sulfur layer rather than a tight passivated sulfur layer is formed on the sulfide surface, which blocks the surface. The sulfur layer would still contain some CuS, which can be oxidized hardly. Elemental analysis (Vario EL III) was performed to obtain the content percentage of precipitates, and the results are shown in Table 1.

Notably, the color of precipitates became lighter and the percentage content of sulfur from elemental sulfur and CuS significantly

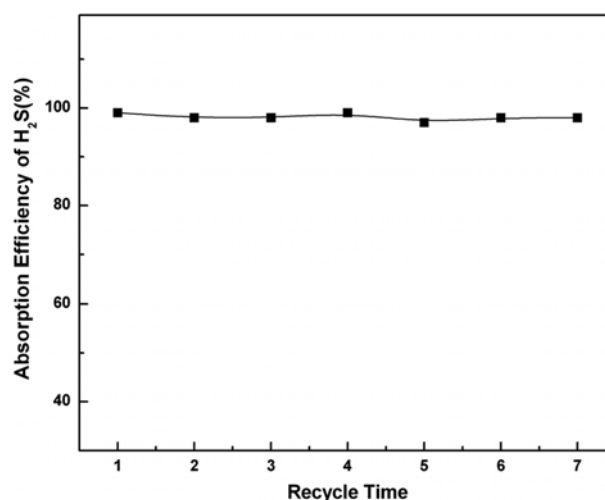


Fig. 10. Effects of CuSO_4 circulation experiment on absorption efficiency. 98% H_2SO_4 : 1.81 wt%, NaCl: 0.30 mol/L, air flow rate: 100 L/h.

increased with the extension of regeneration time, as shown in Table 1. Elemental quantitative analysis of precipitations suggested that CuS content decreased gradually and the reaction product sulfur got more. After regeneration for needed time under good conditions, the CuS content would be lower than 5%.

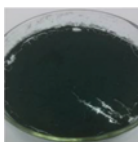
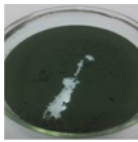
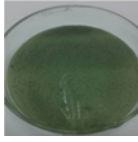
8. Effects of CuSO_4 Circulation Experiment on Absorption Efficiency

A circulation absorption test was carried out in aqueous CuSO_4 solution (100 mL, 0.05 mol/L) containing 0.30 mol/L NaCl and 1.81 wt% H_2SO_4 to study the effect of regenerated CuSO_4 on absorption efficiency. The duration time of inlet gas was 200s and oxidation time was 3 h after absorption (Because of a small amount of CuS, the regeneration efficiency of 3 h approached 100%). The results are shown in Fig. 10. Clearly, after seven times circulation experiment, the removal efficiency of H_2S was no lower than 98%. This explains regenerating will not influence the absorption efficiency. The results show the potential for creating a continuous process to remove H_2S use CuSO_4 in the industry.

CONCLUSIONS

We have successfully developed a selective and efficient method for the H_2S removal through the recycle regeneration of CuSO_4 from CuS. The absorption ratio of H_2S in a CuSO_4 solution was nearly 100% and the regeneration efficiency at specific conditions (323 K, 0.30 mol/L Cl^- , 1.8% acidity, 2 h) surpassed 90%. These results indicate that the presence of NaCl will speed up the oxidation of copper and have little influence on absorption efficiency. Moreover, this new desulfurization technology has many advantages, such as mild reaction conditions (room temperature and constant pressure), reusable absorbent, operational simplicity of the procedure, high regeneration and absorption efficiencies and little waste. Due to these advantages, this new and effective desulfurization technology will be very attractive for academia and industry. The further industrial applications for this new desulfurization technology are currently on going.

Table 1. Elemental analysis of precipitates

No.	Picture	Oxidation time* [h]	Weight [mg]	Content [%]
1		1	3.5440	N: 0.497 C: 1.708 S: 29.67 H: 0.899
2		4	4.1350	N: 0.409 C: 2.734 S: 54.89 H: 0.686
3		8	4.8730	N: 0.297 C: 2.943 S: 88.13 H: 0.643

*98% H_2SO_4 : 1.81 wt%, NaCl: 0.30 mol/L, air flow rate: 100 L/h, 303 K

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