

Research Article

Tea Garden Lateritic Soil as a High-Temperature Desulfurization Sorbent: Effect of Oxygen on Regeneration Process

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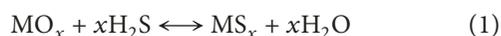
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The lateritic soils collected from a tea garden were used to explore the regeneration process using different O₂ contents for high-temperature desulfurization. The desulfurization and regeneration experiments were carried out using a fixed-bed reactor at 500°C and the gaseous mixture composed of 1% H₂S, 25% CO, 15% H₂, and balance N₂ for the desulfurization process. Experimental results showed that the regenerability is better when the air was used as a regeneration gas and the regeneration time is shortened. Multiple regeneration experiments indicated that lateritic soils can be regenerated by passing air and can thus be reused many times and its regeneration efficiency is slightly better than that regenerated by 1% O₂. The sulfur capacity after air desulfurization/regeneration cycles was examined by elemental analysis with a value ranging from 1.40% to 1.49%, and residual sulfur was detected with a value of 0.12% after the diluted 1% O₂ regeneration. No sulfur was detected for the regenerated lateritic soil after air regeneration. From NMR structural identification, the 6-coordinated octahedral structure of Al and trioctahedral coordinated Si are the major Al-containing and Si-containing compounds. Broad shoulder peaks were detected after regeneration process that may be associated with the formation of aluminosilicate and further reduces the dispersion of iron on the surface of lateritic soils.

1. Introduction

Hot coal gas desulfurization (HGD) is an essential procedure for advanced power generation system, such as the integrated gasification combined cycle (IGCC) and solid oxide fuel cell (SOFC) technologies. One of the crucial criteria in the development of the HGD for IGCC and SOFC is the need for a high sulfur capacity, low overall cost, high utilization, eco-friendly, and regenerable sorbent [1, 2]. Based on the investigation of previous studies, Fe, Cu, Zn, Mn, V, and Co oxides have been paid much attention because of their thermodynamic feasibility, reactivity, and regeneration property [3–6]. The basic desulfurization scheme is expressed by the following reaction:



where MO and MS are the mean metal oxides and metal sulfides, respectively.

Regeneration is an important procedure in the HGD system. Through the regeneration reaction, the metal sulfides can be completely converted into metal oxides, and thus, the metal oxides can be used for numerous cycles. The scheme of regeneration reaction can be represented as follows:



where MS and MO are the mean metal sulfides and metal oxides, respectively. Considering the overall operating cost, the regeneration process has to be operated at high temperature with diluted oxygen to avoid the exothermic reaction and further causes a deactivation of metal oxides. This shortcoming of use of diluted oxygen leads to a long-time regeneration reaction. In the past, we have investigated a series of laterites on the application of high-temperature desulfurization, and the results indicated that laterites are the potential material for high-temperature desulfurization [7, 8].

To our knowledge, no research was reported on the effect of regeneration process for high-temperature desulfurization using laterites. Therefore, the regeneration process of laterites applied for high-temperature desulfurization was evaluated; some regenerating process parameters including different O₂ concentrations, regenerating cycles, and the gaseous product of regenerating reaction were examined. Characterization of lateritic soil before and after regeneration process using different O₂ contents was also performed with several spectroscopic techniques for the investigation of the structural change.

2. Materials and Experimental Procedure

The lateritic soil used in this study was collected from a tea garden in Taiwan. After sampling, unwanted materials such as leaves, plant roots, and small gravel were removed from soil samples and dried at room temperature for a week. Before use, the lateritic soils were ground with an agate mortar and sieved to pass through a 2 mm sieve. The contents of total iron oxides and free iron oxides were 18.45% and 4.66% determined by the inductively coupled plasma analysis after digesting with aqueous regia and dithionite citrate bicarbonate (DCB) procedure [9]. The basic physicochemical properties of the lateritic soil are shown in Table 1.

The experiment was carried out in a bench-scale fixed-bed reactor at 500°C. 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. The quartz fibers were set in the reactor to support the lateritic soils. The gaseous mixture composed of 1% H₂S, 25% CO, 15% H₂, and a balance of N₂ from regulation cylinders. The air and diluted O₂ used in the regeneration process were supplied from the regulation cylinder. The diluted O₂ was prepared with 1% O₂ and a balance of N₂ (99.9% purity, San Fu). Two K-type thermocouples were inserted into the reactor to the positions at the top and bottom of the soil samples to enable the inlet and outlet temperatures to be accurately measured and controlled. Three grams of the lateritic soils was packed in the reactor for each run. The gas flow was controlled at a rate of 100 mL·min⁻¹. The inlet and outlet concentrations of H₂S were analyzed by an online 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 when the outlet concentration of H₂S reached 100 ppm. Following H₂S removal reaction, the reactor was purged with nitrogen gas for 15 min, and then the air and diluted O₂ (1%) were used for regeneration run. The regeneration experiment was terminated when the concentration of SO₂ in the effluent gas was below 50 ppm.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra spectrometer with a Mg K α X-ray radiation source (1253.6 eV). 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 pretreatment. 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 the least-squares method.

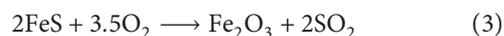
Elementar vario EL III Heraeus CHNOS Rapid F002, equipped with a flash combustion furnace and thermal conductivity detector (TCD), was used to measure the sulfur content of the lateritic soil before and after desulfurization and regeneration process.

Lateritic soil samples were examined with a Rigaku Model D/MAX III-V X-ray powder diffractometer (XRD) equipped with a Ni-filtered Cu K α radiation generated at 30 mA and 40 kV. The diffraction patterns were recorded from 10° to 80° with a scan rate of 3° min⁻¹. The solid-state ²⁷Al MAS (magic angle spinning) NMR and ²⁹Si MAS NMR spectra of the lateritic soil samples were recorded under 9.4 Tesla with operating frequencies of 79.4 and 104.2 MHz, respectively, on a Bruker Avance D SX400 spectrometer. Zirconia rotors were spun in air at 5 kHz.

3. Results and Discussions

First of all, it is very important to explore the effect of other metals on the desulfurization. It is reported that the Fe, Mn, Cu, Zn, and Co have the favorable thermodynamic property for high-temperature desulfurization [3–6]. In the past, we have investigated a great number of soil samples for high-temperature desulfurization, and some important information was proposed [10, 11]. The contents of Cu, Zn, and Co in the normal soil are relatively lower, and their contribution to desulfurization is lesser although they have excellent reactivity with H₂S. As shown in Table 1, the contents of Cu, Zn, Mn, and Co are relatively lower in comparison with Al, Si, and Fe. Therefore, the effect of Cu, Zn, Mn, and Co on desulfurization in this study could be ignored. On the other hand, it is well known that Al₂O₃ and SiO₂ are widely used as carrier (or supports) to prepare the supported catalyst in chemical engineering application because of good dispersion, porosity structure, and heat resistance. Lateritic soil contains large amounts of Al and Si, and due to the long-term weathering in nature, the distribution of Al and Si can be regarded as a homogeneous state and plays the carrier role to support Fe dispersed on the surface of lateritic soil. Our previous research showed that the desulfurization efficiency was less than 1% for lateritic soils after extracting Fe. This indicated that the major desulfurization reaction is attributed to the reaction of H₂S and Fe. The effect of Al and Si on desulfurization and regeneration could also be ignored [10, 11].

In the regenerating process, the product SO₂ is the major component to determine the extent of regeneration for sulfided sorbent. The formation of SO₂ is expressed as follows:



To understand the SO₂ evolution during the regeneration process, the sulfided lateritic soil was regenerated

TABLE 1: The basic physicochemical properties of the tea garden lateritic soil used in this study.

pH (H ₂ O)	Texture	Cu* (ppm)	Zn* (ppm)	Mn* (ppm)	Co* (ppm)	Al* (%)	Si* (%)	Fe* (%)	CEC (cmol·kg ⁻¹)	CBD-Fe (Fe ₂ O ₃) (%)	CBD-Mn (mg·kg ⁻¹)
4.2	Loam	64 ± 3	1621 ± 58	677 ± 42	26.2 ± 1.4	15.84 ± 1.05	21.52 ± 1.57	12.92 ± 1.14	7.8 ± 0.36	4.66 ± 0.22	225 ± 7

*The values were determined by ICP analysis after an aqua digestion at 120°C for 8 h.

with air and diluted O₂, and the outlet concentration of SO₂ was systematically recorded for the multiple regenerating cycles. As shown in Figure 1, the regeneration time ranged between 80 and 100 min when the diluted O₂ was used as a regenerating gas, whereas a very rapid regenerating time can be found when the air was used. This is due to the fact that the air contains more O₂ to increase the regeneration reaction and to shorten the regenerating time. On the other hand, the maximum SO₂ concentrations for diluted O₂ and air were 5612 ppm and 121,032 ppm, respectively. Based on the thermodynamic calculation of the reaction between FeS and O₂, the SO₂ equilibrium concentrations are 5,710 and 118,800 ppm when the diluted O₂ (1% O₂) and air were used as regeneration gases. This result revealed that air can be used as a regeneration gas to replace diluted O₂, and the regeneration reaction obeys (3).

Figure 2 shows the five consecutive regeneration cycles using diluted O₂ (1%) and air as regeneration gases. Note that the breakthrough time after air regeneration was slightly higher than that of the diluted O₂. The average breakthrough time for air regeneration ranged from 27.3 min to 29.9 min, whereas that for diluted O₂ regeneration ranged from 30.3 min to 32.4 min. For better understanding of the actual sulfur capacity in the lateritic soil after desulfurization reaction, the reacted lateritic soils were measured by the elemental analyzer (EA) for sulfur determination. The breakthrough time shown in Figure 2(a) for multiple air regeneration cycles is 32.4 min, 31.7 min, 30.3 min, 31.2 min, and 30.6 min in which sulfur capacity measured by EA is 1.49%, 1.46%, 1.40%, 1.44%, and 1.41%, respectively. For the diluted O₂ (1%) regeneration cycles, the sulfur capacity is 1.34%, 1.31%, 1.33%, 1.27%, and 1.26% which corresponds to the breakthrough time results. EA analysis demonstrated that the regeneration by air is better than that by diluted O₂ because of the higher sulfur content for air regeneration. For both cases, the breakthrough time appeared to have a slight decrease after the first regeneration process. No severe deactivation was observed after five consecutive regeneration cycles for different O₂ contents.

To understand the change in temperature during the regeneration process, the changes in temperature during the regeneration process using different O₂ contents were recorded. In the case of air, the temperature increased rapidly from 500°C to 750°C and remained around 2 min and then gradually decreased. For diluted O₂, the temperature rapidly increased from 500°C to 650°C and the temperature of 650°C maintained around 40 min, indicating that the operation with diluted O₂ has a lower regenerability compared to the air. The increase in temperature for both cases is attributed to the exothermic reaction. It is believed that the exothermic reaction will cause the increase in temperature and thus is beneficial to the regeneration reaction. Although

higher temperature is favorable for the regeneration reaction, it may cause a sintering effect and results in the deactivation of the lateritic soil after multiple regeneration cycles. A series of analyses in lateritic soil after different treatments are tabulated in Table 2. Note that no huge changes in surface area were observed. Approximately 15% and 20% BET surface area were lost after five consecutive cycles for diluted O₂ and air. This implies that the pore structure did not suffer from a severe damage, and the extent of sintering has little effect to the lateritic soil after multiple regeneration cycles. From the XPS analysis, the binding energy for all soil samples was around 711 eV, and the major iron species present in lateritic soil is in the form of Fe³⁺ and is assigned to hematite (α -Fe₂O₃). This result coincides with the observation of XRD, in which a small but detectable peak was measured at $2\theta = 33.21$. This finding strongly implies that the hematite is the major iron species present in the lateritic soil. Furthermore, as shown in Figure 3, a higher binding energy of S_{2p} was observed in the case of 1% O₂ regeneration. In general, two ranges of S_{2p} were commonly observed, namely, around 161–164 eV and 167–170 eV. The range of 161–164 eV is assigned to sulfide and elemental sulfur, whereas the range 167–170 eV is assigned to sulfite and sulfate [12–14]. Based on this information, it is suggested that the XPS spectrum of S_{2p} centered on 168.6 eV is assigned to sulfate. The formation of sulfate is attributed to the reaction between O₂ and FeS during the regeneration process. In the case of air, it is believed that the sulfate can be formed because of the thermodynamically favorable reaction between O₂ and metal sulfide. However, the maximum temperature of 750°C was found when the air was used as a regenerating gas. Under such high temperature, the sulfate is decomposed to SO₂ and metal oxides, and no sulfur species is detected through XPS analysis. From EA analysis, a trace amount of sulfur was detected with a value of 0.12% after the diluted O₂ (1%) regeneration. No sulfur was detected for the regenerated lateritic soil after air regeneration.

Additionally, ²⁷Al MAS NMR and ²⁹Si MAS NMR were also measured and are recorded in Table 1. The chemical shift of ²⁷Al for all soil samples detected at -0.6 ppm and 69 ppm was assigned to a 6-coordinated octahedral structure (Al⁶) and 4-coordinated tetrahedral structure (Al⁴). Al⁴ denotes the structure of aluminum with 3 nearest neighbor Si atoms. For all soil samples, the octahedral phase is the main structure, followed by the tetrahedral phase. With a regression fitting analysis, the proportion of Al⁶ is 82.4%, 75.8%, and 78.3% for fresh and both regenerated soil samples. The proportion of Al⁴ significantly increased and that of Al⁶ decreased after the regeneration reaction. The reasonable explanation of this finding is likely ascribed to the fact that coordination of aluminum underwent significant

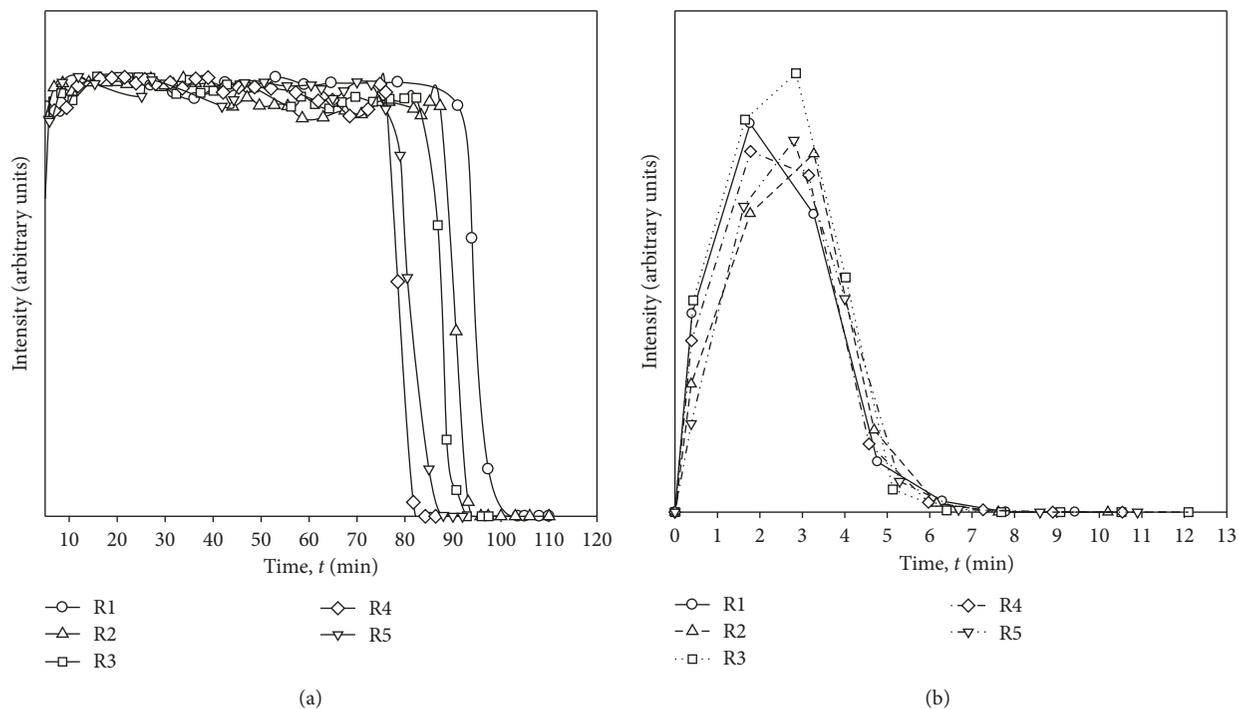


FIGURE 1: Evolution of SO_2 as a function of time using (a) diluted 1% O_2 and (b) air at 500°C .

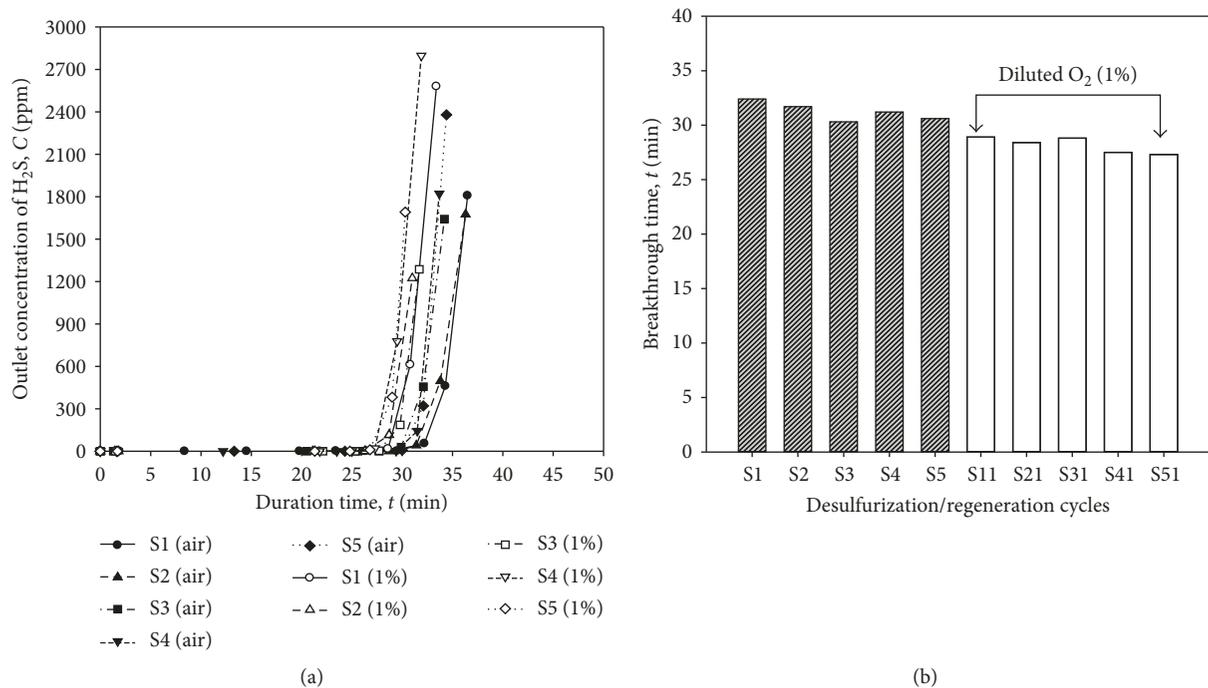


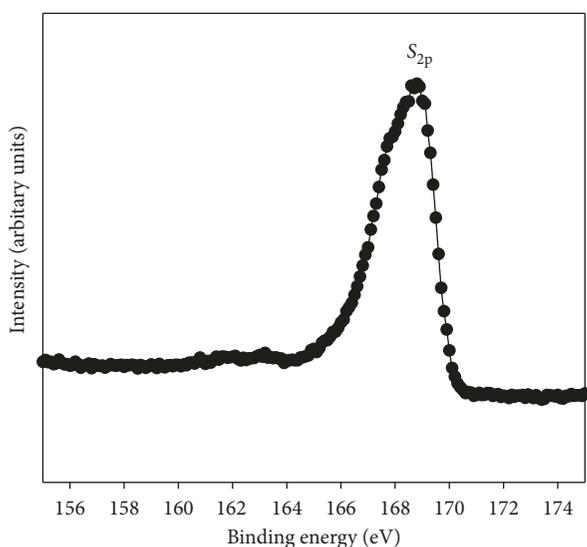
FIGURE 2: (a) Multiple regeneration cycles and (b) breakthrough time profile for different oxygen regeneration treatments.

changes resulting from the dehydroxylation or the formation of aluminosilicate under strong exothermic reaction from the regeneration process [15, 16]. For ^{29}Si NMR, a sharp peak located around -90 ppm was detected, which implies the presence of Q^3 (0 Al) linked to three Si atoms via bridging oxygen atoms and is characteristic of layered

silicates. No obvious signals centered between -103 ppm and -110 ppm were detected for fresh lateritic soil. The resonances between these ranges are associated with the Q^4 (0 Al) site corresponding to the presence of crystalline Si and Si-O-Si trioctahedral structure [17]. As shown in Figure 3, the resonance around -62 ppm was not detected for both

TABLE 2: Spectroscopic and surface area analyses of the lateritic soil under different regenerating operations.

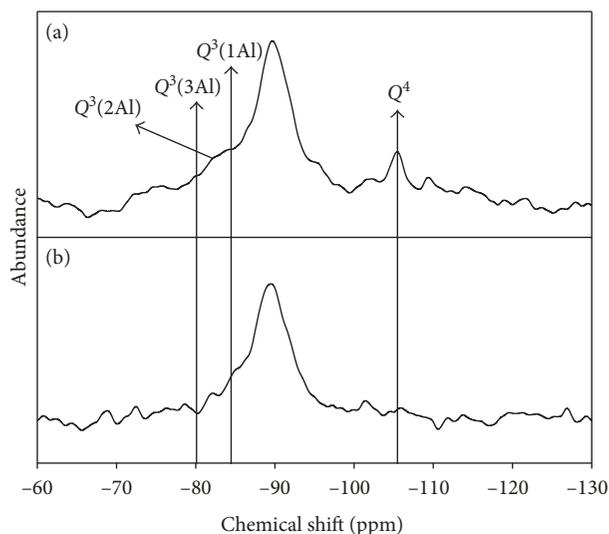
	Fresh soil	Air regeneration	1% O ₂ regeneration
BET surface area	31.4 m ² g ⁻¹	25.5 m ² g ⁻¹	26.3 m ² g ⁻¹
²⁹ Si NMR	Q ⁴ : 0% Q ³ : 87.6%	Q ⁴ : 18.3% Q ³ : 81.7%	Q ⁴ : 14.6% Q ³ : 85.4%
²⁷ Al NMR	Al ⁶ : 82.4% Al ⁴ : 17.6%	Al ⁶ : 75.8% Al ⁴ : 24.2%	Al ⁶ : 78.3% Al ⁴ : 21.7%
XRD	SiO ₂ α-Fe ₂ O ₃ (2θ = 33.2)	SiO ₂ α-Fe ₂ O ₃ (2θ = 33.2)	SiO ₂ α-Fe ₂ O ₃ (2θ = 33.2)
XPS	Fe _{2p} (711 eV)	Fe _{2p} (711.3 eV)	Fe _{2p} (711.2 eV) S _{2p} (168.6 eV)

FIGURE 3: XPS spectrum analysis of S_{2p} for the regenerated lateritic soil after diluted 1% O₂ regeneration.

soil samples, which indicated that no side reaction had taken place between Si and C to form a structure of Si-C linkage [18]. After regeneration process, a resolved signal located around -105 ppm was detected and can be assigned to Q⁴. Moreover, broad shoulder peaks located between -80 ppm and -85 ppm were detected for the regenerated soil. The appearance between these ranges is likely attributed to the Q³ (1 Al), Q³ (2 Al), and Q³ (3 Al), which demonstrates that the Si atoms are surrounded by Al atoms [19, 20]. The formation of Q³ structure linkage with Al atoms may be attributed to a portion of Al released in the free state and reacted with Si to form aluminosilicate minerals, which reflects on the existence of Q³ (1 Al, 2 Al, and 3 Al) detected in the ²⁹Si NMR spectra [21] (Figure 4).

4. Conclusions

It is concluded from this study that the air has a better regenerability than that of diluted O₂ in the regeneration process for high-temperature desulfurization. Spectroscopic

FIGURE 4: ²⁹Si NMR spectra of (a) regenerated soil sample treated by air and (b) fresh soil.

investigation revealed that there were no destructive changes in the structure of the lateritic soil after the regeneration process. From XPS and XRD analysis, it is found that the hematite (α-Fe₂O₃) is the main iron species after the regeneration process. The bonding and distribution between Si and Al were found to be different after the treatment of two regeneration gases. The Q⁴ distribution increased whereas Q³ distribution decreased after the regeneration process. The formation of Q³ structure linkage with Al atoms may be attributed to a portion of Al is released in the free state and reacted with Si to form aluminosilicate minerals.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Authors' Contributions

All authors have contributed to the intellectual content of this paper. Tzu-Hsing Ko conceived and designed the experiments and supervised the data analysis. Chen-Yao Chu carried out the experiments and analysis of the experimental results. Chen-Yao Chu wrote the paper and Tzu-Hsing Ko provided many suggestions and revised this paper. All authors have read and approved the final manuscript.

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