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# Go from $H_2S$ to S in One Step: Use of Heteropoly Compound Solution as Efficient Absorbent and the Effect of Metal Sulfide Additive

Jing Wang [1], Rui Wang [2 +] and Yunqian Ma [2]

[1] State Intellectual Property Office of China, No.6, Xitucheng Road, Haidian District, Beijing, China

[2] School of Environmental Science and Engineering, Shandong University, Jinan, 250100, China

**Abstract.** A new liquid redox method for low sulfur containing gas(with $H_2S$ concentration less than 1000mg/m$^3$) treatment was developed employing the heteropoly compounds of molybdenum and phosphorus. The desulfurization characteristic of the absorbent system of $H_4PVMo_{11}O_{40}$ was investigated by dynamic outlet-gas $H_2S$ concentration detection method. The absorbent system was found to have fairly good absorption-regeneration performance, with a $H_2S$ removal rate of up to 100% in the presence of CuS, hence it is promising in pollution control and resource reclamation.

**Keywords:** hydrogen sulfide, desulfurization, liquid redox, absorption, heteropoly compound

## 1. Introduction

Hydrogen sulfide, as a highly undesirable contaminant existing in industrial gases, such as natural gas and coke oven gas, has long been confirmed to be hazardous material which should be removed to the possible lowest limit for reasons from both environmental restrictions and process requirements. Among the numerous $H_2S$ removal approaches developed by now, liquid redox method has the remarkable advantage in that it can convert $H_2S$ directly to elemental sulfur without causing secondary pollution [1,2]. Furthermore, the device it employed is that of conventional, which is quite economically acceptable compared to the well-known Claus apparatus for sulfur recovery. Recent concern for liquid redox method has been making iron chelate base absorbents the hot point. But iron chelate base absorbent is not as stable as desired, it may give rise to ferric sulfide by-product when reacting with $H_2S$, and there are also some difficulties in its regeneration, hence, the amendment of iron chelate base absorbent is still a problem. It is desirable to develop a new absorbent, good in chemical stability, easy of being regenerated, uncomplicated in composition and capable of oxidizing $H_2S$ to elemental sulfur effectively. An innovative approach to liquid redox process involving the use of heteropoly compounds (HPC) appears to be a promising resolution to $H_2S$ removal and sulfur recovery from industrial gases, to which a detailed introduction will be given in this presentation.

Being a kind of catalyst, HPC has long been applied mainly to act as catalyst for organic synthesis reactions or reagent for chemical analysis, few report has been given by now in the open literatures on its new application in gas purification. Kuznetsova and Yurchenko[3] studied the catalytic effect of the aqueous solutions of several HPC,$PW_{11}M(H_2O)O_{39}^{5-}$(M=Fe, Co, Ni), on the gas phase reaction of $H_2S$ and $O_2$, they found that, under conditions of initial solution pH range from 5 to 7 and at temperature of 20 $^oC$, only $PW_{11}Fe(H_2O)O_{39}^{5-}$ has evident catalytic effect on the oxidation of $H_2S$ by $O_2$. Yang and Chen[4] explored a two-step method of NO decomposition into $N_2$ using a solid state HPC as catalyst without reducing gas, the HPC they used was $H_3PW_{12}O_{40}•6H_2O$, it was shown that, at a space velocity of 5000h$^{-1}$, 70% of NO in a

+ Corresponding author. Tel.: + 86-531-88366367; fax: +86-531-88364513.
*E-mail address*: ree_wong@hotmail.com.

simulated flue gas is absorbed in the fixed bed at 150 $^oC$, when the NO-saturated bed was heated to 450 $^oC$, 68.3% of the absorbed NO is decomposed into $N_2$. Except the reports by the author[5-7], none has been given on the direct removal of $H_2S$ from gas stream with the aqueous solution of HPC.

The HPC investigated in this study is $H_4PVMo_{11}O_{40}$, which can easily gain one or more electron when reacting with $H_2S$, making themselves changed into the reduction forms accordingly, the resultant HPC may be changed reversibly to their original form in the presence of air by losing the electron gained to oxygen. Hence, a circulating process of $H_2S$ conversion with HPC can be formed in the presence of air. This is the principle of the new process for $H_2S$ conversion.

There are two reasons for the author to introduce this newly developed method for $H_2S$ removal. Firstly, the removal of $H_2S$ from industrial gases is a key step for most industrial processes relevant to the direct utllization or further processing of gases, relating to which the new information especially new solution or technique is naturally needed for the improvement of gas industries. Secondly, although the new method is up-to-date, the devices it requires it that of conventional, such as packed column, hence it can be readily industrialized provided the characteristics of the process are better understood.

## 2. Experimental

### 2.1. Absorbent and Gas

All chemicals used were of reagent grade and deionized water was used throughout. The feed gas of constant $H_2S$ concentration, constant-flow rate is prepared by mixing two gas streams of dilute $H_2S$ and pure nitrogen after passing through mass flow controller respectively, the mixed gas stream was analyzed by zinc acetate absorption-iodometric titration method to determine $H_2S$ concentration.

### 2.2. Experimental Methods

The scheme of the experimental flow sheet can be found in literature[5]. With the combination of Pt electrode, calomel electrode and potential analyzer, dynamic redox potential detection was conducted to monitor the whole process of $H_2S$ absorption with HPC and the resultant absorbent regeneration by air stream. In the meantime, online outlet $H_2S$ concentration detection method was also executed with $H_2S$ detector during the process of $H_2S$ absorption. The concentration and rate of the inlet gas stream was controlled at a fixed value with two mass flow controllers. The operation temperature was controlled automatically by a thermostat at a fixed value. To compensate the water loss in the gas-liquid reactor owing to long time operation, the inlet gas stream was pre-humidified by passing through a water saturation tank. The desulfurization product was studied with the aid of Finber 1000 Energy Spectrum.

## 3. Results and Discussion

### 3.1. The Effect of HPC Concentration

To gas absorption, the absorbent concentration plays an important role in the whole process. Results from the effect of the absorbent concentration normally provide basic information for further design of the process equipment. From the experiment, we found a high dependence of the $H_2S$ removal efficiency on HPC concentration, where HPC refers to $H_4PVMo_{11}O_{40}$. In details, the experiments were conducted under condition of: inlet gas, 0.31 l/min; absorption temperature, 30 $^oC$; volume of the absorbent, 200 ml; $H_2S$ concentration, 580 mg/m$^3$. In Figure 1, the $H_2S$ removal efficiency increases markedly as $H_4PVMo_{11}O_{40}$ concentration increases from $3.0\times10^{-4}$ mol/l to $6.0\times10^{-4}$ mol/l, and such tendency diminishes when $H_4PVMo_{11}O_{40}$ concentration increases further. Meanwhile, the adsorption curves tend to level off with time. These indicate that maintenance of desulfurization efficiency at high level as close to 90% requires using of absorbent with concentration higher than $2.5\times10^{-3}$ mol/l, which is economically competitive compared to the iron chelate liquid redox absorbent for $H_2S$ removal.

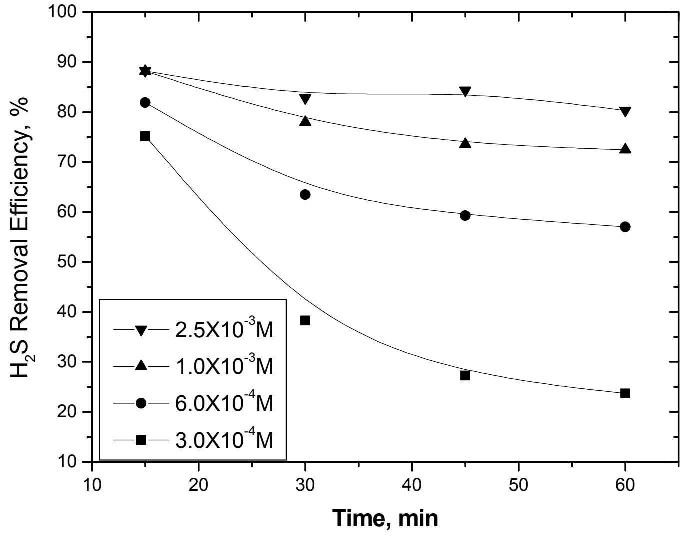


Fig. 1 Effect of $H_4PVMo_{11}O_{40}$ concentration on $H_2S$ absorption

## 3.2. The Effect of Absorption Temperature

With other conditions remained unchanged, the effect of absorption temperature was examined. From the results shown in Figure 2, it can be found that the absorption curve locates within a quite stable position, showing slight tendency of being affected by the change in absorption temperature from 30 to 50 $^oC$. This implies that application of such process requires less or no heat input to maintain favorable absorption temperature. If possible, ambient temperature is a good choice.

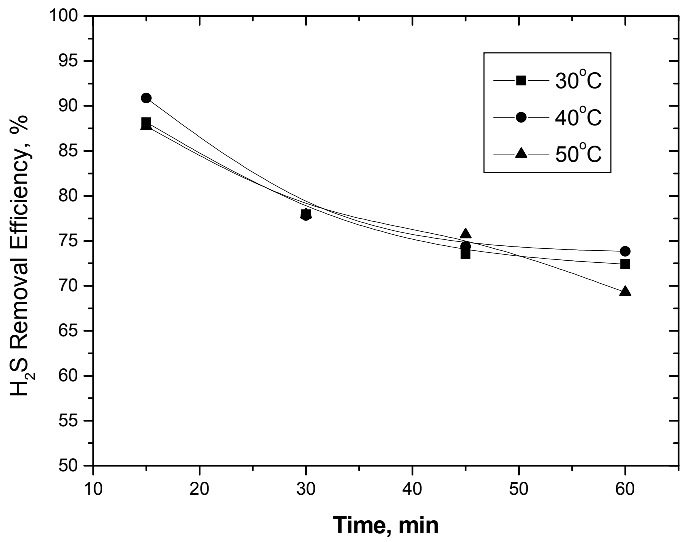


Fig. 2 Effect of temperature on $H_2S$ absorption

## 3.3. The Effect of Inlet Gas $H_2S$ Concentration

The effect of inlet gas $H_2S$ concentration was examined under following conditions: inlet gas, 0.31 l/min; absorption temperature, 30 °C; volume of the absorbent, 200 ml; $H_4PVMo_{11}O_{40}$ concentration, $1\times10^{-3}$ mol/l. The results (Fig.3) show that increasing inlet gas $H_2S$ concentration from 571mg/m³ to 833 mg/m³ leads to a sharp decrease in $H_2S$ removal efficiency while a quite less decline can be observed when inlet gas $H_2S$ concentration increases from 419 mg/m³ to 571 mg/m³. These indicate that practical application should be cautious on the $H_2S$ concentration in the gas to be treated, and $H_4PVMo_{11}O_{40}$ solution of $1\times10^{-3}$ mol/l is applicable to treatment of gas containing $H_2S$ of around 571 mg/m³ or lower.

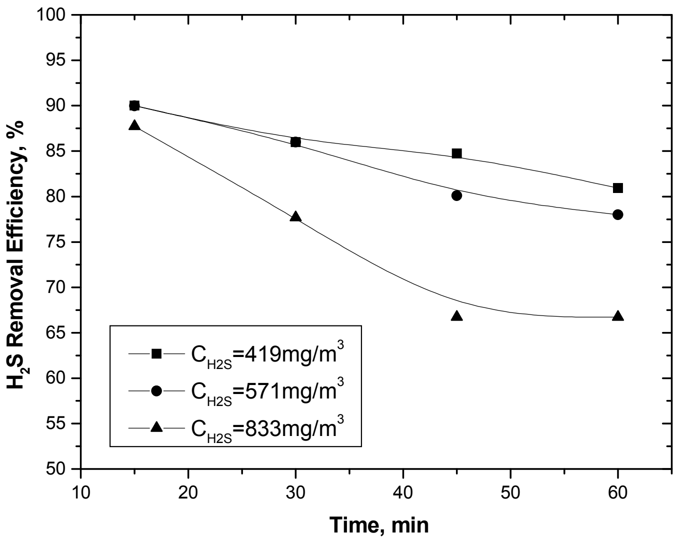


Fig. 3 Effect of inlet gas $H_2S$ concentration on $H_2S$ absorption

## 3.4. The Effect of Metal Sulfide Additive

To improve the desulfurization performance, many additives have been tested, from which metal sulfides have been found to be very effective. Shown in Table 1 are the test results on ZnS, CdS and CuS under the following experimental conditions: inlet gas, 0.50 l/min; absorption temperature, 30 °C; volume of the absorbent, 200 ml; $H_4PVMo_{11}O_{40}$ concentration, $1\times10^{-3}$ mol/l; $H_2S$ concentration, 580 mg/m³; additive/HPC=1:1, molar ratio; duration of the test, 30min. From the results listed in Table 1, it can be seen that the effect of metal sulfides follows the order of ZnS < CdS < CuS, where CuS shows the best enhancement effect on the absorption of $H_2S$.

Table 1 Test results on metal sulfides additives

| | no additive | with ZnS | with CdS | with CuS |
|---|---|---|---|---|
| $H_2S$ Removal Efficiency, % | 83.63 | 84.73 | 88.71 | 100 |

Finally, energy spectrum analysis of the sedimentation products derived from 10 absorption-regeneration cycles with the absorbent systems of $H_4PVMo_{11}O_{40}$ was conducted under conditions of 15kV of accelerating voltage and $1\times10^{-7}$A of electron beam current. We found that the composition of the sedimentation product is sulfur mainly, with little deposition compounds of molybdenum and vanadium.

# 4. Conclusions

The aqueous solution of $H_4PVMo_{11}O_{40}$ can be used as absorbent for $H_2S$ removal. Among the three metal sulphides tested, CuS is the best for enhancing the performance absorbent. The desulfurization product is elemental sulfur mainly with little sedimentation of molybdenum and phosphorus.

## 5. Acknowledgements

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