



The Review of Flue Gas Desulfurization with a Readily Available Metal Ions Liquid Catalytic Oxidation Catalyst-Pulp



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Abstract

Liquid catalytic oxidation technology by transition metal ions is one of the hot topics in the field of flue gas desulfurization. As pulp contains abundant transition metal ions, desulfurization technology by pulp has been investigated. The review introduced pyrolusite pulp desulfurization research, including the main influence factors, desulfurization mechanism analysis, process equipment as well as combined effect of pyrolusite pulp and microbes; the state of industrial application of phosphate pulp desulfurization; the investigation of coal pulp flue gas desulfurization. All the above pulp flue gas desulfurization achieved excellent results, with high SO₂ removal rate and obtaining by-products. Pulp is a kind of cheap and readily available metal ions liquid catalytic oxidation desulfurization catalysts.

Keywords: Pulp; Flue gas desulfurization; SO₂; Liquid catalytic oxidation

Introduction

As one of the main atmospheric pollutants, SO₂ is the immediate cause of acid rain, which can result in dead trees, food production decrease, water acidification, building corrosion, deterioration of ecological environment, and serious harm to human health [1]. SO₂ is mainly derived from flue gas emissions of the thermal power industry, nonmetal mineral products industry, chemical industry and metallurgy industry [2]. Scholars did a lot of research on flue gas desulfurization, and developed more than one hundred kinds of desulfurization methods, divided into dry and wet kinds according to the forming process [3]. In the industrialization methods, limestone-gypsum was used mostly, which was cheap and produced by-product gypsum, while the gypsum was difficult to be used, economic was not obvious, and it caused the secondary pollution [4]. Developing a new desulfurization technology which can not only remove SO₂ from flue gas, but also recycle sulfur resources to get high value by-product will be an effective way to solve SO₂ pollution. In recent years, liquid phase catalytic oxidation flue gas desulfurization technology are paid more and more attention [5,6], such as Mn(II) system, Fe(II) and Fe(III) system, various ions coordinated system, heteropoly acid system, which don't consume catalyst in theory, and can regenerate by changing valence state of transition metal ions, without solid waste and secondary pollution. In addition, it can make valuable by-products, fertilizer, ferrous

sulfate, manganese sulfate, polymeric ferric sulfate, and so on. By investigation, the addition of Mn, Cu, Co to Fe(II) catalyst, not only can play promoting and synergy performance, but also make Fe(II) catalytic activity stable, and the absorbing liquid used to remove SO₂ from smelter flue gas has achieved good effect [7]. From the view of sulfur resource utilization, environment protection and sustainable development, recycling method should be chosen firstly in flue gas desulfurization.

Pulp contains a variety of transition metal ions, which is in favor of SO₂ absorption. In the process of pulp absorbing SO₂, transition metal ions will continue into the solution, becoming cheap metal ions liquid catalytic oxidation desulfurization catalyst [8-10]. Currently, pyrolusite pulp, phosphate pulp and coal pulp are researched for flue gas desulfurization. In this paper, the current study on pulp flue gas desulfurization was introduced.

The Research Status of Pulp Flue Gas Desulfurization Pyrolusite pulp

MnO₂ is the main ingredient of pyrolusite pulp, which is a good antioxidant for treatment SO₂ in flue gas [11]. In acidic environment, Mn²⁺ is the most active reaction medium for SO₂ oxidation [12]. Pyrolusite pulp also contains Fe₂O₃, Al₂O₃, CaO, and other impurities. These impurities have the catalytic oxidation of SO₂, and can free up

in acidic liquid, leading to the catalytic oxidation rate of SO_2 improving 3-10 times than that singly using Fe^{3+} , Fe^{2+} or Mn^{2+} as catalyst. Fan chose pyrolusite, MnO_2 , Fe_2O_3 to modify walnut shell-derived column activated carbon by blending method respectively, and achieved the maximum sulfur capacity of activated carbon loaded by pyrolusite was 227.8mg/g [13]. Using the reaction characteristics of pyrolusite pulp and SO_2 to do flue gas desulfurization and obtain by-products MnSO_4 or dilute sulphuric acid, not only can eliminate secondary pollution in the desulfurization process, realize the comprehensive utilization of lean ore, but also can achieve the goal of recovery of sulfur resources, decrease the desulfurization cost [14,15].

The main influence factors

By investigation, Zhu found that stirring intensity had a dual role on desulfurization and manganese leaching efficiency [16,17]. Under low stirring speed (<500r/min), the desulfurization reaction of MnO_2 and SO_2 in the solution was major; with MnSO_4 as main by-product. Under high stirring speed (>1000r/min) and the catalysis of Mn^{2+} , Fe^{2+} etc., due to the dissolved oxygen concentration in the solution increasing, water absorbing SO_2 and MnO_2 - SO_2 oxidation reaction coexisted, with the mixture of MnSO_4 and dilute sulphuric acid as by-products, which was a new finding that SO_2 in flue gas could be oxidized to rare H_2SO_4 . If MnSO_4 needs to be recycled, stirring speed should be controlled below 500r/min. In order to obtain dilute sulphuric acid, stirring speed should be increased above 1000r/min. Increasing pyrolusite pulp temperature, the reaction rate and mass transfer rate improved, while SO_2 solubility decreased. The experimental results showed that from room temperature to 80 °C, the influence of two aspects offset. Improving the pulp temperature appropriately, was benefit to decrease the generation of $\text{S}_2\text{O}_6^{2-}$ which produced in the side reaction and influenced the quality of MnSO_4 [18]. Hu and Jin indicated that 40 °C was the ideal temperature by experiments [19,20]. Considering energy consumption, fresh pulp doesn't need to be heated as the high flue gas temperature.

Maintaining a low pH value (PH≈1) in desulfurization process, can enhance MnO_2 oxidation ability, and promote its reaction with SO_2 , to increase Mn leaching rate and SO_4^{2-} generation during the same reaction time. Less the rest of MnO_2 in pulp was, faster the desulfurization rate decreased [14]. Sun thought that the low PH was against SO_2 dissolving, and affected the reaction of MnO_2 and SO_2 . In order to speed up the desulfurization rate, it was necessary to add buffer to the reaction system. Hu reported that under the condition of PH 2-3.5, temperature 40 °C, the emission of SO_2 was up to standard, more than 80% Mn could be recycled, and SO_2 absorption rate reached over 90% [19].

For continuous operation equipment, liquid gas ratio (L/V) is an important parameter. With the increase of flue gas flow, the amount of gas into the liquid phase in a unit time rises, but SO_2 in the liquid phase stays for a shorter time, leading that SO_2 contacts with pulp inadequately. Besides, the initial amounts of SO_2 react with pulp quickly, making SO_2 excessive in the subsequent reaction, which reduces the desulfurization efficiency. The larger L/V is, the

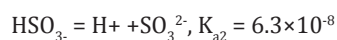
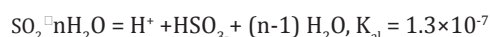
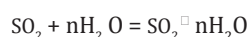
higher SO_2 absorption rate is, and the larger energy consumption and the cost of conveying liquid pumps, pipes and other equipment fee are. When the L/V reached 40, the absorption rate increased not obviously. Comprehensively considering the above factors, it was indicated that 40 was optimal liquid gas ratio [20]. Li et al. [20] also investigated the influence of liquid-solid ratio on the desulfurization rate and Mn leaching rate [15]. She indicated that the higher liquid-solid ratio was, the shorter the duration of high desulfurization rate was, the faster desulfurization rate decreased, at the same time Mn leaching rate improved and SO_4^{2-} generation decreased.

Sun et al. [21] investigated the influence of molar ratio of O_2 and SO_2 (O_2/SO_2) on Mn leaching rate. The results showed that O_2/SO_2 influenced Mn leaching rate and desulfurization efficiency by changing PH, as O_2 and SO_2 could react in the aqueous solution to generate sulfuric acid. The Mn leaching rate and MnSO_4 generation showed an increasing firstly and then decreasing trend with the increasing of O_2/SO_2 . When O_2/SO_2 was below 15, other Mn series by-product generated. O_2/SO_2 was above 20, by-product was only MnSO_4 , for the flue gas with O_2/SO_2 above 30 or below 15, PH value can be adjusted by adding rhodochrosite or sulfuric acid to improve Mn leaching rate and the percentage of MnSO_4 .

Desulfurization mechanism analysis

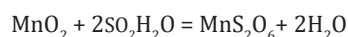
Pyrolusite pulp flue gas desulfurization process is a complex system related to gas, liquid and solid three phase mass transfer, chemical reaction in liquid phase, the liquid-solid surface chemical reaction. It contains the redox reaction and the catalytic oxidation process. Zhu determined the main reaction of the desulfurization system [22]: $\text{MnO}_2 + \text{SO}_2 = \text{MnSO}_4$, the main product in absorbing liquid was MnSO_4 , and its K balance constant was 6.84×10^{35} . The reported mechanism mainly includes the following aspects [23-25]:

(1) The dissolution of SO_2 . As flue gas contacts with pulp, SO_2 immediately dissolves into liquid phase. There is the following balance:



In acidic solution, S (IV) mainly shows HSO_3^- type.

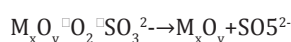
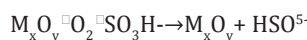
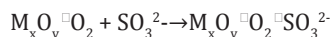
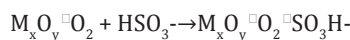
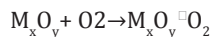
(2) MnO_2 oxidation of SO_2 .



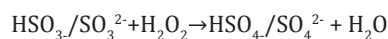
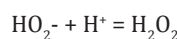
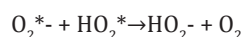
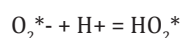
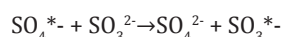
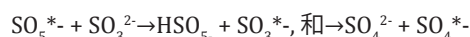
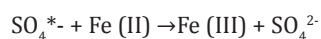
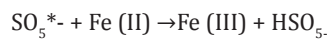
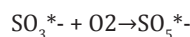
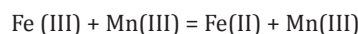
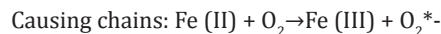
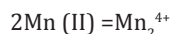
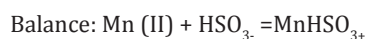
SO_2 and H_2O spread to the surface or inside of MnO_2 . Due to H_2SO_3 strong reducibility and MnO_2 strong oxidizing; the above reaction can run smoothly. Because of Mn^{2+} catalytic oxidation of H_2SO_3 in the existence of O_2 , there will be a sulfuric acid generation. MnS_2O_6 can be easily decomposed in acid medium or high temperature. It also can occur the following reaction:



Liu thought that in the process of catalytic oxidation of SO_2 , various metal oxides (M_xO_y) in pyrolusite pulp were all involved in the reaction [24]. Possible mechanism is as follows:



(3) Mn, Fe and other transition metal liquid phase catalytic oxidation. SO_2 and O_2 dissolving in absorbing liquid can occur catalytic oxidation reaction due to the presence of metal ion. W. Pasiuk thought that as chain reaction, metal ions catalytic oxidation of SO_2 must have HSO_3^- to form complex to cause reactions, with Mn(II) and Fe(II) catalyzing [26,27].



Process equipment

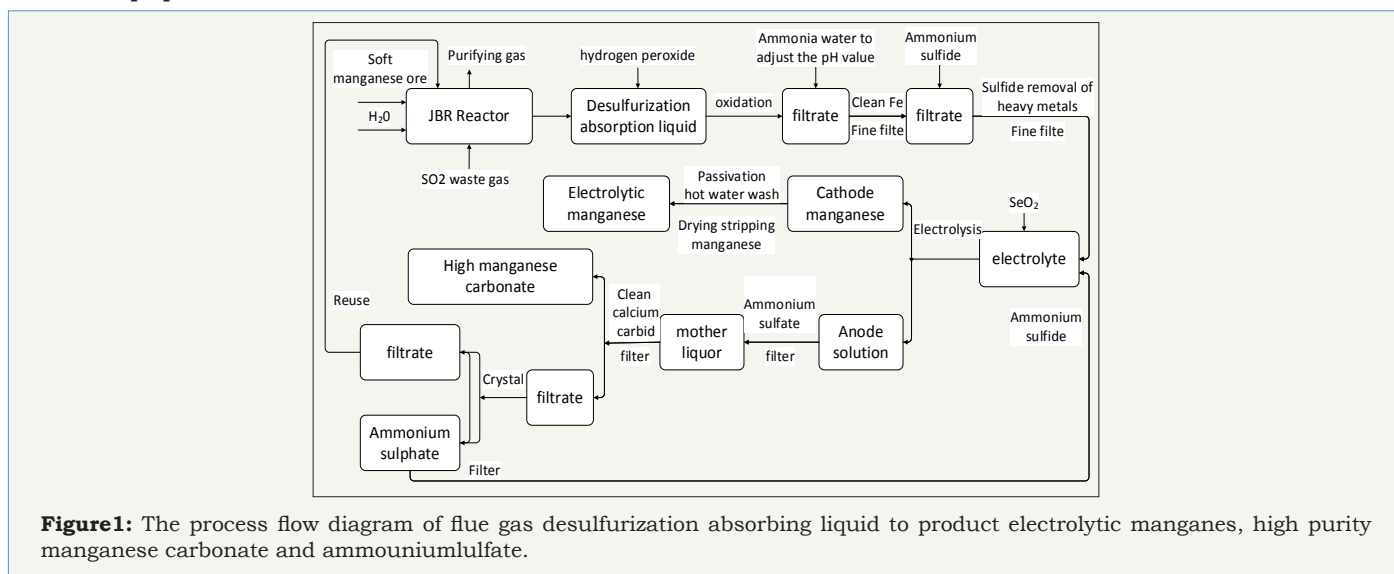


Figure 1: The process flow diagram of flue gas desulfurization absorbing liquid to product electrolytic manganese, high purity manganese carbonate and ammonium sulfate.

Chen believed that it was necessary to ensure the material enough residence time. Due to liquid membrane control in the process, a larger fluid and gas purification equipment was chosen as suitable one, such as bubbling tower sieve plate tower, etc. [28]. Zhu investigated the jet bubbling reactor (JBR), and achieved above 90% desulfurization rate [29]. Ren further researched the influence of JBR process parameters on the desulfurization efficiency and Mn leaching rate, and indicated the optimal structural parameters: the diameter of mixer blade 70mm; the height of blade from the reactor bottom 35mm; the porosity of the periphery jet pipe from the reactor bottom 68mm [30]. Wang used veneer sieve plate tower to absorb SO_2 . The desulfurization rate initially was as high as 80%. When other conditions kept unchanging, the liquid gas ratio

improved from $2.5\text{L}/\text{m}^3$ to $4.5\text{L}/\text{m}^3$, the desulfurization efficiency increased by 13% [31]. Ning dealt with pyrolusite using fire burning to do catalytic oxidation desulfurization [32]. Although the method increased fire burning process, the production rate of MnSO_4 , as well as the utilization of Mn in pyrolusite improved greatly, and the SO_2 removal efficiency could reach 100%. He also did the expanding test in smelter with a foam absorber tower. When the absorbing liquid crystallized once, 95% purity $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was obtained. Sun also opened a new way of flue gas desulfurization with pyrolusite pulp and absorbing liquid reclamation (Figure 1) [33]. He proved that obtaining electrolytic Mn, high purity MnCO_3 and $(\text{NH}_4)_2\text{SO}_4$ in the process of flue gas desulfurization with pyrolusite pulp was feasible and reasonable.

Combined effect of pyrolusite pulp and microbes

Pyrolusite pulp desulfurization research is more focused on the direct use of pyrolusite pulp to absorb SO_2 . As the pyrolusite pulp has surface adsorption, nanometer effect and molecular sieve effect, it can be used as a carrier of microbes. Microbes on the pyrolusite surface participate in the process of sulfur oxidation-reduction, improve the desulfurization efficiency, and are advantage to the sorbent regeneration [34,35].

Dai studied the process of catalytic oxidation of SO_2 by thiobacillus ferrooxidans, manganese oxidizing bacteria and pyrolusite pulp. He thought manganese oxidizing bacteria adhered on pyrolusite pulp, and oxidized Mn (II) to Mn(III), Mn(IV), strengthening the effect of pyrolusite pulp catalytic oxidation of SO_2 . Manganese oxidizing bacteria promoting desulfurization had an adjustment period, and the followed reinforcement increased with the concentration of bacteria improving. The synergies of thiobacillus ferrooxidans and manganese oxidizing bacteria existed and associated with the proportion of microbial composition [36]. Zhang found that the coexistence of pyrolusite pulp and other components had an effect on the desulfurization. Adding bacteria to pyrolusite pulp could restore Fe and Mn ions catalytic activity of SO_2 , realizing the catalyst regeneration and keeping high desulfurization efficiency [37]. Wei selected thiobacillus ferrooxidans and manganese oxidizing bacteria respectively to investigate the oxidation performance and the recovery of the Mn and Fe ions active performance in the system [38]. When Fe (II) and thiobacillus ferrooxidans coexisted, the

conversion rate of SO_3^{2-} reached 0.0153g/ (L•min), better than the chemical oxidation. He indicated that bacteria in pyrolusite pulp had reinforcement for desulfurization, and could realize Fe and Mn catalyst regeneration.

In addition, Sun investigated NO_x removal from flue gas with pyrolusite slurry. It was found that the removal efficiency was depended strongly on the molar ration of NO_2 and NO_x [39]. He also studied the absorption of mixture of SO_2 and NO_x with pyrolusite slurry, indicating that NO was oxidized into NO_2 first by injecting ozone into flue gas stream, and then NO_2 was absorbed from flue gas simultaneously with SO_2 by pyrolusite slurry to form MnSO_4 and $\text{Mn}(\text{NO}_3)_2$ [40,41].

Phosphate pulp

Phosphorite contains abundant transition metal. In the process of phosphate pulp absorbing SO_2 , transition metal ions will continue into the solution, and become cheap liquid catalytic oxidation. Under the condition, H_2SO_4 is prepared and can decompose phosphorite to product H_3PO_4 and CaSO_4 . Fe_2O_3 was thought to be the main active ingredient in phosphate pulp for desulfurization. When MgO content was over 1% in phosphorite, it had adversely effect on the wet production of phosphoric acid and subsequent further process. SO_2 dissolving in water generated sulfurous acid, which could react with MgCO_3 in phosphorite to produce $\text{Mg}(\text{HSO}_3)_2$ with high solubility [3]. The residue-concentrate phosphorite, would be obtained after separating and filtering the solution.

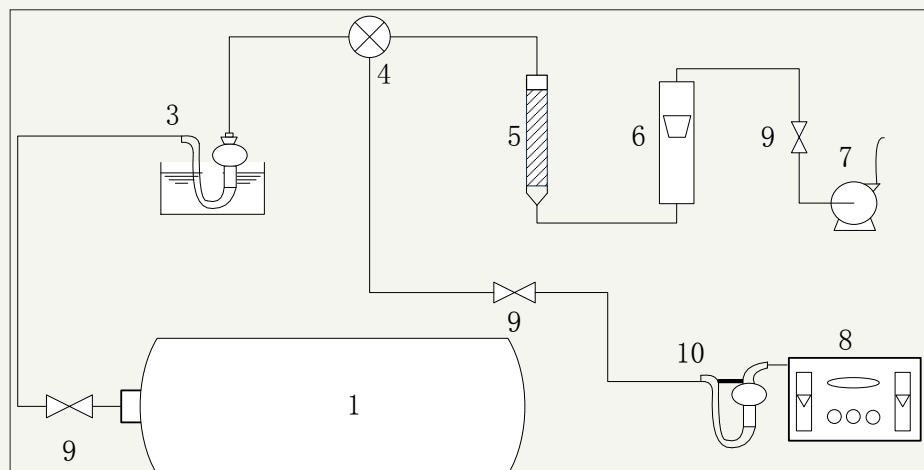


Figure 1: Diagram of experimental apparatus for aqueous catalyzed oxidation desulfurization by phosphorus ore pulp (1-air pocket; 2-thermostat water bath; 3-absorber; 4- tee valve; 5- drying tube; 6- gas flow counter; 7- air pump; 8- atmosphere sampler; 9- globe valve; 10- absorbing tube with multi-orifice).

Liu carried liquid catalytic oxidation desulfurization reaction with low concentration SO_2 and phosphate pulp [42,43] (Figure 2). This method had simple process and high desulfurization efficiency. In the condition of solid-liquid ratio 48%, gas velocity 0.3L/min, and absorption temperature 20 °C, 100% SO_2 removal rate could be kept for 400min. The failure pulp recycled to product phosphorus chemicals, with high economic efficiency. A site experiment on the desulfurization process was conducted in a phosphorus

chemical plant, obtaining the results that 100% SO_2 removal rate could maintain for 335min. She further used microwave to treat phosphorite to generate thermal stress on the surface to change physical properties and maintain chemical properties, resulting that more Fe_2O_3 on the surface improved SO_2 removal efficiency. Kunming University of science and technology has studied phosphate pulp desulfurization technology from the basic test to industrial application, forming the innovative theoretical system

and complete phosphate pulp desulfurization technology system. For ten years development, the technology has realized industrial application.

Coal pulp

Coal mine contains Fe_2S , which can be oxidized under the normal condition. SO_2 and O_2 in the flue gas can react with Fe_2S to form Fe^{3+} , Fe^{2+} , etc. Some scholars selected coal pulp as the absorbent, to investigate SO_2 catalytic oxidation. According to certain proportion, Sun groups prepared coal pulp with coal mine containing Fe_2S 0.32%-1.5% [44]. In the experiments, SO_2 and O_2 concentration in simulation flue gas was controlled 3% and 20% respectively. The temperature above 40 °C, the desulfurization rate could reach more than 99%. They thought that due to the different morphology and surface structure, coal pyrite oxidation efficiency was superior to mineral pyrite. Coal pulp used in liquid catalytic oxidation of SO_2 , on the one hand could make the sulfur in pyrite leach, achieving the purpose of lowering sulfur content and improving the quality of the coal; on the other hand could achieved $\text{Fe}^{2+}/\text{Fe}^{3+}$ system by SO_2 and O_2 reacting with coal pyrite without extra catalyst. Flue gas desulfurization with coal pulp as the absorbent, could not only remove SO_2 and dust, but also reduce impurities (sulfur and iron) content in the coal, avoid the traditional method's problems of high material consumptions and waste residue, which was a kind of environmentally friendly technology, and had a good application prospect.

Discussion and Conclusion

This review has shortly analyzed the state of the art on the pyrolusite pulp, phosphate pulp and coal pulp flue gas desulfurization. The study on pyrolusite pulp flue gas desulfurization has been kept for many years. This paper introduced the main influence factors, desulfurization mechanism analysis and process equipment as well as combined effect of pyrolusite pulp and microbes. The desulfurization process included the dissolution of SO_2 ; MnO_2 oxidation of SO_2 ; Mn, Fe and other transition metal liquid phase catalytic oxidation. Microbes in pyrolusite pulp had reinforcement for desulfurization, and could realize Fe and Mn catalyst regeneration. Using the reaction characteristics of pyrolusite pulp and SO_2 can not only do flue gas desulfurization, but also obtain by-products MnSO_4 or dilute sulphuric acid.

Phosphate pulp desulfurization technology has realized industrial application, with 100% SO_2 removal rate for 335min. Fe_2O_3 is the main active ingredient in phosphate pulp for desulfurization. In the process of phosphate pulp absorbing SO_2 , phosphorus chemicals and other by-products can be obtained. Coal mine contains Fe_2S , which can react with SO_2 and O_2 in the flue gas to form Fe^{3+} , Fe^{2+} , etc. Coal pulp used in liquid catalytic oxidation of SO_2 , not only could make the sulfur in pyrite leach, achieving the purpose of lowering sulfur content and improving the quality of the coal, but also achieved $\text{Fe}^{2+}/\text{Fe}^{3+}$ readily catalyst. There are also various processes in the area of pulp flue gas desulfurization, which need to be further studied. As cheap metal ions liquid catalytic oxidation desulfurization catalyst, pulp has a good application prospect.

Prospective

To summarize the present research situation, the main research directions of this field remained to be further carried out in the future are as follows:

1. In order for better industrial application of pulp flue gas desulfurization, the process mechanisms need a deep understanding. In addition, biotechnology can be combined to cultivate biological species more suitable for the desulfurization.
2. Desulfurization equipment and process need to be further studied. In the published literature, different desulfurization device was used. Each of them has advantages and disadvantages. In addition, the influence factors of reaction, such as the flue gas properties, desulfurization equipment, products outlet, should be considered comprehensively.
3. As a cheap adsorbent, pulp contains a variety of metal oxide and other active ingredients, which can be attempted to use in other fields, such as dealing with greenhouse gas CO_2 . As a whole, the technology of pulp flue gas desulfurization is feasible, and can make full use of lean ore, as well as recover sulfur resources. Microbes can keep the activity of the catalyst and achieve continuous catalytic. The selection of the parameters in the process should be considered comprehensively.

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