Investigation on the Cause of the SO₂ Generation during Hot Gas Desulfurization (HGD) Process

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Abstract: In the integrated gasification combined cycle (IGCC) process, the sulfur compounds present in coal are converted to hydrogen sulfide (H₂S) when the coal is gasified. Due to its harmful effects on sorbent/solvent and environmental regulations, H₂S needs to be removed from the product gas stream. To simulate the H₂S removal process, desulfurization was carried out using a dry sorbent as a fluidizing material within a bubbling, high-temperature fluidized bed reactor. The ZnO-based sorbent showed not only an excellent capacity of H₂S removal but also long-term stability. However, unexpected SO₂ gas at a concentration of several hundred ppm was detected during the desulfurization reaction. Thus, we determined that there is an unknown source that supplies oxygen to ZnS, and identified the oxygen supplier through three possibilities: oxygen by reactant (fresh sorbent, ZnO), byproduct (ZnSO₄), and product (H₂O). From the experiment results, we found that the H₂O produced from the reaction reacts with ZnS, resulting in SO₂ gas being generated during desulfurization. The unknown oxygen source during desulfurization was deduced to be oxygen from H₂O produced during desulfurization. That is, the oxygen from produced H₂O reacts with ZnS, leading to SO₂ generation at high temperature.

Keywords: hot gas desulfurization; hydrogen sulfide; sulfur dioxide; zinc oxide; H₂O

1. Introduction

The coal integrated gasification combined cycle (IGCC) emits sulfur in the form of hydrogen sulfide (H₂S) in the product gas [1–4]. It is necessary to clean the coal-derived H₂S gas in order to prevent gas turbine corrosion and to follow the strict regulations regarding pollutant emission. Recently, the research on power generation using natural gas, biogas, and reforming, etc. has been focused on the reduction of greenhouse gas emissions. These gases usually consist of several acidic pollutants, such as CO₂ and H₂S [5–8]. Generally, a typical chemical plant uses a wet desulfurization method, utilising amines as a sorbent at low temperatures, even though the wastewater treatment after the absorption process is a major problem. On the other hand, hot gas desulfurization (HGD) is regarded as a clean technology that scrubs the concentration of sulfur compounds to one-tenth of the original levels and improves the power generation efficiency at the same time, due to the sulfur compound removal. Various dry desulfurization sorbents (including Zn, Ca, Mn, Fe, Cu, and Ni-based sorbents) have been studied for high removal efficiency over HGD [9–17]. In recent years, most studies have mainly focused on the regenerability and durability of desulfurization sorbents. Additionally, many efforts have been made to find the cause of sulfate formation and zinc volatilization during desulfurization. Although numerous studies on desulfurization are being conducted, there are few studies...
on SO\(_2\) generation during desulfurization. In addition, the reason for SO\(_2\) generation is still unknown [18–20]. There are some studies reporting that the formation of SO\(_2\) is due to the reaction between the side products (ZnSO\(_4\)) of the desulfurization and H\(_2\)O [21–27]. Park et al. [25,26] also observed SO\(_2\) during desulfurization over the reaction between the reducing gases (CO and H\(_2\)) and ZnSO\(_4\), which was produced during the regeneration of sorbent under conditions of a low regeneration temperature and an excessive O\(_2\) injection. The reaction is shown in Equation (1).

\[
\text{ZnSO}_4 + \text{CO(} or \text{H}_2\text{)} \rightarrow \text{ZnO} + \text{SO}_2 + \text{CO}_2 \text{ (or H}_2\text{O)} \quad (1)
\]

Sasaoka et al. [23,24] studied the effect of H\(_2\)O on ZnS formation during desulfurization using a temperature-programed reduction (TPR), reporting that the formation of SO\(_2\) was caused by the reaction of formed ZnS with H\(_2\)O at temperatures above 450 °C, as shown in Equations (2) and (3).

\[
\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \quad (2)
\]

\[
\text{ZnS} + 3\text{H}_2\text{O} \rightarrow \text{ZnO} + \text{SO}_2 + 3\text{H}_2 \quad (3)
\]

Even though there are a few studies that identified the presence of SO\(_2\) during desulfurization, the exact cause of SO\(_2\) gas generation has not yet been investigated.

In this study, experimental investigation was performed to find the reason for the SO\(_2\) generation problems during the desulfurization, as well as the formation of ZnSO\(_4\), a side reaction product. First, the effect of the presence of H\(_2\)O and reducing gases on the SO\(_2\) generation during desulfurization was investigated under both the N\(_2\) and reducing syngas in a fluidized bed reactor. In addition, the effect of the presence of H\(_2\)O only was investigated to identify the detailed HGD reaction mechanism. Based on the experimental works, a more scientific understanding for the SO\(_2\) generation during desulfurization was obtained.

2. Results and Discussion

Figure 1 shows the result of desulfurization and SO\(_2\) generation over fresh sorbent (ZnO) with H\(_2\)S gas (4000 ppm) at temperatures from 500 °C to 650 °C. As shown in Figure 1, no SO\(_2\) gas was produced at below 500 °C, whereas SO\(_2\) gas was formed above 550 °C, even though the removal rate of H\(_2\)S was 100%. This is possibly because SO\(_2\) gas was generated over the oxidation of sulfur compound with an unknown source of oxygen when the ZnS was converted to Zn or ZnO. The SO\(_2\) production rate increased as the operating temperature increased. Even in the absence of oxygen, the SO\(_2\) generation phenomenon indicates that there were other causes of SO\(_2\) generation during ZnS regeneration. To determine the unknown source of oxygen and the conditions for SO\(_2\) generation, experiments were conducted under various conditions.

![Figure 1](image-url). Effect of temperature on SO\(_2\) generation of fresh sorbent in the desulfurization process with 4000 ppm H\(_2\)S.
During the desulfurization, the possible oxygen sources were from (1) oxygen contained in sorbent (ZnO), (2) oxygen from a side product (ZnSO₄) during desulfurization, and (3) oxygen from H₂O generated during desulfurization. Experiments were carried out to investigate the sources of oxygen.

First, an experiment was conducted to check whether the oxygen was from the ZnO sorbent, as shown in Figure 2. The sulfided sorbent (ZnS) and fresh sorbent (ZnO) were mixed at a ratio of 1:1, and then we evaluated whether SO₂ gas was generated at 550 °C with N₂ atmosphere. The presence of SO₂ gas would indicate that ZnS was regenerated by ZnO, resulting in the generation of SO₂. We confirmed that no SO₂ gas was generated at 550 °C for 100 min under the N₂ condition. SO₂ gas was detected following regeneration under 3 vol. % O₂ at 650 °C, but no SO₂ gas was produced at 550 °C under N₂ atmosphere. From this result, we concluded that the ZnO was not an oxygen supplier for the generation of SO₂ because the SO₂ gas was not detected after holding ZnS with ZnO at the high temperature of 550 °C.

![Figure 2. Effect of oxygen in the sorbent itself on the SO₂ generation.](image)

Secondly, the formation of ZnSO₄ was analyzed using X-ray diffraction (XRD) to determine whether the SO₂ generation was from a side reaction of the desulfurization. Figure 3 shows the XRD patterns of the sorbents (SC-229TD, before and after the first desulfurization, after the first regeneration, and after the second desulfurization). The desulfurization was conducted at 550 °C and 4000 ppm H₂S. Then, the sorbent was regenerated at 650 °C under a 3% O₂ condition. As shown in the XRD patterns, the ZnO peak was mainly assigned in the fresh sorbent, and some NiO peak was found. Al- or Si-based compounds used as support were not detected. In the case of the sulfided sorbent, unreacted ZnO, sulfided ZnS, and NiS were found in the XRD patterns. The SiO₂ peaks identified in the XRD patterns were the inert material (sand) mixed with sorbent. In the sorbent after regeneration, the ZnS and NiS peaks disappeared as they existed as ZnO and NiO, which were in the same phase as before the desulfurization reaction. From these results, it can be concluded that the ZnSO₄ phase was not produced by side reactions during the desulfurization and regeneration, which leads to the conclusion that the generation of SO₂ gas was not by ZnSO₄.
Thirdly, an experiment was carried out by injecting H$_2$O using a water pump to investigate the effect of H$_2$O on the SO$_2$ production. Figure 4 shows the results of SO$_2$ generation over the sulfided sorbent with the temperature range from 475 °C to 650 °C with 20% H$_2$O (N$_2$ balance). The maximum concentrations of SO$_2$ were 20 ppm at 550 °C, 100 ppm at 600 °C, and 200 ppm at 650 °C. An increase in temperature shortened the initial time of SO$_2$ generation and increased the concentration of SO$_2$ with the presence of water vapor. The sulfided sorbent emitted SO$_2$ at 550 °C and above, although oxygen gas was not present. The formation of SO$_2$ was due to the reaction between the ZnS and injected H$_2$O, which led to the regeneration of ZnS to ZnO. A previous work reported that the presence of water vapor can prevent the formation of ZnSO$_4$ because it promotes the conversion of sulfate (SO$_4^{2-}$) to sulfite (SO$_3^{2-}$), which is easier to be decomposed or removed from the surface of sorbent than sulfate species [28]. Figure 5 shows the effect of temperature on the consumption of reactant, and the generation of products during the regeneration by H$_2$O, using Outukumpu HSC 5.1 software. The concentrations of ZnS and H$_2$O decreased from about 450 °C, and the product SO$_2$ gas was also produced without oxygen during the regeneration. The desulfurization was thermodynamically favorable at the lower temperature. The activity of the reaction gradually decreased above 450 °C. Although the temperature was set for desulfurization, the regeneration over H$_2$O started from 450 °C. The concentration of products (SO$_2$, H$_2$, ZnO, and H$_2$S) increased as the temperature increased. These results indicate that the regeneration of ZnS
is thermodynamically possible, even at the desulfurization temperature, when water is present. Additionally, the results gained using the HSC 5.1 software are consistent with the results shown in Figure 4. From these results, it can be concluded that the H$_2$O produced from desulfurization was the major oxygen supplier, which is reactive with ZnS, leading to SO$_2$ generation during desulfurization.

Figure 4. Effect of temperature on the SO$_2$ generation in HGD process with 20% H$_2$O balanced by N$_2$.

An additional experiment was carried out to confirm SO$_2$ generation under the condition of actual reducing gases (CO and H$_2$), as shown in Figure 6. The desulfurization of...
3600 ppm H$_2$S was conducted at 550 °C under the reducing gas mixture (6.5% CO, 2.95% H$_2$, 0.15% CO$_2$, and N$_2$ balance). In the absence of reducing gases, ZnS was regenerated to ZnO by H$_2$O produced during desulfurization. Additionally, SO$_2$ gas was generated, as shown in Figure 5, whereas the ZnS was not regenerated during desulfurization in the presence of reducing gases.

![Figure 6. Variation in gas composition in the desulfurization process using 3600 ppm H$_2$S containing reducing gas (6.5% CO, 2.95% H$_2$, 0.15% CO$_2$ balanced by N$_2$).](image)

It is expected that the H$_2$O generated during desulfurization can be formed over the water gas shift (WGS) reaction with reducing gases as shown in Equation (4).

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4)$$

However, the production of H$_2$ through the WGS reaction was very low, as the amount of H$_2$O (the reactant term) was already at a very low concentration due to a low concentration of H$_2$S for desulfurization (3600 ppm). As shown in Figure 6, the concentrations of CO and H$_2$ were detected as being as low as below 1% at the beginning of the reaction. The CO$_2$, injected at a concentration of 0.15%, increased to 2%. Due to the lower reduction temperature of NiO than ZnO, NiO can be partially reduced to Ni metal over the reducing gases of CO and H$_2$ by producing CO$_2$ gas (4). Additionally, as shown in Equations (5)–(8), the ZnS does not produce SO$_2$ because it is reduced by CO or H$_2$ [28–31].

$$\text{ZnS} + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{S} \quad (5)$$

$$\text{ZnS} + \text{CO} \rightarrow \text{Zn} + \text{COS} \quad (6)$$

$$\text{ZnO} + \text{COS} \rightarrow \text{ZnS} + \text{CO}_2 \quad (7)$$

$$\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2 \quad (8)$$

Various possibilities were considered for the reason behind SO$_2$ generation during the desulfurization of H$_2$S. It is clear that ZnS was able to be regenerated by H$_2$O, resulting in the production of SO$_2$ in the N$_2$ atmosphere. However, in the reducing gas stream, H$_2$O can actively participate in the WGS reaction. Additionally, the metal oxide sorbent can be reduced by CO and H$_2$. Thus, the SO$_2$ gas was not produced under the simulated syngas
stream. Further study is needed to check whether the desulfurization sorbent affects the reduction gas composition beside the H$_2$S removal.

3. Materials and Methods

SC-229TD sorbent, manufactured by Korea Electric Power Corporation Research Institute (KEPCO RI) was used as a high-temperature desulfurization sorbent. The major components of the sorbent are active materials (40–50 wt% ZnO, 5–10% NiO) and support (Al$_2$O$_3$, SiO$_2$). The SC-229TD sorbent was sieved to have a controlled particle size from 106 to 212 µm. The bulk density was 1001.64 kg/m$^3$. The sorbent or mixture of sorbent and sand (weight ratio, 1:9) were filled to the height of 0.4 m in a fluidized bed reactor. Air was injected at 400 °C for 1 h to remove moisture and impurities before the desulfurization. The desulfurization experiment was started when no gases were detected, except for the balance gas of N$_2$. The detailed conditions of the experiment are shown in Table 1.

Table 1. Experimental conditions of desulfurization.

| H$_2$S Desulfurization | Regeneration |
|------------------------|-------------|
| Temperature (°C)       | 450–650     | 650         |
| Pressure               | ambient     | ambient     |
| Flow rate (mL/min)     | 2000        | 2000        |
| H$_2$S: 0.4, or H$_2$S: 0.36 |
| Gas composition (Vol.%)| CO: 6.5,    | O$_2$: 3,    |
|                        | H$_2$: 2.95, | N$_2$: balance |
|                        | CO$_2$: 0.15, |             |
|                        | N$_2$: balance |             |

Figure 7 shows the batch fluidized bed reactor used in this study. The fluidized bed reactor consists of a main reactor, a gas and water injection system, an electric furnace for maintaining the reactor temperature, and an on-line gas analyzer for analyzing the concentration of exhaust gas. The main reactor is made of stainless steel (SUS 310) with an inner diameter of 0.05 m, a thickness of 0.003 m, and a height of 0.7 m. The temperature of the reactor was controlled based on the internal temperature of the reactor (K-type thermocouple), by using an electric furnace temperature with a temperature indicator. The temperature was measured at a height of 0.2 m from the bottom of the reactor. The differential pressure of the fluidized bed was measured by installing a differential pressure transducer and pressure indicator at a height of 0.01 m and 0.58 m from the reactor bottom. The H$_2$S gas was supplied to the reactor using a mass flow controller (MFC) for desulfurization. The operating temperature range was from 450 °C to 650 °C. For the sorbent regeneration, O$_2$ gas (3 vol.%) was used. The outlet gases from the reactor were automatically analyzed in real time with an on-line gas analyzer (Hartmann & Braun Co., Advance Optima) [32]. In addition, thermodynamic equilibrium data were calculated using the HSC 5.1 program. The ratio of ZnS and H$_2$O was assumed to be 1:1, and was calculated on the basis of 1 bar from 200 to 700 °C.
Figure 7. Schematic diagram of the experimental setup used with a batch type fluidized bed reactor for the HGD process.

4. Conclusions

In the integrated gasification combined cycle (IGCC) process, the sulfur compounds present in coal are converted to hydrogen sulfide (H\textsubscript{2}S) when the coal is gasified. Due to the corrosive properties of H\textsubscript{2}S, it deactivates the sorbent/solvent for CO\textsubscript{2} capture, due to its harmful effects; its release to the environment is also subject to environmental regulations. Thus, H\textsubscript{2}S needs to be removed from the produced gas stream. To simulate the H\textsubscript{2}S removal process, the desulfurization reaction was carried out using dry sorbent in a fluidized bed reactor at high temperatures. The ZnO-based sorbent used in this work showed not only an excellent capacity, but also long-term stability. However, SO\textsubscript{2} gas at a concentration of several hundred ppm was measured during the desulfurization process, where it was found that SO\textsubscript{2} gas was generated when the desulfurized ZnS was converted to Zn or ZnO by reacting with an unknown source of oxygen during desulfurization. The unknown oxygen source during desulfurization was deduced to be oxygen from H\textsubscript{2}O produced during desulfurization. That is, the oxygen produced from H\textsubscript{2}O reacted with ZnS, leading to SO\textsubscript{2} generation at a high temperature.

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References

1. Ben-Slimane, R.; Hepworth, M.T. Desulfurization of hot coal-derived fuel gases with manganese-based regenerable sorbents. 1. Loading (sulfidation) tests. *Energy Fuels* 1994, 8, 1175–1183. [CrossRef]

2. Cheah, S.; Carpenter, D.L.; Magrini-Bair, K.A. Review of mid- to high-temperature sulfur sorbents for desulfurization of biomass- and coal-derived syngas. *Energy Fuels* 2009, 23, 5291–5307. [CrossRef]

3. Feng, Y.; Mi, J.; Wu, M.; Shangguan, J.; Fan, H. In situ preparation and regeneration behaviors of zinc oxide/red clay desulfurization sorbents. *Energy Fuels* 2017, 31, 1015–1022. [CrossRef]

4. Giuffrida, A.; Romano, M.C. On the Effects of Syngas Clean-Up Temperature in Igccs, ASME Turbo Expo 2010: Power for Land, Sea, and Air, 2010; American Society of Mechanical Engineers: New York, NY, USA, 2010; pp. 661–670.

5. Nakhjiri, A.T.; Heydarinasab, A.; Bakhtiarz, O.; Mohammadi, T. Numerical simulation of CO$_2$/H$_2$S simultaneous removal from natural gas using potassium carbonate aqueous solution in hollow fiber membrane contactor. *J. Environ. Chem. Eng.* 2020, 8, 104130. [CrossRef]

6. Wang, J.; Song, Z.; Cheng, H.; Chen, L.; Deng, L.; Qi, Z. Multilevel screening of ionic liquid absorbents for simultaneous removal of CO$_2$ and H$_2$S from natural gas. *Sep. Purif. Technol.* 2020, 248, 117053. [CrossRef]

7. Raabe, T.; Mehne, M.; Rasser, H.; Krause, H.; Kureti, S. Study on iron-based adsorbents for alternating removal of H$_2$S and CO$_2$ from natural gas and biogas. *Chem. Eng. J.* 2019, 371, 738–749. [CrossRef]

8. Zulkifi, N.N.; Masdar, M.S.; Wan Isahak, W.N.R.; Abu Bakar, S.N.H.; Abu Hasan, H.; Mohd Sofian, N. Application of response surface methodology for preparation of znac2/cac adsorbents for hydrogen sulfide (H$_2$S) capture. *Catalysts* 2021, 11, 545. [CrossRef]

9. Gupta, R.P.; Gangwal, S.K.; Johnson, E.W. Integration and Testing of Hot Desulfurization and Entrained-Flow Gasification for Power Generation Systems. Volume 2, Evaluation of Zinc Loss from Zinc Titanate Sorbents during Hot Gas Desulfurization: Final Report, 1 October 1987–31 October 1993; Texaco Montebello Research Lab.: Montebello, CA, USA, 1993.

10. Huang, L.; Wang, G.; Qin, Z.; Dong, M.; Du, M.; Ge, H.; Li, X.; Zhao, Y.; Zhang, J.; Hu, T. In situ xas study on the mechanism of reactive adsorption desulfurization of oil product over Ni/ZnO. *Appl. Catal. B Environ.* 2011, 106, 26–38. [CrossRef]

11. Jung, S.Y.; Jun, H.K.; Lee, S.J.; Lee, T.J.; Ryu, C.K.; Kim, J.C. Improvement of the desulfurization and regeneration properties of mgo-based sorbents promoted with alkali metal nitrates at high pressure for the sorption enhanced water gas shift process. *Process Saf. Environ. Prot.* 2018, 116, 219–227. [CrossRef]

12. Jung, S.Y.; Lee, S.J.; Lee, T.J.; Ryu, C.K.; Kim, J.C. H$_2$S removal and regeneration properties of zn–al-based sorbents promoted with various promoters. *Catal. Today* 2006, 111, 217–222. [CrossRef]

13. Jung, S.Y.; Lee, S.J.; Park, J.J.; Lee, S.C.; Jun, H.K.; Lee, T.J.; Ryu, C.K.; Kim, J.C. The simultaneous removal of hydrogen sulfide and ammonia over zinc-based dry sorbent supported on alumina. *Sep. Purif. Technol.* 2008, 63, 297–302. [CrossRef]

14. Kim, H.N.; Lee, D.-H.; Lee, S.-Y.; Hwang, T.-S.; Ryu, H.-J. Reaction characteristics of wgs catalyst for sewgs process in a pressurized fluidized bed reactor. *Trans. Korean Hydrog. New Energy Soc.* 2012, 23, 337–345. [CrossRef]

15. Ko, T.-H.; Chu, H.; Chaung, L.-K. The sorption of hydrogen sulfide from hot syngas by metal oxides over supports. *Chemosphere* 2005, 58, 467–474. [CrossRef] [PubMed]

16. Hwang, B.W.; Lim, J.H.; Chae, H.J.; Ryu, H.-J.; Lee, D.; Lee, J.B.; Kim, H.; Lee, S.C.; Kim, J.C. CO$_2$ capture and regeneration properties of mgo-based sorbents promoted with alkali metal nitrates at high pressure for the sorption enhanced water gas shift process. *Process Saf. Environ. Prot.* 2018, 116, 219–227. [CrossRef]

17. Barba, D. Catalysts and processes for H$_2$S conversion to sulfur. *Catalysts* 2021, 11, 903. [CrossRef]

18. Lee, J.B.; Ryu, C.K.; Yi, C.K.; Jo, S.H.; Kim, S.H. Screening of zinc-based sorbents for hot-gas desulfurization. *Energy Fuels* 2008, 22, 1021–1026. [CrossRef]

19. Lee, T.J.; Kwon, W.T.; Chang, W.C.; Kim, J.C. A study on regeneration of zinc titane sorbents for H$_2$S removal. *Korean J. Chem. Eng.* 1997, 14, 513–518. [CrossRef]

20. Park, N.-K.; Jung, Y.-K.; Kim, B.-S.; Ryu, S.-O.; Lee, T.-J.; Kim, K.-S. Behavior of zinc based sorbents for hot gas desulfurization. *Theor. Appl. Chem. Eng.* 2002, 8, 4493–4496.

21. Siritwardane, R.V.; Gardner, T.; Poston, J.A.; Fisher, E.P.; Miltz, A. Spectroscopic characterization of nickel containing desulfurization sorbents. *Ind. Eng. Chem. Res.* 2000, 39, 1106–1110. [CrossRef]

22. Seo, J.-H.; Beak, C.; Kwon, W.; Ahn, J.; Cho, K. Trends in research and technical development of sorbents for hot gas desulfurization for H$_2$S removal. *J. Korean Inst. Resour. Recycl.* 2016, 25, 14–27.

23. Sasaoka, E.; Hatori, M.; Yoshimura, H.; Su, C.; Uddin, M.A. Role of H$_2$O in oxidation of spent high-temperature desulfurization sorbent Fe$_2$O$_3$ and cux in the presence of O$_2$. *Ind. Eng. Chem. Res.* 2001, 40, 2512–2517. [CrossRef]

24. Sasaoka, E.; Hatori, M.; Sada, N.; Uddin, M.A. Role of H$_2$O in oxidative regeneration of zns formed from high-temperature desulfurization zno sorbent. *Ind. Eng. Chem. Res.* 2000, 39, 3844–3848. [CrossRef]

25. Park, N.-K.; Lee, Y.J.; Han, G.B.; Ryu, S.O.; Lee, T.J. Preparation and reactivity test of nano size ZnO for hot gas desulfurization. *Theor. Appl. Chem. Eng.* 2006, 12, 540–543.

26. Park, N.-K.; Lee, D.H.; Lee, J.-D.; Chang, W.C.; Ryu, S.-O.; Lee, T.-J. Effects of reduction of metal oxide sorbents on reactivity and physical properties during hot gas desulfurization in igcc. *Fuel* 2005, 84, 2158–2164. [CrossRef]

27. Park, N.-K.; Lee, D.H.; Jun, J.H.; Lee, J.D.; Ryu, S.O.; Lee, T.J.; Kim, J.-C.; Chang, C.H. Two-stage desulfurization process for hot gas ultra cleanup in igcc. *Fuel* 2006, 85, 227–234. [CrossRef]
28. Siriwardane, R.V.; Woodruff, S. Ftr characterization of the interaction of oxygen with zinc sulfide. *Ind. Eng. Chem. Res.* **1995**, *34*, 699–702. [CrossRef]

29. Yu, J.; Chang, L.; Li, F.; Xie, K. A review on research and development of iron-based sorbents for removal of hydrogen sulfide from hot coal gases. *Front. Chem. Eng. China* **2010**, *4*, 529–535. [CrossRef]

30. Westmoreland, P.R.; Gibson, J.B.; Harrison, D.P. Comparative kinetics of high-temperature reaction between hydrogen sulfide and selected metal oxides. *Environ. Sci. Technol.* **1977**, *11*, 488–491. [CrossRef]

31. Wen, Y.; Wang, G.; Wang, Q.; Xu, C.; Gao, J. Regeneration characteristics and kinetics of Ni/ZnO–SiO$_2$–Al$_2$O$_3$ adsorbent for reactive adsorption desulfurization. *Ind. Eng. Chem. Res.* **2012**, *51*, 3939–3950. [CrossRef]

32. Siriwardane, R.V.; Poston, J.A. Interaction of H$_2$S with zinc titanate in the presence of H$_2$ and CO. *Appl. Surf. Sci.* **1990**, *45*, 131–139. [CrossRef]