

Performance of New Liquid Redox Desulfurization System of Heteropoly Compound in Comparison with that of Iron Chelate

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Abstract—In order to achieve a comprehensive understanding of the performance of the heteropoly compound (HPC) absorbent systems for H₂S removal developed before this study, a comparable study was made concerning the desulfurization characteristics, sulfur loading capacity (SLC) and desulfurization product composition, taking Fe-EDTA system as a standard. The desulfurization effect of HPC multicomponent absorbent system can be greater than that of Fe-EDTA system during long time of operation; the regeneration effects of HPC and Fe-EDTA system are similar. The SLC of single HPC is almost the same as that of the Fe-EDTA system, and the multicomponent system of HPC has SLC which is 12.93% higher. Furthermore, the desulfurization product from HPC system contains sulfur mainly, which is superior to that from Fe-EDTA system. Hence, HPC absorbent system developed would be of promising application value.

Key words: Heteropoly Compounds, Absorbent, Desulfurization, Regeneration, Absorption

INTRODUCTION

Being a harmful impurity in industrial gases such as natural gas, coke-oven gas and semiwater gas, H₂S can not only cause pipe and equipment corrosion, catalyst poisoning, but also seriously threaten personal safety. Because of both environmental restrictions and process requirements, the removal of H₂S becomes of great importance during the utilization of industrial gases.

Among the numerous desulfurization methods developed to date [Riesenfeld et al., 1979; Maddox, 1990 (Chinese edition)], the liquid redox method has attracted the most attention in that it enables the simultaneous removal of H₂S and the recovery of elemental sulfur, meeting the development trend of pollution control and resource reclamation. In particular, in the cases where the H₂S concentration in the feed gas is low, the liquid redox method is an economically acceptable alternative compared to the conventional amine absorption-Claus process for sulfur recovery. The typical liquid redox absorbent system industrialized is iron chelate. Aqueous Fe (III) solutions are capable of removing H₂S from a gas stream, in which the species reacting with H₂S is FeOH²⁺ [Asai et al., 1997]. But such solution systems are not stable for H₂S removal; hence iron chelate solution systems were developed. In an iron chelate absorbent system, ferric ion is stabilized by combining with chelating agents such as EDTA (ethylene diamine tetraacetic acid), NTA (nitrilotriacetic acid), SSAL (sulfosalicylic acid), etc. [Dalrymple et al., 1989; Neumann et al., 1984]. Since iron chelate base absorbent is not always stable during application, the corresponding amendment is still underway. At present, the main concern about the liquid redox process is to develop new absorbent system - more stable, cheaper and simpler in composition. A new liquid redox absorbent system employing the corresponding heteropoly compound of molybdenum and phosphorus as active constituent was determined by the author

to have these advantages.

During the past years, heteropoly compounds (HPC) have been used mainly to act as catalysts in chemical industries for organic synthesis [Kozhevnikov, 1998]. However, no report has been given on the new application of aqueous solution of HPC in the field of gas purification. By employing HPC, the author developed a novel liquid redox method of H₂S removal from low sulfur containing industrial gases in previous study [Wang, 1999, 2002a, b]. The HPC investigated includes H₃PMo₁₂O₄₀ and its sodium salt, Na₂H₃PMo₁₂O₄₀. Both can easily gain one or more electrons when reacting with H₂S, making themselves changed into the reduction forms accordingly; the resultant HPC may be oxidized back to their original form in the presence of air by losing the electron gained to oxygen. Hence, a circulating process of H₂S conversion with HPC can be formed in the presence of air, where the net contribution of HPC is catalyst (Fig. 1). This is the principle of the new liquid redox process for H₂S conversion, in which the catalytic effect is based on the redox property of HPC.

In order to achieve a comprehensive understanding of the performance of the absorbent system of HPC, by taking Fe-EDTA system as a standard, a comparable study was made concerning the desulfurization characteristics, regeneration, sulfur loading capacity and desulfurization product composition, to which a detailed introduction will be given in this paper.

EXPERIMENTAL

1. Absorbents and Gases

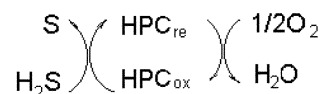


Fig. 1. Basic principle of the new process of H₂S removal with HPC.

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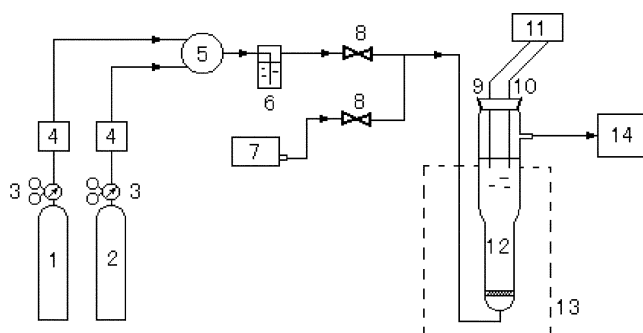


Fig. 2. Scheme of the experimental flow sheet.

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|----------------------------|--|
| 1. Nitrogen vessel | 9. Pt electrode |
| 2. H ₂ S vessel | 10. Calomel electrode |
| 3. Pressure meter | 11. Potential analyzer |
| 4. Mass flow controller | 12. Multi-orifice-plate gas liquid reactor (hole diameter: 50-70 μm) |
| 5. Gas mixer | 13. Thermostat |
| 6. Water saturation tank | 14. H ₂ S detector |
| 7. Air pump | |
| 8. Gas valve | |

The HPC investigated in this study was Na₂H₂PMo₁₂O₄₀. The absorbent systems of HPC include single HPC system and multicomponent system of HPC. The former refers to the aqueous solution of Na₂H₂PMo₁₂O₄₀ only, and the latter refers to that formed by the addition of NaVO₃, NaCl and Na₂CO₃ to the aqueous solution of Na₂H₂PMo₁₂O₄₀. The Fe-EDTA system is comprised of NH₄Fe(SO₄)₂, EDTA, Na₂CO₃ and NaHCO₃, and it is also applied in the form of aqueous solution. All the chemicals involved were of reagent grade and deionized water was used throughout. Gases used in this study included N₂ and H₂S, all of standard grade (with the purity of 99.99%). The feed gas of constant-flow H₂S gas was prepared by mixing two gas streams of dilute H₂S and pure nitrogen after passing through mass flow controllers, respectively.

2. Experimental Method

The experimental flowchart was shown in Fig. 2. A multi-orifice plate glass absorption reactor (hole diameter: 50-70 μm) was used to investigate the desulfurization characteristics of the absorbent system. Online outlet H₂S concentration detection method was conducted with H₂S detector (AIM 450, Germany) during the whole process of desulfurization. Meanwhile, dynamic redox potential detection was carried out to monitor the whole process of H₂S absorption and absorbent regeneration, with Pt and calomel electrodes as measuring and reference electrodes, respectively. The regeneration of the resultant solution from desulfurization was conducted by the switching of air stream to the absorption reactor at a constant rate.

Under experimental conditions for H₂S absorption, the feed gas stream flowed at constant rate, V_1 , and the H₂S concentration in the feed gas, C_{in} , also remained unchanged, whereby the amount of H₂S entered the absorption reactor during absorption for time span, t , can be determined as,

$$m_{in} = V_1 C_{in} t \quad (1)$$

In the meantime, the residual H₂S in the outlet gas stream of the absorption reactor was removed completely with zinc acetate solution contained in a gas scrubber before final discharge; the resultant solution was then analyzed by iodometry. The amount of H₂S absorbed determined by iodometry is equal to that of H₂S emitted

from the absorption reactor, m_{out} . Hence, sulfur loading capacity (SLC) of the absorbent can be determined as,

$$SLC = m_{in} - m_{out} \quad (2)$$

To investigate the sedimentation products derived from many times of absorption-regeneration cycles, Energy Spectrum (Finber 1000 Energy Spectrum) analysis of the sedimentation products was made under conditions of 15 kV of accelerating voltage and 1×10^{-7} A of electron beam current.

RESULTS AND DISCUSSION

1. Characteristics of Desulfurization

In the investigations undertaken, the absorbent system (HPC or Fe-EDTA) was used to remove H₂S from the gas stream and to be regenerated by air subsequently, forming an absorption-regeneration cycle. The regenerated absorbent solution was used to remove H₂S in the next operation cycle. The experiment conducted using the original absorbent to absorb H₂S for the first time was numbered "run1"; the resultant solution was then regenerated by air and reused to absorb H₂S for the second time, and the corresponding absorption experiment was termed "run2". The resultant solution derived from "run2" was regenerated by air again, which may give rise to the next experiment of "run3". All the experiments of "run1, run2, run3" were conducted under the same conditions as listed in the figure captions (Fig. 3 to Fig. 5).

The results of the outlet H₂S concentration change with time in the absorbent system of HPC are illustrated in Fig. 3 and Fig. 4. Fig. 5 corresponds to the result of Fe-EDTA system under the same operation conditions. Apparently, the desulfurization effect of single HPC during the three times of absorption-regeneration cycles (Fig. 3) is to some extent inferior to that of Fe-EDTA as shown in Fig. 5. In view of this, additives having positive effect on desulfurization were introduced into the absorbent system, resulting in the optimized absorbent system, i.e., multicomponent system of HPC. As a whole, a multicomponent system of HPC, which is superior to single HPC, is competitive with Fe-EDTA. This is reflected in

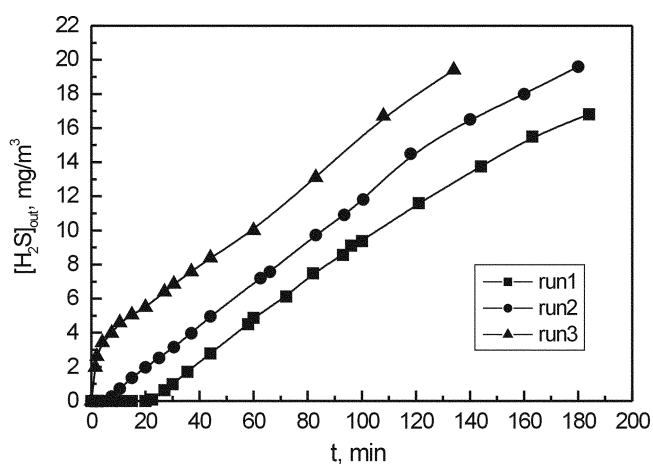


Fig. 3. The desulfurization effect of single HPC system.

Absorption: $T=30^\circ\text{C}$, $V=75\text{ mL}$, $G_f=0.5\text{ L/min}$, $[\text{Na}_2\text{H}_2\text{PMo}_{12}\text{O}_{40}]=1.25 \times 10^{-2}\text{ mol/L}$, $[\text{H}_2\text{S}]_{in}=240.72\text{ mg/m}^3$. Regeneration: $T=55^\circ\text{C}$, $G_{ar}=1.39\text{ L/min}$, regeneration time: 50 min.

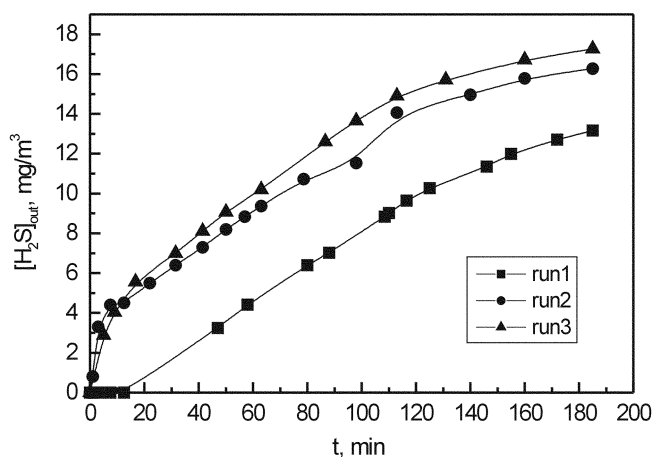


Fig. 4. The desulfurization effect of multicomponent HPC system.

Absorption: $T=30^{\circ}\text{C}$, $V=75\text{ mL}$, $G_f=0.5\text{ L/min}$, $[\text{H}_2\text{S}]_m=240.72\text{ mg/m}^3$, $[\text{Na}_2\text{CO}_3]=1.101\text{ g/L}$, $[\text{Na}_2\text{HPMo}_{12}\text{O}_{40}]=1.25\times 10^{-2}\text{ mol/L}$, $[\text{NaVO}_3]=1.158\times 10^{-3}\text{ mol/L}$, $[\text{NaCl}]=1.0\text{ g/L}$. Regeneration: $T=55^{\circ}\text{C}$, $G_{air}=1.39\text{ L/min}$, regeneration time: 50 min.

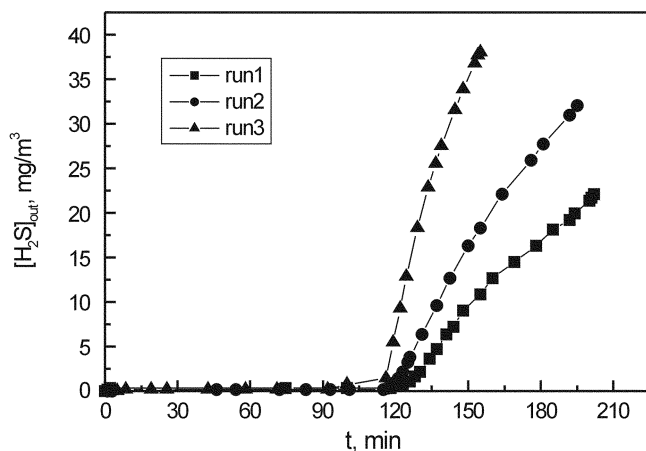


Fig. 5. The desulfurization effect of Fe-EDTA system.

Absorption: $T=30^{\circ}\text{C}$, $V=75\text{ mL}$, $G_f=0.5\text{ L/min}$, $[\text{H}_2\text{S}]_m=240.72\text{ mg/m}^3$, $[\text{EDTA}]=1.376\times 10^{-2}\text{ mol/L}$, $[\text{Na}_2\text{CO}_3]=6.256\text{ g/L}$, $[\text{NaHCO}_3]=31.256\text{ g/L}$, $[\text{NH}_4\text{Fe}(\text{SO}_4)_2]=1.25\times 10^{-2}\text{ mol/L}$. Regeneration: $T=55^{\circ}\text{C}$, $G_{air}=1.39\text{ L/min}$, regeneration time: 50 min.

the H_2S absorption effect, regeneration time and also the sulfur loading capacity to be discussed in the next section. The outlet H_2S concentration during desulfurization with multicomponent system of HPC is lower than that with Fe-EDTA system when the operation time exceeds 160 mins (Fig. 4 and Fig. 5), indicating that the new absorbent system has better and consistent performance in long-time operation. The difference in desulfurization behavior of these two systems lies in the starting point of outlet H_2S concentration increase and the subsequent growth rate. Compared to the absorbent system of Fe-EDTA, the outlet H_2S concentration in the case of HPC systems (Fig. 3 and Fig. 4) increases at the same time of absorption or just after a short time delay; the subsequent growth rate is much lower and with fairly good repeatability among all the three absorption-regeneration cycles. The higher alkalinity that Fe-EDTA system possesses is the exact cause of the above phenom-

ena; the net desulfurization effect of Fe-EDTA chelate complex is unnecessarily greater than single HPC. Since, for $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}$, it can reversibly gain two electrons during redox reaction, corresponding to the iteration between $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}^{\text{VI}}$ and $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}^{\text{V}}$ Mo_2O_4 [Wang, 2002b]. But Fe-EDTA itself can only have one electron transferred within the iteration between Fe^{III} -EDTA and Fe^{II} -EDTA during the same process [Martell et al., 1996]. Thus, the sulfur-loading capacity of HPC single or multicomponent system may be expected to be comparable with that of Fe-EDTA system.

In the above study, emphasis was given on the effect of H_2S removal of the absorbent systems; experiments were conducted with all other parameters, including that of regeneration, being equal. As the performance of absorbent system regeneration is also of practical importance to the liquid redox desulfurization process, a contrasting study was also made, by the method of dynamic redox po-

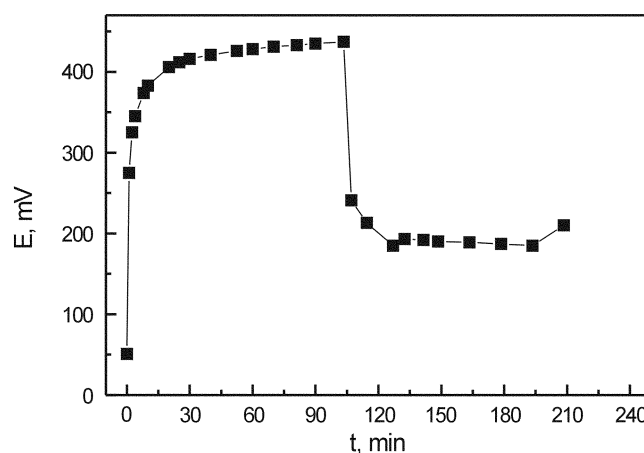


Fig. 6. Dynamic redox potential curve of desulfurization with HPC.

Absorption: $G_f=0.5\text{ L/min}$, $[\text{H}_2\text{S}]_m=877.22\text{ mg/m}^3$, $[\text{Na}_2\text{HPMo}_{12}\text{O}_{40}]=2.0\times 10^{-2}\text{ mol/L}$, $T=12^{\circ}\text{C}$, $V=75\text{ mL}$. Regeneration: $T=12^{\circ}\text{C}$, $G_{air}=1.47\text{ L/min}$.

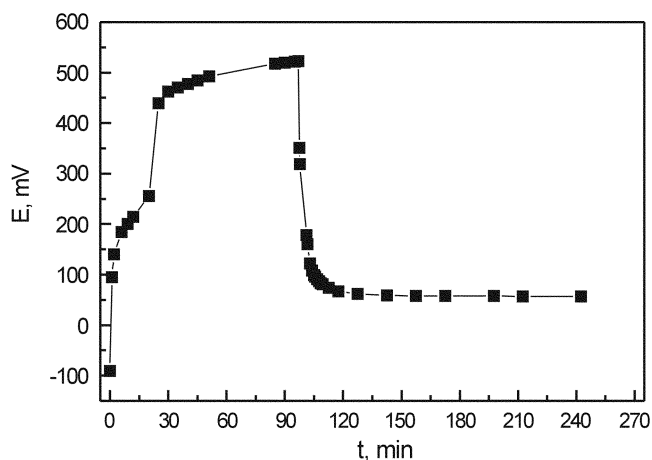


Fig. 7. Dynamic redox potential curve of desulfurization with Fe-EDTA system.

Absorption: $T=12^{\circ}\text{C}$, $V=75\text{ mL}$, $G_f=0.5\text{ L/min}$, $[\text{H}_2\text{S}]_m=877.22\text{ mg/m}^3$, $[\text{EDTA}]=1.117\times 10^{-2}\text{ mol/L}$, $[\text{Na}_2\text{CO}_3]=5.08\text{ g/L}$, $[\text{NaHCO}_3]=25.38\text{ g/L}$, $[\text{NH}_4\text{Fe}(\text{SO}_4)_2]=1.015\times 10^{-2}\text{ mol/L}$. Regeneration: $T=12^{\circ}\text{C}$, $G_{air}=1.47\text{ L/min}$.

tential detection. In the experiments of dynamic redox potential detection, the calomel electrode (i.e., the reference electrode) is anode, and Pt electrode, cathode. Hence, during the stage of H_2S removal, the redox potential of the absorbent solution increases with the increase of the absorption time until reaching an asymptotic maximum; during the stage of regeneration, the redox potential of the absorbent solution decreases with the increase of the regeneration time until reaching an asymptotic minimum. Hence, a similar shape of the dynamic redox potential curve should be gained during the whole process of absorption-regeneration, regardless of the liquid redox absorbent system investigated. This has been verified from the comparison between Fig. 6 and Fig. 7. Taking the initial value of the redox potential, corresponding to the starting point of absorption as a base for evaluation, the resuming levels of the redox potential of the two absorbent systems after being regenerated by air are roughly identical. The resuming levels of the redox potential are 74% for the system of Fe-EDTA and 71% for HPC. Defining the time span between the starting point of regeneration and the attainment of asymptotic minimum of the redox potential as the regeneration time, the two absorbent systems can be found to have almost the same regeneration time, which is approximately 36 mins. Hence, the regeneration performance of the absorbent system of HPC is competitive with that of Fe-EDTA system from the viewpoint of application.

2. Sulfur Loading Capacity

As the performance of the absorbent system also depends on the sulfur loading capacity (SLC) it possesses, experiments were conducted to measure the SLC of the absorbent systems under equal conditions of 20 °C in operation temperature, 240.72 mg/m³ of H_2S concentration in the feed gas stream flowing at the rate of 0.5 L/min, and 75 ml of absorbent solution contained in the absorption reactor. The end point of the experiment was set to be the moment when the H_2S concentration in the outlet gas attains 23.60 mg/m³. The test results of SLC are listed in Table 1.

It is apparent that the SLC of single HPC is almost the same as that of the gross effect of Fe-EDTA system. As the absorbent system of Fe-EDTA contains a large amount of alkalinity components, its SLC is greater than the net contribution of Fe-EDTA chelate complex itself. The multicomponent system of HPC has the SLC being 12.93% higher than that of Fe-EDTA system, indicating the positive contribution of the additives. It should be stated that the multicomponent system of HPC used here is an optimized one, i.e., whose composition was optimized through experiments arranged by ortho-

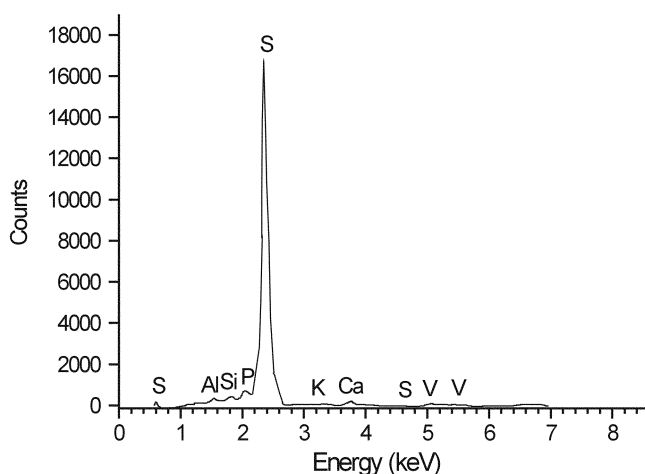


Fig. 8. ES diagram of the sedimentation product from multicomponent system of HPC.

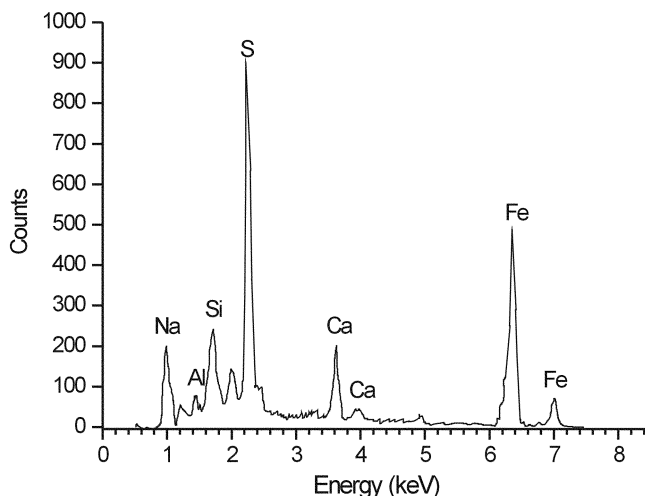


Fig. 9. ES diagram of the product from Fe-EDTA system.

onal layout. The concentrations of Na_2CO_3 and $NaVO_3$ in the system both have an upper limit, although their isolated effects on the H_2S absorption are both positive. From the contrast results of SLC gained in Table 1, it is reasonable for us to be elated with the new absorbent systems of HPC.

3. Desulfurization Product Analysis

Table 1. Test results of SLC

Absorbent system	SLC
HPC Single: [$Na_2HPMo_{12}O_{40}$]= 1.012×10^{-3} mol/L	1.14 mol H_2S /molHPC
HPC Multicomponent System: [$Na_2HPMo_{12}O_{40}$]= 1.012×10^{-3} mol/L, [Na_2CO_3]=0.08914 g/L, [$NaVO_3$]= 0.9375×10^{-4} mol/L, [NaCl]=0.08096 g/L.	1.31 mol H_2S /molHPC
Fe-EDTA System: [$NH_4Fe(SO_4)_2$]= 1.015×10^{-3} mol/L, [EDTA]= 1.117×10^{-3} mol/L, [Na_2CO_3]=0.508 g/L, [NaHCO ₃]=2.538 g/L	1.16 mol H_2S /molFe-EDTA

Test conditions: [H_2S]_{in}=240.72 mg/m³, [H_2S]_{out}=23.60 mg/m³, T=20 °C, V=75 ml.

Apparently, the sedimentation product from HPC system contains sulfur mainly, with little deposition compounds of vanadium and phosphorus (Fig. 8), indicating that HPC is chemically stable during many times of absorption-regeneration cycles. The presence of vanadium and phosphorus detected may derive from the adsorption of anions of NaVO_3 and HPC on sulfur sediment in solution. In contrast, large amount of deposition by-product can be found in the sedimentation product from Fe-EDTA system as shown in Fig. 9, especially that of ferric compounds, indicating that the Fe-EDTA absorbent system is unstable during the process of absorption-regeneration cycles. Hence, the chemical stability of the absorbent system of HPC is superior to that of Fe-EDTA.

CONCLUSIONS

1. The desulfurization effect of HPC absorbent system can be greater than that of Fe-EDTA system during long time of operation.

2. The regeneration performance of the absorbent system of HPC is competitive with that of Fe-EDTA system. The resuming levels of the redox potential are 74% for the system of Fe-EDTA and 71% for HPC. The two absorbent systems can be found to have almost the same regeneration time, which is approximately 36 mins.

3. The SLC of single HPC is almost the same as that of Fe-EDTA system; the multicomponent system of HPC has SLC which is 12.93% higher.

4. The desulfurization product of HPC system contains sulfur mainly, superior to that of Fe-EDTA system which contains large amount of ferric by-product deposition.

As a whole, the HPC absorbent systems developed would be of promising application value.

NOMENCLATURE

C_{in} , $[\text{H}_2\text{S}]_{in}$: the H_2S concentration in the feed gas [mg/m^3]
 E : redox potential [mV]
 G_{air} : regeneration air flow rate [L/min]
 G_f : feed gas flow rate [L/min]
 m_{in} , m_{out} : the amount of H_2S entered and emitted from the absorption reactor [mg]
 t : time [min]

T : temperature [$^{\circ}\text{C}$]
 V : volume of the liquid [mL]
 V_1 : feed gas flow rate [L/min]

Subscripts and Superscripts

in : inlet
 out : outlet
 ox : oxidation
 re : reduction

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