Chemical Analysis of High Moisture Content of Flue Gas Desulfurization Gypsum

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Abstract. In order to solve the problem of high moisture content of flue gas desulfurization gypsum in coal-fired power plants, after eliminating the reasons of system equipment, chemical analysis of relevant samples was carried out by thermogravimetric analyzer, laser particle size analyzer, ICP and other instruments. Results show that the main reason for the high moisture content of desulfurization gypsum is the high magnesium content in limestone, which results in the faster nucleation rate of gypsum crystals and the difficulty of aggregation and growth of gypsum crystals. This increases the difficulty of dewatering gypsum with dewatering belt.

1. Introduction
Limestone wet desulfurization is a common choice for flue gas desulfurization in coal-fired power plants. Gypsum, as a by-product of flue gas desulfurization, can be used for industrial or building materials. In actual operation, the problem of high moisture content of desulfurization gypsum often occurs, which has a direct impact on the quality of gypsum. There are two main reasons for this problem: one is the failure of relevant equipment, such as insufficient vacuum of dehydration belt, damage of filter cloth and poor operation effect of gypsum cyclone; the other is the poor quality of gypsum slurry itself, which can be identified by chemical composition analysis.

A coal-fired power plant has four 320MW units, which use limestone-gypsum wet flue gas desulfurization. The desulfurization gypsum treatment system adopts two-stage dehydration, the first stage is gypsum cyclone, then the gypsum cyclone underflow enters the vacuum belt dehydrator for the second stage dehydration. After dehydration, gypsum is transported to the outside.

In the actual operation process, the problem of high moisture content of desulfurization gypsum occurred many times in the plant. For the desulfurization gypsum of the power plant, a continuous tracking for a week is carried out. The change trend of gypsum moisture content is showed in Table 1. The moisture content of gypsum is between 12% and 25%, which obviously exceeds the general requirement of less than 10% moisture content of gypsum.

Table 1. Moisture content of gypsum

| Monitoring Date | 2019/6/3 | 2019/6/4 | 2019/6/5 | 2019/6/6 | 2019/6/7 | 2019/6/8 | 2019/6/9 |
|-----------------|----------|----------|----------|----------|----------|----------|----------|
| moisture content of gypsum /% | 12.09 | 21.52 | 14.30 | 21.77 | 16.57 | 18.31 | 24.25 |
2. Chemical analysis
After checking, the vacuum degree of dewatering belt, the thickness of gypsum, the quality of filter cloth and the treatment effect of absorption tower all meet the requirements, eliminating the possibility of equipment failure of desulfurization system, and then analyzing from the chemical point of view.

2.1 thermogravimetric analysis
The gypsum, gypsum cyclone underflow and slurry of three absorption towers in operation were dried, and then the solid phase was taken for thermogravimetric analysis. Test results are showed in Table 2. The main component of solid phase in slurry of three absorption towers is CaSO₄·2H₂O, which is over 90%. The content of CaCO₃ in slurry of 1# and 2# absorption tower is less than 3%, while the content of CaCO₃ in slurry of 4# absorption tower is as high as 6.36%. This is due to the fact that remaining CaCO₃ can not react with SO₂ in time after the 4# absorption tower was just put into operation, which results in relatively high CaCO₃ content in slurry. Considering that the content of CaCO₃ in gypsum is only 1.76%, combined with operation experience, it can be judged that the high content of CaCO₃ in slurry of 4# absorption tower is not the main reason for the high moisture content of gypsum. Composition analysis of gypsum shows that the content of CaSO₃·1/2H₂O reaches 97.63%, which meets the requirement. CaSO₃·1/2H₂O was almost not detected in slurry of three absorption towers, underflow of gypsum cyclone and gypsum.

Table 2. Thermogravimetric analysis results

| items       | unit | 1#absorption tower slurry | 2#absorption tower slurry | 4#absorption tower slurry | underflow of gypsum cyclone | gypsum          |
|-------------|------|--------------------------|--------------------------|--------------------------|----------------------------|-----------------|
| CaSO₄·2H₂O  | %    | 96.84                    | 97.93                    | 92.21                    | 94.79                      | 97.63           |
| CaCO₃       | %    | 1.37                     | 0.98                     | 6.36                     | 4.72                       | 1.76            |
| CaSO₃·1/2H₂O | %    | ND                       | ND                       | ND                       | ND                         | ND              |

In general, when the concentration of CaSO₃ in slurry is high, the formation of CaSO₄·2H₂O crystal will be affected, thus the dehydration performance of gypsum will be reduced[1]. However, the CaSO₃·1/2H₂O in the absorption tower of this plant is almost completely converted to CaSO₄·2H₂O, which shows that the forced oxidation performance is favorable and there is no problem of excessive CaSO₃ content. The effects of incomplete CaCO₃ reaction and inadequate CaSO₃ oxidation were eliminated by thermogravimetric test.

2.2 Particle size analysis
The particle size of gypsum and absorption tower slurry is analyzed by laser particle size analyzer. The particle size distribution is showed in Figure 1.

![Particle size distribution](image)
The analysis of particle size distribution shows that there is a common problem in gypsum and slurry. Within the particle size range of less than 10 micron, there are numerous and dense particles, shown in the spectrum, there is a certain "tailing" on the left side of the curve. These tiny particles could plug the hole of the dewatering belt and increase the resistance of the belt to dewatering, thus affects the moisture content of gypsum.

The particle size distribution is digitized in Table 4. Among them, $D_{40}$ indicates the size of a sample when the cumulative particle size distribution reaches 40%. Its physical meaning is that the particles with smaller particle size account for 40% and those with larger particle size account for 60%. $D_{10}$, $D_{50}$ and $D_{90}$ have the same meaning.

Table 3. Particle size distribution results

| item  | gypsum (μm) | #1 slurry (μm) | #2 slurry (μm) | #4 slurry (μm) |
|-------|-------------|----------------|----------------|----------------|
| $D_{10}$ | 8.74       | 6.81           | 6.47           | 5.74           |
| $D_{50}$ | 33.6       | 31.1           | 29.9           | 28.3           |
| $D_{40}$ | 29.3       | 26.8           | 25.8           | 24.3           |
| $D_{90}$ | 59.9       | 56.2           | 55.0           | 52.7           |

The European Gypsum Industry Association stipulates that the $D_{40}$ of desulfurization gypsum shall not be less than 32μm. While in the actual measurement, $D_{40}$ of 1#, 2# and 4# absorption tower slurry is 26.8, 25.8 and 24.3μm, respectively, and gypsum’s $D_{40}$ is 29.3μm, which are significantly lower than the standard requirements. The composition of gypsum meets the requirements, but the particle size is lower than the limit. It shows that the gypsum nuclei in the absorption tower slurry can not proceed to gather together and grow into large crystals.

2.3 Components Analysis of ICP

ICP was used to analyze the component of slurry. It was found that all the indexes of slurry were normal, except for magnesium content. The magnesium contents in the slurry of three absorption towers are all high. The lowest of these three slurry is 4# absorption tower slurry, which reaches 1682 mg/L. The content of magnesium in gypsum is as high as 0.98% by ICP test after alkali melting.

Table 4. Slurry components results

| item  | unit | #1 slurry | #2 slurry | #4 slurry |
|-------|------|-----------|-----------|-----------|
| Ca    | mg/L | 843.0     | 721.4     | 957.5     |
| Mg    | mg/L | 2174      | 1831      | 1682      |
| Mn    | mg/L | 10.18     | 7.11      | 6.86      |
| Na    | mg/L | 237.6     | 179.2     | 194.7     |
If desulfurization slurry contains too much magnesium, the nucleation rate of gypsum crystal increases a lot. In the process of gypsum crystallization, the smaller the number of gypsum nuclei, the more favorable for the growth of gypsum crystals, the more likely it is to grow into ideal thick rhombus or prism; conversely, excessive gypsum nuclei will slow down the growth of gypsum crystals and tend to produce more slight crystals. Research results show that when MgO contents of slurry reaches to 1%, the proportion of gypsum crystal size less than 20 micron will increase from 23.0% to 39.7%. Finally, the crystal will be too tiny, and the dehydration performance and application of solid by-products will be deteriorated.

For further analysis, it is necessary to search the source of magnesium. Combined with the desulfurization system, there are three main sources of magnesium in the absorption tower slurry: the introduction of magnesium in the industrial water added to the tower, the introduction of flue gas when the performance of electrostatic precipitator is poor, and the excessive content of magnesium in the desulfurization limestone itself. After eliminating the first two problems, the composition of limestone is analyzed. The result is as follows: 53.7% CaO, 2.18% MgO, 0.10% Fe₂O₃, others below 0.10%. The composition of limestone is normal, except for magnesium. The content of magnesium in limestone is as high as 2.18%, which is far beyond the requirement that the content of Mg in limestone is less than 0.5%. It almost shows that the magnesium in the slurry of absorption tower is brought in by limestone.

So far, the main reason for the high moisture content of gypsum in this plant is the high magnesium content of limestone used in desulfurization, which results in the smaller size of gypsum and the difficulty of dehydration.

3. Conclusion

3.1 The main components of solid phase in gypsum and slurry of absorption tower can be detected by thermogravimetric analysis technology. The reaction degree and forced oxidation performance of limestone in absorption tower can be determined according to the content of CaSO₄·2H₂O、CaCO₃、CaSO₄·1/2H₂O.

3.2 The distribution of different particle sizes in gypsum and slurry can be analyzed by laser particle size analyzer, which is a direct characterization of the crystallization of gypsum.

3.3 In actual production, excessive magnesium content of limestone will affect the crystallization of gypsum in absorption tower, resulting in more nuclei and more crystals of small size, increasing the difficulty of dehydration of gypsum belt and higher moisture content of gypsum. Therefore, it is necessary to strengthen the control of limestone composition.

References

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