Research on the integration of flue gas desulfurization and dust removal in oil shale refining

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Abstract. The flue gas of oil shale retort is characterized by high humidity, low sulfur content and tar content, which makes it impossible for traditional flue gas desulfurization facilities to deal with such flue gas normally. By collecting flue gas parameters at the inlet and outlet of the original desulfurization tower of oil shale dry distillation flue gas, and combining with computational fluid dynamics numerical simulation, this paper analyzes the fault reasons of each step in the process of desulfurization of oil shale dry distillation flue gas. Through experimental study, the flocculation characteristics of suspended solids and petroleum substances in desulfurization circulating liquid were analyzed. The results show that the low concentration of Na2CO3, Ca(HO)2, CaO desulfurizer can promote the flocculation, Ca(HO)2, CaO desulfurizer is beneficial to the removal of petroleum substances. The original wet limestone-gypsum desulfurization system was transformed into the wet sodium carbonate desulfurization and dust removal integrated system. The method of flocculation and sedimentation is used to remove sludge and petroleum substances, which can ensure the normal operation of the system and the emission of flue gas up to the standard.

1. Introduction
Oil shale is a kind of sedimentary rock with high ash content and combustible organic matter. Shale oil can be obtained by low-temperature retorting of oil shale, which is similar to crude oil and can be made into gasoline, diesel oil or fuel oil. Low temperature retorting refining of oil shale can comprehensively utilize low-grade oil shale, improve the added value of oil shale, and bring good economic and social benefits[1]. However, the flue gas produced by low-temperature retorting of oil shale has the characteristics of high humidity, low temperature and containing oil components. At present, the purification technology for this kind of oily flue gas is not mature. Low temperature retorting of oil shale is still facing severe challenge of atmospheric environmental protection [2,3].

In an oil shale refinery project, the comprehensive utilization technology of medium and low temperature retorting components was adopted, and oil shale was used as raw material for retorting and pyrolysis to produce oil. The traditional flue gas purification method is adopted in the oil shale refining project, and the purification effect is poor. Due to the low temperature, high humidity and tar content of flue gas produced by the process, the desulfurization tower can not be used normally. The flue gas produced by this process contains CO, H2, hydrocarbon and other combustible gases. In order to avoid the risk of explosion in the spark discharge of electrostatic precipitator due to high O2 content, electrostatic precipitator is not suitable for flue gas dust removal[4]. Due to the high humidity and low temperature of flue gas, if the filter dust collector is used for flue gas dust removal, the filter
membrane will be blocked in a short time [5]. In view of this kind of high humidity and low temperature oily and dusty flue gas, this paper puts forward the scheme and research analysis of transforming the original desulfurization into an integrated device of desulfurization and dust removal, which has a certain reference significance for the purification of high humidity and dusty oily flue gas.

2. Fault analysis

2.1. Composition of flue gas

Under the condition of full load, the flue gas volume of this system is 66990 Nm³/h, the inlet flue gas temperature is 115℃, and the outlet flue gas temperature is 75℃. In order to analyze the fault causes of the desulfurization system, the automatic smoke (gas) tester was used to detect the flue gas composition at the inlet and outlet of the desulfurization tower, and the results are shown in table 1.

| Composition | Inlet(mg/Nm³) | Outlet(mg/Nm³) |
|-------------|---------------|----------------|
| Dust        | 1822          | 813            |
| Tar         | 87            | 26             |
| SO₂         | 398           | 126            |
| CO₂         | 15.3%         | 14.2%          |
| CO           | 4.04%         | 4.09%          |
| CₙHₘ        | 9.49%         | 9.61%          |
| O₂           | 2%            | 2%             |
| N₂           | 68.59%        | 68.94%         |

Note: The percentage of gas composition is volume fraction.

2.2. Distribution analysis of desulfurization tower field

SolidWorks software is used to establish a three-dimensional model with the size ratio of 1:1. Then the model is imported into ICEM CFD for grid generation. According to the above conditions, through ANSYS FLUENT software, the standard K-ε model was used to simulate the process in the desulfurization tower. The numerical simulation results are shown in Figure 1. According to the numerical simulation results, the gas flow distribution in the desulfurization tower is extremely uneven. After the flue gas enters the desulfurization tower through the inlet flue of the desulfurization tower, the gas flow on one side of the inlet flue is very small and eddy current is formed, while the gas flow on the other side is large and the flow rate is too high. Due to the uneven distribution of gas flow in the desulfurization tower, the amount of flue gas on the left side is more than that on the right side, so the slurry sprayed in the tower can not fully contact with the flue gas, which will seriously affect the desulfurization efficiency. And the side with large amount of flue gas, due to the fast flow rate of flue gas, will carry a large number of particles into the demister, resulting in the blockage of the demister.
2.3. Failure analysis
Based on the above analysis, it is considered that the desulfurization process of the project adopts the circulating mode in the tower, and the flue gas carries a large amount of dust into the desulfurization tower. After a long time of operation, the dust content in the circulating slurry increases continuously and cannot be discharged in time, which makes the suspended solids such as sludge and tar in the circulating slurry accumulate continuously, resulting in the rapid increase of the load of the slurry circulating pump and the decrease of the circulating flow, Spray nozzle is difficult to form spray. Moreover, due to the uneven distribution of the flow field after the flue gas enters the desulfurization tower, the gas flow near the inlet flue is very small, and the gas flow is concentrated on the other side. The flue gas on this side will carry a large number of particles into the demister to form sludge. With the accumulation of tar in the flue gas in the demister, the oil sludge mixture will gradually form, and the viscosity of the oil sludge will increase due to the existence of tar, The oil sludge in the mist eliminator cannot be washed out in time by the backwashing system, which results in the complete blockage of the mist eliminator with the passage of time, resulting in the failure of the desulfurization process and affecting the operation of the whole oil shale refining system.

3. Experimental research and analysis
In order to realize the function of desulfurization and dust removal at the same time, it is necessary to remove the suspended solids and petroleum in desulfurization circulating liquid by flocculation precipitation method, so as to achieve the purpose of desulfurization slurry recycling. However, whether the desulfurization circulating liquid can be treated by flocculation and precipitation method is studied in this paper.

3.1. Experimental study on flocculation of desulfurization circulating slurry

3.1.1 Experimental methods
The temperature of the water sample is 57 °C. The pH value of water sample measured by pH meter is 7.51, and the pH value is adjusted to 7 by dropping hydrochloric acid. The composite flocculant
system was composed of 40 mg/L polyaluminum chloride coagulant and 50 mg/L LH-3 organic polymer flocculant.

Take 200ml water sample after adjusting pH value into a glass beaker. Considering the extreme temperature of desulfurization circulating liquid, heat the water sample to 65 ℃, and gradually add the compound flocculant solution into the beaker with a plastic syringe in ml and quickly stir it. Observe the floc forming and precipitation speed, and do three experiments to determine the dosage of 5ml. After mixing the complex flocculant with sewage water sample, the whole process is completed in 65 ℃ water bath constant temperature bath. Then ss-1z type suspended solids analyzer was used to measure the suspended solids in raw water and after flocculation, and infrared spectrophotometer was used to measure the oil content in raw water and after flocculation. Three experiments were conducted to get the average value.

3.1.2 Experimental results and analysis
The experimental results are shown in Table 2. According to the experimental data, the composite flocculant system composed of polyaluminum chloride coagulant and LH-3 organic polymer flocculant has good flocculation effect on the circulating liquid of desulfurization tower, and most of the suspended solids have been removed, as shown in Figure 2. The analysis shows that the dust, oil and other suspended solids in the circulating liquid of desulfurization tower can be removed by flocculation precipitation method.

| Raw water | Water after flocculation |
|-----------|--------------------------|
| SS (mg/L) | 835 | 82 |
| Petroleum class (mg/L) | 329 | 67 |

3.2. Experimental study on the effect of desulfurizer on flocculation
In order to study and analyze the influence of desulfurizer on flocculation effect, three kinds of desulfurizers Na₂CO₃, CaO and Ca(HO)₂, which are commonly used in industrial flue gas desulfurization, are selected. The influence of 3 kinds of desulfurizers with different concentrations on flocculation effect of desulfurization circulating liquid is studied and analyzed through experimental research.

3.2.1 Experimental methods
Take 200ml of the water sample after adjusting the pH value into beakers 1, 2 and 3, add Na₂CO₃ to beaker 1, CaO to beaker 2 and Ca (HO)₂ to beaker 3, and stir evenly to dissolve the drug. Then, 5ml compound flocculant system was added into three beakers according to the method in 2. After mixing and stirring, the whole process was completed in 65 ℃ water bath constant temperature bath. The content of suspended solids and petroleum before and after flocculation was determined by the same method. The dosage of three desulfurizers were 10, 40, 70, 100, 130, 160 and 200 mg/L respectively. Six groups of experiments were conducted, and each group was conducted three times, and the average value was finally taken.

3.2.2 Experimental results and analysis
According to the experimental data, with the increase of the concentration of the three desulfurizers in the desulfurization circulating liquid, the removal rate of suspended solids (SS) in the circulating liquid by the composite flocculant system first increased, and the removal rate of suspended solids began to decrease when the desulfurizer reached a certain concentration, as shown in Figure 3. When the concentration of desulfurizer is high, Ca(HO)₂ has the most obvious effect on the reduction of the
removal rate of suspended solids, while Na₂CO₃ has relatively weak effect on the removal rate of suspended solids. With the increase of the concentration of Ca (HO)₂ and CaO in the circulating liquid, the removal rate of petroleum in the circulating liquid increased slightly at first, and then remained stable.

With the increase of the concentration of Na₂CO₃ in the desulfurization circulating liquid, the removal rate of petroleum in the circulating liquid by the composite flocculant system increased first and slightly. When the concentration of Na₂CO₃ reached a certain amount, the removal rate of petroleum decreased significantly to 62.2%, as shown in Figure 4. The results show that when the composite flocculant system composed of polyaluminum chloride coagulant and LH-3 organic polymer flocculant is used to flocculate the circulating liquid of desulfurization tower, the low concentration of desulfurizer Na₂CO₃, Ca(OH)₂ and CaO can promote the flocculation, while the high concentration of desulfurizer is not conducive to flocculation.

![Figure 3. Effect of flocculant on SS removal from circulating liquid](image1)

![Figure 4. Effect of flocculant on petroleum removal from circulating liquid](image2)
4. Transformation plan

After the desulfurization system is transformed into an integrated system of desulfurization and dust removal, the process flow of desulfurization and dust removal is shown in Figure 5. The sodium carbonate slurry preparation system sends the fresh sodium carbonate slurry to the regulating tank, and the slurry circulating pump lifts the sodium carbonate slurry to the spray layer of the desulfurization and dust removal tower to form mist droplets, which fully contact with the flue gas from bottom to top during the falling process in the tower. In this process, the slurry absorbs $\text{SO}_2$ in the flue gas to generate $\text{Na}_2\text{O}_3$, and part of the particles in the flue gas are also infiltrated and absorbed, which are carried into the liquid storage tank at the bottom of the absorption tower. Under the action of slurry agitator, the sediment is suspended and discharged to the outside of the tower with slurry to the circulating pool. In the middle area of the circulating tank, the air supplied by the oxidation fan passes through the oxidation air pipe network arranged in the circulating tank to enter the tank. Under the action of the slurry agitator, the air entering the slurry tank forms tiny air bubbles, evenly passes through the circulating tank, and oxidizes the $\text{Na}_2\text{O}_3$ in the circulating tank to $\text{Na}_2\text{SO}_4$. The slurry containing sludge is suspended under the action of agitator mixing and oxidation fan blowing. It enters the high-efficiency flocculation cyclone precipitator through the sewage lift pump, and the flocculated sludge precipitates to the sludge area. After a period of time, the sludge is transported to the pressure filter dehydrator through the sludge lift pump, and the sludge cake formed after full dehydration is sent out, and the desliming sewage flows back into the circulating liquid tank. The clarified water in the high efficiency flocculation cyclone settler enters the regulating tank to realize slurry circulation.

5. Conclusion

(1) The dust content of the flue gas at the entrance of the desulfurization tower is too high, and the desulphurization process adopts the internal circulation mode, which makes the dust content in the circulating slurry increase continuously and can not be discharged in time. This causes the load of the slurry circulation pump to increase sharply, the circulating flow becomes smaller, the spray nozzle of the spray layer is hard to form spray, and the flow field distribution in the desulfurization tower is uneven, which is the reason for the failure of the original desulfurization tower.

(2) The composite flocculant system composed of 40 mg/L polyaluminum chloride coagulant and 50 mg/L LH-3 organic polymer flocculant has good flocculation effect on circulating liquid of desulfurization tower, and can remove most suspended solids and petroleum in circulating liquid of desulfurization tower.
(3) According to the flocculation effect of compound flocculant on circulating liquid, low concentration of Na₂CO₃, Ca(OH)₂ and CaO desulfurizer can promote flocculation, while high concentration of desulfurizer is not conducive to flocculation and precipitation to remove suspended solids. Ca(OH)₂ and CaO desulfurizers are beneficial to the removal of petroleum. When the concentration of Na₂CO₃ desulfurizer is low, it is beneficial to the removal of petroleum. When the concentration reaches a certain amount, the removal rate of petroleum decreases obviously.

(4) The content of SO₂ in the flue gas of oil shale retort is relatively low, so the original desulfurization system can be transformed into the wet sodium carbonate desulfurization and dust removal integrated system, and the mode of external circulation can be adopted. For circulating slurry, sludge and petroleum substances can be removed by high-efficiency flocculation sedimentation method, which can ensure the normal operation of desulfurization and dust removal integration.

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