Feasibility Application of Cu-Contaminated Soil on the Removal of H2S from Hot Coal Gas

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In this study Cu-contaminated soils were chosen as a candidate material for the removal of hydrogen sulfide (H2S) from hot coal gas. Experimental results showed that the H2S was significantly reduced below 10 ppm when the Cu-contaminated soils were reacted with H2S. The optimal removal temperature of H2S was found to be at 923 K in the operating conditions. In addition to Cu species, free Fe oxides in the contaminated soils also performed an active species to react with H2S and enhanced the overall sulfur capacity. Through the XPS analysis, Fe sulfide (FeS) and Cu sulfide (CuS) were the major products after removal experiments. Regeneration experimental results also indicated that the Cu-contaminated soils can be regenerated by pass air and thus be reused for many times. [doi:10.2320/matertrans.M2014393]

(Received November 6, 2014; Accepted January 8, 2015; Published February 25, 2015)

Keywords: copper-contaminated soil, hydrogen sulfide, hot coal gas, regeneration

1. Introduction

Hydrogen sulfide (H2S) is a well-known toxic and corrosive gas and a number of technologies have been widely developed for achieving better removal efficiency. In the past, activated carbon adsorption and wet absorption are the major technologies for removal of H2S.1−3 However, not all H2S containing gases can be treated by adsorption and wet absorption. For example, the gases containing H2S released from coal gasification processes accompany high temperature and relatively higher content of H2S as well as further increase the overall removal efficiency when adsorption and wet absorption are used for capable of H2S removal. To overcome this disadvantage, a novel removal method has been developed based on the thermodynamic consideration. A representative scheme can be represented as follows:

\[ \text{MO}_x + x\text{H}_2\text{S}_y \leftrightarrow \text{MS}_x + x\text{H}_2\text{O}_y \]  

where MOx is metal oxides and MS is metal sulfides. Several metal oxides have been proposed for removal of H2S in this system. Copper oxides are recognized as one of the favorable thermodynamic properties for H2S removal and continuously to be the leader metal in this system.

Soil contamination is a serious environmental problem in highly industrialized countries. In particular, contaminated soils with heavy metals, such as Zn, Ni, Cu, Pb, and Cr have been recognized as the troublesome problem. Since contaminated soils contain high concentration of metals, some of metals may play active species to react with H2S to form metal sulfides for achievement above system. On the other hand, to date no much applied information is found for the use of metal contaminated soils. For this reason, Cu-contaminated soils were chosen as a candidate for the removal of H2S at high temperature because of higher content of Cu and favorable thermodynamic property with H2S.

In this study, Cu-contaminated soils were used and evaluated to assess its performance on the high-temperature removal of H2S in a fixed bed reactor under simulated conditions. In addition, multiple regeneration experiments were conducted in order to understand regeneration property. Characterization of Cu-contaminated soil was also performed with X-ray photoelectron spectroscopy for investigation of Cu species after reaction processes.

2. Experimental Procedure

The tested soils were collected from one of the severely contaminated sites polluted by copper metal and was recognized by the Environmental Protection Administration of Taiwan. Contaminated soils were sampled at a depth of 0–15 cm from a site. Unwanted materials, such as leaves, tree root and small gravel were removed from soil sample and then dried at room temperature for a week. The collected soils were ground with an agate mortar and sieved to pass through a 2-mm sieve. The contents of total Cu and Fe are 8,820 and 116,573 mg·kg−1, respectively based on the inductively coupled plasma (ICP) analysis. The free Fe content is 12,371 mg·kg−1 based on the dithionite-citrate-bicarbonate (DCB) procedure.4) On the other hand, the content of Mn, Zn, Ca, Mo, V, Co, W and Sr in Cu-contaminated soil is very small and their contribution on H2S removal would be ignored in this system.

The hot coal gases consisted of 1% H2S, 25% CO, 15% H2, 10% H2O and a balance of N2 from regulation cylinders, which were similar to the quenched exit gas of the typical KRW coal gasifier. The reactor consisted of a quartz tube, 1.6 cm i.d., 2.0 cm o.d., and 150 cm long, located inside an electric furnace. Quartz fibers were set in the reactor in order to support samples. Two K-type thermocouples were inserted exactly into the reactor near the positions on the top and bottom of the samples packing to measure and control the inlet and outlet temperatures. Three grams of soils were...
packed in the reactor for each run. The gas flow was controlled at 100 mL·min\(^{-1}\). Before experiment proceeding, a pure nitrogen gas (purity 99.99\%) was fed into the reactor for 30 min at 823 K to remove adsorbed water and impure materials coated on the surface of samples. The inlet and outlet concentration of \(\text{H}_2\text{S}\) was analyzed by an on-line gas chromatograph (HP, GC-5890) equipped with a flame photometry detector (FPD). The breakthrough time was defined as the time from the beginning of the reaction to the point outlet \(\text{H}_2\text{S}\) concentration reached 100 ppm. Following \(\text{H}_2\text{S}\) removal reaction, the reactor was purged with nitrogen gas for 15 min, and then regeneration run was begun at 923 K with air. The regeneration experiment was terminated when the concentration of \(\text{SO}_2\) in the effluent gas was below 50 ppm.

X-ray Photoelectron Spectroscopy (XPS) chemical analyzing instrument is a VG Micro Lab. MKIII XPS analyzing instrument with a Mg K\(\alpha\) X-ray radiation source (1253.6 eV). The sample was initially tapped on a sample supporting plate. The plate was then placed in a pretreatment chamber attached to the instrument. The chamber pressure was then decreased from 100 to 1.33 \(\times 10^{-10}\) kPa via a turbo pump. The time needed to reach the final pressure was approximately 4 hrs. A gate valve between the pretreatment chamber and a vacuum chamber was then opened after the pre-treatment. The sample was moved to the vacuum chamber for analysis. The pressure in the vacuum chamber was maintained at 1.33 \(\times 10^{-10}\) kPa via an ion pump. The data analysis procedure generally involved background subtraction by a Shirley-type integral profile and a curve fitting procedure by a least-squares method. The chemical shifts of the 2p\(_{3/2}\) transitions of Cu and Fe were scanned and recorded. The experimental errors were estimated to be \(\pm 0.2\) eV for the photoelectron peak binding energy positions.

Elementar vario EL III Heraeus CHNOS Rapid F002, equipped with a flash combustion furnace and thermal conductivity detector (TCD) was used for determination of sulfur content after experimental processes.

3. Results and Discussions

A series of temperatures ranging from 773–1023 K were conducted and experimental result was shown in Fig. 1. As shown, the optimal temperature for the use of Cu-contaminated soils appears to be around 873–923 K and the breakthrough time is estimated about 16 min through the experimental observation. It is surprisingly that the experimental breakthrough time remains about 9 min, which confirms the presence of another active element as well as may be acted as the important role with \(\text{H}_2\text{S}\). On the other hand, a change in color from gray to black on exposure to \(\text{H}_2\text{S}\) was significantly observed during the stage of experiment. This finding was consistent with the result obtained by Joyner \textit{et al.} in which their research shown that the color of Fe based catalyst turned into black when the \(\text{H}_2\text{S}\) was introduced into a reactor.\(^5\) The color change implied the structure change from Fe oxides to Fe sulfide (\(\text{FeS}/\text{FeS}_2/\text{FeS}_1–x\)).

In this study, X-ray fluorescence (XRF) was used to determine a series of the potential metals for high temperature desulfurization. Results indicated that no vanadium, tungsten, cobalt and molybdenum were detected and the contents of zinc, manganese were 123 and 205 ppm, respectively. Therefore, it is believed that their contributions on \(\text{H}_2\text{S}\) removal would be ignored. It is undoubtedly that the Fe oxides presented in the Cu-contaminated soils are another active species to react with \(\text{H}_2\text{S}\) and enhances the overall removal efficiency in this study.

The sulfur capacity is another important factor to assess the performance of Cu-contaminated soil. A series of measured tests for the determination of sulfur content were performed and tabulated in Table 1. The theoretical breakthrough time and theoretical sulfur capacity are calculated based on the following reactions:

\[
\text{Fe}_2\text{O}_3(s) + 2\text{H}_2\text{S}(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{FeS}(s) + 3\text{H}_2\text{O}(g) \quad (2)
\]

\[
2\text{CuO}(s) + \text{H}_2\text{S}(g) + \text{H}_2\text{O}(g) \rightarrow \text{Cu}_2\text{S}(s) + 2\text{H}_2\text{O}(g) \quad (3)
\]

where the \(\text{Fe}_2\text{O}_3\) and \(\text{CuO}\) represent the Fe and Cu content in the Cu-contaminated soil. Both contents of \(\text{Fe}_2\text{O}_3\) and \(\text{CuO}\) were digested by the DCB method and aqua regia, respectively and determined their concentration using ICP. Based on the contents of \(\text{Fe}_2\text{O}_3\), \(\text{CuO}\) and the mass flow rate of \(\text{H}_2\text{S}\), the theoretical breakthrough time and theoretical sulfur capacity can be accurately determined. Note that the theoretical breakthrough time and sulfur capacity for the case of 923 K appears to have the best performance among all the test temperatures. Experimental breakthrough time of 16 min
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Table 1 Sulfur capture capacity determined from different analyses for Cu-contaminated soils.

<table>
<thead>
<tr>
<th></th>
<th>Theoretical breakthrough time (t/min)</th>
<th>Experimental breakthrough time (t/min)</th>
<th>Theoretical sulfur capacity (mass%)</th>
<th>Experimental sulfur capacity determined from breakthrough time (mass%)</th>
<th>Actual sulfur capacity determined from element analysis (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh (773 K)</td>
<td>16.0</td>
<td>8.2</td>
<td>0.69</td>
<td>0.37</td>
<td>0.39</td>
</tr>
<tr>
<td>Fresh (823 K)</td>
<td>16.0</td>
<td>10.2</td>
<td>0.69</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>Fresh (873 K)</td>
<td>16.0</td>
<td>15.5</td>
<td>0.69</td>
<td>0.67</td>
<td>0.68</td>
</tr>
<tr>
<td>Fresh (923 K)</td>
<td>16.0</td>
<td>16.0</td>
<td>0.69</td>
<td>0.69</td>
<td>0.71</td>
</tr>
<tr>
<td>Fresh (973 K)</td>
<td>16.0</td>
<td>9.5</td>
<td>0.69</td>
<td>0.41</td>
<td>0.40</td>
</tr>
<tr>
<td>Fresh (1023 K)</td>
<td>16.0</td>
<td>8.2</td>
<td>0.69</td>
<td>0.36</td>
<td>0.35</td>
</tr>
</tbody>
</table>

for the case of 923 K is also close to the theoretical breakthrough time, which implies that the Cu oxides can be completely used and converted to copper sulfide (obey the above assumed reaction). Furthermore, the sulfur capacity for all temperatures determined by an elemental analysis nearly corresponds to the results obtained from the experimental calculation.

The reaction equation shown in the introduction is a simple desulfurization reaction to elucidate the interaction between metal oxides and H₂S. In fact, coal gas contains large amounts of reductive gases, mainly CO and H₂, which results in complex reactions taking place in this system. Additionally, other compounds such as tar, CH₄, C₃H₈, CS₂ and other hydrocarbon compounds are also widely to be found in coal gas. It is not easy to elucidate the overall reaction when above-mentioned compounds are taken into account. Due to instrument limitation, only main compounds including H₂, CO, CO₂ and H₂O were focused in this study. A further study will be done on the effect of operating factors (including with/without H₂, CO, CO₂ and H₂O), thermodynamic properties and the formation of gaseous by-products for the use of Cu-contaminated soil.

On the basis of above findings, it is concluded that the Cu-contaminated soils can be used as materials for the removal of H₂S from hot coal gas and possible reactions for H₂S removal may be attributed to the reactions 2 and 3.

To verify the major solid-state structures after reaction, the reacted Cu-contaminated soils were analyzed by X-ray diffraction (XRD) and XPS, respectively. Unfortunately, no Cu, Fe and other metal sulfides species were identified from XRD analysis. This result may be attributed to the relatively lower contents of Cu and Fe or the metal sulfides are in form of amorphous. In summary, no important findings were obtained from the analysis of XRD. For better understanding the reaction products, XPS is used to survey the chemical state of Cu-contaminated soil after reaction. The XPS spectra of Fe₂p together with fitting regression results for the reacted Cu-contaminated soils were plotted in Fig. 2. Four Fe peaks were found and fitted. A fitting signal centered around 707 eV is assigned to the binding of Fe(II)-S. No fitting results were matched for the Fe sulfide compounds such as FeS₂/Fe₁₋₂S/FeS₁₋₂ based on the fitting regression simulation. Aside from the first peak centered around 707 eV was assigned to Fe(II)-S. The other fitting peaks were found and assigned to the other form of Fe-S or Fe-O. The second peak centered around 709 eV is an awkward position because the binding of Fe(II)-S and Fe(II)-O are around this position. In fact, Fe is a very complex component in soil mineral compositions. Some Fe ion exists in the form of single Fe oxides such as Fe₂O₃, FeOOH, Fe₂O₄ etc. and the other Fe ion presents in the form of Fe-O-Si or Fe-O-Al within the minerals lattices including kaolins, micas, chlorites etc. These minerals have strong binding force between Fe and other elements so that their influence on the reaction with H₂S can be neglected.

Figures 3 and 4 show the XPS spectra of Cu₂p together with the fitting results for the fresh and reacted Cu-contaminated soil. For the fresh Cu-contaminated soil a broad peak centered at 932.6 eV is observed and four fitting peaks (931.4, 932.1, 932.8 and 933.1 eV) were also found. As reported, the peak at 935 eV revealed the appearance of Cu²⁺ species strongly interacting with other metals. As expected, no peaks located at 935 eV were found, indicating the appearance of Cu in Cu-contaminated soil probably present in the form of free or oxide states. The form of free and oxide states are in favor of reaction with H₂S and inspection of results presented in Table 1 shows that the agreement between the experimental and theoretical breakthrough time is fairly good. Unlike fresh Cu-contaminated soil, a narrow and sharp peak was detected for the reacted one. This observation was consistent with the result obtained.
by Skrzypski et al. in which their research shown that the fresh Cu/ZnO based-sorbent has a broad Cu XPS spectra and a narrow Cu peak was measured for the sulphide sample. In addition to narrow and sharp feature, the binding energy of Cu shifts to lower energy (931.5 eV), indicating the appearance of Cu$^{+}$ in a sulphide environment. The Cu$_2$S would be the main sulphide metal.

A fortuitous feature of using contaminated soil for the removal of H$_2$S is that it can be regenerated and thus be reused after oxidation treatment. To test the regeneration characterization of Cu-contaminated soil for H$_2$S removal, thirty successive reaction/regeneration cycles were evaluated under the same conditions. Table 2 summarizes the breakthrough times and sulfur capacities determined by different analyses for thirty successive reaction/regeneration cycles. It is evident that experimental breakthrough time slightly decreases with regeneration cycle. No huge deactivation is observed after thirty regeneration cycle. The sulfur capture capacity determined from breakthrough time and element analysis for different regeneration cycle almost appears to have the identical value. Compared with the first and twenty regeneration cycle, approximately 11.6% sulfur capacity is decreased, also implying that the efficiency of regeneration at least remains as high as 88% and is acceptable for use in this system.

Although Cu-contaminated soil is capable of H$_2$S from hot coal gas, the overall sulfur capacity is relatively lower than the commercial and lab-made metal oxides, which cause the major barriers for the future development. To overcome this disadvantage, the Cu-contaminated soil will be chosen as a candidate to modify its crystalline phase by addition other metals. The formation of spinel structure of bi-metals will be undertaken in the coming experimental procedure.

4. Conclusion

Results of this research suggested that the Cu-contaminated soils could effectively remove H$_2$S from hot coal gas within the operation conditions. A series of temperatures were evaluated and found that the suitable operation temperature for use contaminated soil is experimentally estimated at about 923 K. Free Fe oxides present in contaminated soils play another active species to react with H$_2$S and enhance the overall sulfur capacity. FeS and Cu$_2$S were found to be the major species in the reacted sample. In regeneration experiments, no significant severe degeneration occurs to the contaminated soil after the thirty reaction/regeneration processes. The findings of this study showed that the contaminated soils have the potential to be the high-temperature material for removal of H$_2$S as well as provides...
new aspect and application for the treatment of heavy metals contaminated soils.

Acknowledgments

This work was partially funded by Tzu Hui Institute of Technology with a grant No. THIT-103011. The authors gratefully acknowledge the constructive comments of anonymous reviewers.

REFERENCES


