Reaction Mechanism of Simultaneous Removal of H$_2$S and PH$_3$ Using Modified Manganese Slag Slurry

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Abstract: The presence of phosphine (PH$_3$) and hydrogen sulfide (H$_2$S) in industrial tail gas results in the difficulty of secondary utilization. Using waste solid as a wet absorbent to purify the H$_2$S and PH$_3$ is an attractive strategy with the achievement of “waste controlled by waste”. In this study, the reaction mechanism of simultaneously removing H$_2$S and PH$_3$ by modified manganese slag slurry was investigated. Through the acid leaching method for raw manganese slag and the solid–liquid separation subsequently, the liquid-phase part has a critical influence on removing H$_2$S and PH$_3$. Furthermore, simulation experiments using metal ions for modified manganese slag slurry were carried out to investigate the effect of varied metal ions on the removal of H$_2$S and PH$_3$. The results showed that Cu$^{2+}$ and Al$^{3+}$ have a promoting effect on H$_2$S and PH$_3$ conversion. In addition, the Cu$^{2+}$ has liquid-phase catalytic oxidation for H$_2$S and PH$_3$ through the conversion of Cu(II) to Cu(I).

Keywords: phosphine; hydrogen sulfide; manganese slag; metal ions; reaction mechanism

1. Introduction

The presence of phosphine (PH$_3$) and hydrogen sulfide (H$_2$S) in industrial gases can result in reduced feed gas quality, excessive equipment corrosion, and catalyst deactivation and poisoning, limiting industrial gas recovery and utilization [1], especially yellow phosphorus off-gas. In addition, H$_2$S, as a highly toxic, corrosive gas, can not only cause air pollution but also eye irritation and breathing problems. Even exposure to small amounts of H$_2$S will pose a serious threat to humans [2]. Additionally, PH$_3$ may cause immediate death if one is exposed to a concentration level of 50 ppm, according to the National Institute for Occupational Safety and Health (NIOSH) [3]. Therefore, it is desirable to remove them from the point of view of the highly efficient use of industrial gases and human health.

Currently, the wet process has more advantages for simultaneously removing H$_2$S and PH$_3$ compared to the dry process, due to lower cost and easier preparation process [4,5]. However, the wet process for the removal of H$_2$S and PH$_3$ could rapidly consume oxidant, thus leading to a decrease in removal efficiency [4]. Hence, there is an urgent need to modify the traditional wet method to meet stricter environmental laws. In recent years, the use of metal ore, tailings, and metal smelting slag to remove industrial waste gas has attracted the attention of researchers [6–8]. Smelting slag contains a large number of transition metals such as Fe, Mn, and basic oxides, which could have been favorable for absorption of PH$_3$ and H$_2$S in the wet process due to the liquid phase catalytic oxidation ability of transition metals and higher alkalinity of basic oxides such as CaO, MgO, etc. The liquid catalytic
oxidation by transition metals can be favorable for the oxidation of gas pollutants, thus being conducive to absorbing H₂S or/and PH₃ [9-11]. At present, China has become the largest manganese producer, consumer, and exporter, and has emitted more than 2 × 10⁶ tons of manganese slag (MS) every year, which mainly originate from the manganese metallurgy process. Piling manganese slag waste has caused color stain and pollution in the composition of soil and surface water and contaminated groundwater and rivers due to surface runoff [12]. Therefore, there is a pressing need to dispose of MS in a green and highly efficient manner. The chemical compositions of MS are rich in Mn-based oxides and contain a number of basic oxides, which make it possible to become a highly efficient absorbent for the removal of H₂S and PH₃.

According to our previous studies [13], modified manganese slag (MS) slurry was used to remove H₂S and PH₃ and proved a great absorbent. However, a detailed investigation of the reaction mechanism was still lacking. Thus, our research extends the knowledge into the reaction mechanism of H₂S and PH₃ using modified MS slurry. In this paper, the emphasis was laid on the role of modified MS slurry in removing H₂S and PH₃. In addition, to understand the liquid phase catalytic oxidation ability of modified MS slurry, we simulated the composition of MS slurry in the form of different metal salt solutions based on the actual composition of electrolytic MS. In addition, XPS (X-ray photoelectron spectrometer), IC (ion chromatography), and XRF (X-ray fluorescence) and XRD (X-ray diffraction) techniques were used to investigate the samples’ surface information. Thus, a mechanism of simultaneous removal of PH₃ and H₂S using modified MS slurry was proposed.

2. Results and Discussion

2.1. Effect of Different Component Slurry after Acid Leaching on Simultaneous Removal of H₂S and PH₃

In order to investigate the mechanism of simultaneous removal of H₂S and PH₃ using modified MS slurry, the acid leaching method was used to treat the raw MS. Thus, the majority of soluble metal ions can be leached and transferred from the solid phase of raw MS to the aqueous solution. It can be seen from Figure 1 that XRD results show that the main mineral phases of raw MS were 3CaO·SiO₂ (C₃A), 2CaO·SiO₂ (C₂A), CaO, Al₂O₃, and merwinite. These components were acid-soluble, which can be decomposed by the acid solution. Table 1 also shows that the main elements in raw MS were Si, Ca, and Mn. Thus, through acid leaching and then filtering, the active components mainly including metal ions could be removed from the raw MS.

![Figure 1. XRD pattern of raw manganese slag.](image-url)
whereas Group 3 (metal chlorides) obtained the higher PH3 removal efficiency relative to those of the other groups, with the order being metal chlorides > metal nitrates > metal sulfates. In order to achieve a better understanding of the variation in PH3 and H2S conversion by different metal salts, the reaction products in aqueous solutions were detected by the IC method. The IC results, as shown in Figure 4, showed that the generated PO43− and SO42− concentrations in Group 3 increased with the reaction proceeding, which indicated that the H2S and PH3 could be converted to PO43− and SO42−, respectively. Thus, the addition of metal sulfates inhibited higher H2S and PH3 conversion efficiency because the generation of SO42− was accelerated and inhibited the oxidation of PH3 when the copper concentration was increased.

As shown in Figure 2, the 100% H2S removal efficiency of modified MS slurry (MS + CuSO4 group) can maintain 7 h while the 65% PH3 removal efficiency of modified MS slurry can maintain 5 h. In addition, the acid leaching residues and CuSO4 slurry can only obtain around 7% H2S removal efficiency and approximately 9% PH3 removal efficiency. Compared with the simultaneous removal of H2S and PH3 by modified MS slurry, the acid leaching residue and CuSO4 slurry obtained a poorer removal efficiency due to the consumption of active components after the acid leaching method. Additionally, the raw MS and Cu2+ have a synergistic effect on the removal of H2S and PH3. Thus, leached metal ions in slurry have a leading role in removing H2S and PH3. The mixture of MS and CuSO4 slurry obtained the best PH3 conversion efficiency while the effect of CuSO4 solution was not obvious. According to our previous report [13], the increase in PH3 conversion efficiency can be ascribed to the oxidation ability of Cu2+ and Mn2+ from MS, thus inhibiting the formation of CuS/Cu2S.

Table 1. XRF analysis of electrolytic manganese slag (wt.).

| Element       | Ca   | Si   | Mn   | Al   | Mg   | S    | O    |
|---------------|------|------|------|------|------|------|------|
| Raw electrolytic manganese slag | 25.54 | 13.09 | 11.33 | 4.80 | 3.54 | 1.87 | 37.48 |

2.2. Effect of Simulated Modified MS Slurry on Simultaneous Removal of H2S and PH3

The metal ions leached from MS during the reaction period played a leading role in removing H2S and PH3. Thus, to gain more insight, the modified MS slurry was simulated in the form of metal salts based on the real component composition. The various simulated metal salts species (including metal nitrates, metal chlorides, and metal sulfates) were investigated and the simulated contents were listed in Table 2. The H2S and PH3 removal efficiency by simulated modified MS slurry is shown in Figure 3. The results showed that the three groups obtained a 100% H2S conversion efficiency; whereas Group 3 (metal chlorides) obtained the higher PH3 removal efficiency relative to those of the other groups, with the order being metal chlorides > metal nitrate > metal sulfates. In order to achieve a better understanding of the variation in PH3 and H2S conversion by different metal salts, the reaction products in aqueous solutions were detected by the IC method. The IC results, as shown in Figure 4, showed that the generated PO43− and SO42− concentrations in Group 3 increased with the reaction proceeding, which indicated that the H2S and PH3 could be converted to PO43− and SO42−, respectively. Thus, the addition of metal sulfates inhibited higher H2S and PH3 conversion efficiency because the generation of SO42− was accelerated and inhibited the oxidation of PH3 when the copper concentration was increased.

![Figure 2](image_url)  
Figure 2. Effects of different component slurry after acid leaching on simultaneous removal of (a) H2S and (b) PH3 by manganese slag before and after acid leaching. Experimental conditions: H2S concentration = 800 ppm; PH3 concentration = 400 ppm; gas flow rate = 110 mL min−1; reaction temperature = 35 °C; Oxygen content = 1 vol%; stirring rate = 800 r/min.
was at relatively high concentration, according to our previous study [13]. In other words, more sulfates existing in the solution led to lower PH₃ conversion efficiency. Hence, the metal chloride was chosen for the following experiments.

### Table 2. Composition of simulated modified manganese slag slurry.

| Samples                      | Composition (wt.%), Total Mass = 3 g, Balanced in SiO₂ |  |
|------------------------------|--------------------------------------------------------|---|
|                              | Ca²⁺ | Mg²⁺ | Mn²⁺ | Al³⁺ | Extra Added Cu²⁺ |
| Group 1 (metal nitrates)     | 25.54| 3.54 | 11.33| 4.80 | 0.01 mol         |
| Group 2 (metal chlorides)    | 25.54| 3.54 | 11.33| 4.80 | 0.01 mol         |
| Group 3 (metal sulfates)     | 25.54| 3.54 | 11.33| 4.80 | 0.01 mol         |

**Figure 3.** Effect of different simulated modified manganese slag (MS) slurry on simultaneous removal of H₂S and PH₃ by manganese slag before and after acid leaching. Experimental conditions: H₂S concentration = 800 ppm; PH₃ concentration = 400 ppm; gas flow rate = 110 mL min⁻¹; reaction temperature = 35 °C; Oxygen content = 1 vol %; stirring rate = 800 r/min.

**Figure 4.** Ion concentration in Group 3 (metal chloride) as a function of time (50× dilution).
2.3. Effect of Single and Multi-Metal Ions on Simultaneous Removal of H$_2$S and PH$_3$

To further explore the role of metal ions in removing H$_2$S and PH$_3$, we provide a series of experiments to examine the effect of metal ions on H$_2$S and PH$_3$ removal. It can be seen from Figure 5 that all groups can achieve 100% H$_2$S removal efficiency. The highest PH$_3$ conversion efficiency of Cu$^{2+}$ + Al$^{3+}$, Cu$^{2+}$ + Ca$^{2+}$, Cu$^{2+}$ + Mg$^{2+}$, and Cu$^{2+}$ + Mn$^{2+}$ were 95.52%, 89.45%, 87.43%, and 81.63%, respectively. The Al$^{3+}$ + Cu$^{2+}$ group obtained higher PH$_3$ conversion efficiency relative to that of Cu$^{2+}$ alone, which indicated that the Al$^{3+}$ and Cu$^{2+}$ have a synergistic effect on PH$_3$ removal. The addition of Mg$^{2+}$, Ca$^{2+}$, and Mn$^{2+}$ slightly reduced the PH$_3$ conversion efficiency compared to those of the Cu$^{2+}$ group and Al$^{3+}$ + Cu$^{2+}$ group. Thus, the analysis emphasis was laid on the Al$^{3+}$ + Cu$^{2+}$ group, and the reaction products in long-term experiments are analyzed in the next section (Section 2.4).

\[
\text{Cu}^{2+} + \text{H}_2\text{S} \rightarrow \text{CuS} + 2\text{H}^+ \quad (1)
\]

![Figure 5](image_url)  
Figure 5. Effect of different single and multi-metal ions (metal chlorides) on simultaneous removal of H$_2$S and PH$_3$. Experimental conditions: H$_2$S concentration = 800 ppm; PH$_3$ concentration = 400 ppm; gas flow rate = 110 mL min$^{-1}$; reaction temperature = 35 °C; Oxygen content = 1 vol %; stirring rate = 800 r/min.

2.4. Reaction Mechanism of Metal Ions to Simultaneous Removal of H$_2$S and PH$_3$

To understand the effect of Al$^{3+}$ combined with Cu$^{2+}$ on simultaneous removal of H$_2$S and PH$_3$, the long-term experiments were carried out and the variation in the pH value of solution, solid or aqueous products is analyzed in this section. For the Cu$^{2+}$ group, Figure 6a shows that the PH$_3$ conversion efficiency increased initially and then decreased with the reaction proceeding, accompanied by a gradual decrease in the pH value. The XRD results in Figure 6b indicate that the main reaction product was CuS, Cu$_8$S$_5$, and CuCl, which resulted from the reaction between H$_2$S and Cu$^{2+}$ (Equation (1)). Meanwhile, the H$^+$ ion was increased, thereby leading to a decrease in pH value. The Al$^{3+}$ + Cu$^{2+}$ group showed a similar conversion trend for H$_2$S and PH$_3$. However, the reaction products of the Al$^{3+}$ + Cu$^{2+}$ group became different. It can be seen from Figure 6d that the Al$_2$(SO$_4$)$_3$, CuSO$_4$, Cu$_4$(SO$_4$)(OH)$_6$, 2H$_2$O, and CuS were the main reaction products for removing H$_2$S while AlPO$_4$, AIP, and Cu$_8$O$_2$(PO$_4$)$_2$ were the main reaction products for removing PH$_3$. When Al$^{3+}$ was added into the solution, the pH value slowly decreased during 5 h of initial reaction time, which indicated that Al$^{3+}$ could inhibit the rapid decline of pH value, although the pH value subsequently decreased dramatically.
whereas the sulfate content (91.4%) was dominant in the Al⁺³ + Cu²⁺ group. This can be explained by noting that the B. E. of 169.8 eV appeared [16] and the sulfate content further increased from 7 h to complete reaction, which indicated that CuS was further oxidized to CuSO₄.

As shown in Figure 7c, when the Al³⁺ + Cu²⁺ group reacted for 1 h, phosphate was formed, since the PO₄³⁻ content increased from 51.7% to 69.8%, up to 94.4% in the final. The variation of the P valence state in the Cu²⁺ group as shown in Figure 7d was the same as for the Al³⁺ + Cu²⁺ groups with the reaction proceeding. For the Al³⁺ + Cu²⁺ group, as shown in Figure 6d, only CuS and Cu₈S₅ were the main reaction products for removing H₂S while CuCl, Al₂(SO₄)₃, Cu₅O₂(PO₄)₂, Cu₄(SO₄)(OH)₆·2H₂O, and CuS were the main reaction products for removing H₂S while the B. E. of 169.8 eV appeared [16] and the sulfate content further increased from 7 h to complete reaction, which indicated that part of Cu²⁺ was converted to Cu⁺ as evidenced by the formation of CuCl.

To understand the effect of Al³⁺ combined with Cu²⁺ on simultaneous removal of H₂S and PH₃, we conducted several XPS studies for the reaction products of the Cu²⁺ group and Al³⁺ + Cu²⁺ groups. For the Al³⁺ + Cu²⁺ group, as shown in Figure 7a, the binding energy (B. E.) centered at about 159.4 eV for S 2p₁/₂ could be attributed to S²⁻ [14], which indicated that CuS was generated in the Al³⁺ + Cu²⁺ group. In addition, the B. E. located at 164.2 eV may be ascribed to polysulfide species [15], which indicated that CuS/Cu₈S₅ was oxidized in the existence of oxygen. With the reaction further proceeding, the sulfate was formed as evidence that the B. E. of 169.8 eV appeared [16] and the sulfate content further increased from 7 h to complete reaction, which indicated that CuS was further oxidized to CuSO₄ by oxygen in the presence of the water environment [17]. This was consistent with the XRD results as shown in Figure 6d. For the Cu²⁺ group, the variation in S valence state in the initial reaction period was similar to the Al³⁺ + Cu²⁺ group. However, with further increase of the reaction time, the content of the polysulfide species (53.2%, calculated by XPS data as shown in Table 3) was the same as the sulfate content (46.8%); whereas the sulfate content (91.4%) was dominant in the Al³⁺ + Cu²⁺ group. This can be explained by noting that the addition of Al³⁺ could effectively accelerate the CuS oxidation, thus generating more sulfate species.
Figure 7. XPS spectra of Al$^{3+}$ + Cu$^{2+}$ group and Cu$^{2+}$ group with different reaction time for surveys of (a,b) S 2p, (c,d) P 2p, and (e,f) Cu 2p.
Table 3. XPS data of Al\textsuperscript{3+} + Cu\textsuperscript{2+} group and Cu\textsuperscript{2+} group with different reaction time for surveys of S 2p; P 2p, and Cu 2p.

| Sample | Element | Parameter |
|--------|---------|-----------|
| Cu\textsuperscript{2+} Group | S | 1 h | 4 h | Complete Reaction |
| Position (eV) | 164.2 | 159.4 | 169.8 | 164.9 | 169.7 | 163.6 |
| Atomic ratio (%) | 68.2 | 31.9 | 40.4 | 59.6 | 46.8 | 46.5 | 6.7 |
| Substance | S\textsubscript{4} | S\textsuperscript{2-} | SO\textsubscript{4}\textsuperscript{2-} | S | SO\textsubscript{4}\textsuperscript{2-} | S | S\textsubscript{n} | S\textsubscript{n} |
| P | Position (eV) | 134.2 | 131.3 | 134.2 | 131.4 | 131.4 | 134.1 |
| Atomic ratio (%) | 39.9 | 60.1 | 64.7 | 35.3 | 100.0 |
| Substance | PO\textsubscript{4}\textsuperscript{3-} | P\textsuperscript{3-} | PO\textsubscript{3}\textsuperscript{2-} | P\textsuperscript{5-} | PO\textsubscript{4}\textsuperscript{3-} |
| Cu | Position (eV) | 935.1 | 932.7 | 932.8 | 935.3 | 932.3 | 934.6 |
| Atomic ratio (%) | 87.9 | 12.1 | 15.2 | 84.8 | 70.2 | 29.8 |
| Substance | CuSO\textsubscript{4} | CuS | CuS | CuSO\textsubscript{4} | CuS | CuSO\textsubscript{4} |

| Al\textsuperscript{3+} + Cu\textsuperscript{2+} Group | S | 1 h | 4 h | Complete Reaction |
|--------|---------|-----------|
| Position (eV) | 164.2 | 159.4 | 169.8 | 164.9 | 169.7 | 163.6 |
| Atomic ratio (%) | 78.4 | 21.6 | 74.2 | 25.8 | 91.4 | 8.6 |
| Substance | S\textsubscript{n} | S\textsuperscript{2-} | SO\textsubscript{4}\textsuperscript{2-} | S | S\textsubscript{n} | S\textsubscript{n} |
| P | Position (eV) | 133.6 | 131.0 | 134.0 | 131.5 | 134.1 | 131.0 |
| Atomic ratio (%) | 51.7 | 48.3 | 69.8 | 30.2 | 94.4 | 5.6 |
| Substance | PO\textsubscript{4}\textsuperscript{3-} | P\textsuperscript{3-} | PO\textsubscript{3}\textsuperscript{2-} | P\textsuperscript{5-} | PO\textsubscript{4}\textsuperscript{3-} | P\textsuperscript{3-} |
| Cu | Position (eV) | 934.9 | 932.6 | 935.2 | 935.3 | 935.0 | 932.3 | 932.6 |
| Atomic ratio (%) | 83.5 | 16.5 | 86.5 | 13.5 | 73.6 | 26.4 |
| Substance | Cu(II) | Cu(I) | Cu(II) | Cu(I) | Cu(II) | Cu(I) |

\(^{1}\text{s}\textsubscript{n} \text{refers to the polysulfide species.}\)

As shown in Figure 7c, when the Al\textsuperscript{3+} + Cu\textsuperscript{2+} group reacted for 1 h, phosphate was formed, since the peak at 134.6 eV could be attributed to PO\textsubscript{4}\textsuperscript{3-} while the B. E. of 131.0 eV may be ascribed to P\textsuperscript{3-}. With an increase in reaction time, the PO\textsubscript{4}\textsuperscript{3-} content increased from 51.7% to 69.8%, up to 94.4% in the final. The variation of the P valence state in the Cu\textsuperscript{2+} group as shown in Figure 7d was the same as for the Al\textsuperscript{3+} + Cu\textsuperscript{2+} group; but the generation rate of phosphate in the Cu\textsuperscript{2+} group was slower than that of the Al\textsuperscript{3+} + Cu\textsuperscript{2+} group. When the reaction time was for 1 h, the relative phosphate content in the Cu\textsuperscript{2+} group was 39.9%, thus leading to a slower increased PH\textsubscript{3} conversion efficiency than the Cu\textsuperscript{2+} group. The faster conversion of PH\textsubscript{3} to phosphate resulted in accelerated PH\textsubscript{3} absorption in the initial period of reaction.

It can be seen from Figure 7e that the B. E. located at around 934.9 and 932.6 eV in the Al\textsuperscript{3+} + Cu\textsuperscript{2+} group could be attributed to Cu(II) and Cu(I), respectively [18]. The relative Cu\textsuperscript{2+} content in the Al\textsuperscript{3+} + Cu\textsuperscript{2+} group was 83.5% for 1 h of reaction time and then decreased to 73.6% until the complete reaction, which indicated that part of Cu\textsuperscript{2+} was converted to Cu\textsuperscript{+} as evidenced by the formation of CuCl and Cu\textsubscript{8}S\textsubscript{5} by the XRD technique. From Figure 7f, it can be seen that the ratio of Cu(II)/Cu(I) in the Cu\textsuperscript{2+} group decreased dramatically relative to the Al\textsuperscript{3+} + Cu\textsuperscript{2+} group, which indicated that Cu\textsuperscript{2+} ion had a liquid-phase catalytic oxidation effect on removing H\textsubscript{2}S and PH\textsubscript{3} through variation in the valence state of Cu\textsuperscript{2+} to Cu\textsuperscript{+}.

Based on the above analysis, the metal ions played a leading role in removing H\textsubscript{2}S and PH\textsubscript{3}. The reaction process can be summarized as follows (Equations (2)–(13)):

\[
\text{H}_2\text{S} \leftrightarrow \text{HS}^- + \text{H}^+ \leftrightarrow \text{S}^{2-} + 2\text{H}^+ \tag{2}
\]

\[
\text{Me}^{2+} + \text{H}_2\text{S} + 2\text{H}_2\text{O} \rightarrow \text{MeS} \downarrow + 2\text{H}^+ \quad \left(\text{Me}^{2+} = \text{Cu}^{2+}\right) \tag{3}
\]

\[
\text{CuS(s)} \rightarrow \text{Cu}^{2+} (\text{aq}) + \text{S}^{2-} \quad \left(\text{Me}^{2+} = \text{Cu}^{2+}\right) \tag{4}
\]

\[
8\text{Cu}^{2+} + \text{PH}_3 + 4\text{H}_2\text{O} \rightarrow 8\text{Cu}^+ + \text{PO}_4^{3-} + 11\text{H}^+ \tag{5}
\]
\[ 4\text{Cu}^+ + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Cu}^{2+} + 4\text{OH}^- \]  
\[ \text{Cu}^+ + \text{O}_2 \rightarrow \text{Cu}^{2+} + \text{O}_2^- \]  
\[ \text{O}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{S} \downarrow + 2\text{H}_2\text{O} \]  
\[ \text{S} + 1.5\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \]  
\[ (\text{CuS})_n + \text{O}_2 \rightarrow (\text{CuS})_{n-1}(\text{CuS})^{*+} + \text{O}_2^{*-} \]  
\[ \text{Cu}^{2+} + \text{H}_2\text{O} \rightarrow \text{Cu}^+ + \text{H}^+ + \text{OH}^* \]  
\[ 2\text{OH}^* \rightarrow \text{H}_2\text{O}_2 \]  
\[ 4\text{H}_2\text{O}_2 + \text{S}^{2-} \rightarrow \text{SO}_4^{2-} + 4\text{H}_2\text{O} \]

3. Materials and Methods

3.1. Materials

The manganese slag samples were collected from Wenshan, China. The electrolytic manganese slag is firstly dried at 105 °C in the oven for 12 h, then mechanically ground by ball mill and sieved to 200 mesh (74 µm) for use. The standard gases include N\(_2\) (≥99.99%), H\(_2\)S/N\(_2\) (1.00% H\(_2\)S, v/v), PH\(_3\)/N\(_2\) (1.00% PH\(_3\), v/v), and O\(_2\) (≥99.99%), all of which were purchased from Dalian Special Gases Co., Ltd., Dalian, China.

3.2. Acid Leaching Procedure and Preparation of Modified MS Slurry

First, the electrolytic manganese slag was weighed and transferred into a three-necked flask. Then, 2 mol L\(^{-1}\) hydrochloric acid solution was taken into the three-necked flask with the connecting condensing device. The solid-to-liquid ratio of the slag to the acid solution was 1:6. The acid leaching temperature was set at 100 °C for 60 min. After acid leaching, the acid-leached solution was filtered. Then, filter residue and filtrate were obtained. The obtained filter residue was named as acid leaching residue. The acid leaching residue was then mixed with deionized water to obtain a 40 mL acid leaching residue slurry. Furthermore, the acid leaching residue was mixed with 0.01 mol CuSO\(_4\), named as acid leaching residue + CuSO\(_4\). The mixture of acid leaching residue and CuSO\(_4\) was added into 40 mL deionized water to prepare the acid leaching residue + CuSO\(_4\) slurry. The modified MS slurry was obtained by a mixture of 3 g MS, 40 mL deionized water, and 0.01 mol CuSO\(_4\), named MS + CuSO\(_4\). In addition, the 3 g of raw MS was added to 40 mL deionized water to prepare the raw MS slurry, named MS. The CuSO\(_4\) solution also was prepared by adding a mixture of 40 mL deionized water and 0.01 mol CuSO\(_4\), named CuSO\(_4\).

3.3. Analytical Method

The solid samples were characterized by XPS technology to obtain the information of S 2p, P 2p, and Cu 2p that were measured by the ESCALAB 250 X-ray photoelectron spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with a resolution of 0.45 eV (Ag) and 0.82 eV (PET). The sensitivity of the instrument is 180 kbps (200 µm, 0.5 eV). The anions in the solutions were detected by ICS-600 (Thermo Fisher Scientific, Waltham, MA, USA). The ion chromatography is equipped with an AS12A anion separation column consisting of sodium carbonate and sodium bicarbonate. The instrument is turned on for 1–2 h, and the background conductance is less than 30 µs to start measurement. XRD method was used to determine the phase structure of the solid samples prior and after H\(_2\)S and PH\(_3\) absorption experiments by a D/MAX-2200 X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu Kα ray, at a voltage of 36 kV, at a current of 30 mA, with scanning range between 10 and 90°, and at a scanning speed of 5°/min.
3.4. Catalytic Activity Test

The experiment device for evaluating the activity of the remover is shown in Figure 8. The simulated flue gas consists of O₂, H₂S, PH₃, and N₂, all of which were supplied by gas cylinders (1a–1d), and their concentration were 1 vol %, 800 ppm (parts per million by volume), 400 ppm, respectively, with a total gas flow rate of 110 mL/min. The gas flow in each gas path is controlled by mass flow controllers (2) (Beijing Seven-Star Electronics Co., Ltd., Beijing, China) with a digital display (4) (Beijing Seven-star Electronics Co., Ltd., Beijing, China), then all of the gases were mixed in the mixing tank (5) (J.K Fluid Technology, Jiaxing, China). The mixed gas will reach the desired concentration by adjusting the mass flow controllers, and be analyzed by gas chromatography (6) (FULI-9790II gas chromatography, FULI Instrument Co., Ltd., Taizhou, China). Then, the mixed gas passes through three-necked flask (10) combined with the constant temperature magnetic stirrer (DF-101S, INESA Scientific Instrument Co., Ltd., Shanghai, China), contacting the prepared modified manganese slag slurry in which mixed gas will react with the slurry. During the reaction process, the pH value of slurry was measured by pH meter (PHS-3C, INESA Scientific Instrument Co., Ltd., Shanghai, China). Moreover, the tail gas will first be analyzed by a gas chromatography and then be removed in the tail gas treatment system (9) (scrubbed by the 5 wt.% KMnO₄ solution with 5 wt.% H₂SO₄).

![Figure 8. Experimental device diagram of extractant activity evaluation. 1a, 99.99% O₂ cylinder gas; 1b, 1 vol % H₂S cylinder gas; 1c, 1 vol % PH₃ cylinder gas; 1d, 99.99 vol % N₂ cylinder gas; 2, mass flow meter; 3, on-off valve; 4, digital display; 5, gas mixing tank; 6, FULI-9790II gas chromatography; 7, data analysis; 8, constant temperature magnetic stirrer; 9, exhaust gas absorption bottle; 10, three-necked flask.](image)

The calculation method for the conversion efficiency of PH₃ and H₂S is shown in Equation (14).

\[
\text{PH₃(H₂S) conversion efficiency \%} = \frac{\text{PH₃(H₂S)}_{\text{inlet}} - \text{PH₃(H₂S)}_{\text{outlet}}}{\text{PH₃(H₂S)}_{\text{inlet}}} \times 100
\]

(14)

where PH₃ inlet and H₂S inlet refer to the inlet concentrations of PH₃ and H₂S at the initial of the reactor, respectively, in mg/m³; and PH₃ outlet and H₂S outlet refer to the outlet concentrations of PH₃ and H₂S at the end of the reactor, respectively, in mg/m³.

4. Conclusions

In this study, modified MS slurry was systematically carried out toward simultaneously removing H₂S and PH₃. On the basis of different characterization techniques, we investigated the reaction mechanism of removing H₂S and PH₃ by modified MS slurry. The main findings of this study are as follows:
(1) Through acid leaching experiments, the liquid-phase part after filtration has a leading role in removing H$_2$S and PH$_3$. The highest PH$_3$ conversion efficiency of leaching residue slurry + CuSO$_4$ group can only obtain 15.14%, which indicated that the main active components were consumed by the acid leaching method.

(2) By simulation of the modified MS slurry with metal ions based on real chemical composition, the catalytic activity for H$_2$S and PH$_3$ is relative to the types of metal salts, with the order being metal chlorides > metal nitrates > metal sulfates. All of the metal salts can obtain 100% H$_2$S removal efficiency. In addition, the metal chlorides can maintain above 70% PH$_3$ conversion efficiency for 10.5 h and the highest PH$_3$ conversion efficiency was 86.85%; whereas the highest PH$_3$ removal efficiency of the metal nitrates and metal sulfates can only obtain 47.36% and 27.24%, respectively. Furthermore, Al$^{3+}$ and Cu$^{2+}$ has a synergistic effect on removing H$_2$S and PH$_3$ compared to Ca$^{2+}$, Mg$^{2+}$, and Mn$^{2+}$ combined with Cu$^{2+}$ groups.

(3) H$_2$S was oxidized to element S and sulfate due to the reaction between Cu$^{2+}$ and H$_2$S and part of the H$_2$S oxidation by O$_2$, while the PH$_3$ was oxidized to PO$_4^{3-}$ by liquid-phase catalytic oxidation of metal ions with the conversion of Cu$^{2+}$ to Cu$^+$. 

(4) The best PH$_3$ and H$_2$S conversion efficiency was obtained by the modified MS slurry (MS + CuSO$_4$), and the maximum removal efficiency of H$_2$S and PH$_3$ were 100% and ~78%, respectively. The simple modification process for raw MS through adding Cu$^{2+}$ can effectively improve the H$_2$S and PH$_3$ conversion relative to fresh MS, which can be attributed to the synergistic effect of different metal ions. However, the added Cu$^{2+}$ in the modified MS slurry would be consumed by conversion of Cu$^{2+}$ to CuS/Cu$_2$S, thereby leading to the deactivation of modified MS slurry.

Author Contributions: J.B. and X.W. contributed equally. Conceptualization, X.S. (Xin Sun) and P.N.; methodology, 3 (4) The best PH$_3$ conversion efficiency of leaching residue slurry + CuSO$_4$ group can only obtain 15.14%, which indicated that the main active components were consumed by the acid leaching method.

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