

# Study on Removing Methanthiol with Chlorine Dioxide

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| Received: 8 August 2013; | Accepted: 11 December 2013; | Published online: 16 July 2014; | AJC-15547 |
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In this paper, the experimental device of chlorine dioxide (ClO<sub>2</sub>) solution removing methanthiol (CH<sub>3</sub>SH) gas was designed and the removal process was studied. The absorbent of residual ClO<sub>2</sub>, the amount of ClO<sub>2</sub>, the reaction temperature, the pH value of ClO<sub>2</sub> solution and the air flow effect on the removal rate of CH<sub>3</sub>SH were studied. The optimum conditions of removing CH<sub>3</sub>SH are as follows: the mixed lye of NaOH and Na<sub>2</sub>S as the absorbent of residual ClO<sub>2</sub> and the molar ratio of NaOH and Na<sub>2</sub>S 1:1, the molar ratio of CH<sub>3</sub>SH and ClO<sub>2</sub> 1:2.5, the temperature 35 °C, the pH value of ClO<sub>2</sub> solution 2, the compressed air flow 0.75 m<sup>3</sup>/h. Under this conditions, the results show that the concentration of CH<sub>3</sub>SH is reduced from the initial 1.457 g/m<sup>3</sup> to 0.032 mg/m<sup>3</sup>, the removal rate of CH<sub>3</sub>SH attains to 99.8 %, which meets level 3 national emission standards.

Keywords: ClO<sub>2</sub> solution, CH<sub>3</sub>SH gas, Kraft mill.

## **INTRODUCTION**

The malodorous pollutants generated from the kraft mill are mainly the total reduced sulfides (TRS), whose main ingredients includes four chemicals, such as hydrogen sulfide (H<sub>2</sub>S), methanthiol (CH<sub>3</sub>SH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS),  $etc^1$ . The CH<sub>3</sub>SH is generated in the production process of the kraft pulp mill, which is also a typical kind of atmospheric odor pollutants. The boiling point of CH<sub>3</sub>SH is 6.8°C, which is a colourless gas with a strong smell of rotten cabbage leaves at room temperature. Its olfactory threshold is 0.15  $\mu$ g/m<sup>3</sup> (lower than 1 ppbv) and the stink can easily be perceived. The CH<sub>3</sub>SH is water-insoluble, but it is soluble in ethanol, benzene and other organic solvents. In addition, CH<sub>3</sub>SH gas is a type of neurotoxin and it has a strong stimulation to human mucous membranes. A small amount of CH<sub>3</sub>SH inhaled may damage human nervous and respiratory system, a medium amount of CH<sub>3</sub>SH caused headache, nausea and even narcotism of differentt degree, a high concentrations of CH<sub>3</sub>SH can cause respiratory paralysis and even death. In view of all the hazards of odor pollutants, many countries have established control standards of stink pollutions and published the Prevention Act. Many countries have brought CH<sub>3</sub>SH into monitoring stink pollutants and in our country the publication of "Emission standards for odor pollutants" has stipulated that the CH<sub>3</sub>SH level 3 emission limits is from 0.02 to 0.0350  $mg/m^3$ .

In the paper, the main subjects are that in the self-designed reactor the  $CH_3SH$  gas fully mixs and reacts with the atomized  $ClO_2$  liquid by compressed air, the unreacted  $ClO_2$  gas is absorbed by lye and the residual  $CH_3SH$  gas is absorbed by ethanol. At last, the residual non-condensable gases are discharged into the atmosphere.

## **EXPERIMENTAL**

1 % (mol/mol) of CH<sub>3</sub>SH standard gas was purchased from the foshan of KODI gas chemical industry co., LTD. The ClO<sub>2</sub> solution was obtained from Guangxi Nanning Phoenix Pulp & Paper. Other reagents are analytical grade.

Agilent 6890N gas chromatograph (with Agilent G1888 Headspace Sampler), the self-made absorption device of CH<sub>3</sub>SH gas.

**Solution preparation and calibration:** 0.1 mol/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> standard solution, 0.1 mol/L iodine standard solution, 0.1 mol/L HCl solution as well as ClO<sub>2</sub> solution are prepared and calibrated<sup>2</sup>. Determination of the concentration of CH<sub>3</sub>SH<sup>3</sup>, the procedures are as follows: (1) Take 200 mL absolute ethanol into a 500 mL brown reagent bottle, then lead slowly the CH<sub>3</sub>SH standard gas into the bottle for 20 min and the solution of CH<sub>3</sub>SH absolute ethanol is obtained. The prepared solution is stored airtightly in the refrigerator at 4 °C after calibration. (2) Calibration method: Take 10 mL the prepared solution into a 250 mL conical flask, add 15 mL absolute ethanol and 15 mL 0.025 mol/L silver nitrate solution into the flask, shake for

5 min and add 3 to 5 mL iron alum indicator (dissolve 40 g iron alum with 60 mL distilled water, add 20 mL nitric acid, then make the solution volume reach 100 mL by adding the distilled water. Remove the nitrogen oxides in the solution by boiling before using the solution and dilute with water 4 times) into the same flask and then titrate the solution until the colour of light pink appearing with 0.025 mol/L ammonium thiocyanate (a mL) and then continuely titrate the solution until the colour (b mL). At last, titrate with ammonium thiocyanate solution (c mL) until the colour of the solution becomes the microlight pink that is the endpoint colour. The concentration of CH<sub>3</sub>SH is calculated as follows:

$$C = \frac{48 \times 0.025 \times (15 - a + b - c)}{10}$$
(1)

where: C - the concentration of  $CH_3SH$ , g/L; a, c = the titrated volume of 0.025 mol/L ammonium thiocyanate solution, mL; b = the titrated volume of silver nitrate solution, mL.

Gas chromatography conditions about the detection of methanthiol content: Headspace sampling method: heating box 60 °C, quantitative tube 70 °C, transmission line 80 °C, balance time of headspace vial 3 min, injected time 1 min.

**Gas conditions:** Inlet temperature 150 °C, spliting ratio 1:9, chromatographic column temperature 150 °C, running time 15 min. Column: GS-Q (the U.S. J&W CO.) 30.0 m × 0.53 mm × 0.00  $\mu$ m, FID detector, hydrogen flow 35 mL/min, air flow 300 mL/min, nitrogen flow 35 mL/min.

**Methylmercaptan standard curve:** Standard concentration of 0.41g/L CH<sub>3</sub>SH ethanol solution was diluted to 0.0082, 0.0123, 0.0164, 0.0205, 0.0246, 0.0287, 0.0328, 0.0369 and 0.041 g/L. The different concentrations of standard solution were taken 1 mL into headspace vial, which was measured in the headspace gas chromatography in accordance with a predetermined chromatographic conditions. Every standard solution was done 3 parallel times and the average value of the peak area was obtained. Draw CH<sub>3</sub>SH linear standard curves with the concentration of CH<sub>3</sub>SH solution for abscissa and the peak area for ordinate. The results are showed in Fig. 1. The regression equation is Y = 1184.5X-2.6064, the correlation coefficient R<sup>2</sup> is 0.998.



**Technological diagram:** The technological diagram of the experiment is shown in Fig. 2. The experimental devices are mainly consisted of atomizing device of  $ClO_2$  solution, reaction apparatus of stench, alkali absorber tower and residual gas absorption apparatus.



Fig. 2. Technological diagram of the experimental device. 1. Air compressor 2. Water bath 3. Plastic air pipe 4. CH<sub>3</sub>SH standard cylinders 5. Relief valve 6. Flowmeter 7. Atomizer 8-1. Separatory funnel 9. Reactor 8-2. Separatory funnel 10-1. Liquid distributor 11. Alkali absorber tower 12. Plastic filler 8-3. Separatory funnel 10-2. Liquid distributor 13. Residual gas absorption tower 14. Wire filler

The main role of  $ClO_2$  atomization device is to atomize  $ClO_2$  liquid into 5-50 µm tiny droplet under the driving of compressed air. Moreover,  $ClO_2$  has strong oxidation, which can instantly reacts with the CH<sub>3</sub>SH gas to produce odorless sulfonate and sulfones<sup>4</sup>. The main effect of the stench reactor is that the CH<sub>3</sub>SH gas and atomized  $ClO_2$  liquid sufficiently mix and react in the apparatus. The main effect of alkali absorber tower is to absorb residual  $ClO_2$  and CH<sub>3</sub>SH gas and further to be removed by the lye in the alkali absorber tower. The residual gas absorption device is used to absorb the residual CH<sub>3</sub>SH with absolute ethanol and the removal effect of CH<sub>3</sub>SH is evaluated through analyzing the CH<sub>3</sub>SH content in the absorption liquid.

The compressed air is produced by the air compressor 1, then the air goes through plastic compressed air pipe 3 and the air is heated by the water in electric water bath 2. The ClO<sub>2</sub> liquid sheding from separatory funnel 8-1 is fogged into 5-50 µm tiny droplet by the atomizer 7 under the driving of compressed air. The CH<sub>3</sub>SH gas sheds from CH<sub>3</sub>SH standard cylinder 4 into the reactor 9 through the pressure relief valve 5 and flowmeter 6. In the reactor 9, the CH<sub>3</sub>SH gas sufficiently mixs and reacts with atomized ClO<sub>2</sub> droplets. Those mixtures of the unreacted ClO<sub>2</sub>, Cl<sub>2</sub> and CH<sub>3</sub>SH are leaded into the alkali absorber 11. After the mixtures go through the plastic filler 12, they are sbsorbed by alkali absorbents, which shed from separating funnel 8-2 and are evenly distributed by liquid distributor 10-1. The waste liquid flows from the bottom of the alkali absorber tower 11. The residual gas mixtures in the alkali absorber tower 11 are leaded into gas absorption tower 13. After the residual gases go through wire filler 14, they are sbsorbed by the absolute ethanol, which sheds from separating funnel 8-3 and is evenly distributed by the liquid distributor 10-2. The waste liquid flows from the bottom of the residual gas absorption tower 13 after the ethanol absorbent absorbs those residual gas mixtures. At last, the residual non-condensable gases are discharged into the atmosphere from the top of tower 13.

**Experimental device airtightness test:** The purpose is to check the airtightness of the experimental apparatus. The specific experimental steps is to put the exhaust pipe at the top of gas absorption tower 13 into a flask contained water. 250 mL distilled water is loaded into the separatory funnel 8-1 in advance, which is guided slowly into the reactor 9. Then check whether there is any bubble in the flask.

Selection of absorbent in alkali absorber tower: During the process of reaction there will be large amounts of  $ClO_2$ and  $Cl_2$  gas generated from  $ClO_2$  droplets and these gases will be leaded into the residual gas absorption tower. If these gases will not be dealt with promptly, they would have effect on detecting the content of residual  $CH_3SH$  gas. Moreover, if the residual  $ClO_2$  and  $Cl_2$  are directly discharged into the atmosphere, they would pollute the air. Therefore, it is necessary to set the absorption device to remove the residual  $ClO_2$  and  $Cl_2$ .

The ClO<sub>2</sub> and Cl<sub>2</sub> can dissolve into lye (for example NaOH and Na<sub>2</sub>S) with strong oxidizability. Because the S<sup>2-</sup> of Na<sub>2</sub>S solution has reductibility, the NaOH and Na<sub>2</sub>S must be added during cooking process in a sulfate pulp mill, which can be used to absorb these oxidizability gas. In accordance with the literature<sup>5</sup>, the mixed lye of NaOH and Na<sub>2</sub>S can absorb and remove ClO<sub>2</sub> and Cl<sub>2</sub>. In the experiment, the NaOH solution, the Na<sub>2</sub>S solution and the mixed liquid of NaOH and Na<sub>2</sub>S, are used as absorbents. In the absorption solution, the content of ClO<sub>2</sub> and Cl<sub>2</sub> is titrated with 0.1 mol/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> standard solution and the content is expressed with the available chlorine content. The calculation formula is as follows:

$$M = \frac{[(250 + V) \times C - V_1 C_1] \times 35.5}{1000}$$
(2)

where, M = Available chlorine content of residual gas, g; V = Titrated volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, mL; C = Concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, mol/L; V<sub>1</sub> = Volume of iodine standard solution, mL; C<sub>1</sub> = Concentration of iodine standard solution, mol/L; 35.5 = 1 mol Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> quality corresponding to a chlorine atom.

**Blank experiments of chlorine dioxide removing CH<sub>3</sub>SH:** Because CH<sub>3</sub>SH may be adsorbed by the experimental device and the gases may flow badly within the experimental device, which both effect the removal rate of CH<sub>3</sub>SH. The feasibility of experiment equipment is tested by detecting the recovery rate of CH<sub>3</sub>SH through proceeding blank experiment. The formula of CH<sub>3</sub>SH recovery rate is as follows:

$$N = \frac{n_{CH_3SH recovery}}{n_{total CH_3SH}} \times 100 \%$$
(3)

$$n_{CH_{3}SH \text{ recovery}} = \frac{V \times (Y + 2.6064)}{1184.5 \times 48}$$
(4)

$$n_{\text{total CH}_3\text{SH}} = \frac{L \times t \times w}{22.4} \tag{5}$$

where: N = the removal rate of CH<sub>3</sub>SH,  $n_{CH_3SH recovery}$  = the content of CH<sub>3</sub>SH in ethanol absorbent, mol,  $n_{total CH_3SH}$  = the content of standard CH<sub>3</sub>SH gas passed into, mol, V = the volume of absolute ethanol absorbent, L, Y = the peak area of gas chromatographic, L = the flow of CH<sub>3</sub>SH gas, L/min, t = the leaded time of CH<sub>3</sub>SH gas, min, w = the concentration of CH<sub>3</sub>SH gas, 1 % (mol/mol) The recovery rate of CH<sub>3</sub>SH is 98.87 % after the blank experiment has been proceeded. Therefore, it is possible that CH<sub>3</sub>SH is adsorbed little by the self-designed apparatus, that the gas flowability is good in the experimental device. The absolute ethanol on absorption effect of CH<sub>3</sub>SH is good. So it can be considered that the self-made experimental apparatus would be feasible.

Experiments of ClO2 removing CH3SH: In this experiment, absolute ethanol is used as the absorbent of residual CH<sub>3</sub>SH gas according to the properties that CH<sub>3</sub>SH can be dissolved into the organic solvent, such as alcohol, ether, ester. The experimental procedures are as follows: (1) The device is connected and the airtightness of system is inspected. The 7 g/L ClO<sub>2</sub> liquid is added to the separatory funnel 8-1, in addition, the alkali absorbent is added to the alkali absorber tower 11 and the separatory funnel 8-2. Then absolute ethanol is added to the separatory funnel 8-3. (2) First open inlet switch of compressed air device and the air flow is controlled at 0.75  $m^{3}/h$ . Then open the switch of funnel 8-1 and the ClO<sub>2</sub> solution is leaded into the reactor 9 with the flow of 40 mL/min. At the same time, absolute ethanol flows into absorption tower 13 with the rate of 250 mL/min. Within 5 min, the standard methanthiol gas is leaded into the reactor 9 with the speed of 0.85 L/min, after at the end of leading into CH<sub>3</sub>SH gas the flow of compressed air is increased to 1.25 m<sup>3</sup>/h to purge the CH<sub>3</sub>SH gas in devices and the time of purge is 3 min. (3) After the end of the purge, stop add absolute ethanol, then collect absolute ethanol absorbent solution and store hermetically at 4 °C refrigerator. The CH<sub>3</sub>SH content in absolute ethanol absorbent solution is measured by headspace gas chromatography<sup>6</sup>.

## **RESULTS AND DISCUSSION**

**Choice of absorbent:** The absorbents of NaOH solution, Na<sub>2</sub>S solution and mixed lye of NaOH and Na<sub>2</sub>S are selected as absorbent solution to conduct the experiment of screening efficient absorbent. Under the same adding amount of chlorine and CH<sub>3</sub>SH conditions, the content of available chlorine in each absorbent solution is detected to screen out the efficient absorbent solution.

The results are found that the colour of NaOH solution becomes yellow-green when it is used to absorb the residual ClO<sub>2</sub> and Cl<sub>2</sub>, the reason may be that most of the absorbed ClO<sub>2</sub> has no reaction with the NaOH solution, which only dissolves into the lye with the form of ClO<sub>2</sub> molecular. And the ClO<sub>2</sub> with relatively strong volatility easily escapes from solution into the residual gas absorption tower and whose available chlorine content is higher. So it is not very satisfactory with the absorbent of NaOH solution. When Na<sub>2</sub>S solution is used as absorbent to absorb the residual ClO<sub>2</sub> and Cl<sub>2</sub>, the absorbent effect is good, but it is found that the S<sup>2-</sup> is oxidized into elemental sulfur and adhered on the filler.

The cooking lye contains of NaOH and Na<sub>2</sub>S in a kraft pulp mill. In view of the above results, the mixed lye of NaOH and Na<sub>2</sub>S is investigated on the absorption effect of ClO<sub>2</sub> and Cl<sub>2</sub> and the proportion of the NaOH and Na<sub>2</sub>S should also be determined. The molar ratio of NaOH and Na<sub>2</sub>S, respectively 1:0.5, 1:1, 1:1.5 and 1:2, is investigated in order to determine the influence of absorbing ClO<sub>2</sub> and Cl<sub>2</sub>. The experimental results are found that when the molar ratio of NaOH and Na<sub>2</sub>S is 1:1, under the same adding amount of chlorine and CH<sub>3</sub>SH condition, the content of available chlorine in the absorbent is higher and the turbidity and yellow precipitation disappear, so that the mixed alkali of NaOH and Na<sub>2</sub>S is good absorbent and their molar ratio is 1:1.

**Methanthiol gas chromatogram:** The standard CH<sub>3</sub>SH 1 % (mol/mol) is filled into headspace bottle with water displacement method and the gas is sealed in the bottle and detected by headspace gas chromatography. Fig. 3 is the gas chromatogram of the CH<sub>3</sub>SH. From the Fig. 3, the results are obtained that the retention time of CH<sub>3</sub>SH is from 4.45 min to 4.60 min, which can be used to carry out CH<sub>3</sub>SH qualitative analysis. The gas chromatogram of the CH<sub>3</sub>SH ethanol solution is shown in Fig. 4.



**Effects of the dosage of chlorine dioxide on the removal rate of CH<sub>3</sub>SH:** The effects of the molar ratio of CH<sub>3</sub>SH and ClO<sub>2</sub> on removing CH<sub>3</sub>SH were investigated, which molar ratio were respectively 1:1, 1:1.5, 1:2, 1:2.5, 1:3. The experimental results are shown in Table-1.

As shown in Table-1, with increasing molar ratio of  $CH_3SH$  and  $ClO_2$  the  $CH_3SH$  content in the residual gas is gradually reduced and the removal rate of  $CH_3SH$  is gradually improved. When the molar ratio increases to 1:2.5, the increasing trend about the removal rate of  $CH_3SH$  becomes gentle, while the content of available chlorine in the absorbent has been increased substantially. The reasons may be that when the molar ratio increases to 1:2.5 the content of  $CH_3SH$  is in excess, which makes the concentration of available chlorine in alkali absorbent increases greatly. Therefore, the molar ratio of  $CH_3SH$  and  $ClO_2$  1:2.5 is optimal.

| TABLE-1                          |   |  |
|----------------------------------|---|--|
| EFFECTS OF DIFFERENT MOLAR RATIO |   |  |
| ON CH₃SH REMOVAL RATE            |   |  |
|                                  | - |  |

| Molar<br>ratio | CH <sub>3</sub> SH<br>recovery (%) | Removal rate of<br>CH <sub>3</sub> SH (%) | Concentration of<br>available chlorine in<br>alkali absorbent(g/L) |
|----------------|------------------------------------|---|--|
| 1:1            | 38.90                              | 60.41                                     | 0.04   |
| 1:1.5          | 34.92                              | 64.34                                     | 0.06   |
| 1:2            | 29.67                              | 69.54                                     | 0.08   |
| 1:2.5          | 27.95                              | 71.24                                     | 0.13   |
| 1:3            | 27.47                              | 71.71                                     | 0.18   |
| Conditio       | ns: the molar rati                 | o of NaOH and Na <sub>2</sub> S           | S 1: 1, the pH of $ClO_2$  |

solution 2, the temperature 35 °C, the air flow  $0.75 \text{ m}^3/\text{h}$ . Other experimental conditions are the same as 1.3.5

Effects of different temperature on the removal rate of CH<sub>3</sub>SH: The reactivity of the reactants increased while enhancing appropriately the reaction temperature. The temperature in the reaction system is controlled by adjusting the temperature of the compressed air within the compressed air hose with the constant temperature water bath. Five different temperatures of 25, 30, 35, 40 and 45 °C were investigated. The results are shown in Table-2.

| TABLE-2   |                                  |                       |                        |  |
|---|----------------------------------|-----------------------|------------------------|--|
| EF  | EFFECTS OF DIFFERENT TEMPERATURE |                       |                        |  |
|   | ON CH SH REMOVAL RATE            |                       |                        |  |
|   | onten                            |                       |                        |  |
| Temperature   | CH <sub>3</sub> SH               | Removal rate          | Concentration of       |  |
| (°C)  | recovery                         | of CH <sub>3</sub> SH | available chlorine in  |  |
|   | (%)                              | (%)                   | alkali absorbent (g/L) |  |
| 25  | 28.53                            | 70.66                 | 0.11                   |  |
| 30  | 28.29                            | 70.90                 | 0.12                   |  |
| 35  | 27.95                            | 71.24                 | 0.12                   |  |
| 40  | 28.73                            | 70.46                 | 0.08                   |  |
| 45  | 28.92                            | 70.28                 | 0.09                   |  |
| Conditions: The molar ratio of NaOH and Na <sub>2</sub> S 1:1, the molar ratio of |                                  |                       |                        |  |
| CH Sh and ClO 1:25 the pH of ClO solution 2 the air flow 0.75                     |                                  |                       |                        |  |

CH<sub>3</sub>Sh and ClO<sub>2</sub> 1:2.5, the pH of ClO<sub>2</sub> solution 2, the air flow 0.75  $m^3/h$ .

Table-2 shows that, when the temperature is increased from 25 to 35 °C the removal rate of CH<sub>3</sub>SH and the concentration of available chlorine are increased slowly, whereas these values are reduced slightly when the temperature is increased to 35 °C. The reason is that when the temperature is elevated moderately the reactivity of ClO<sub>2</sub> and CH<sub>3</sub>SH is improved and a part of the ClO<sub>2</sub> gas volatilizes from the small atomized liquid into alkali absorber tower, the removal rate of CH<sub>3</sub>SH and the concentration of available chlorine are both increased. But when the temperature is raised to 35 °C the decomposition rate of  $ClO_2$  decomposing into  $Cl_2$  and  $O_2$  is accelerated, so the effect of ClO<sub>2</sub> absorbing CH<sub>3</sub>SH is weakened and the concentration of available chlorine is reduced. So the temperature has little influence on the CH<sub>3</sub>SH removal rate, which are more conducive to industrialization realization. Therefore, the reaction temperature of 35 °C is determined.

Effects of the pH value of ClO<sub>2</sub> solution on the removal rate of CH<sub>3</sub>SH: Since chlorine dioxide has strong oxidability under the acidic or alkaline conditions, the effects of pH value on the removal rate CH<sub>3</sub>SH were investigated when the pH value was respectively 2, 5, 7, 10, 12. The pH value is adjusted with 6 mol/L HCl solution and 100 g/L NaOH solution. The experimental results are shown in Table-3.

| TABLE-3   |          |                       |                        |
|---|----------|-----------------------|------------------------|
| EFFECTS OF pH VALUE ON CH <sub>3</sub> SH REMOVAL RATE                            |          |                       |                        |
|   | CH₃SH    | Removal rate          | Concentration of       |
| pН  | recovery | of CH <sub>3</sub> SH | available chlorine in  |
|   | (%)      | (%)                   | alkali absorbent (g/L) |
| 1   | 27.85    | 71.44                 | 0.09                   |
| 2   | 27.95    | 71.24                 | 0.10                   |
| 5   | 29.25    | 69.95                 | 0.11                   |
| 7   | 30.37    | 68.84                 | 0.12                   |
| 10  | 31.62    | 67.61                 | 0.43                   |
| 12  | 34.06    | 65.19                 | 1.61                   |
| Conditions: The molar ratio of NaOH and Na <sub>2</sub> S 1:1, the molar ratio of |          |                       |                        |
| CH SH and ClO 1.2.5 the temperature 35 °C the air flow 0.75 m <sup>3</sup> /h     |          |                       |                        |

Table-3 showed that with the raise of the pH value, the  $CH_3SH$  removal rate is reduced gradually while the concentration of available chlorine is increased gradually. Two reasons are as follows. One is that the stability of  $CIO_2$  solution increases with the pH values increasing<sup>7</sup>, which reduces the  $CIO_2$  decomposition rate and the  $CIO_2$  volatility from the solution. The other is that  $CIO_2$  generates easily chlorate and chlorite under higher pH value conditions, which reduces the reactivity of  $CH_3SH$ . When the pH value is 1 and 2, the removal rate of  $CH_3SH$  is almost same. And the acidity is higher, the corrosion is greater. Therefore, the pH value of 2 is better.

Effects of air flow on the removal rate of CH<sub>3</sub>SH: Although CH<sub>3</sub>SH can be oxidized into sulfonic acid or sulfonate by ClO<sub>2</sub> instantly, the mixed time and effect of ClO<sub>2</sub> and CH<sub>3</sub>SH gas both affect reaction. In this experiment, the residence time of ClO<sub>2</sub> and CH<sub>3</sub>SH in the reactor is adjusted by controlling the flow of compressed air. When the flow of compressed air is little, ClO<sub>2</sub> and CH<sub>3</sub>SH gas have a long residence time in the reactor and mix uniformly. But when the compressed air flow are big, the mixed gas of ClO<sub>2</sub> and CH<sub>3</sub>SH quickly are purged into the alkali absorber tower, the residence time is short and these gases mix unevenly and the reaction is not sufficient. The compressed air flow of 0.5, 0.75, 1 and 1.25 m<sup>3</sup>/h are investigated in order to evaluate the effect on the CH<sub>3</sub>SH removal rate. The experimental results are shown in Table-4.

| TABLE-4<br>EFFECTS OF COMPRESSED AIR FLOW<br>ON CH₃SH REMOVAL RATE  |                                       |  |   |
|---|---------------------------------------|--|---|
| Air flow<br>(m³/h)  | CH <sub>3</sub> SH<br>recovery<br>(%) | Removal rate<br>of CH <sub>3</sub> SH<br>(%) | Concentration of<br>available chlorine in<br>alkali absorbent (g/L) |
| 0.5   | 15.88                                 | 83.17  | 0.14  |
| 0.75  | 27.95                                 | 71.24  | 0.08  |
| 1.0   | 37.16                                 | 62.13  | 0.10  |
| 1.25  | 43.85                                 | 55.52  | 0.13  |
| Conditions: The maler ratio of NeOH and Ne S 1:1 the maler ratio of |                                       |  |   |

Conditions: The molar ratio of NaOH and Na<sub>2</sub>S 1: 1, the molar ratio of  $CH_3SH$  and  $ClO_2$  1:2.5, the temperature 35 °C, the pH of  $ClO_2$  solution

Seen from Table-4, the CH<sub>3</sub>SH removal rate decreases rapidly with the increase of air flow, which show that when the compressed air flow is smaller ClO<sub>2</sub> and CH<sub>3</sub>SH mix more evenly, the efficiency of removing CH<sub>3</sub>SH is higher. But the residence time of CH<sub>3</sub>SH in the reactor is prolonged when the air flow is small, which augments the investment of the reactor and also increases the cost of pipe. And when the compressed air flow is increased more than  $0.75 \text{ m}^3$ /h, the ClO<sub>2</sub> gas quickly is purged into the alkali absorber tower by the compressed air, such that in the alkali absorbent the concentration of available chlorine increases. In conclusion, the flow of compressed air  $0.75 \text{ m}^3$ /h is better.

**Removal of CH<sub>3</sub>SH experiment under the optimal conditions:** The optimal conditions are obtained for removing CH<sub>3</sub>Sh with ClO<sub>2</sub> solution. The conditions are as follows: The absorbent of residual ClO<sub>2</sub> gas is the mixed lye of NaOH and Na<sub>2</sub>S, the molar ratio of the mixed lye is 1:1, the molar ratio of CH<sub>3</sub>SH and ClO<sub>2</sub> is 1:2.5, the temperature is 35 °C, the pH value of ClO<sub>2</sub> solution is 2, the flow of compressed air is  $0.75 \text{ m}^3$ /h. Under this optimum conditions, the experiment of removing CH<sub>3</sub>SH is conducted and the results are shown in Table-5.

| TABLE-5<br>RESULTS OF REMOVING CH3SH UNDER<br>THE OPTIMAL CONDITIONS |   |   |  |
|--|---|---|--|
| CH <sub>3</sub> SH recovery<br>(%)                                   | Removal rate of<br>CH <sub>3</sub> SH (%) | Concentration of available<br>chlorine in alkali<br>absorbent (g/L) |  |
| 0.198  | 99.80                                     | 0.09  |  |
|  |   |   |  |

Table-5 showed that the removal rate of CH<sub>3</sub>SH is 99.80 %, the concentration of available chlorine is 0.09 g/L and the concentration of CH<sub>3</sub>SH gas reduces from the initial 1.457 g/m<sup>3</sup> to 0.032 mg/m<sup>3</sup>. The emission concentration of 0.032 mg/m<sup>3</sup> reaches level 3 national emission standards.

#### Conclusion

The optimal conditions of removing  $CH_3SH$  with  $CIO_2$  are obtained, they are as follows: the absorbent of residual  $CIO_2$  gas is the mixed lye of NaOH and Na<sub>2</sub>S, the molar ratio of the lye is 1:1, the molar ratio of  $CH_3SH$  and  $CIO_2$  is 1:2.5, the temperature is 35 °C, the pH value of  $CIO_2$  solution is 2, the flow of compressed air is 0.75 m<sup>3</sup>/h. Under the conditions, the removal rate of  $CH_3SH$  is 99.80 % and the concentration of  $CH_3SH$  reduces from the initial 1.457 g/m<sup>3</sup> to 0.032 mg/m<sup>3</sup>, which reaches level 3 emission standards stipulated by the state.

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