Feasibility Analysis and Key Issues of Using Limestone Sludge in Power Plant Desulfurization System

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Abstract. Comparative analysis of limestone sludge in recycled water and desulfurization limestone is made in the chemical composition, reaction activity, crystallization properties and pH of Slurry. The results show that the limestone sludge in recycled water is possible to be used as a desulfurizer. Due to the large amount of impurities and lower reactivity of limestone sludge, the overall performance index values of limestone sludge are lower than that of desulfurization limestone. If it wants to be used as a desulfurizer, the further research on the using conditions of recycled water limestone sludge in desulfurization system and the possible impact of the reuse of desulfurization system on the stable operation of the system are needed.

Keywords: limestone sludge, reaction activity, desulfurization system.

1. Introduction
In recent years, urban sewage reuse as the reclaimed water reuse project has opened up a new way to solve the problem of water resources [1]. According to the National Standard of the People's Republic of China 5085-2007 "Dangerous Waste Identification Standard", the sludge produced by the water lime softening treatment system belongs to Class II general industrial solid waste. If it is accumulated for a long time, it will not only occupy a large amount of land, but also cause serious erosion to the soil. The main component of the sludge is CaCO₃, and the desulfurizer used in the limestone-wet flue gas desulfurization technology is a calcium-based alkaline substance with similar physical and chemical properties. In theory, the sludge can be used as a wet desulfurization system. In this paper, the main components of the limestone sludge and desulfurized limestone, the pH value, the reactivity, the reaction crystallization performance, etc. are analyzed and compared, and the research is applied to the wet flue gas desulfurization system of thermal power plant [2]-[3].

2. Production of limestone sludge in water
The reclaimed water limestone sludge is a solid waste with CaCO₃ as the main component produced during the process of softening of the reclaimed water lime. The reclaimed water lime softening method is as follows: adding lime milk, participating in (1)-(4) softening reaction, controlling the pH of the effluent to 10.3~10.5, generating a large amount of CaO₃ crystal to reduce the temporary
hardness of water, and simultaneously generating the crystal nucleus. Other impurities can act as agglomeration and adsorption [4]-[6].

\[
\text{CO}_2 + \text{Ca (OH)}_2 = \text{CaCO}_3 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Ca (HCO}_3\text{)}_2 + \text{Ca (OH)}_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{Mg(HCO}_3\text{)}_2 + \text{Ca(OH)}_2 = 2\text{CaCO}_3 + \text{Mg(OH)}_2 + 2\text{H}_2\text{O} \quad (3)
\]

\[
\text{MgCO}_3 + \text{Ca (OH)}_2 = \text{CaCO}_3 + \text{Mg (OH)}_2 \quad (4)
\]

In order to improve the precipitation effect of the process, an appropriate amount of coagulant is generally added during the treatment, and the charged body of the dispersed suspension, CaCO₃ crystal, organic matter, organic slime and colloid is destabilized by compressing the electric double layer. Under the action of mechanical mixing and polymer coagulant bridging and net trapping, the collision of particulate matter becomes larger, which makes the pollutants more likely to settle. The main product of the reclaimed water lime treatment system is CaCO₃. In theory, the product of the water treatment system can be used as a desulfurizer for the desulfurization system.

3. Analysis of the difference in reaction performance between limestone sludge and desulfurized limestone

3.1. Main component indicators

The limestone powder samples from the desulfurization system of one of the North China thermal power plant and the sludge samples dehydrated from the water limestone mud in the sewage treatment plant were used as comparative analysis objects, mainly for Ca, Mg, acid insoluble, iron and organic matter. Conduct an analysis to understand the quality and changes of different manufacturers, different batches of desulfurized limestone and reclaimed water limestone sludge. The test standard is based on the power standard 1483-2015 "Test method for chemical and physical properties of limestone-gypsum wet flue gas desulfurization system", GB/T 15057.6-1994 "Determination of iron content in limestone for chemical industry - phenanthroline spectrophotometry", CJ /T 221—2005 “Sewage Treatment Plant Sludge Inspection Method”, etc. Desulfurization limestone samples and reclaimed water limestone sludge samples of different time periods were selected as physical and chemical indicators. The analysis results are shown in Table 1.
Table 1. The physical and chemical analysis results of simples.

| Test Items              | Test Standards       | Test Results (mg/L)                        |
|------------------------|----------------------|--------------------------------------------|
|                        |                      | Reclaimed water limestone sludge samples   | Desulfurization limestone samples |
| 1 pH value             | GB 6920-1986         | 8.31                                       | 6.41                             |
| 2 Suspended solids     | GB 11901-1989        | 112                                        | -                                |
| 3 ammonia nitrogen     | HJ 535-2009          | 0.399                                      | 14.0                             |
| 4 COD                  | HJ 828-2017          | 56                                         | 995                              |
| 5 LAS                  | GB 7494-4987         | 0.16                                       | 0.35                             |
| 6 total phosphorus     | GB 11893-89          | 4.19                                       | 1.57                             |
| 7 nitrite nitrogen     | GB 7393-1987         | 0.015                                      | 0.808                            |
| 8 total residual chlorine | HJ 586-2010         | 0.015                                      | 0.21                             |
| 9 total hardness       | GB 7477-1987         | 2.17×10³                                   | 2.47×10⁴                         |
| 10 Pb                  | GB 7475-1987         | 0.092                                      | 0.973                            |
| 11 As                  | HJ 694-2014          | 0.0068                                     | 0.0010                           |
| 12 Cd                  | GB 7475-1987         | 0.010                                      | 0.134                            |
| 13 Mn                  | HJ/T 344-2007        | 0.03                                       | 57.3                             |
| 14 Fe                  | HJ/T 345-2007        | 0.29                                       | 1.26                             |
| 15 Ca                  | GB/T 15452-2009      | 868                                        | 8.28×10⁴                         |
| 16 Mg                  | GB/T 15452-2009      | <2                                         | 233                              |

It can be seen from Table 1 that the main components of desulfurized limestone and reclaimed water limestone sludge are Ca, Mg, and acid insoluble. The Ca mass fraction of desulfurized limestone is 8.28×10⁴ mg/L; the Ca mass fraction of reclaimed water limestone sludge is 868 mg/L. Compared with desulfurized limestone, the quality of reclaimed water limestone sludge is relatively poor.

3.2. Slurry pH value
20 g of desulfurized limestone and reclaimed water limestone sludge samples were weighed separately, and 80 mL of deionized water was added to prepare a slurry having a mass fraction of 20%. The pH value of the slurry was analyzed by a pH meter. The test results showed that the pH of the limestone sludge slurry was 8.31, the pH of the desulfurized limestone slurry was 6.41, and the pH of the limestone slurry was much higher than that of the desulfurized limestone slurry.

3.3. Reactive activity
A sample of desulfurized limestone and a sample of water limestone sludge in a certain day were selected as the research object of the reaction. The test standard was based on DL/T 943-2005 "Determination of the reaction rate of limestone powder for flue gas wet desulfurization". The following four samples were designed for reactivity analysis: desulfurization limestone sample, reclaimed water limestone sludge sample, 75% desulfurized limestone sample and 25% reclaimed water limestone sludge sample (mixed by mass ratio). A sample of a 50% desulfurized limestone sample and a 50% reclaimed water limestone sludge sample. The sample reactivity analysis results are shown in Figure 1.
Figure 1. Reactivity analysis results of four samples. a, 100% desulfurization limestone, b, 75% desulfurized limestone with 25% reclaimed water limestone sludge, c, 50% desulfurized limestone with 50% reclaimed water limestone sludge, d, 100% reclaimed water limestone sludge sample.

Figure 1 shows as the reaction time reaches 2 h, the limestone conversion rate of the reclaimed water limestone sludge is 12.27% lower than that of the desulfurized limestone, and the reaction rate is low.

3.4. Reaction crystallization properties
In order to analyze the difference in the crystallization properties of the limestone lime sludge and the desulfurized limestone, it is determined whether the impurity component in the sludge will affect the crystallization reaction of the desulfurized gypsum, and the gypsum crystallization reaction test is carried out[7]. A schematic diagram of the gypsum crystallization test reaction device is shown in Fig.2.

Figure 2. Schematic diagram of the gypsum crystallization test reaction device

During the test, firstly, a concentration of 0.6 mol/L Na$_2$SO$_4$ solution was placed in the sample storage tank. 100 mL of 0.6 mol/L CaCl$_2$ solution was added to the crystallization reactor, and the Na$_2$SO$_4$ solution was passed through a peristaltic pump. A 9 mL/min injection rate was added to the reactor at a constant temperature of 50 °C. The analyzer was used to monitor the change of conductivity of the solution in the reactor, and the crystal growth process was analyzed according to
the change of conductivity. Then, the reclaimed water limestone sludge and desulfurized limestone samples were used respectively, and the 0.6 mol/L CaCl$_2$ solution was replaced by the equivalent of calcium ion concentration to analyze the difference of reaction crystallization properties between the reclaimed water limestone sludge and the desulfurized limestone. The crystallization performance test results are shown in Figure 3.

![Conductivity Curves](image)

**Figure 3.** The conductivity curves of the crystallization reactions with different calcium ion solutions

It can be seen from Fig. 3 that the CaCl$_2$ solution is titrated to a non-impurity reaction, and when the conductivity of the solution in the reactor is lowered to 21.10 mS/cm, a large amount of visible crystal is formed. After replacing the CaCl$_2$ solution in the limestone sludge sample and the desulfurized limestone sample, the conductivity tends to be stable when the conductivity is decreased to 15 mS/cm. At this time, CaSO$_4$·2H$_2$O crystals appear in the solution, and the crystallization time is compared with the analytical pure solution. The crystallization time was delayed by about 20 min. It can be seen that the reaction crystallization performance of the reclaimed water limestone sludge and the desulfurized limestone is similar, and the crystallization reaction time of the reclaimed water limestone sludge is slightly higher than that of the desulfurized limestone.

### 4. Conclusion and recommendations

By analyzing and comparing the differences in reaction performance between water limestone sludge and desulfurized limestone in a power plant, the following conclusions are drawn.

1. The main components of both are the same, all of which are Ca, Mg, and acid insoluble.
2. When the reaction time reaches 2 h, the limestone conversion rate of the reclaimed water limestone sludge is 12.27% lower than that of the desulfurized limestone, and the reaction rate is low.
3. The reclaimed water limestone sludge contains more elements than desulfurized limestone. These secondary components are important factors in determining whether it can be used as a desulfurizer.

Comprehensive analysis shows that the reclaimed water limestone sludge has the potential to be used as a desulfurizer. However, sludge limestone contains more impurities and lower reactivity, and its overall performance index is worse than that of desulfurized limestone. If it is to be used as a desulfurizer, further intermediate tests and industrial tests are needed to determine the final conditions of use.
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