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Original Research Paper

Research on H_2S Removal by the Ferric Oxide Process

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ABSTRACT

The removal of hydrogen sulphide by using the method of dry desulphurization in a normal temperature iron oxide is introduced in this paper. The experiment has been conducted by using the ferric oxide as the desulphurizer in the waste red mud and added wood chips and calcium oxide for the removal of hydrogen sulphide. Also, the desulphurization efficiency of desulphurizer is researched in different drying temperatures and different ratio conditions, and the best condition of removing hydrogen sulphide is studied. The results of the studies show that the best conditions of removing hydrogen sulphide are 80% of red mud, 5% of wood chips and 15% of calcium oxide at 110°C drying temperature; 85% of red mud, 5% of wood chips and 10% of calcium oxide at 130°C drying temperature; and 70% of red mud, 5% of wood chips and 25% of calcium oxide at 150°C drying temperature. In three different drying temperatures, the best ratio is 85% of red mud, 5% of wood chips, 10% of calcium oxide, and the best drying temperature is 130°C. This test also provides technical support for further industrial utilization.

INTRODUCTION

Hydrogen sulphide is a kind of colourless, highly toxic and acidic gas. It has a strong smell of rotten egg and, a very small amount of hydrogen sulphide may bring harm to people. In humid conditions, it also corrodes concrete and steel (Shuang Zhang 2013). Many industrial productions are accompanied by hydrogen sulphide emissions, such as oil refining, food handling, coking plant, chemical fibre plant, paper mill, effluent disposal and so on (Lei Yan 2012). Besides, sulphur dioxide is produced after the combustion of hydrogen sulphide, which can cause serious pollution in the atmospheric environment. For this reason, the concentration of hydrogen sulphide is strictly limited in China and some foreign countries in different environments (Bingnan Ren & Ping Ning 2009), and desulphidation must be conducted before chemical tail gas emission. So, whether it is from the environment or the production, hydrogen sulphide must be removed from the exhaust gases (Zhaohua Li 2002). Therefore, the research on efficient removal of hydrogen sulphide has got important significance.

According to the different desulphurization process, the methods for removing hydrogen sulphide gas can be divided into dry and wet method. There are many frequently-used methods of dry desulphurization, including ferric oxide method, zinc oxide method, manganese oxide method, activated carbon method and molecular sieve method, etc. Desulphurizer used by ferric oxide method has abundant resources, economic raw materials, so ferric oxide method is the most practical method (Jie Yan 2011). In this paper, the desulphurization efficiency of desulphurizer is researched in different drying temperatures and different ratio conditions by using ferric oxide method. Based on this, in order to provide the basis for the production application, the best condition of removing hydrogen sulphide is studied.

MATERIALS AND METHODS

Materials

The experimental device: There are two main types of experimental devices, including experiment equipment of absorption and analysis device.

***Experiment equipment of absorption*:** Four absorption bottles, one filled tower, one LZB-3F glass rotameter, one dust concentration measuring instrument by static pressure balance type, one desiccator, two tubualted bottles, one hydrogen sulphide generator. The hydrogen sulphide absorption flow is shown in Fig. 1.

***Analysis device*:** One buret, several 250mL iodine flasks, several 500mL and 1000mL volumetric flasks, one 10mL cylinder, one 100mL and 20mL suction pipette, several 50mL and 500mL beakers.

Reagents: 0.1mol/L iodine stock solution and 0.01mol/L iodine standard solution, 0.1mol/L stock solution of sodium thiosulphate and 0.01mol/L standard solution of sodium thiosulphate, glacial acetic acid, 30g/L zinc acetate solution, starch indicator, 0.5% water solution, zinc acetate and concentrated sulphuric acid, calcium chloride.

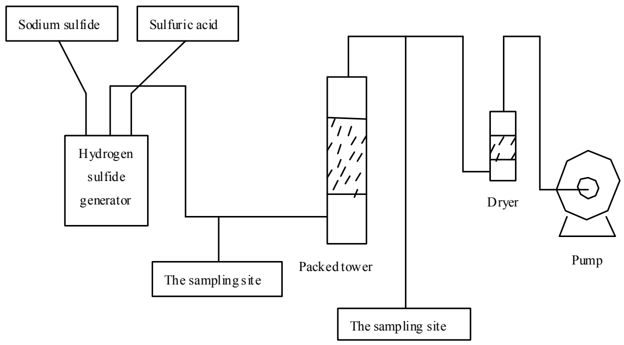

Fig. 1: Hydrogen sulphide absorption flow chart.

The composition of desulphurizer: (1) There are seven types of ferric oxide as desulphurizer, like α-Fe_2O_3, α-$Fe_2O_3 \cdot H_2O$, β-Fe_2O_3, β-$Fe_2O_3 \cdot H_2O$, γ- Fe_2O_3, γ-$Fe_2O_3 \cdot H_2O$ and amorphous Fe_2O_3, but the useful desulphurizer is only α-$Fe_2O_3 \cdot H_2O$ and γ-$Fe_2O_3 \cdot H_2O$ (Li et al. 2007). There are several desulphurizers used frequently in China. They are natural marsh ore, artificial ferric oxide, scraps iron mud in the pigment factory and sulphuric acid plant, shaping desulphurizer of pyrite cinder, red mud from a steelmaking converter and shaping desulphurizer. The red mud is found in abundant as a raw material in Handan iron and steel group company. So we have given a try to use this raw material.

(2) There are three bonding agents used frequently, including cement, polyvinyl alcohol and calcium oxide (Ling Liu 2012). For this experiment, calcium oxide has been chosen as the bonding agent. It does not only make shaping better and cheaper, but also improve the product alkalinity and activation adsorption (Ailing Ren 2000). The building lime from a school construction site was used as a source of calcium oxide in our experiment.

(3) Wood chip can be taken as a raising agent. It requires a very little amount of consumption and can be obtained from the woodworking room.

Methods

The process principle of desulphurization by ferric oxide method: The ferric oxide type desulphurizer is a high efficiency gas purifying agent processed by taking the ferric oxide as the main active component and adding other accelerators. The reaction principle of the main reaction and of the ferric oxide type desulphurizer absorbing H_2S and desulphurizer regeneration is given in the following equations.

The desulphurization reaction:

$$Fe_2O_3 \cdot H_2O + 3H_2S = Fe_2S_3 \cdot H_20 + 3H_2O$$

$$Fe_2O_3 \cdot H_2O + 3H_2S = 2FeS + S + 4H_2O$$

The regeneration reaction:

$$Fe_2O_3 \cdot H_2O + 3/2O_2 = 2\ Fe_2O_3 \cdot H_2O + 3S$$

$$2FeS + 3/2O_2 + H_2O = Fe_2O_3 \cdot H_2O + 2S$$

Firstly, H_2S dissolves in a water film, which exists on the surface of desulphurizers. The dissociation products are the HS^- and S^{2-} ions. Secondly, the ions react with ferric oxide, then generating iron sulphide and ferrous sulphide (Bo Wang 2013). The products of the reaction can be converted into ferric oxide and sulphur after contacting oxygen in the air where there is water condition. Finally, the desulphurization accompanies the regeneration process, until the surface of ferric oxide is mostly sulphur or other impurities to lose activity.

The absorption of hydrogen sulphide: A 100mL zinc acetate is added to the four absorption bottles respectively. The tubualted bottle with sodium sulphide and sulphate is opened. Then the absorption bottle is connected to the proper position in the gas path. When the reaction is stable, gas flow is regulated to enter the bottle. We stop to aerate and take the absorption bottle out after turning milky white in the bottle. At a certain time interval, we put others absorption bottles, and then record flow meter readings, temperature and atmospheric pressure.

The determination of hydrogen sulphide: At the beginning, removing the absorption bottle, we put the absorption liquid and precipitate in the iodine flask. Then, 20mL iodine standard solution and 2-3mL glacial acetic acid is added in the absorption bottle to dissolve the precipitate attached to the bottle wall. After that, we also put it in the iodine flask. Next, we use sodium thiosulphate to titrate with it till pale yellow colour appeared. Upon the addition of the starch indicator, the solution turns blue and is kept for one minute. The end, we need to get the same amount of iodine, zinc acetate and sodium thiosulphate to make the blank experiment.

The calculation formula of the hydrogen sulphide content:

$$H_2S\ (mg/m^3) = (V_1\text{-}V_2) \times C \times 17.04 \times 1000/(V_0 \times f) \quad ...(1)$$

Where, V_2 is the volume of a standard solution of sodium thiosulphate needed titration in the blank experiment. V_1 is the volume of a standard solution of sodium thiosulphate in the experiment. C is the concentration of a standard solution of sodium thiosulphate. The mmol weight of hydrogen sulphide is 17.04, f is the coefficient, which the sample gas volume converts into standard volume and f = (273/273 + temperature°C) × (pressure mm Hg 0.1333/760 × 0.1333).

The process of preparing desulphurizers: The process of

Table 1: The ratio table of desulphurizers component at 110°C drying temperature.

Number	Red mud (%)	Wood chips (%)	Calcium oxide (%)	Remarks
First	50	5	45	
Second	60	5	35	
Third	70	5	25	
Fourth	80	5	15	
Fifth	85	5	10	
Sixth	90	5	5	
Seventh	50	5	45	Water mixing
Eighth	70	25	5	

Table 2: The ratio table of desulphurizers component at 130°C drying temperature.

Number	Red mud (%)	Wood chips (%)	Calcium oxide (%)	Remarks
First	50	5	45	
Second	60	5	35	
Third	70	5	25	
Fourth	80	5	15	
Fifth	85	5	10	
Sixth	90	5	5	

Table 3: The ratio table of desulphurizers component at 150°C drying temperature.

Number	Red mud (%)	Wood chips (%)	Calcium oxide (%)	Remarks
First	50	5	45	
Second	60	5	35	
Third	70	5	25	
Fourth	80	5	15	
Fifth	85	5	10	

preparing three group desulphurizers at different drying temperatures is as follows. Firstly, the three components of appropriate quality were taken . Secondly, the three components are mixed thoroughly and put in the drying box with a specific temperature. Lastly, the drying temperature time is kept as 2 hours.

RESULTS AND ANALYSIS

110°C drying temperature: According to the ratio, the composition of desulphurizers is divided into eight groups in the 110°C drying temperature condition (Table 1).

Through the above experimental method and the calculation, we eventually get the hydrogen sulphide concentration and desulphurization efficiency of each group in any time interval. The curve chart of several group's desulphurization efficiency is shown in Fig. 2.

Experimental results show that the desulphurization efficiency is not high in the first and the seventh group, and

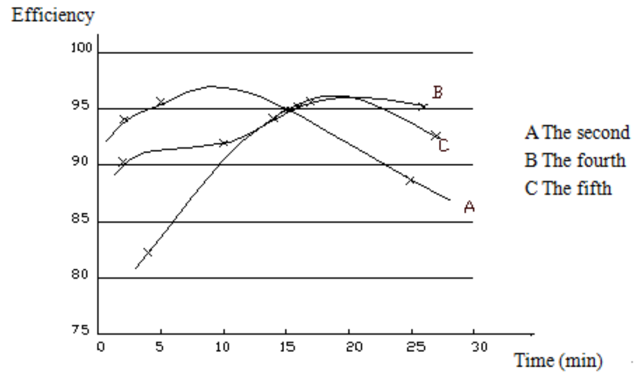

Fig. 2: The comparison chart of desulphurization efficiency varies with time.

desulphurization time is very short in the third, sixth and eighth group. They are not good desulphurizers, so we do not compare these groups.

As can be seen from Fig. 2, the fourth group from the individual efficiency and desulphurization time is better than the other groups. Therefore, the fourth group is the best.

130°C drying temperature: According to the ratio, the composition of desulphurizers is divided into six groups in the 130°C drying temperature conditions (Table 2).

Through the above experimental method and the calculation, we eventually get the hydrogen sulphide concentration and desulphurization efficiency of each group in any time interval. The curve chart of several groups desulphurization efficiency has been shown in Fig. 3.

Experimental results show that the saturation time is short in the second group and the efficiency drops rapidly in a short time. While the desulphurization efficiency of the first group and the third group is obviously less than the other three groups. They are not suitable as a desulphurizer, so we do not compare these several groups.

As can be seen from Fig. 3, the fifth group from the individual efficiency and desulphurization time is better than the other groups. Therefore, the fifth group is the best.

150°C drying temperature: According to the ratio, the composition of desulphurizers are divided into five groups in the 150°C drying temperature conditions. It is shown in Table 3.

Through the above experimental method and the calculation, we get eventually the hydrogen sulphide concentration and desulphurization efficiency of each group in any time interval. The curve chart of severaulphroups desulphurization efficiency is shown in Fig. 4.

Experimental results show that the saturation needs a long period of time and the desulphurization efficiency is

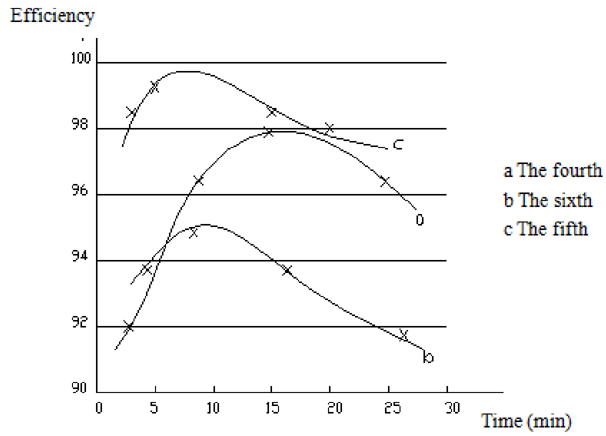

Fig. 3: The comparison chart of desulphurization efficiency varies with time.

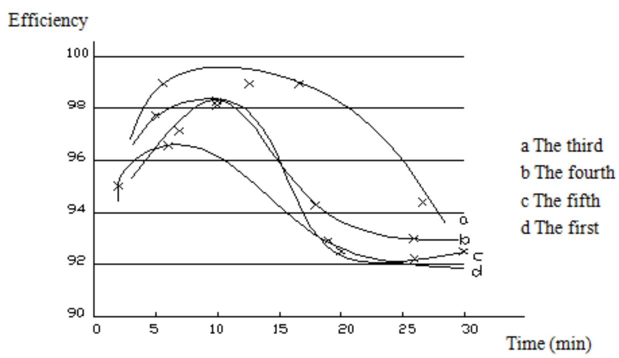

Fig. 4: The comparison chart of desulphurization efficiency varies with time.

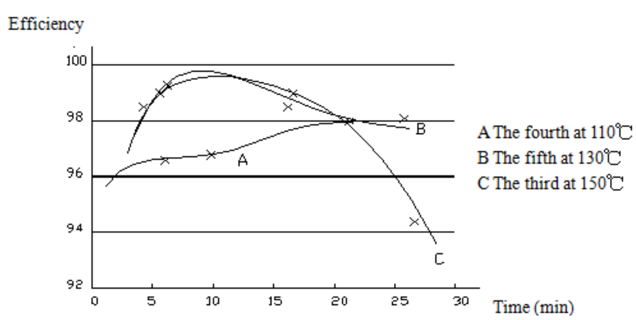

Fig. 5: The comparison chart of desulphurization efficiency varies with time.

not high in the second group. So only the rest of the four groups are compared.

As can be seen from Fig. 4, the third group from the individual efficiency and desulphurization time is better than the other groups. Therefore, the third group is the best.

The comparison of desulphurization effect in three different drying temperatures: From the above experimental results, we obtain the best ratio of the effect desulphurization component for each temperature. The comparison chart is shown in Fig. 5 for three different drying temperatures.

As can be seen from Fig. 5, the three curves, the best ones in desulphurization efficiency, varies with time at 110°C, 130°C and 150°C drying temperatures respectively. Although the effect of the three kinds desulphurizing agent is better and can maintain more than 90%, B (the fifth at 130°C) has the best effect, and the best ratio is 85% of red mud, 5% of wood chips, 10% of calcium oxide. Because the red mud content is higher, the temperature is moderate, and the desulphurizing agent for the ratio can activate the activity.

CONCLUSIONS

According to the above analysis, we can draw the following conclusions:

1. The best ratio is 80% of red mud, 5% of wood chips, 15% of calcium oxide at 110°C drying temperature.
2. The best ratio is 85% of red mud, 5% of wood chips, 10% of calcium oxide at 130°C drying temperature.
3. The best ratio is 70% of red mud, 5% of wood chips, 25% of calcium oxide at 150°C drying temperature.
4. In above three different drying temperatures, the best ratio is 85% of red mud, 5% of wood chips, 10% of calcium oxide, and the best drying temperature is 130°C.

REFERENCES

Ailing, Ren, Bin, Guo and Baohua, Zhou 2000. Preparing high efficiency ferric oxide type desulphurizer with industrial wasts. Environmental Engineering, 18(4): 40-43

Bingnan, Ren and Ping, Ning 2009. Research on adsorption of H_2S by modified activated carbon. Guangdong Chemical Industry, 36(3): 3-5.

Bo, Wang 2013. Application of the ferric oxide method gas desulfurization process in ceramic production. Resources Economization & Environmental Protection, (11): 75-77.

Li, F., Zhang, J., Jiang, A., Shao, C., & Yan, B. (2007). Research progress of desulfurizer at a low temperature. Chemical Industry and Engineering Progress, 26(4): 519-525.

Jie, Y., Hong, L., Kecai, L., Kai, T. and Wenjing, Y. 2011. Research progress of removing H_2S by dry method. Sichuan Chemical Industry, 14(5): 27-31.

Lei, Yan, Quan, Liu and Shuang, Zhang, Wang, W. D., Wanf, Y. J. and Jing, R. Y. 2012. Response surface optimization for hydrogen sulfide removal using fermentation broth produced by acidithiobacillus ferrooxidans. Biotechnology, 22(6): 86-88.

Ling, Liu 2012. Oil and gas desulfurization theory and case analysis. Coal Technology, 31(8): 212-213.

Shuang, Zhang, Zhibao, Chen and Lei, Yan et al. 2013. Immobilization research of acidithiobacillus ferrooxidans by Ca-alginate. Journal of Heilongjiang Bayi Agricultural University, 25(3): 75-77.

Zhaohua, Li 2002. Process research study on catalytic oxidative deodorization of odorant from petroleum refining. Petroleum Refinery Engineering, 32(4): 52-55.