Application research on high efficiency desulfurization technology of reducing calcium-sulfur ratio in circulating fluidized bed boiler

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Abstract. Based on current status of desulfurization calcium-sulfur ratio on active 150MW CFB boiler running poor economically, the actual influencing factors of the low desulfurization efficiency are studied combined with the desulfurization mechanism. In a typical load of 150MW CFB boiler, the degree of key factors influence on calcium-sulfur ratio is analyzed. On this basis, high efficiency technologies for improving the desulfurization efficiency and reducing calcium-sulfur ratio are proposed one by one for the influencing factors, and the application of technology is implemented on 150MW CFB boiler. The experiment is arranged to test desulfurization calcium-sulfur ratio of the boiler furnace before and after the implementation of the technology. The results show that the comprehensive operating calcium-sulfur ratio of the unit is reduced by 70% after the the application, and the technology has a good effect on significantly reducing calcium-sulfur ratio.

1. Introduction
Circulating fluidized bed (CFB) power generation technology has been rapidly developed in China and abroad for nearly three decades, due to its extensive coal quality adaptability and excellent environmental performance[1]. China's CFB boilers have reached the world's leading level in terms of stand-alone capacity, installed scale and technological advancement. By 2018, large-capacity CFB boilers of 410 t/h above have been put into operation in more than 440, and the total installed capacity has exceeded 82.3 GW[2]. The supercritical CFB boiler units with independent intellectual property rights have been put into operation in more than 30 units, and the capacity of single unit reaches 600MW. At present, most CFB boiler units are equipped with an in-furnace desulfurization system. With the application of ultra-low emission technology for semi-dry desulfurization system outside the furnace[3], the in-furnace desulfurization system will be still essential. However, for the early design of CFB boilers burning high-volatility coal, the desulfurization efficiency is not good due to the high bed temperature, the obvious contradiction between SO₂ removal and suppression of NOx formation in the furnace, which results in high calcium-sulfur ratio and poor economics of the unit. Due to the rapid development of CFB boiler and equipment technology update in recent years, calcium-sulfur ratio generally reaches the design value, and operating value of some is even lower than 2[4]. Therefore, it is possible to carry out research on the high efficiency desulfurization technology of reducing calcium-sulfur ratio in the furnace for the early CFB boiler. At the same time, with the implementation of
technical upgrading projects such as addition point optimization, operation adjustment optimization and maintenance process level improvement, it can provide a necessary test platform for research. 

Previously, through the analysis of desulfurization mechanism and related experimental research, the main factors affecting the desulfurization efficiency are confirmed, including the reaction temperature and atmosphere, particle size and quality of desulfurizer[5]. The factors lead to low efficiency in actual operation, and relevant measures need to be made to increase the desulfurization efficiency to reduce calcium-sulfur ratio. The factors such as the efficiency improvement of separator can improve the bed temperature and desulfurization efficiency, which has been widely verified in engineering applications. Therefore, this work was carried out on the key factors affecting the desulfurization efficiency on actual operation of 150MW CFB boiler. The effect of low desulfurization efficiency was analyzed, the relevant optimization and adjustment technologies were implemented. The test was arranged to determine the degree of reduction on calcium-sulfur ratio after technical optimization. This provides technical basis for optimization and transformation of reducing calcium-sulfur ratio.

2. Experimental object
A 150MW CFB boiler with M-type arrangement has 6 coal feeders correspond to 6 coal inlets, 2 cyclone separators and seal pots with 4 legs, which are evenly distributed along the front and rear wall. There are 8 limestone feed openings. The 4 limestone feed openings in the front wall are arranged on the left and right sides of the two coal inlets, and that in the rear wall are arranged on the leg of seal pot. The boiler adopts integrated combustion technology of desulfurization and denitration in the furnace[6]. The desulfurization adopts the method of spraying limestone, and the denitration is staged combustion inhibition of NOx in the furnace, which of the emission standard is 200 mg/Nm³. The design value of calcium-sulfur ratio is 2.3, but the operating value is about 11.5. The analysis of coal quality and limestone content is shown in Table 1.

3. Study on key actual factors of desulfurization
3.1. The low-oxygen operation
The desulfurizer generally used for SO₂ removal mainly is limestone. In the furnace of CFB boiler, limestone enters the boiler furnace through the pneumatic conveying system. Limestone is first endothermic and decomposed into CaO and CO₂, and then CaO reacts with SO₂. The reaction formula is as follows:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]  
\[ -183 \text{kJ/mol} \]

\[ \text{CaO} + \frac{1}{2}\text{O}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 \]  
\[ +486 \text{kJ/mol} \]

For CFB boilers, the operating oxygen of the boiler is generally represented by the air preheater inlet oxygen. The air preheater inlet oxygen has no significant effect on SO₂ emission alone. But when the air preheater inlet oxygen is less than a certain value about 2.4-2.7%, the desulfurization efficiency drops sharply. When it’s increased, the efficiency is improved. Therefore, the oxygen is required to participate in the desulfurization reaction, and an excessively low oxygen concentration causes a decrease in the efficiency.

The desulfurization and suppression of NOx formation in the furnace are mutually influential and contradictory. Due to poor NOx suppression effect of 150MW CFB boiler, a mode of low-oxygen operation is adopted to control NOx emission, but the desulfurization reaction
requires an oxidizing atmosphere, resulting in a significant decrease of the efficiency and an increase of the operating calcium-sulfur ratio. It’s shown in Figure 1 that in the case of stable operation of the unit, as the air preheater inlet oxygen is adjusted to less than 2%, the desulfurization efficiency decreases significantly. To ensure that the SO₂ emission is up to standard, the mass flow rate of limestone feeder increases, and excessive limestone is injected, which causes higher calcium-sulfur ratio.

![Figure 1.](image1.png)

**Figure 1.** Low-oxygen operation leads to excessive addition of desulfurizer under 100% load.

3.2. Boiler operating bed temperature

Relevant research shows that the optimal desulfurization reaction temperature of CFB boilers is 800-900°C[7], which is the operating temperature of CFB boiler. Limestone entering the furnace is decomposed to get porous CaO, which reacts with SO₂. When it rises to above 900°C, CaO is sintered, and generated a large molar volume of CaSO₄ covers the surface of desulfurizer, causing partial pores on the surface of CaO to be clogged and inactivated. In addition, at a higher temperature, especially in a reducing atmosphere, CaSO₄ is decomposed and releases SO₂, which reduces the sulfur retention rate.

The temperature measurement points of CFB boilers are different, which leads to a slight difference in optimal temperature. The distribution of the bed temperature is uneven, and the operating bed temperature is higher than 900 °C or lower than 800 °C, which deviates from optimal temperature and leads to the decrease of desulfurization efficiency.

The average bed temperature of 150MW CFB boiler is higher than 900 °C under high load, and the deviation of bed temperature is more than 100 °C. It is shown in Figure 2 that because of the particle size of the coal suddenly thinning, the average value of boiler operating bed temperatures increases under 80% load at a oxygen of 2.0%, and the desulfurization efficiency decreases. In order to ensure SO₂ emission up to standard, the mass flow rate of limestone feeder increases, and the amount of limestone increased significantly, which leads to higher operating calcium-sulfur ratio.

![Figure 2.](image2.png)

**Figure 2.** Increasing boiler bed temperature leads to excessive addition of desulfurizer under 80% load.
3.3. Particle size of desulfurizer
The particle size of desulfurizer has an important influence on the desulfurization efficiency, which should be matched with the efficiency of the separator. When the particle size is too small, the part of desulfurizer will be entrained by the flue gas to the boiler tail. Although the specific surface area of the particle is increased, which is beneficial to the desulfurization reaction, it is difficult for too small particles to be effectively trapped by the separator. It’s not conducive to the recycling of desulfurizer, and the performance is that the amount of CaO in the fly ash is higher than that in the bottom slag. If the particle size of desulfurizer is too coarse, the specific surface area of the particle is reduced, and the effective component of the central part is hard to react with SO2. A large amount of coarse particles are not effectively utilized and discharged with the bottom slag, which directly affects the desulfurization efficiency in the furnace.

The 150 MW unit uses finished desulfurizer product, and the particle size is uneven. It’s shown in Figure 3 that the share of >1mm exceeds 20%, and that of <0.5 mm is about 50%, resulting in low utilization rate of desulfurizer. It’s shown in Figure 4 that in the case where the ratio of bottom slag to fly ash is 1:1, the content of CaO in the bottom slag is higher than that in the fly ash. It indicates that the coarse particle fraction of desulfurizer is higher than fine particle. Excessive limestone is discharged through the bottom slag or fly ash, which is characterized by higher levels of CaO.

![Figure 3. Particle size distribution of collected desulfurizer sample.](image)

![Figure 4. The content of CaO in the fly ash and bottom slag in the case of the bottom slag to fly ash 1:1.](image)

4. High efficiency desulfurization technology and application

4.1. Operation adjustment technology
The purpose of operation adjustment technology is mainly to provide good conditions for desulfurization reaction in the operation, including improving bed pressure, the optimization of primary and secondary air ratio, etc. According to different measures taken, the effect of reducing calcium-sulfur ratio is different, which is expected to be 10-30%.

For boilers operating at low bed pressure and high bed temperature, improving bed pressure can be adopted, which can reduce operating bed temperature and improve the uniformity with the
increase of effective materials. It’s beneficial to suppression of NOx formation and desulfurization reaction in the furnace.

The optimal ratio of primary and secondary air should be optimized, which can be used in the case that the air ratio of the boiler is not good, or that the oxygen distribution in the cross section of the furnace is uneven. The share of primary air is appropriately increased under different loads to improve the uniform distribution of oxygen in the furnace.

In view of the good operation mode of graded combustion, the upper and lower secondary air ratio are optimized. It can take the principle of the strong wind above and small wind below, matching wind pressure and uniform oxygen, which can reduce original NOx emission and increase the amount of operating oxygen to improve the desulfurization efficiency.

On 150 MW CFB boiler, the above operation adjustment technology is comprehensively taken to test Ca/S under different stable loads. The results are shown in Figure 5 that compared with the value before adjustment, the calcium-sulfur ratio of 100 MW load after adjustment is reduced by 13%, and that of 120 MW load is decreased from 11.2 to 8.7. The calcium-sulfur ratio of 140 MW load after adjustment is reduced by 26%.

4.2. Denitration technology
The main measure to solve the low-oxygen operation is to increase means of controlling the NOx emission, such as denitration system added. The denitration system of CFB boiler generally adopts SNCR denitration technology, which reduces NOx by spraying NH3/Urea in the inlet of the separator. Because of added system, the relationship between desulfurization and suppression of NOx formation is removed, and the oxygen of the boiler is restored to the design value of 3.5%. This provides a better oxidizing atmosphere for desulfurization, and the effect of reducing calcium-sulfur ratio can be more than 30%.

The 150MW CFB boiler uses a low-oxygen operation mode to control NOx emission standards. After the SNCR system modified, the control method of NOx is more flexible. The operating oxygen returns to the normal range. Through testing, the results show in Figure 6 that calcium-sulfur ratio is decreased from 9.3 before to 5.3 after the transformation, which is reduced by about 43%.
4.3. Adjustment of particle size distribution of desulfurizer

The particle size of limestone can be referred to the standard requirement, as shown in Figure 7. According to the distribution standard, the particle size of limestone is controlled to be between 0-1 mm, and the median particle size $d_{50}$ is between 150 and 250 $\mu$m. Therefore, controlling particle size of desulfurizer within a reasonable range can improve desulfurization efficiency. For CFB boilers, $>1$mm of the limestone should be eliminated as much as possible. If it’s not guaranteed, it should not exceed 5%, and the median particle size of limestone should meet the standard requirement. The calcium-sulfur ratio is expected to be reduced by 10-30% though improving the particle size of desulfurizer.

The particle size distribution of desulfurizer on 150MW CFB boiler is unreasonable, so adjustment optimization of particle size is carried out. After the adjustment, the ratio of particle size less than 1mm is from 80% of the total to 96%, and $d_{50}$ of which is about 500 $\mu$m to 350 $\mu$m, which is shown in Figure 3 and 8. Compared with the value before adjustment, the particle size is more uniform after adjustment.

![Recommended Limestone Grain Size](image)

**Figure 7.** Recommended limestone grain size passing through the sieve.

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![Particle size distribution of collected desulfurizer sample after adjustment](image)

**Figure 8.** Particle size distribution of collected desulfurizer sample after adjustment.

Figure 9 shows the change in the limestone feeder before and after adjustment. When load rate of the unit is the same, the cumulative amount of limestone are significantly lower than before adjustment, which is reduced by 20%. It shows that as the particle size of limestone is reduced, the amount of limestone is reduced in the same situation.

It’s shown in Figure 10 that the content of CaO in the bottom slag is lower than that in the fly ash. Compared with the value before adjustment, the content of CaO in the bottom slag is reduced by 25% after adjustment of particle size, and that in the fly ash is reduced by 8%. It indicates that it results in an increase in the utilization rate of limestone after taking adjustment measure of particle size distribution of desulfurizer.
4.4. Application effect of technology

After adopting high efficiency desulfurization technology of operation adjustment, SNCR denitration system and adjustment of particle size of desulfurizer, the technology of reducing calcium-sulfur ratio is solidified into the normal operation of the unit, and 150MW CFB boiler has a significant reduction in the overall operating calcium-sulfur ratio.

To illustrate the comprehensive application effect on the technology, the data related to the calcium-sulfur ratio in the case of the same power generation are collected before and after the application, and the comprehensive calcium-sulfur ratio is calculated. The result is shown in Figure 11 that compared with the value before the application of the technology, the comprehensive operating calcium-sulfur ratio of the unit is reduced by 70% from 11.5 to 3.4 after the the application, and the application effect is obvious.

Figure 9. The cumulative amount of limestone decreased with the adjustment of particle size under 70% load.

Figure 10. The content of CaO in the fly ash and bottom slag after adjustment of particle size.

Figure 11. The comprehensive calcium-sulfur ratio before and after the application of the technology on 150MW CFB boiler.
5. Conclusions
The key factors affecting the desulfurization efficiency in the furnace are studied on active 150MW CFB boiler. This work qualitatively analyzes the effect of boiler operating bed temperature, low oxygen operation and particle size of desulfurizer on calcium-sulfur ratio. For different factors, the high efficiency desulfurization technology is proposed and applied one by one to 150MW boiler, which of the effect of reducing calcium-sulfur ratio is tested under a certain load. Adopting operation adjustment technology for improving bed pressure, optimization of primary and secondary air ratio, optimization of the upper and lower secondary air, can reduce calcium-sulfur ratio by 20%. For low-oxygen operation, it leads to the desulfurization efficiency dropping sharply, but the SNCR system can be added to restore the operating oxygen to the design value, which is expected to reduce calcium-sulfur ratio by 43%. The reasonable particle size distribution of desulfurizer matched with the separator can reduce calcium-sulfur ratio by 20%. The expected goals of reducing calcium-sulfur ratio for the technology are achieved.

The verification test of technical application effect is carried out on 150MW CFB boiler. By adopting high efficiency desulfurization technology of operation adjustment, SNCR denitration system and adjustment of particle size of desulfurizer, the desulfurization efficiency and calcium-sulfur ratio are improved, the comprehensive operating calcium-sulfur ratio is reduced from 11.5 to 3.4 after the the application, which is reduced by 70%. It shows that the technology has a good effect on reducing calcium-sulfur ratio, which has obvious reference significance in practical engineering project.

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