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Advancement of Environmental Sustainability: A Comparative Analysis of Flue Gas Desulfurization Technologies in China's Energy Sector

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Abstract: This paper provides an in-depth analysis of the various flue gas desulfurization technologies employed in the context of China's rapidly growing energy sector. With the nation's industrial expansion leading to unprecedented levels of sulfur dioxide (SO2) emissions, the need for efficient and effective desulfurization methods is paramount. This study systematically examines multiple desulfurization techniques, including limestone-gypsum, ammonia alkali, dual alkali, magnesium oxide, organic amine methods. The research evaluates each method based on its operational mechanics, efficiency, economic feasibility, environmental impact, and suitability for China's specific industrial conditions. Limestone-gypsum desulfurization, while prevalent, is contrasted with emerging alternatives that offer potential advantages in terms of efficiency, cost, and environmental sustainability. Special attention is given to innovative approaches such as magnesium oxide and organic amine methods, which demonstrate high efficiency and lower ecological footprints. The findings of this study indicate a trend towards more sustainable and cost-effective desulfurization techniques, highlighting the need for continued research and development in this field.

1. Introduction

The dawn of the 21st century heralded a period of explosive growth for the Chinese economy, paralleled by an escalating demand for energy. This surge in energy requirement has been predominantly met by coal and petroleum, which are the primary sources for combustion-based power generation. The transformation of these fossil fuels into electrical energy, while instrumental in fueling economic expansion, has given rise to substantial environmental concerns, particularly in terms of pollution.

A significant environmental challenge is the emission of sulfur dioxide (SO_2), a by-product of fossil fuel combustion. China has notably led global rankings in sulfur dioxide emissions for several consecutive years, a testament to the scale of its industrial and energy-generating activities[1]. According to the 2020 China Ecological Environment Status Bulletin released by the Ministry of Ecology and Environment, areas affected by acid rain, primarily caused by sulfur dioxide and its derivatives, covered approximately 466,000 square kilometers in 2020[2]. This area represents about

4.8% of China's total landmass, with the prevalent form of acid precipitation being sulfuric acid-type rain due to the high concentration of sulfate anions.

The issue of sulfur dioxide emissions is not just an environmental concern but also a pressing public health matter, given the harmful effects of acid rain and air pollution on human health and ecosystems. Therefore, the urgent need for effective sulfur dioxide emission control strategies is not only a response to environmental degradation but also a proactive step towards sustainable development and public health preservation.

The urgency to curtail SO_2 emissions in China is a critical aspect of its broader environmental protection and sustainable development goals. This thesis aims to explore and analyze various desulfurization techniques, assessing their feasibility, efficiency, and practical implications in the context of China's unique environmental, economic, and industrial landscape.

2. Limestone (Lime) – Gypsum Desulfurization

The limestone (lime) – gypsum method is the most technically mature, widely applied, and stable desulfurization process in the world. Its notable advantages include: first, high desulfurization efficiency (in some cases, with a Ca/S ratio of 1[3], the efficiency can exceed 90%); second, high utilization rate of the absorbent, which can be greater than 90%; and third, high equipment operation rate (which can reach over 90%). This method has nearly thirty years of operational experience. The gypsum by-product can be recycled or disposed of.

The primary reaction in this process occurs in the absorption tower. The absorbent delivered to the tower, a limestone slurry, mixes with flue gas cooled by the flue gas re-heater before entering the tower. The sulfur dioxide in the flue gas reacts with the calcium carbonate in the absorbent slurry and oxygen from the air pumped in to produce gypsum. The desulfurized flue gas then passes through a demister to remove droplets and is heated by the flue gas re-heater before being discharged into the atmosphere through a chimney. The process uses calcium oxide or calcium carbonate slurry to absorb sulfur dioxide in a wet scrubbing tower.

Due to the complexity of the chemical reactions occurring in the absorption tower, the complete reaction process is not yet fully understood. However, the main reactions are as follows[4]:

The dissociation of water:

$$H_2O \rightarrow H^+ + OH^- \tag{1}$$

Absorption of SO_2:

$$SO_2(g) \rightarrow SO_2(ag) \tag{2}$$

$$SO_2(ag) + H_2O \rightarrow H^+ + HSO_3^- \tag{3}$$

$$HSO_3^- \rightarrow H^+ + SO_3^{2-} \tag{4}$$

Dissolution of solid $CaCO_3$:

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \tag{5}$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \tag{6}$$

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2(aq) \tag{7}$$

Oxidation of HSO3- in the presence of oxygen:

$$2HSO_3^- + O_2 \rightarrow 2H^+ + 2SO_4^{2-} \tag{8}$$

Crystallization of $CaSO_4$ and $CaSO_3$:

$$Ca^{2+} + SO_3^{2-} + H_2O \rightarrow CaSO_3 \cdot 1/2\ H_2O \tag{9}$$

$$Ca^{2+} + SO_4^{2-} + H_2O \rightarrow CaSO_4 \cdot 1/2\ H_2O \quad (10)$$

The by-product of the limestone (lime) – gypsum desulfurization process is gypsum, which can be recycled and reused. This process is technologically mature, with high desulfurization efficiency (90% to 98%), suitable for large-capacity units, adaptable to various types of coal, reliable in performance, and uses absorbents that are abundant and inexpensive. The by-products are easily recyclable. However, the initial investment and operating costs are high, it consumes a large amount of water, and requires more space compared to other processes, presenting certain difficulties for existing power plants without reserved desulfurization space. This process is widely used in the United States, Japan, and Germany and is the most applied and technically mature desulfurization process in the world, holding about 90% of the global market share. In China, the Luohuang Power Plant in Chongqing introduced two sets of limestone (lime) – gypsum flue gas desulfurization equipment from Mitsubishi Heavy Industries in Japan, equipped with two 360MW generator sets, achieving a desulfurization efficiency of 95% and producing about 400,000 tons of gypsum by-products annually. Other desulfurization projects like the Chongqing Power Plant (2*200MW) and the Banshan Power Plant (2*125MW) also adopted the limestone (lime) – gypsum desulfurization process.

However, drawbacks of this method include high demand for limestone, relatively high operation and maintenance costs, and potential corrosion to processing equipment. Additionally, the generated gypsum must be properly handled to avoid environmental issues.

3. Ammonia Alkali Desulfurization

Ammonium hydroxide or ammonium sulfite solution is used as the absorbent, converting absorbed sulfur dioxide into ammonium sulfite—ammonium bisulfite. Decomposing the washed absorbent with acid (acidification) produces sulfur dioxide and the corresponding ammonium salts, known as the ammonia-acid method. Direct processing of the absorbent into ammonium sulfite, substituting caustic soda in the papermaking industry, is the ammonia-ammonium sulfite method. As China is a major grain and fertilizer producer, the by-products of the ammonia alkali method, being fertilizers themselves, hold significant value. The desulfurization rate of the ammonia alkali method is high, and with two-stage absorption, the sulfur dioxide concentration in the exhaust can be reduced to less than one part per million[5].

The chemical reaction between ammonia and sulfur dioxide produces ammonium sulfate and ammonium sulfite. This reaction mechanism can be simplified into the following two main steps:

$$NH_3 + SO_2 + H_2O \rightarrow NH_4HSO_4 \quad (11)$$

$$NH_4HSO_3 + NH_3 \rightarrow (NH_4)_2SO_3 \quad (12)$$

In actual industrial applications, the ammonia desulfurization system needs optimization for high efficiency and low energy consumption. This may include adjusting the supply of ammonia, controlling reaction temperature and pressure, and ensuring proper system maintenance. Advantages of the ammonia method include high removal efficiency for SO2 and the ability to produce useful by-products. However, challenges such as ammonia escape and equipment corrosion must be considered in the design and operation phases.

4. Dual Alkali Desulfurization

In this method, sodium alkali or ammonia alkali solutions absorb sulfur dioxide. The resulting solution then reacts with an alkali, converting the absorbed sulfur dioxide into insoluble CaSO4 and regenerating the absorbent liquid. This method uses inexpensive limestone to treat flue gases, being economical and avoiding the clogging issues present in the wet lime-limestone method.

Reaction Principles:

Using the first alkali: In the first stage, sodium carbonate is commonly used as the first alkali. It reacts with SO2 in the flue gas to form sodium sulfite and sodium sulfate.

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \tag{13}$$

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \tag{14}$$

Regeneration and using the second alkali: The second stage involves regenerating the solution. This step typically uses calcium hydroxide as the second alkali. It reacts with sodium bisulfite to convert it into insoluble calcium sulfite and regenerate sodium hydroxide.

$$2NaHSO_3 + Ca(OH)_2 \rightarrow CaSO_3 + 2NaOH + H_2O \tag{15}$$

$$CaSO_3 + 1/2O_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{16}$$

The advantages of the dual alkali desulfurization method include effective removal of sulfur dioxide from flue gases and the production of valuable gypsum as a by-product. Moreover, as it uses two types of alkalis, this method has a high desulfurization efficiency and can adapt to different flue gas conditions. However, its drawbacks include relatively high operating costs and the need for careful maintenance and management of the processing equipment to avoid corrosion and clogging issues.

5. Magnesium Oxide Desulfurization

China boasts a rich reserve of magnesium oxide, with approximately 16 billion tons identified, accounting for about 80% of the world's total. The most significant advantage of magnesium oxide desulfurization over calcium-based methods is that it prevents scaling and blockage in equipment. Magnesium hydroxide, magnesium sulfate, and magnesium sulfite are all soluble in water, ensuring the safe and effective operation of the entire desulfurization system. Moreover, controlling the pH value between 6.0 to 6.5 in magnesium oxide desulfurization can mitigate equipment corrosion to a certain extent. In terms of chemical reactivity, magnesium oxide is far superior to calcium-based desulfurization agents. Additionally, since magnesium oxide has a lower molecular weight than calcium carbonate and calcium oxide, its desulfurization efficiency under similar conditions is higher than that of calcium-based methods. Generally, the desulfurization efficiency of magnesium oxide can reach 95% to 98% or more, while the efficiency of the limestone-gypsum method is around 90% to 95%. The unique advantages of magnesium oxide desulfurization allow for reductions in the corresponding values during the structural design of absorption towers, calculation of circulating slurry volume, and power selection of equipment. The investment cost of a magnesium oxide desulfurization system is generally more than 20% lower compared to calcium-based desulfurization[6].

First, magnesium oxide reacts with water to form magnesium hydroxide:

$$MgO+H_2O \rightarrow Mg(OH)_2 \tag{17}$$

Then, magnesium hydroxide reacts with sulfur dioxide to produce magnesium sulfite:

$$Mg(OH)_2+SO_2 \rightarrow MgSO_3+H_2O \tag{18}$$

$$MgSO_3+1/2O_2 \rightarrow MgSO_4 \tag{19}$$

6. Organic Amine Desulfurization

Organic amine desulfurization is a commonly used flue gas desulfurization technology in industrial production, especially suitable for flue gases with lower concentrations of sulfur dioxide. This method mainly uses organic amine compounds as absorbents. In the desulfurization tower, an organic amine solution is sprayed or brought into contact with the flue gas. Common organic amines include diethanolamine, methyldiethanolamine, and triethanolamine. These organic amines chemically react with sulfur dioxide in the flue gas to form soluble amine salts. This process is generally reversible, allowing the release of sulfur dioxide from the amine solution in subsequent steps[7].

For example, the reaction of methyldiethanolamine with sulfur dioxide can be represented as:

$$2MEA+SO_2 \rightarrow (MEA)_2SO_2 \tag{20}$$

Regeneration of Organic Amines: The organic amine solution that has absorbed sulfur dioxide is then sent to a regeneration tower. In the regeneration tower, the amine salts are decomposed by heating or reducing pressure, releasing sulfur dioxide and regenerating the organic amines.

For example, for methyldiethanolamine:

$$(MEA)_2SO_2 \rightarrow 2MEA+SO_2 \tag{21}$$

The released sulfur dioxide can be further processed, such as being converted into sulfuric acid or liquid sulfur. The treated flue gas, with significantly reduced sulfur dioxide concentration, can be safely discharged into the atmosphere. The regenerated organic amine solution is recycled back to the desulfurization tower for a new round of absorption. The advantages of organic amine desulfurization include efficient sulfur dioxide absorption capability and suitability for flue gases with low sulfur dioxide concentrations. Moreover, this method operates under relatively mild temperature and pressure conditions, reducing corrosiveness to equipment. However, drawbacks of this method include higher operational costs, particularly in the procurement and regeneration of organic amines, as well as potential issues with amine solution leakage and volatilization, requiring effective management and control.

7. Conclusion

This comprehensive study of flue gas desulfurization (FGD) methods in China's energy sector underscores the critical need for effective strategies to mitigate sulfur dioxide (SO2) emissions, a byproduct of the country's rapid industrialization and energy production. Our analysis of different FGD techniques—limestone-gypsum, ammonia alkali, dual alkali, magnesium oxide, organic amine—reveals varied efficacy, economic viability, and environmental impacts, each presenting unique advantages and challenges.

This thesis highlights that no single FGD method is universally optimal; rather, the choice depends on specific industrial requirements, regional characteristics, and environmental regulations. It is evident that balancing economic growth with environmental sustainability is a complex but vital endeavor for China. The move towards more sustainable and economically viable FGD technologies is not only an environmental imperative but also a strategic necessity for the country's ongoing industrial development.

In conclusion, the journey towards reducing SO2 emissions in China is multifaceted, involving technological innovation, economic considerations, and regulatory measures. The successful implementation of effective desulfurization strategies is crucial for ensuring a sustainable and environmentally conscious future for China's energy sector.

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