

Red soil as a regenerable sorbent for high temperature removal of hydrogen sulfide from coal gas

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Abstract

In this study, hydrogen sulfide (H₂S) was removed from coal gas by red soil under high temperature in a fixed-bed reactor. Red soil powders were collected from the northern, center and southern of Taiwan. They were characterized by XRPD, porosity analysis and DCB chemical analysis. Results show that the greater sulfur content of LP red soils is attributed to the higher free iron oxides and suitable sulfidation temperature is around 773 K. High temperature has a negative effect for use red soil as a desulfurization sorbent due to thermodynamic limitation in a reduction atmosphere. During 10 cycles of regeneration, after the first cycle the red soil remained stable with a breakthrough time between 31 and 36 min. Hydrogen adversely affects sulfidation reaction, whereas CO exhibits a positive effect due to a water-shift reaction. COS was formed during the sulfidation stage and this was attributed to the reaction of H₂S and CO.

Results of XRPD indicated that, hematite is the dominant active species in fresh red soil and iron sulfide (FeS) is a product of the reaction between hematite and hydrogen sulfide in red soils. The spinel phase FeAl₂O₄ was found during regeneration, moreover, the amount of free iron oxides decreased after regeneration indicating the some of the free iron oxide formed a spinel phase, further reducing the overall desulfurization efficiency.

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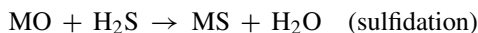
Keywords: Hydrogen sulfide; Red soil; High temperature; Free iron oxides; Spinel

1. Introduction

It is well known that integration gasification combined cycle (IGCC) and molten carbonate fuel cell (MCFC) processes are advanced power generation technologies with high efficiency power generation and good environmental performance. The advantages of IGCC and MCFC systems over pulverized coal fired power generation are higher power generation efficiency, lower air pollutants emission, smaller water consumption and simpler plant configuration [1,2]. Therefore, IGCC and MCFC are expected to be the main spearhead in the future for power required. Coal gasification generates large amounts of pollutants, such as particles, hydrogen sulfide and hydrogen chloride representing a serious problem. Among these pollutants, hydrogen sulfide (H₂S) has attracted the most attention because of

its severe corrosive property and relatively high concentration (almost 1%).

Several commercial techniques are available for removal of hydrogen sulfide, including wet absorption by MDEA, sodium carbonate, sodium hypochlorite or adsorption by active carbon [3–6]. However, the disadvantage of these commercial techniques for the purification of coal gas is that hot coal gas must be cooled to ambient temperature and then preheated to a high temperature before can be used in a gas turbine. To avoid heat loss and save energy, high temperature desulfurization technology has been widely developed and appears to be the major technique for removal of hydrogen sulfide from hot coal gas. The basic high temperature sulfidation reaction scheme can be represented as follows:

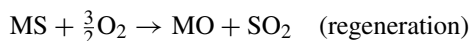


where MO and MS are the metal oxide and metal sulfide, respectively. The sulfide sorbent can be regenerated through reaction

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with diluted air:



Owing to their low cost, calcium oxide and its related species (such as dolomite and limestone) have been widely applied in the literature [7,8]. However, such sorbents possess some drawbacks; for example, the products of sulfidation are toxic and cannot be regenerated, so solid waste is formed. Of all solid metal oxides, copper oxides have the superior thermodynamic equilibrium constants and widely used in high-temperature desulfurization. The most important weakness of copper oxide is that it is reduced to elemental copper in a reducing atmosphere, reducing the efficiency with which it removes H_2S by a factor of about 10 [9]. Zinc oxide is attractive because it exhibits favorable sulfidation thermodynamics and can eliminate H_2S at concentrations below 10 ppm [10,11]. Unfortunately, zinc oxide is reduced to metallic zinc, which vaporizes when the temperature exceeds 823 K [12].

To overcome the reduction of copper oxide and the vaporization of zinc oxide, a series of mixed metal oxides were developed as high-temperature desulfurization sorbents such as ZnFe_2O_4 , LaCu_2O_4 , Cu–Cr and Cu–Ce [13–15]. Although these metal oxides or mixed metal oxides exhibit good removal efficiency. Manufacture of these sorbents results in an additional expenditure for H_2S removal in IGCC system.

Red soil, or so-called lateritic soil, is a residual product of a wide variety of intensive chemical weathering processes that affect rocks under strongly oxidizing and leaching conditions. Studies have shown that red soils include an abundance of iron in such forms as hematite (Fe_2O_3), magnetite (Fe_3O_4) and goethite (FeOOH) [16,17]. These iron oxides are called free iron oxides according to soil taxonomy. The term of free iron oxides are used here to include all iron not present in the crystal lattice of component minerals.

The main objective of this study is to elucidate the feasibility and potential of using red soil as a regenerable sorbent in the H_2S removal from coal gas at high temperature for the IGCC system. Characterization of red soil was also employed in order to observe the changes in structure before and after reaction.

2. Materials and methods

Various red soils investigated in this study were collected from different areas in Taiwan. They are called Pingchen series (PC), Houli series (HL), Dadusan series (DS) and Loupi series (LP) corresponding to Taiwan soil classification systems. The

physical and chemical properties of four red soil series are tabulated in Table 1. Unwanted materials such as leaves, tree roots and pebble were removed from samples and the samples were dried at the ambient temperature for a week. Prior to use, red soils were ground and sieved to the required particle size.

The sulfidation experiment was carried out in a bench scale fixed-reactor at atmospheric pressure. The reactor consisted of a quartz tube, 1.6 cm i.d., 2.0 cm o.d. and 150 cm long, inside an electric furnace. The quartz fibers were set in the reactor to support the red soil. Three grams of red soil was loaded on the center of the reactor for experiments. Two K-type thermocouples were inserted into the reactor to the positions at the top and bottom of the packed sorbent to enable the inlet and outlet temperatures to be measured and controlled. The temperature for sulfidation and regeneration processes was controlled within ± 5 K based on the multiple checks. The gaseous mixture composed of 1% H_2S , 25% CO , 15% H_2 and balance of N_2 from regulation cylinders. All mass flow meters were calibrated using an IR soap bubble meter and the concentrations of all species were calculated at STP condition. The inlet and outlet gas (H_2S) was analyzed by gas chromatograph (Shimadzu, GC-14B) equipped with a flame photometry detector (FPD). A six-port sampling valve with a 500 μl sampling loop was used to sample the gases for analysis. All the outlet gases from the reactor were sampled with an on-line autosampling system and analyzed by a FPD every 3 min. In sulfidation and regeneration experiments, the weight hourly space velocity (WHSV) was calculation set at $2000 \text{ ml}^{-1} \text{ h}^{-1} \text{ g}$. The sulfidation experiment was terminated when the outlet H_2S concentration from the reactor exceeded 1000 ppm. Following the sulfidation run, the reactor was purged with N_2 gas for 15 min and regeneration experiment was performed at 773 K with air under the identical space velocity. The regeneration run was terminated when the SO_2 concentration of the effluent was below 50 ppm. In this study, the breakthrough time was defined as the time from the beginning of the sulfidation to the time when the H_2S concentration at the outlet reached 100 ppm.

The surface area, pore volume and distribution of pore sizes were measured using a Micromeritics ASAP 2010 instrument using adsorption of nitrogen at 77 K. The surface area was calculated by BET equation.

X-ray powder diffraction (Rigaku D/max III-V XRD) was performed to identify crystalline phases and the surface structure of red soils. A diffractometer, using nickel filtered $\text{Cu K}\alpha$ radiation (40 kV and 30 mA), was used to record diffraction patterns from 5° to 90° at a speed of 3° min^{-1} .

Table 1
The physical and chemical properties of the tested red soil series in this study

Red soil series	Taxonomy	Soil matrix	Texture ^a	Munsell color (moist)	pH (H_2O)	Free iron oxide ^b (g/kg)	Total iron oxide ^c (g/kg)
Pingchen	Kandiperox	Diluvial	C	5YR4/6	4.06	38.56	104.36
Houli	Paleudult	Diluvial	CL	2.5YR4/5	4.40	37.23	94.65
Dadusan	Paleudult	Diluvial	SiCL	5YR5/4	4.36	27.62	89.27
Loupi	Hapludox	Diluvial	C	10YR3/4	4.02	42.80	117.25

^a C, CL, and SiCL represent as clay, clay loam and silty clay loam, respectively.

^b DCB extraction.

^c Aqua regia digestion.

The surface of the red soils was observed using a scanning electron microscope equipped with an EDS analyzer (SEM/EDS). The same instrument was used to record an X-ray mapping. The samples were coated with platinum to prevent discharge.

The free iron oxides in the red soils were selectively dissolved using the dithionite citrite bicarbonate (DCB) method, as follows [18]. Place 1 g of red soils in a 100 ml polypropylene centrifuge tube. Add 40 ml of 0.3 M sodium citrate and 5 ml of 1 M sodium hydrogen carbonate to a water bath held at 353 K for 30 min. Add 0.5 g of sodium dithionite to the mixture, shaking frequently for 20 min. Following this digestion run, add 10 ml saturated sodium chloride solution to promote flocculation. The suspension was centrifuged at 2200 rpm for 20 min and filtered through 0.2 μm membrane filters. The supernatant was quantified to 100 ml with distilled water and then determined the concentration of iron by inductively coupled plasma (ICP).

3. Results and discussion

3.1. Feasible and reactivity of various red soil series

Fig. 1 plots the breakthrough time as a function of the outlet concentration of H_2S for the tested red soil series. Noted that the outlet concentrations of H_2S are less than 10 ppm for all tested red soil series prior to breakthrough, indicating all red soil series can be used as sorbents for the removal of H_2S . Meanwhile, during the sulfidation run, the color of red soil changes significantly from red to dark black, indicating that iron oxides (red) are converted to iron sulfide (dark black). As shown in Fig. 1, the LP series shows the best breakthrough time followed by the PC and the HL series. The DS series shows the shortest breakthrough

time. The desulfurization capacities for the tested red soil series follow the order: LP > PC > HL > DS. A reasonable explanation for different H_2S removal efficiency may be explained from different content of free iron oxides. As shown in Table 1, it can be found that the LP red soil series has the highest free iron oxides content among tested samples. DS series has the lowest iron oxides content while PC and HL series have similar contents. This result is consistent with the sulfidation test, which established that the LP series has the best breakthrough time whereas DS series has the shortest breakthrough time. The sulfur uptake can be roughly estimated by a known concentration of H_2S and flow rates as well as a loading weight of red soils. The sulfur uptakes for DS, HL, PC and LP are estimated about 1.31, 1.61, 1.63 and 1.83 g-S/100 g-soils, respectively. The relationship between sulfur uptake and free iron oxides is investigated and shown in Fig. 2. With higher content of free iron oxides, the larger sulfur uptake is observed. Additionally, a good R^2 value could be obtained between sulfur uptake and free iron oxides, suggesting free iron oxides play an important role to react with H_2S . Although other red soil series have lower breakthrough time compared to LP. Nevertheless, they can reduce the concentration of H_2S below to 10 ppm before breakthrough. These findings conclude that the red soils can be considered as a candidate sorbent for the removal of H_2S from coal gas. Since the LP series has better sulfur capacity, therefore, LP series is chosen as a candidate and is carried out the experiments for the sequence of this study.

3.2. Effect of sulfidation temperature

To understand the effect of sulfidation temperature on the removal of H_2S , LP red soil was performed at different temperature ranges of 673–873 K and is shown in Fig. 3. Obviously, the breakthrough time decreases significantly with increasing sulfidation temperature. The sulfur uptakes are evaluated approximately 1.39, 1.83 and 1.89 g-S/100 g-soils for 873, 773 and 763 K, respectively. This finding is consistent with the results

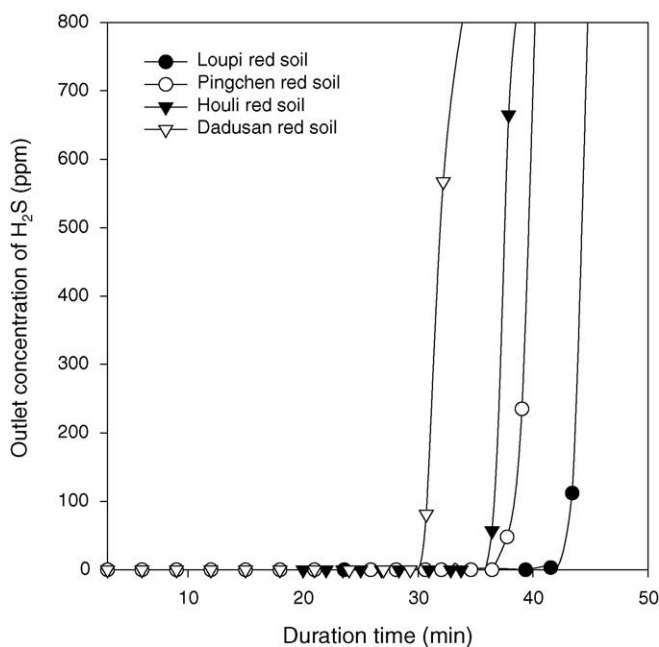


Fig. 1. Breakthrough curves for H_2S removal using various red soil as sorbents at 773 K (3 g of red soil loading, $\text{WHSV} = 2000 \text{ ml h}^{-1} \text{ g}^{-1}$, flow = 100 ml min^{-1} , 1% H_2S ; CO 25%; H_2 15%; with balance N_2).

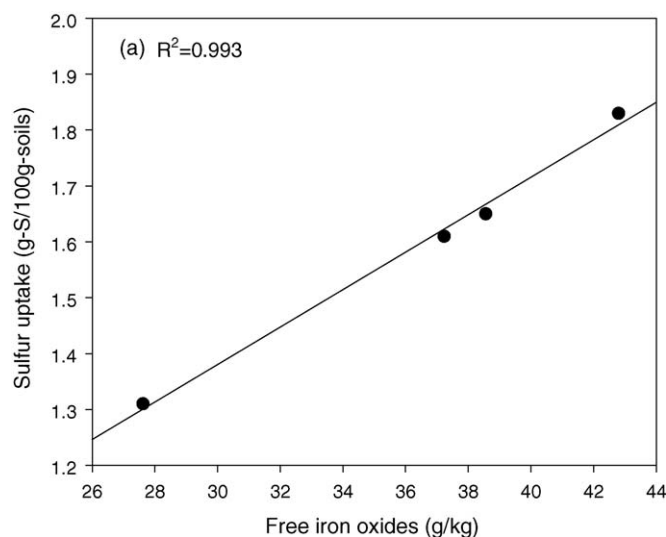


Fig. 2. The relationship between sulfur uptake and free iron oxide content.

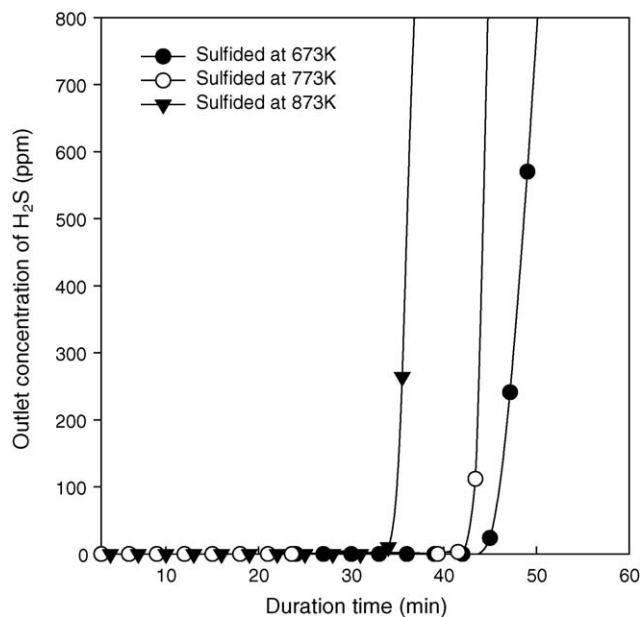
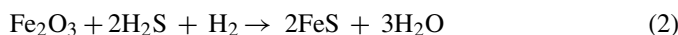
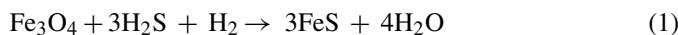


Fig. 3. Effect of the sulfidation temperature on sulfidation behavior with LP red soil (3 g of red soil loading, WHSV = 2000 ml h⁻¹ g⁻¹, flow = 100 ml min⁻¹, 1% H₂S; CO 25%; H₂ 15%; with balance N₂).

obtained by Yumura and Furimsky, in which the results showed that breakthrough time decreased from 32 to 15 min as the temperature increased from 873 to 1023 K when Fe₂O₃ was used as a hot coal gas desulfurization sorbent [19]. Interestingly, a high temperature has a detrimental effect on the removal of H₂S. Although iron oxides have high sulfur sorption capacity and are highly reactive towards H₂S, such reactions are limited to a low-Btu coal gas and temperatures lower than 773 K. A higher temperature (>773 K) detrimentally affects the reaction of H₂S because Fe₂O₃ or Fe₃O₄ is reduced to FeO in a reduction atmosphere at high temperatures. The FeO has been shown to have an unfavorable reaction with H₂S [20,21]. To explain this result, the equilibrium constants for sulfidation reaction with various iron oxides were calculated based on thermodynamic. Fig. 4 presents the equilibrium constants as a function of temperature in sulfidation conditions with various iron oxides. In this figure, (1), (2) and (3) denote Fe₃O₄, Fe₂O₃ and FeO, respectively. Their sulfidation reactions are speculated and expressed as follows:



As seen from the figure, the sulfidation equilibria of Fe₃O₄ and Fe₂O₃ are vastly superior to that of FeO. In a reduction atmosphere, iron oxides initially suffer reduction and following is sulfidation reaction. However, if the temperature exceeds 773 K, Fe₃O₄ will be reduced to wüstite (FeO), an unfavorable reactant with H₂S.

This result seems unfavorable for the use red soil as a sorbent at high temperatures. However, recent studies have revealed that desulfurization system components become prohibitively expensive as the operating temperature increases and the opti-

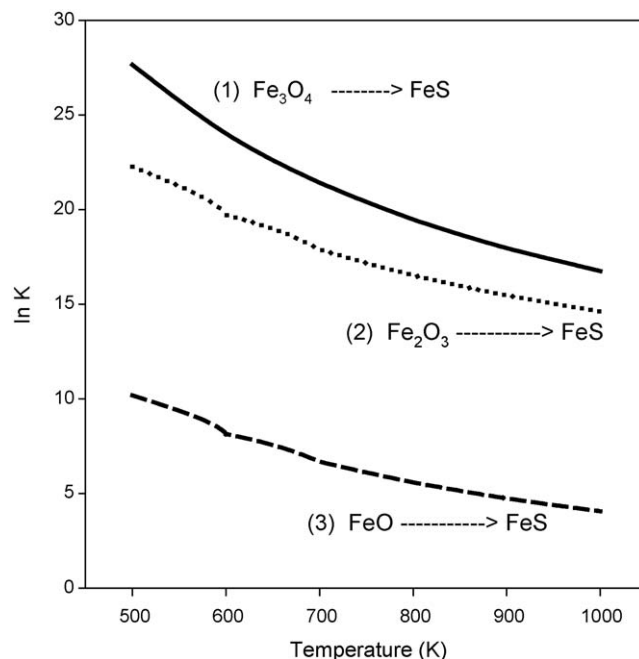
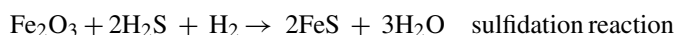


Fig. 4. Equilibrium constants for the removal of H₂S with various iron oxides.

imum desulfurization temperature is controlled between 623 and 823 K [22,23]. Over such a range of temperatures, the efficiency of the process and its technical viability reduce the overall cost of the process. Additionally, many sorbents can reduce the concentration of H₂S below the maximum tolerable level (less than 10 ppm) because the thermodynamic equilibrium is favorable from 623 to 823 K. These findings are evidence that red soil can be developed as a suitable sorbent for high temperature removal of H₂S from coal gas.

3.3. Influence of carbon monoxide and hydrogen

In addition to hydrogen sulfide, carbon monoxide and hydrogen are the main products of coal gasification. Their influence on sulfidation is crucial. Fig. 5 shows the influence of carbon monoxide and hydrogen on the breakthrough curve. The concentration of carbon monoxide and hydrogen are varied from 0% to 40%. In the carbon monoxide run, the feed gas consists of 1% H₂S, 15% H₂, a variable proportion of CO and the balance is N₂. In the hydrogen run the feed gas consists of 1% H₂S, 25% CO, with a variable proportion of H₂ and the balance is N₂. As shown, breakthrough times are depended on the concentrations of carbon monoxide and hydrogen. Although carbon monoxide and hydrogen are reduction gases, they have opposite influence on sulfidation behavior. Carbon monoxide has a positive effect and hydrogen appears to have a negative effect, which is consistent with our previous study [24]. These positive and negative effects can be explained by the water-shift reaction and sulfidation reaction:



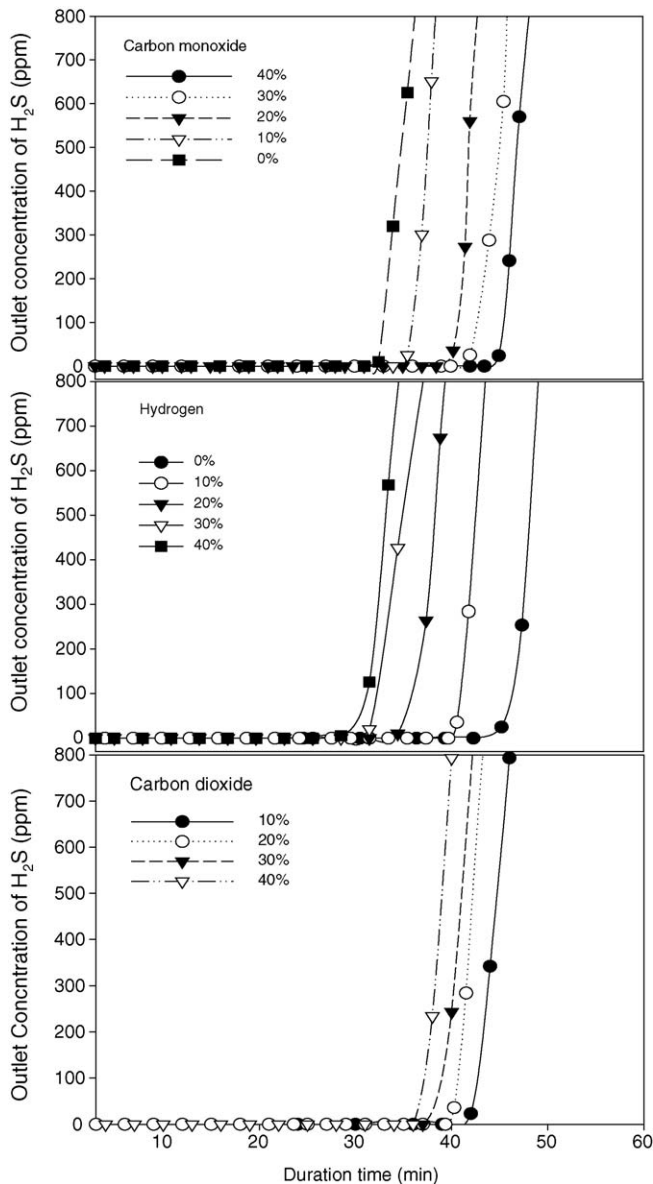


Fig. 5. H₂S breakthrough curves for LP red soil in 10 sulfidation/regeneration cycles (3 g of red soil loading, WHSV = 2000 ml h⁻¹ g⁻¹, flow = 100 ml min⁻¹, 5% O₂ with balance N₂).

During the sulfidation stage, the outlet gases were introduced to an on-line FTIR and was confirmed that the presence of CO₂ and H₂O, indicating that the water-shift is taken place at the operation conditions [25]. As the concentration of carbon monoxide is increased, the water-shift reaction favors toward right side according to LeChatelier's principle, implying that H₂O is consumed via water-shift reaction. A lower H₂O content favors the sulfidation reaction, therefore, increasing the concentration of carbon monoxide enhances desulfurization progress. On the other hand, increasing the concentration of hydrogen favors the left side of the water-shift reaction, resulting in the formation of H₂O. Similarly, the progress of sulfidation is inhibited by the formation of excess H₂O from the water-shift reaction associated with sulfidation.

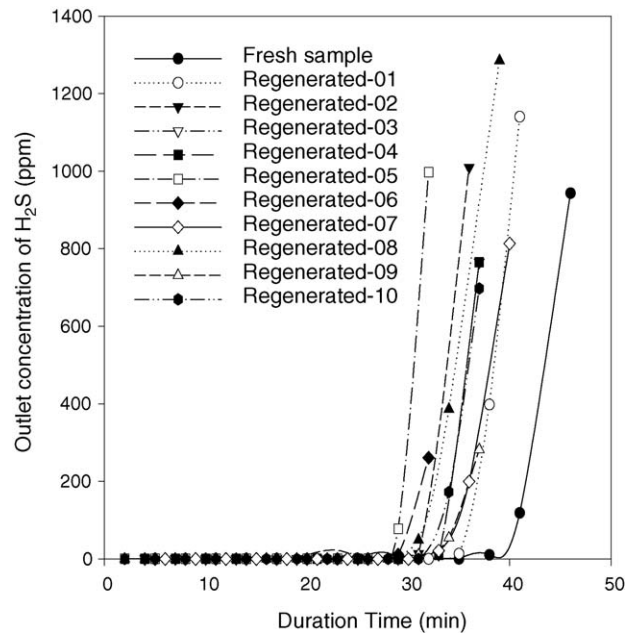


Fig. 6. Effect of the concentrations of carbon monoxide and hydrogen for the removal of H₂S at 773 K (3 g of red soil loading, WHSV = 2000 ml h⁻¹ g⁻¹, flow = 100 ml min⁻¹, 1% H₂S and balance N₂).

On the basis of this theory, it is expected that increasing the concentration of carbon dioxide will inhibit sulfidation. The sulfidation experiment was performed in various concentrations of carbon dioxide (from 0% to 40%) to test this hypothesis. As expected, carbon dioxide appears to have a negative effect, corresponding to the hypothesis of the water-shift reaction.

3.4. Evaluation of durability of LP red soil

The durability of the sorbent is a key point in determining its commercial attractiveness. Regeneration experiments were carried out with diluted air to prevent an intensely exothermic reaction and sintering. In this study, a regeneration experiment was carried out at 773 K using a gas with 5% O₂ and the balance N₂. Fig. 6 plots sulfidation breakthrough curves for each of 10 successive sulfidation/regeneration cycles. The time required for the fresh red soil to take on the appearance of H₂S was approximately 40 min, about 36 min in cycle 01 and about 31 min in cycle 10. The breakthrough time decreased slightly as the cycle number increased. Although the breakthrough time decreased slightly, however, the efficiency of regeneration remained as high as 70% and the breakthrough time of the 10 cycles was between 31 and 36 min.

3.5. Thermodynamic considerations for carbonyl sulfide formation

Although the simulated gas includes only hydrogen sulfide, an additional significant sulfur compound was detected after breakthrough in the effluent gas. This compound was identified as carbonyl sulfide (COS) via analysis of FPD and on-line FTIR.

The evolution of H₂S and COS curves in Fig. 7 show that COS is an effluent gas whose breakthrough curve is similar to

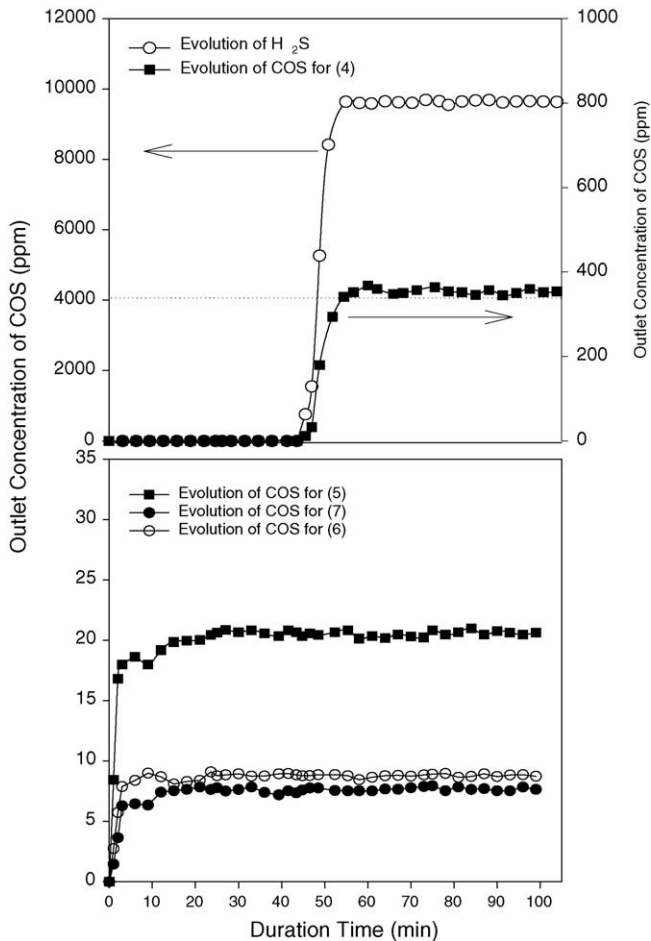
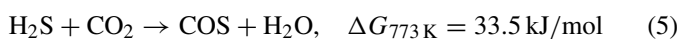


Fig. 7. Evolution of H₂S and COS during the sulfidation test. (Dash-line represents equilibrium concentration of COS for reaction (4).)

that of H₂S. COS is seen to be absent from the outlet gas until H₂S breakthrough. After breakthrough, COS is detected in effluent gas, because in the presence of red soil, sulfidation reaction is thermodynamically favorable. To further understand the formation mechanism of COS, COS is assumed to be formed in a gas reaction and a gas–solid reaction during sulfidation. Gas and gas–solid reactions that form COS are described as follows:

Gas reaction



Gas–solid reaction

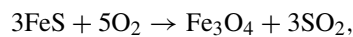


Clearly, higher concentration of COS is formed in the gas reaction than that in the gas–solid reaction, which yields a very low COS concentration. This result also can be explained via thermodynamic properties. The equilibrium constants at 773 K for reactions (4)–(7) are 0.022, 5.82×10^{-3} , 1.16×10^{-5} and 1.17×10^{-5} , respectively. These values indicate that the thermodynamics of the gas reaction are more favorable than those

of the gas–solid reaction. The concentration of COS appears to be a steady state at about 60 min, approaching 370 ppm. This value is slightly higher than the equilibrium COS concentration of 367 ppm calculated under operation conditions. This finding implies that COS may be formed in the gas reaction, and mostly from the reaction of H₂S and CO.

3.6. Characterization of fresh, sulfided and regenerated red soil

X-ray diffraction was used to determine the crystalline phases in the red soils. Table 2 describes the crystalline phases of the fresh, sulfided and regenerated red soils (after 10 cycles). In the case of fresh red soil, the major crystalline phases are hematite, goethite, kaolinite, quartz, gibbsite, micas and illite. Unlike hematite and goethite, kaolinite, quartz, gibbsite, micas and illite are not active materials for H₂S, these clay minerals act as carriers and enhance the dispersion of hematite, further increasing the collision frequency between iron oxide and hydrogen sulfide. The crystalline phases of the sulfided red soil, corresponding to the first sulfidation run show the presence of the expected major sulfided specie, FeS (iron sulfide) and without FeS₂ (iron pyrite). Al₂O₃ was also detected by XRD, having been formed, by the thermal decomposition of gibbsite at high temperature. Maghemite and magnetite are found in regenerated red soils, indicating that FeS is converted to iron oxides and regeneration reaction is complete. However, hematite is not detected after regeneration, implying that regeneration reaction may proceed via the following reaction:



$$\Delta G_{773\text{K}} = -1434.12 \text{ kJ/mol}$$

Remarkable, a spinel structure FeAl₂O₄ was detected by XRD at $2\theta = 18.2^\circ$. This spinel phase was also found after regeneration in a previous study [26], in which Fe₂O₃ was used as the candidate sorbent supported on γ -Al₂O₃, such material is inactive for H₂S removal at high temperature. This result suggests that free iron oxides partially form spinel structure with aluminum during the regeneration process. As shown, the free iron content of the regenerated red soil is less than that of the fresh sample. Approximately 11.8% of the free iron oxide is disappeared after regeneration, showing that the formation of the spinel phase, AlFe₂O₄, resulting from the reaction of free iron oxides and aluminum in the regeneration process.

Table 2 also shows the BET surface area and the diameter of pores of the fresh, sulfided and regenerated red soils. The BET surface area is lowest and pore diameter highest in the regenerated red soil perhaps because the micropores were sintered at high temperature, so only slight sintering occurred. Approximately 80% of the surface area of BET is maintained after regeneration, indicating that sintering is insignificant. On the other hand, no significant change was found in the SEM observation (not shown). In the case of EDS, indeed, we have observed the presence of sulfur after sulfidation process. This confirms that the H₂S is removed by red soil and sulfur is well dispersed in the surface of the red soil.

Table 2
Characterization of crystalline phase, pore structure and free iron oxide content of fresh, sulfided and regenerated red soil

Red soil status	Crystalline phase	BET surface area (m ² /g)	Average pore diameter (Å)	Carbon ^a (%)	Free iron oxide (g/kg)
Fresh	α-Fe ₂ O ₃ (Hematite) γ-FeOOH (Goethite) Si ₂ Al ₂ O ₅ (OH) ₄ (Kaolinite) SiO ₂ (Quartz) Al(OH) ₃ (Gibbsite) Micas Illite	31.4	111.3	1.8	42.8
Sulfided	FeS (Mackinawite) Si ₂ Al ₂ O ₅ (OH) ₄ (Kaolinite) SiO ₂ (Quartz) Al ₂ O ₃ Micas Illite	21.4	171.2	4.0	41.3
Regenerated	γ-Fe ₂ O ₃ (Maghemite) Fe ₃ O ₄ (Magnetite) FeAl ₂ O ₄ (Hercynite) Si ₂ Al ₂ O ₅ (OH) ₄ (Kaolinite) SiO ₂ (Quartz) Al ₂ O ₃ Micas Illite	25.4	174.6	2.4	37.8

^a Determinated by elemental analysis.

Carbon contents in different status for LP red soils were also measured and recorded. Red soils contain organic matter and, carbon represented of 1.76% of the fresh red soil. Over double that amount of carbon is found in the sulfided red soil, implying that large copious quantities of soot are formed during the sulfidation experiment and probably ascribe to the disproportionation of CO to CO₂ and C [27,28]. Some of carbon is oxidized by oxygen during regeneration process, and the carbon content of regenerated red soil is lower than that of sulfided sample but higher than that of fresh sample.

Although red soils undergo some changes in structures such as the formation of a spinel phase, some free iron oxides disappears and soot is formed. The removal efficiency of up to 70% is retained after 10 cycles of regeneration. This result indicates that red soil can be used as an effective regenerable sorbent for removal of hydrogen sulfide from coal gas at high temperatures.

4. Conclusions

High temperature removal of hydrogen sulfide from coal gas by means of natural red soil was conducted to assess their feasibility in a laboratory-scale fixed-bed reactor. Results obtained from breakthrough curves reveal that the tested red soils are capable of achieving less than 10 ppm H₂S concentration in appropriate operation conditions. In the sulfidation temperature range of 673–873 K, it is shown that the breakthrough time is decreased with sulfidation temperature for red soil.

After regeneration, the desulfurization efficiency maintains approximately 70% compared to the fresh sample. No huge deterioration occurs in the regeneration process. The desulfurization efficiency is related with CO and H₂ content. CO is a positive effect, while H₂ is negative effect. This result can be explained

via water-shift reaction. From the analyses of XRD and DCB, the content of free iron oxides decreases after regeneration process and probably is associated with the formation of spinel, AlFe₂O₄.

Appreciable amount of by-product, COS, is formed after breakthrough and this is identified through the gas reaction. On the basis of the knowledge of thermodynamic and calculation, the major reaction for COS formation is attributed to the interaction of CO and H₂S.

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