Study on influencing factors of sulfur particle size in chelated iron in oxidation process

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Abstract. The insoluble elemental sulfur with particle size less than 10 μm is produced in the solution through chelated iron-based method, while the sulfur recovery is generally through the aggregation sedimentation filtration method. In this paper, the influence of desulfurization solution parameters on the size of sulfur are investigated, and the indispensable conditions for the formation of large-size sulfur are discussed. Meanwhile, in order to obtain the conditions for large sulfur particles generation, the influence of the concentration of sulfur modifier on the Zeta potential of desulfurization solution and the change of sulfur particle size were studied.

1. Introduction

With the increasing attention of the government and people to environmental protection, the requirements for H2S removal and sulfur recovery are becoming more and more strict. At present, physical, chemical absorption method, conventional dry method and adsorption method all have respective applications for different purpose, however the shortcomings are very obvious, and there is the problem of secondary pollution. Iron based wet oxidation-reduction desulfurization has been widely used in all walks of life in China in recent years due to its large sulfur capacity, high purification efficiency and wide application range. One of the key steps of chelated iron method is to solve the problem of sulfur blocking the pipeline and equipment, and to maintain the unblockage of the process unit.

Under the condition of low temperature, S6 would be generated in the chelated iron desulfurization solution. The newly generated sulfur is hydrophobic in micron scale, which is easy to adhere to the equipment and float on the liquid surface in both absorption and regeneration tower, causing continuous foaming and making the unit unable to operate. Therefore, in recent years, solving the problem caused by elemental sulfur generated from chelated iron based liquid phase oxidation-reduction process has become new focus of research.
2. Forming conditions of elemental sulfur in chelated iron desulfurization process

The chelated iron method of liquid phase oxidation-reduction desulfurization uses iron ions as catalyst, redox potential difference of which is employed to oxidize HS- dissolved in desulfurization solution to form elemental sulfur. The reaction mechanism is as follows:

desulfurization reaction:

$$H_2S + 2Fe^{3+}L \rightarrow 2H^+ + S_\downarrow + 2Fe^{2+}L$$ ………………… (1)

regeneration reaction:

$$2Fe^{2+}L + 2H^+ + 1/2O_2 \rightarrow 2Fe^{3+}L + H_2O$$ …………………… (2)

total reaction equation:

$$H_2S + 1/2O_2 \rightarrow H_2O + S_\downarrow$$ ……………………………….. (3)

where L represents complex agent.

From Nernst equation:

$$\frac{1}{2} \log_{10} 2 = \frac{E^0_{S/H_2S} + 0.059 \log \left[ \alpha^2 H^+ \right]}{aH_2S}$$ …………………… (4)

$$= E^0_{S/H_2S} + 0.059 \log \alpha^2 H^+ + 0.0295 \log \frac{1}{aH_2S}$$ …………………… (5)

$$= E^0_{S/H_2S} + 0.059 \log pH - 0.0295 \log \alpha H_2S$$ …………………….. (6)

As

$$E^0_{S/H_2S} = 0.141V, \log \alpha H_2S = -0.99 + \log pH_2S$$ ……………….. (7)

Therefore

$$E_{S/H_2S} = 0.1702 - 0.059 \log pH - 0.0295 \log pH_2S$$ …………………… (8)

Chelated iron desulfurization solution, a typical alkaline buffer system, generally containing salt ions such as OH-, CO$_3^{2-}$, HCO$_3^-$, S$_2$O$_3^{2-}$, which have great mutual influence induced by electric potential. Figure 1 shows the change of desulfurization solution potential and H$_2$S content in tail gas with pH of 8.5, absorption time of 15 seconds and hydrogen sulfide content in feed gas of 15.0g/m$^3$. When the outlet pressure was 0.3MPa, H$_2$S content is 10mg/m$^3$ and pH is 8.5, the theoretical value of $E_{S/H_2S}$ was $-220$mv.

![Figure 1. H$_2$S content in tail gas with redox electrode potential.](image)

As shown in Figure 1, when the redox electrode potential is -200mV, the oxidation absorption performs unsatisfactory, and the tail gas exceeds 10ppm. The redox electrode potential of the complex Fe$^{3+}L$ is about 0.1V, which is much higher than that of the H$_2$S (g)/S pair (-220mv) (pH = 8.5), providing enough impetus for the reaction. HS$^-$ oxidation reaction is very fast, so that the balance moves to the direction of sulfur generation, which can make the H$_2$S content in tail gas to be extremely...
Thus, to ensure complete oxidation to sulfur, the potential of absorption solution should be kept above -100mV.

3. Experimental effect of desulfurization solution parameters on sulfur particle size

The composition of chelated iron desulfurization solution is complex, involving gas-solid-liquid three-phase reaction and many side reactions. The conversion of H$_2$S to elemental sulfur can be influenced by many factors. The experimental simulation of different factors involves the parameters of iron ion concentration, solution alkalinity and air regeneration time, and the influence of the parameters on the average particle size of sulfur is investigated.

3.1. Effect of iron ion concentration

The change of sulfur particle size is shown in Fig. 2 when solution of iron ion concentration of solution was prepared to 300ppm, 500ppm, 1500ppm, 3000ppm and 5000ppm, similar to concentrations commonly used in industrial self-circulation process and conventional process flow. Other parameters remained unchanged.

The higher the iron ion concentration is, the larger the sulfur capacity is, which would accelerate the formation of sulfur particles. However, as shown in Fig. 2, when the iron ion concentration increased from 300ppm to 5000ppm, the sulfur particle size did not increase significantly, and was distributed in scale of 2-4 microns. 500 ppm is the common concentration in self circulation process, and 5000 ppm concentration of iron ion is for high sulfur capacity desulfurization. Increasing the iron ion concentration alone could not significantly enlarge the size of newly formed sulfur particles.

3.2. Alkalinity effect

In the process of desulfurization, H$_2$S first reacts with the alkali of the solution, and then hydrogen sulfide ions form sulfur. When the sulfur capacity is large, a large number of hydrogen sulfide ions enter into the regeneration area. Change the alkalinity of desulfurization solution without adding sulfur modifier, and the determination results are shown in Fig. 3.

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![Figure 2. Relationship between iron concentration and particle size.](image1)

![Figure 3. Relationship between alkalinity and particle size.](image2)
In the process of alkalinity increasing from 0.05mol/l to 0.6mol/l without Sulfur Modifier, the particle size of newly formed sulfur fluctuates from 4.6 μm to 6.7 μm, but none of them is more than 10 μm. The experimental results show that the particle size of newly formed sulfur can not be improved only by the change of basicity.

3.3. Effect of solution regeneration time
In general process, the sulfur solution is regenerated in the regeneration tower while air, solution, and sulfur form a gas-solid-liquid three-phase. The solid sulfur surface will change after experiencing the assaulted of air in the solution. With the air in a turbulent state, the experiment was carried out at the regeneration time of 10 minutes to 30 minutes to determine the particle size of the sulfur particles.

![Figure 4. The relationship between regeneration time and particle size.](image)

In Figure 4, the results indicated that the particle size will increase along with the longer regeneration time. The core reason should be that sulfur particles interact between gas, solid and liquid for a long time, and the particles collide and bond with each other. Under prolonged action, sulfur particles will agglomerate and become larger, forming larger-sized sulfur particles.

The average sulfur particle diameter is less than 10 microns while no sulfur modifier is added. Meanwhile, the average particle size tends to increase as the solution regeneration time increases. The parameters of the solution have no significant effect on the sulfur particle size, and sulfur foam is easily formed. In the previous researches on complex iron-based desulfurization, the process is unsmooth due to the fact that sulfur was too fine and easy to bond.

4. Study on the influence of sulfur modifier on sulfur formation
As mentioned above, the desulfurization solution without sulfur modifier cannot cause the sulfur aggregate and settle. Next, the investigations on the effect of adding sulfur modifiers to the complexed iron desulfurization solution on the particle size of sulfur, the effect of H2S absorption by the desulfurization solution, and the conditions for aggregation and sedimentation of desulfurization solution are conducted as follows.

4.1. Experimental conditions
The laboratory adopts the conventional process conditions, the solution after completely regenerated of absorption desulfurization solution, and the pH value of the absorption desulfurization solution is 8.5; the hydrogen sulfide content of the feed gas is 15 g/L; and the iron ion concentration is 3000 ppm.

4.2. Influence of sulfur modifier concentration on sulfur particle size
Under the above experimental conditions, sulfur modifiers of different concentrations were added to the desulfurization solution. After continuous experiments for 48 h, the newly generated sulfur in the regeneration tower is adopted for particle size test, and the average particle size data is shown in Figure 5.
Figure 5. The Relationship between sulfur modifier and sulfur particle size.

Since the sulfur modifier is a surfactant, the addition of a small amount of sulfur modifier can significantly change the surface tension of the desulfurization solution. The surface tension of the desulfurization solution dropped from 60 N/m to about 30 mN/m after adding sulfur modifier. As shown in Figure 5, along with the concentration of sulfur modifier increases, the sulfur particle size increases accordingly. When the sulfur modifier reaches a certain concentration, the particle size will not increase significantly in pace with the increase of sulfur modifier concentration. Thus, the results implied that a suitable concentration range is existed for the sulfur modifier. Different modifiers have different effects on the particle size. For the sulfur modifier employed by the Natural Gas Research Institute, the concentration of 40-70 ppm is recommended in industrial equipment.

4.3. Influence of sulfur modifier on desulfurization effect
The addition of sulfur modifier significantly changes the surface tension of the solution and affects the absorption of H₂S by the desulfurization solution. The study on the tail gas H₂S concentration changes under different sulfur modifier concentration conditions are conducted as follows.

Figure 6. Influence of sulfur modifier on desulfurization effect.

As shown in Figure 6, when the concentration of sulfur modifier is not high, the H₂S content in the tail gas is also not high, and it has little effect on H₂S entering the solution from gaseous state to form HS-. When the H₂S content in the purified gas is less than 10 ppm, the sulfur recovery rate is larger than 99.99%. When the concentration of the solution modifier is greater than 90 ppm, as the concentration increases, the H₂S content in the purified gas is larger than 10 ppm, which exceeds the emission standards. Meanwhile, it is also found that when the concentration of sulfur modifier is large, the surface of the desulfurization solution will continues to foam and difficult to regenerate the solution.

4.4. Sulfur accumulation and settlement conditions
After adding sulfur modifier, sulfur particles would form water-soluble small particles in the early stage. At a certain Zeta potential, the sulfur particles in the solution form a suspension and micelles. Along with numerous particles collide with each other, under the function of sulfur modifier, the suspension will break through the micellar concentration limit, lead to aggregate and settle.
instantaneously. In present work, the zeta potential of the sulfur-containing particle solution was monitored to determine the aggregation and sedimentation. When the Zeta potential is -32.4 mV, the sulfur particle size distribution is described in Figure 7. In addition, when the particle size is relatively fine, the potential distribution interval is relatively narrower.

Figure 7. Correspondence diagram of Zeta potential and particle size distribution.

![Figure 7](image)

As shown in Figure 8, when the zeta potential of the desulfurization solution changes transiently, the average particle size of sulfur will be larger, that is, the process of suspension aggregation changes in the solution. According to the experimental results, when the zeta potential of the desulfurization solution changes from -8 mV to -2.0 mV suddenly, the sulfur will accumulate and the particle size will increase from less than 5 μm to more than 30 μm.

5. Study on the relationship between sulfur particle size distribution and sulfur slurry sedimentation

Sulfur coagulates to form a sulfur slurry, and the initially formed sulfur slurry has graceful fluidity and will not agglomerate. A laser particle size measuring instrument was employed to measure the particle size distribution of the sulfur slurry, and the sulfur doping time under different particle size distribution conditions was measured at the same time to obtain the lowest value when the size was greater than 80%. The experimental results are summarized as follows:

| 80% Particle size | >5 μm | 10 μm | 30 μm | 50 μm |
|-------------------|-------|-------|-------|-------|
| Settling time (s)  | >600  | 164   | 38    | 15    |

As shown in Table 1, when the newly formed sulfur particle size is less than 5 μm while the sulfur sedimentation time is larger than 10 minutes, the desulfurization solution is easy to form a suspension. When the sulfur particle size is larger than 50 μm with 15 s settling time, an easy-flowing sulfur slurry
is formed. In on-site production, most manufacturers determine whether to filter by measuring the settling time.

![Figure 9. The particle size is less than 5 μm](image1)

![Figure 10. Average particle size is larger than 50 μm](image2)

As Figure 9 depicted, when the average particle size of sulfur is less than 10 μm, the solution forms a obviously suspension. When the particle size is larger than 50 μm, the sulfur mostly forms flocs, which is easy to form a sulfur slurry.

6. Conclusion
Chelated iron-based desulfurization to form water-soluble elemental sulfur requires the addition of sulfur modifiers. The sulfur slurry formed is liquidity and limited to agglomerate.

(1) The ion concentration of the complexed iron-based desulfurization solution, the alkalinity of the solution, and the air regeneration time have little influence on the particle size of the newly generated sulfur.

(2) Sulfur modifier is the main factor affecting the particle size of sulfur, which will affect the particle size of sulfur, the desulfurization solution regeneration capacity and the Zeta potential.

(3) When more than 80% of the sulfur particle size is larger than 50 μm, flocculent sulfur is formed, which is easy to settle and filter.

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