# Improving the desulfurization performance of $CaCO_3$ with sodium humate

**Run Feng[1], Zhiguo Sun[1,4], Wenqing Zhang[2] , Hao Huang[3], Haihang Hu[1], Li Zhang[1] and Hongyong Xie[1]**

[1] School of Environmental Science and Engineering, Shanghai Polytechnic University, Shanghai 201209, China;
[2] School of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China;
[3] Shanghai Maring Diesel Engine Research Institute, Shanghai 201108, China

[4]zgsun@sspu.edu.cn

**Abstract.** The influence of these factors on desulphurization efficiency was studied by changing the amount of calcium carbonate, the concentration of sulfur dioxide, the liquid flow rate of absorbent and the air flow rate, the optimum working condition was determined by the research of limestone-gypsum desulphurization process commonly used in industry. By changing the amount of calcium carbonate， we conclude that the volume of water in the desulfurization efficiency does not increase with the adding amount of calcium carbonate. The optimum conditions were determined : at the condicion of the concentration of 500ppm of sulfur dioxide, 10g calcium carbonate, 150L/h liquid flow and the minimum air flow rate of 6.75$m^3$/h, the highest desulfurization efficiency was close to 100% when sodium humate was not added , but the holding time was only about 5 minutes. After adding 3g of humic acid, the desulfurization efficiency was improved obviously, and the instantaneous efficiency of 100% lasting for about 40 minutes. It can be seen that, calcium carbonate in the addition of humic acid sodium can significantly improve the absorption of calcium carbonate performance of $SO_2$.

## 1. Introduction

Limestone-gypsum method is the most widely used flue gas desulfurization method in China. According to statistics, the current popular industrial desulfurization method quantity is only about 10[1], generally divided into dry, semi-dry and the wet desulfurization which is accounted for the vast majority method. Many scholars at home and abroad on a variety of additives for desulfurization efficiency mechanism research, and on this basis to develop new synergist. The ideal desulfurization additive should have good pH buffering effect, low price, low volatility, non-toxic harmless and so on. Dong Peng[2] suggested that the organic acid can slow down the rate of reducing the pH of the absorbent, reduce gas phase and liquid mass transfer resistance, the mass transfer resistance and the organic acid surface activity,and then to increase the effective mass transfer area of the desulfurization reaction, Lower pH conditions to achieve a higher desulfurization rate. Hezhiqiang [3] suggested that the surface activity of organic acid additives can reduce the sedimentation rate of particles in the slurry, thereby reducing the risk of scaling the desulfurization system, making the system more reliable operation. Wang Naiguang [4,5] studied the process of desulfurization of organic acids on the turbulent sphere, and believed that the adipic acid had the strongest invigoration effect and the citric

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

acid had the strongest buffering effect. The study also found that humic acid in the limestone desulfurization system can effectively improve the desulfurization efficiency and help solve the scaling problems [6].

At home and abroad, organic additives have been widely recognized and promoted. Studies have shown that the addition of suitable organic additives to the limestone desulfurization slurry can increases the desulfurization rate and limestone utilization, and can also reduces operating costs [7-11]. Humic acid behaves nature of colloidal, it insoluble in water, the carboxyl and phenolic hydroxyl of its molecules can make it acidic, and the alkali metal salt is soluble in water. The sodium humate is a multi-functional polymer compounds, it contains hydroxyl, quinone, carboxyl and other more active groups, with a large internal surface area, has strong adsorption, exchange, complexation, chelating ability. Especially when humic acid act as ore flotation agent and waste gas treatment agent, humic acid shows a strong vitality, achieved significant economic results, and its price is relatively low. Therefore, the limestone-gypsum desulfurization technology is more mature, add humic acid sodium, the absorption of sulfur dioxide must promote the effect.

## 2. Materials and methods

### *2.1. Experimental materials*

Powdered HA–Na (AR) was provided by Aladdin Reagent (Shanghai) Co., Ltd., in Shanghai. $CaCO_3$ (AR) from Sinoharm Chemical Reagent Co. Ltd. (SCRC).

### *2.2. Experimental process*

The main reaction of the experiment in the equipment is in the spray absorption tower, taking the control variable method to change the calcium carbonate quality, gas flow, liquid flow, the amount of sodium humate and other aspects of a single variable to find out whether the best conditions in this experiment and to ensure whether the sodium humate has a positive effect on the experiment.

First, the effects of different amounts of calcium carbonate on the limestone-gypsum desulphurization process were studied. 10 g of calcium carbonate was weighed in a 2000 ml beaker with an electronic balance. In the electronic balance on the quality of plastic drums and peeled, and then gradually added in the plastic bucket of tap water, finally weigh 5kg tap water. Add tap water in a 2000 ml beaker and stir for 15 minutes with a glass rod, then transfer it to a water tank and continue to add tap water to the 2000 ml beaker, and try to disperse it as much as possible in the tap water and finally transfer to the tank. Cover the tank and open the air pump, then open the sulfur dioxide cylinder to stabilize and maintain the sulfur dioxide inlet concentration at around 800ppm. Opening the pump to start the reaction, and observe the display on the import of export concentration changes and sulfur dioxide removal efficiency for every 5min. When the absorption efficiency of sulfur dioxide is only about 10%, shut down the first pump and then close the air pump (to avoid the air pump first causing liquid reflux). And then weigh 50g and 250g of calcium carbonate respectively, in the conditions of other experiment unchanged to record the results of the experiment to determine the most appropriate quality of calcium carbonate. In the use of the best calcium carbonate content, change one of the conditions such as gas flow, liquid flow, to determine the conditions for the impact of the experiment. Finding the optimum experimental conditions, and finally add sodium humate to determine whether there is a catalytic effect to verify the results. The simple device diagram of the experimental reaction system is shown in Figure 1.

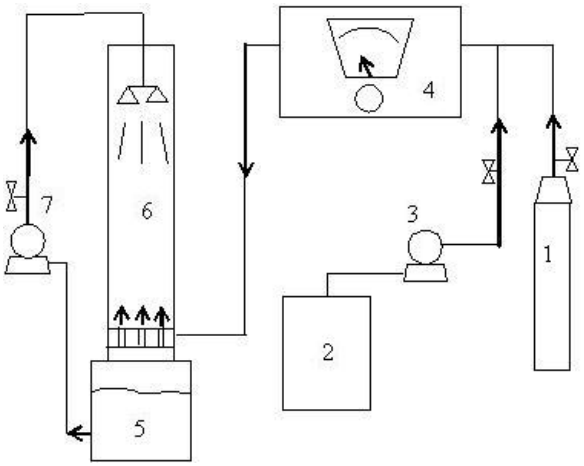


**Figure 1.** Schematic diagram of the experimental reaction system.(1.$SO_2$ cylinders, 2.Mixing tank , 3.Air pump, 4. Flow meter, 5.Reflow box, 6.Spray tower, 7.Water pump)

## 3. Results and discussion

### *3.1. The effect of calcium carbonate on the removal rate of sulfur dioxide*

As can be seen from Figure 2, the increase in the quality of calcium carbonate, to a certain extent, can promote the ability of removing sulfur dioxide. When the mass of calcium carbonate increased from 10 g to 100g, the efficiency of desulfurization increased significantly; 10g and 100g of calcium carbonate mass both act more efficient than 250g calcium carbonate to a large extent. So the best working conditions of the determination of calcium carbonate need to be further determined, the remove of sulfur dioxide absorption diagram of two kinds of calcium carbonate desulfurization drawed as follow.

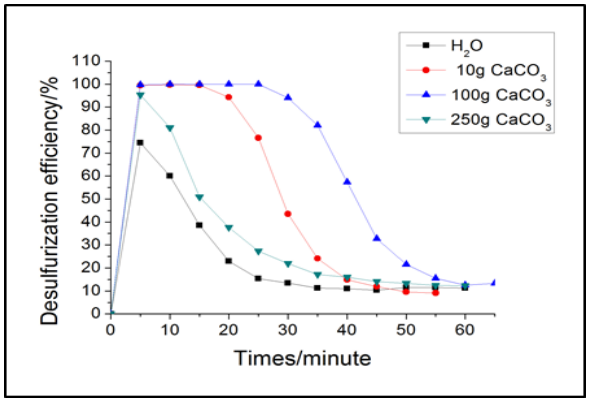


**Figure 2.** Effect of $CaCO_3$ on desulfurization efficiency.

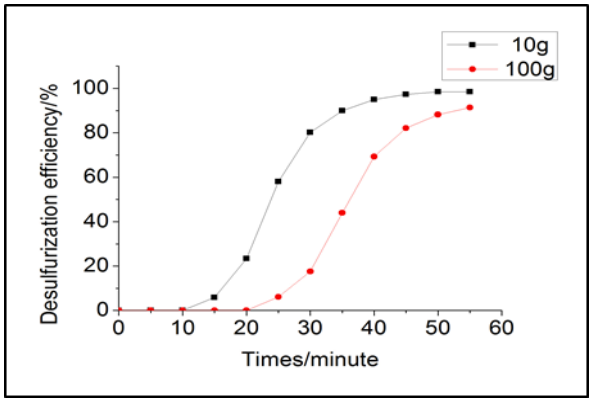


**Figure 3.** Effect of $CaCO_3$ on $SO_2$ absorption.

As can be seen from Figure 3, the addition of 10 g of calcium carbonate to absorb sulfur dioxide is high and the high desulfurization efficiency lasting time is short. The final yield of 10 g of calcium carbonate was better than that of 100 g of calcium carbonate, and the optimum amount of calcium carbonate was determined to be 10 g. Calcium carbonate is a slightly soluble salt, and excess calcium carbonate solution prevents $SO_2$ from entering the liquid phase to reduces the solubility of $SO_2$.

### *3.2. Effect of gas inlet concentration on removal rate*

Under the 10 g calcium carbonate, 15m$^3$/h air flow, 100L/h liquid flow experimental conditions, change the adjustment of the instrument rotor flowmeter and sulfur dioxide cylinder valve to make the sulfur dioxide inlet concentration in 500ppm, 800ppm and 1200ppm up and down floating. As can be seen from Figure 4, when the inlet concentration of sulfur dioxide is low, the effect of the limestone-gypsum desulfurization process is good, and the efficiency of the sulfur dioxide concentration at 500 ppm in the same time period is above the efficiency of 800 ppm and 1200 ppm. When the sulfur dioxide concentration is 800 ppm, the enclosed area and the efficiency of each time period are all higher than 1200 ppm, and the optimum inlet concentration of sulfur dioxide can be determined to be 500 ppm. It can be seen that high concentrations of $SO_2$ will consume too much calcium carbonate solution, and so that decrease the removal efficiency of $SO_2$.

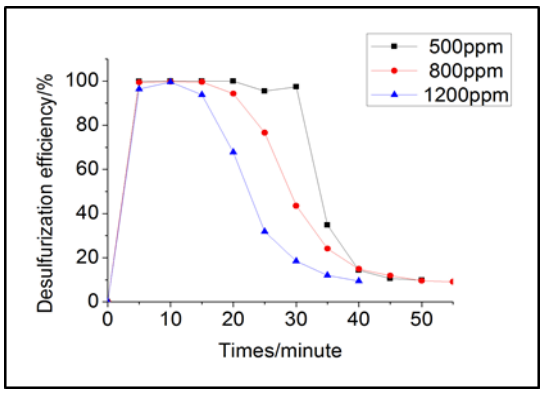


**Figure 4.** Effect of $SO_2$ inlet concentration on desulfurization efficiency.

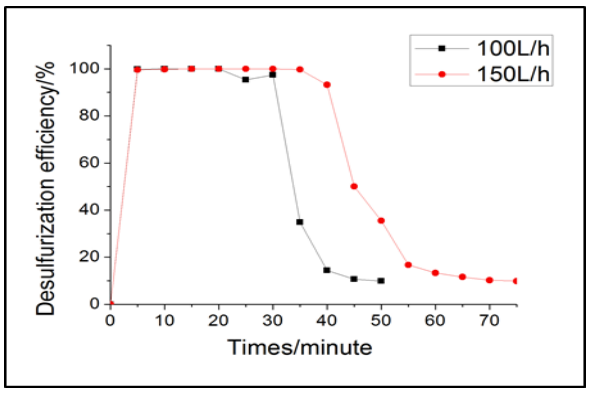


**Figure 5.** Effect of liquid flow on desulfurization efficiency.

### *3.3. Effect of liquid flow on sulfur dioxide removal rate*

When the best sulfur dioxide concentration is 500ppm, maintain the air flow rate is 15m$^3$/h, the amount of calcium carbonate added is 10g, the pump valve is changed and the liquid valve of the inlet pump is adjusted. The liquid flow rate is 100L/h and 150L/h. As can be seen from Figure 5, increasing the liquid flow rate can prolong the sulfur dioxide removal time, so the liquid flow rate at the optimum working conditions is 150 L/h. Increasing the flow rate of liquid can reduce the mass transfer resistance between gas-liquid two-phase films to improve the solubility of $SO_2$, and then to improve the removal efficiency of $SO_2$.

### *3.4. Effect of air flow on sulfur dioxide removal rate*

At present, it has been determined that the optimum conditions are: sulfur dioxide concentration 500ppm, liquid flow 150L/h, calcium carbonate mass 10g, by adjusting the air pump valve, change the air flow of 6.75 m$^3$/h and 10.85 m$^3$/h. As is shown in Figure 6, the air flow rate of the air pump has an effect on the efficiency of desulfurization of sulfur dioxide. The air flow rate of 10.85 m$^3$/h of removal efficiency of 100% is longer 20 minutes than at a speed of 6.75 m$^3$/h, so the optimum air flow rate for stable air pump flow is 6.75 m$^3$/h. Increasing the air flow reduces the concentration of $SO_2$ gas in the vicinity of the gas-liquid mass transfer interface, and the absorption efficiency of $SO_2$ is reduced to avoid the removal efficiency.

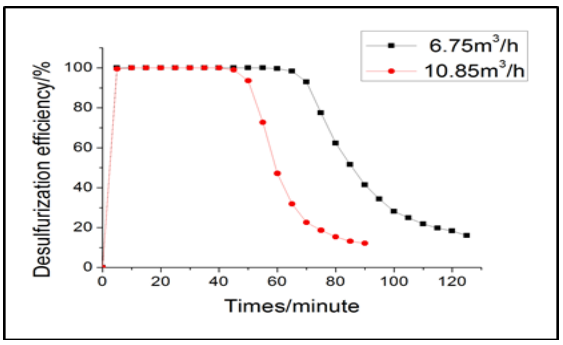


**Figure 6.** Effect of air flow on desulfurization efficiency.

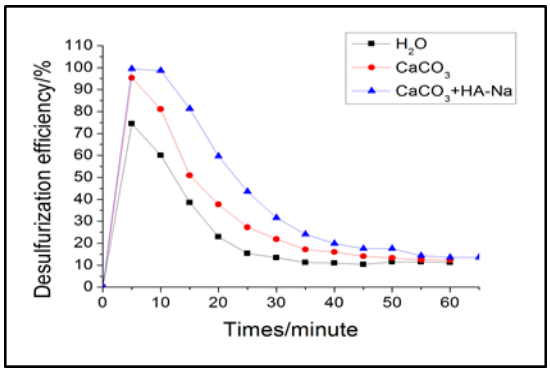


**Figure 7.** Effect of sodium humate on the promotion $SO_2$ absorption.

*3.5. Effect of Sodium Humate on $SO_2$ Removal*

As is shown in Figure 7, the blank experiment has a certain absorption effect on sulfur dioxide. Because the sulfur dioxide has a certain solubility, so the absorption efficiency of sulfur dioxide in the experiment is improved. At the same time, it can be seen that the absorption efficiency of sulfur dioxide after adding humic acid sodium is the highest, and the duration of the reaction is about 5 to 10 minutes longer than that of the other reaction.

*3.6. Effect of Sodium Humate concent on the Removal Rate of Sulfur Dioxide*

The above experiment determined the best working conditions for 10 g of calcium carbonate, 150 L/h of liquid flow rate, 6.75 $m^3$/h of air flow, maintaining the sulfur dioxide inlet concentration at 500 ppm under experimental conditions. Change the amount of sodium humate to determine whether the humic acid sodium limestone-gypsum desulfurization process desulfurization efficiency to promote the role. In Figure 8, the addition of 1g and 3g of sodium humate to the limestone-gypsum desulfurization of the working conditions have a role in promoting function. Their instantaneous efficiency of the data curve are not added in the upper part of the map of humic acid, so the addition of sodium humate can promote the role of the process. And the data curve of adding 3 g of humic acid sodium was added to the data curve of 1 g of humic acid sodium, so to some extent, with the increase of humic acid sodium content, the humic acid sodium had a certain amount of limestone-gypsum wet desulfurization process enhancement.

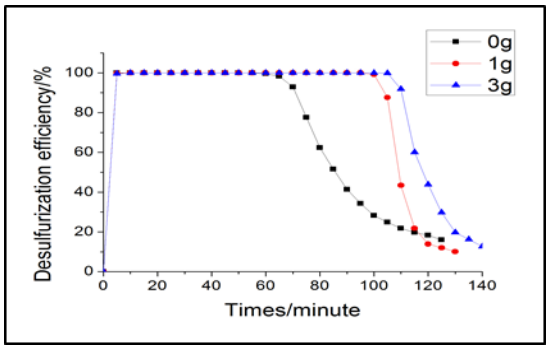


**Figure 8.** Effect of sodium humate efficiency.

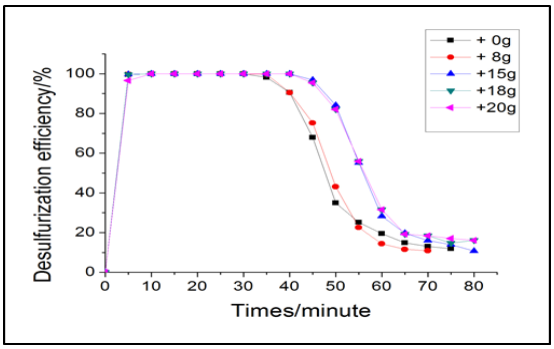


**Figure 9.** Demonstrating the effect of desulfurization sodium humate on limestone-gypsum.

### *3.7. Validation of sodium humate limestone - gypsum $SO_2$ removal rate*

Experiments have confirmed that humic acid on the limestone-gypsum desulfurization in the best conditions to promote the role, the following is to verify whether the humic acid sodium on the limestone-gypsum desulfurization process in the sulfur dioxide inlet concentration of 800ppm, calcium carbonate content of 50g, liquid flow rate of 100L/h and the air pump output air flow of 15$m^3$/h still has a role in promoting. The experiment was repeated by adjusting the amount of sodium humate added. The results obtained are shown in Figure 9. Sodium humate has a catalytic effect on limestone-gypsum desulfurization. When the amount of sodium humate is 8g and the amount of calcium carbonate is large, the promoting effect of sodium humate is very small.

## 4. Conclusions

It is found that the diffusion constant of $SO_2$ in gas phase is much larger than that of liquid phase diffusion constant. So the main resistance of $SO_2$ migration is concentrated in the liquid film. The results show that the $H^+$ produced by the dissolution of $SO_2$ is produced by the ionization of the organic acid additive and the anions present in the liquid film are transferred to the liquid phase body, which reduces the diffusion resistance of $SO_2$ and improves the diffusion resistance of $SO_2$. The solubility of $SO_2$ through the liquid film increases the solubility of SO2 [12-17]. The presence of $H^+$ in the liquid film formed on the outer surface of the solid phase increases the solubility of $CaCO_3$ and improves the desulfurization efficiency [18, 19]. By Henry law, the concentration of $SO_2$ free molecules in the liquid phase is much lower than that absorbed by pure water due to the addition of the reactive reactants, so that the equilibrium partial pressure of $SO_2$ is greatly reduced. In the case of total pressure, greatly enhance the absorption of the driving force to speed up the absorption rate [20]. By controlling the reaction conditions, the maximum instantaneous removal rate was 100%, which was about 26% higher than that of the blank control group. At the concentration of 500ppm sulfur dioxide, add 10g of calcium carbonate, 150L/h liquid flow and the minimum air flow 6.75$m^3$/h, this is not adding humic acid sodium when the best conditions, the highest efficiency close to 100%. But the maintenance time is only 5 minutes; at the condition of adding 3g humic acid sodium, the desulfurization efficiency was significantly improved, the instantaneous efficiency of 100% to maintain 40 minutes. In the best working conditions, a certain limit of the effect of sodium humate promoted with the increase in humic acid sodium increased. When the amount of sodium humate added exceeds a certain limit, such as 15g, the addition of sodium humate to the experiment to promote almost no effect.

## Acknowledgement

The authors gratefully acknowledge financial support by the Natural Science Foundation of Shanghai (Nos. 15ZR1416900, 16ZR1412600), State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University (No.LK1518), and Cultivate discipline fund of Shanghai Second Polytechnic University (No.XXKPY1601).

## References

[1] Juan Li, Feng Qian, Qinfang Zhang 2005 Study on Flue Gas Desulfurization Additive *Environmental Science and Technology* **28**(21) 181-183
[2] Peng *Dong*, Hongwei Cao 2004 Rushan Bie Experimental Study on the Effect of Organic Acid Additives on Wet Desulfurization *Journal of Harbin Institute of Technology* (3) 334-337
[3] Zhiqiang *He*, Peng Zhou, Ming Zhang 2011 Experimental Study on Application of Organic Acid Additives in Limestone-Gypsum Desulfurization *Journal of China Electromechanical Engineering* **31**(23) 34-40
[4] Yuxia Han, Naiguang Wang, Xin Li 2007 Experimental Study on Strengthening the Flue Gas Desulfurization Process of Limestone by Organic Acid Additive *Power Engineering* **27**(2) 278-281
[5] Naiguang Wang Naer A, Qiwang Liu 2008 Experimental Study on Wet Flue Gas

Desulfurization of Organic Limestone Enhanced Limestone *Journal of ChinaElectromechanical Engineering* **28**(17) 61-65
[6] Chenchang Xiao 2006 Study on fouling performance of humic acid sodium in wet limestone flue gas desulfurization system *Environmental Pollution and Prevention* **28**(11) 814-816
[7] Shengyu Liu, Wende Xiao 2006 Modeling and simulation of a bubbling SO2 absorber with granular limestone slurry and the organic acid additive *Chemical Engineering &Technology* **29**(10) 1167-1173
[8] Shengyu Liu, Wende Xiao 2006 New wet flue gas desulfurization process using granular limestone and organic acid additives *International Journal of Chemical Reactor Engineering* **16**(A4)
[9] Yin Zhang 2013 Research Progress of Wetting Desulfurization of Limestone by Additive Technology *information* (5) 168-169
[10] Faen Shi, Haining Wang 2005 Study on New Additive for Wet Desulfurization of Lime Industrial *Safety and Environmental Protection* **31**(2) 8-10
[11] Minli Liu 2010 Selection of Additives in Flue Gas Desulfurization Technology *Science and technology communication* **10**(2) 105-107
[12] Liyan Dong, Yupeng Liu, Baohua Song 2015 Experimental Study on Enhanced Desulfurization by Compound Synergist *Thermal power generation* **44**(8) 116-120
[13] Lijun Lu, Honghui Fang 2015 Experimental study on semi-dry flue gas desulfurization ash used in steel slag composite material *Characterization of Minerals, Metals, and Materials* 541-547
[14] LI Chao,LIU Jianmin,LV Jing 2012 The study on efficiency improving and energy saving of wet flue gas desulfurization system *Northeast Electric Power Technology* (5) 4-8
[15] Bin Guo, Jingfeng Bian, Ailing Ren 2010 Physical and Chemical Properties of Semi-Dry Desulfurization Ash of Sintered Flue Gas[J] *Journal of Central South University* 41(1) 387-392
[16] Yin Chen, He Yang, Hongbao Liang 2011 Research Progress on Decarbonization and Decarbonization of Natural Gas *Petrochemical* **40**(5) 565-570
[17] Yong Jia, Qin Zhon, Xuyou Fan 2010 Modeling of ammonia-based wet flue gas desulfurization in the spray scrubber *Korean J Chem Eng* **28**(4) 1058-1064
[18] Hongwei Chen, Zhenghui Zhao, Xinzhang Huang 2012 Activated Decarburization Desulfurization Characteristics of Steam Activated Calcium Based Absorbents *Journal of Chemical Industry* **63**(8) 2566-2575
[19] Zheng Wang, Jiangguo Wang, Shouqi Bing 2011 Influencing factors of limestone-gypsum wet flue gas desulfurization efficiency *Gas and heat* **31**(9) 1-4
[20] De Ding, Qinhu Zhao, Minghui Liu 2012 Application and Analysis of Organic Acid Desulfurization Additive in Thermal Power Plant *Technical application* (11) 70-74