A Review of Coal Desulfurization Technology

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Abstract

China's air pollution is mainly soot type, and its main pollutants are mainly soot, SO_2 and NO_x .The main task of controlling air pollution in China is to reduce SO_2 and NO_x emissions.It is urgent to find an effective and economical technology of sulfur removal.For this reason, this article comprehensively introduces several methods of desulfurization, and points out the characteristics, principles, and applications of each method which provides scientific basis for the selection of methods and realizes efficient and clean utilization of coal.

Keywords

Coal; desulfurization; technology; methods.

1. Introduction

Coal plays a very important role in the world's conventional fossil energy. The main pattern of the world's energy is fossil energy, and the energy pattern of China is "rich coal, poor oil and little gas", which determines the dominant role of energy in China as coal.The next table is the energy consumption structure of our country in recent years[1].

Table 1.Energy consumption structure in China in recent years

Year	Coal/%	Petroleum/%	Natural gas/%	Hydropower, nuclear power and wind power/%
1990	76.2	16.6	2.1	5.1
2000	67.9	23.2	2.4	6.7
2006	69.4	20.4	3.0	7.2
2009	68.7	18.0	3.4	9.9
2010	69.2	17.4	4.0	9.4
2014	66.0	17.1	5.7	11.2
2015	64.0	18.1	5.9	12.0
2016	62	18.3	6.0	13.7

As can be seen from Table 1, in recent years, although the proportion of coal in the energy consumption structure has dropped slightly, it still occupies about 5/7 of energy consumption.Although the proportion of coal has declined rapidly in the last two years, it still occupies a dominant position in the primary energy consumption in China, and the coal consumption will still dominate in the first energy consumption for a long period of time.

Because of the poor endowment conditions of coal resources in China, 40% of the coal reserves are low quality coal resources with high impurities, such as mineral and sulfur, and the clean utilization technology of coal has not been paid enough attention. It is an indisputable fact that coal utilization is caused by environmental pollution.

About 80% of the raw coal in our country is used for direct combustion. In air pollution, 80% of dust and 90% of SO_2 come from coal combustion.In 1995, the national emission of smoke and dust was about 17 million 200 thousand tons, SO_2 emissions were about 23 million 700 thousand tons, of which the SO_2 produced by burning coal accounted for about 90%, CO_2 accounted for 83%, CO accounted for 71%, NO_X accounted for 70%, and dust accounted for 60%.The mean concentration of SO_2 in the atmosphere of our country is 100mg/m^3, which is the 2.5-1.7 times of world sanitary fabric (40~60mg/m^3), and the concentration of NO_2 in pulverized coal boiler is 800-1000mg/m^3, which exceeds the standard of 40%-60%.The acid rain area has an expanding trend, the acid rain control area accounts for 8.4% of the land area, and the SO_2 pollution control area accounts for 3% of the land area. It not only causes the loss of agriculture and forestry, but also causes the corrosion of the buildings and bridges. The annual economic loss is about 8 billion yuan, and it also causes great harm to the health of the people.

At present, environmental pollution has become one of the important reasons restricting coal development. Desulfurization of high sulfur coal is an important way to reduce coal pollution to the environment.From the perspective of coking coal, although China has abundant coal resources, high-quality coal, especially high-quality coking coal, accounts for a small proportion.According to statistics, coking coal accounts for about 27% of the coal reserves in China. With the increasing demand for coking coal in China in recent years, the shortage of high quality coking coal resources is becoming more and more serious, and some coking enterprises have begun to use coking coal with high sulfur content.Studies have shown that the sulfur content in coke has a great impact on the energy consumption of blast furnace ironmaking and the quality of molten iron. For every 0.1% increase in sulfur content in coke, the ironmaking coke ratio increases by 1.5%, while the blast furnace production capacity decreases by 2.5%. Moreover, the quality of steel products is affected, and the SO_2 produced in the coking process will generate strong acid rot candle coking equipment.From the angle of power coal, about 90% of SO_2 is produced by coal combustion, which not only causes environmental pollution but also causes great harm to human health. It can be combined with drift dust into the human lung, causing a variety of malignant diseases, and the harm to plants is very great. The combination of SO_2 in air and water can form acid rain and can make it possible. In the coal washing project, the coal with high sulfur content is often very heavy on the equipment, and some basic substances (such as limestone, etc.) need to be added to alleviate the corrosion of the equipment.Therefore, it is very urgent and meaningful to carry out desulphurization research on high sulfur coal, either in terms of economic efficiency or in solving environmental pollution[2].

2. The Occurrence of Sulfur in Coal

Sulfur content in coal is expressed as St and D, including inorganic sulfur and organic sulfur.Based on the dry basis, according to the total sulfur content, according to the national standard GB17608, the coal can be divided into the following five categories, and table 2 is the total sulfur classification of coal.

Table 2. Classification of total sulfur in coal

Category	Special low sulfur coal	low-sulfur coal	Middle sulfur coal	Middle high sulfur coal	High sulfur coal
Total sulfur content	≤0.50%	0.51%-0.90%	0.91%-1.50%	1.51%-3.00%	>3.00%

Sulfur, which is trapped in coal in a free state, is called elemental sulfur.Organic sulfur, pyrite sulfur and elemental sulfur are combustible sulfur. Since sulphur sulfur remains in the residue after coal

combustion, it is called fixed sulphur.Inorganic sulfur mainly includes pyrite sulphur, sulphur sulphur and trace elemental sulfur.Sulphate sulfur exists in different forms of sulfate, such as barium sulfate ($BaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), etc.Pyrite sulfur is the main existence form of pyrite sulfur, and pyrite sulfur is a square crystal, mainly in the form of nodular, lenticular, lump and disseminated form in coal, and the proportion of pyrite sulfur in pyrite is less. It is a trapezoid crystal and mostly radiate.In addition to the above two species, there are other small amounts of inorganic sulfides, such as ($CuFeS_2$), arsenopyrite ($FeAsS_2$), galena (PbS), and flash catalpa (ZnS).Inorganic sulfur is mostly attached to coal particles, which mainly acts as a physical function. It can remove part of through coal washing[2].

Organic sulfur usually refers to sulfur in organic structure of coal molecules, and the molecular structure of coal is mainly composed of macromolecular aromatic compounds.The study shows that the molecular structure of coal is quite complex. Most experts think that it is similar to the structure of polymer, but it is different from the general polymer because it does not contain a unified monomer, and the form of organic sulfur in coal is also complicated.Sulfur and oxygen are similar in nature, so the types of sulfur and oxygen containing functional groups in coal are similar, mainly in the following categories: fat and aromatic mercaptan; fat, aromatic sulfides; fat, aromatic and mixed two sulphides; thiophene (single and complex thick rings); thioquinones and thiones.

3. Research Status of Coal Desulfurization Technology

According to the order of sulfur removal from coal combustion, the existing coal desulfurization technology is divided into three categories: coal desulfurization before coal combustion, desulfurization in coal combustion and desulphurization after coal combustion.This paper introduces desulfurization before coal combustion and desulphurization in combustion.

3.1 Pre Combustion Desulfurization Technology of Coal [3]

Desulfurization before coal combustion is the removal of sulfur from coal before combustion.This method can avoid the form change of sulfur in the combustion, reduce the sulfur content in the flue gas and the corrosion of the tail flue, and avoid the bad effects on the following links of combustion and coking, thus reducing the operation and maintenance cost of the coal industry.

3.2 Desulphurization Technology in Coal Combustion

In the process of coal combustion, the components of sulfur, nitrogen and chlorine in coal are explained to gas in the coal gas to form harmful gases and corrosion related equipment. Especially for the system of coal gasification combined cycle, these harmful gases enter the gas turbine and corrode the blade of the unit, and these harmful gases are emitted into the atmosphere with the gas combustion. It can also cause pollution, so removing harmful components from coal combustion is an indispensable part[3].These harmful gases mainly include sulfur gas and HCl, HCN, NO_X and other components.Sulfide produced by coal combustion can be divided into two categories: inorganic sulfide and organic sulfide.Inorganic sulfides are mainly H_2S and a small amount of COS (carbonyl sulfur) and mercaptan, and organic sulfides are converted almost entirely to H_2S at high temperatures, so in general, most of the sulfur is in the form of H_2S, which is equal to the removal of the vast portion of the harmful gases by removing H_2S.Desulfurization is usually carried out using limestone or dolomite [4].

The desulfurization process takes place in the gasifier, so there is no need to install additional desulphurization device. The equipment investment is small and the system structure is simple.Because the desulphurizer does not regenerate reaction process, the removal of the furnace usually uses cheap limestone or dolomite, the main component is $CaCO_3$ or $CaCO_3$ $MgCO_3$, the main chemical reaction equation is [5]:

Calcination of limestone and dolomite:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1}$$

$$CaCO_3 \cdot MgCO_3 \rightarrow CaCO3 \cdot MgO + CO_2 \tag{2}$$

$$CaCO_3 \cdot MgO \rightarrow CaO \cdot MgO + 2CO_2 \tag{3}$$

Limestone was removed from the H2S reaction:

$$CaCO_3 + H_2S \rightarrow CaS + H_2O + CO_2 \tag{4}$$

$$CaO + H_2S \rightarrow CaS + H_2O \tag{5}$$

Dolomite removal of H_2S reaction:

$$CaCO_3 \cdot MgO + H_2S \rightarrow CaS \cdot MgO + H_2O + CO_2 \tag{6}$$

$$CaO \cdot MgO + H_2S \rightarrow CaS \cdot MgO + H_2O \tag{7}$$

On the one hand, $CaCO_3$ can react directly or react with calcination to generate CaO and H_2S.However, under normal conditions, the vulcanization of CaO after calcination reaction is more thorough than that of $CaCO_3$.This indicates that the roasting reaction of limestone is very important for improving the performance of desulfurization.

4. Conclusion

Based on the above technologies, we can conclude that under different conditions or conditions, the desulphurization methods are different and the desulphurization effects are different.Therefore, we need to choose the best technology according to the specific situation.

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