



High temperature hydrogen sulfide adsorption on activated carbon

II. Effects of gas temperature, gas pressure and sorbent regeneration

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Received 30 March 1999; accepted 30 October 1999

Abstract

Several types of activated carbon sorbents were evaluated for removal of H₂S at high temperatures (400–600°C) in an integrated gasification combined cycle (IGCC) power generation process. Part I of this series of papers discussed the effects of gas composition and metal addition. Here we examine the effects of gas temperature, gas pressure and sorbent regeneration. Adsorption experiments with a zinc-impregnated activated carbon sample produced almost identical breakthrough times at varied temperatures (400–600°C). High pressure (10 atm) adsorption experiments showed significantly longer breakthrough times at 10 atm compared to 1 atm. Gaseous H₂ sample regeneration was found to be the most effective regeneration method of the variety of methods analyzed, with all previously H₂S adsorbed sulfur being removed in a H₂ regeneration experiment. While additional research is necessary to further evaluate sample regeneration and multi-cycle adsorption/regeneration, results of temperature and pressure effect experiments are encouraging for IGCC applications. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Activated carbon; B. Surface treatment, Gasification; C. Adsorption

1. Introduction

In part I of this series of papers a short introduction was given detailing the motivation behind this research [1]. In brief, the purpose of this research was to determine the viability of using carbon-based sorbents for removal of H₂S at high temperatures (400–550°C) in an integrated

gasification combined cycle (IGCC) power generation process. In the past decade, much research has focused on using metal-based sorbents for H₂S removal in IGCC processes, but to our knowledge, no researchers have examined using carbon-based sorbents for high temperature sulfur removal [2]. In part I, we detailed the methods used to prepare the activated carbon sorbents, showed which sorbents had the greatest potential as a high temperature sulfur sorbent, and examined the effects of inlet gas composition on H₂S capacity for various activated carbon sorbents. Here we examine the effects of gas temperature and pressure on H₂S adsorption capacity. Also, since any sorbent to be used in an IGCC process must be regenerable due to economic considerations, we will examine methods for removing chemically bound sulfur from the activated carbon sorbents, so that the sorbents can be reused.

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2. Experimental

2.1. Materials

The activated carbon sorbents used for high temperature (400–600°C) H₂S adsorption in this study were prepared from an Illinois bituminous coal (IBC-102). The sorbents were subjected to various chemical treatments, such as nitric acid (HNO₃) oxidation, metal (Zn and Cu) impregnation, and thermal desorption of oxygen functional groups to determine the best sorbent for high temperature H₂S adsorption. Detailed procedures for preparing the activated carbon samples were presented in part I of this series [1].

2.2. High pressure H₂S adsorption experiments

The sorbent materials were tested in a laboratory scale high temperature and high pressure (HTHP) fixed-bed reactor at the Research Triangle Institute (RTI) in Research Triangle Park, North Carolina. The experimental set-up consisted of a gas delivery system, a fixed-bed reactor, and a gas analysis system. In the gas delivery system, a simulated fuel gas of a desired composition was generated using compressed gas cylinders, mass flow controllers (MFCs), and high pressure syringe pumps. Steam was added to the mixed dry gas by vaporizing liquid water and injecting it into the gas stream at a controlled rate using a high pressure syringe pump. The reactor is a 1.0-cm inner diameter stainless steel pipe with a porous alumina plate at the bottom to support the sorbent. The inside of the reactor was Alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. Pressure inside the reactor was controlled by a back pressure regulator (BPR) and measured using an electronic pressure sensor. Thermocouples were positioned to measure the temperatures of the preheated feed gas, the sorbent bed, and the product gas. Tests were conducted with a simulated coal gas containing (vol.%) 12% H₂, 18% CO, 6% CO₂, 0.55% H₂S, 5% H₂O, and balance N₂. Outlet H₂S concentration was monitored using a gas chromatograph (GC). Steam in the gas was condensed out before the gases were sent to the GC.

A typical run consisted of loading 4 cm³ of the carbon-based sorbent and heating the reactor to a desired temperature of 550°C with continuous flow of N₂ at the desired pressure. Once the desired temperature was attained, the flow of fuel gas to the reactor was started and the concentration of H₂S was measured periodically in the effluent gas. When the H₂S concentration reached ~500 ppmv, the run was stopped. In all the runs, space velocity (SV) remained constant at 2000 h⁻¹ (2000 scm³/cm³/h). At the end of the run, the sorbent was cooled in N₂ and removed from the reactor. A gas chromatograph (GC) with a flame photometric detector was used to measure the sulfur gases in the reactor effluent. Gas samples were taken

approximately every 3 min with the GC to generate H₂S breakthrough curves.

2.3. Regeneration experiments

Several types of regeneration experiments, both liquid and gas phase, were performed during this study. Possible methods for carbon sorbent regeneration that were investigated included air, steam, air and steam, HNO₃, KOH, thermal desorption, and H₂. SO₂, elemental sulfur, and H₂S are possible useful products of regeneration. After an H₂S adsorption experiment had been conducted and the sulfur content of a sample had been determined, a sample could then be used in a regeneration experiment.

Aqueous regeneration mainly focused on treatment of sulfided carbon sorbents with hydrogen peroxide (H₂O₂) and HNO₃. Selected samples were placed in a beaker and mixed in an aqueous solution to remove chemically adsorbed sulfur. For regeneration experiments with H₂O₂, 30% by volume H₂O₂ was used. Typically, 30 ml of H₂O₂ in H₂O were added to a beaker containing 3 g of activated carbon sample and continuously stirred. The solution reacted vigorously and exothermically and raised the solution temperature to 70°C for ~20 min. Once the reaction slowed, 30 ml more of H₂O₂ in H₂O were added. This was repeated several times for some of the regeneration experiments. Repeated H₂O₂ treatment was found to degrade carbon sorbents and reduce their average particle size. Regeneration experiments with HNO₃ were performed in a continuously stirred beaker with 30 ml HNO₃ and 3 g activated carbon sample. The HNO₃-activated carbon solution was heated at 70°C for 1 h. Regeneration in potassium hydroxide (KOH) was also performed in a continuously stirred beaker. About 30 ml of a 1.3 M solution of KOH was used with 3 g of activated carbon. The KOH-activated carbon solution was mixed for 1 h. Total sulfur was measured after regeneration experiments to determine how much sulfur was removed and compared to the sulfur content before regeneration.

Other selected activated carbon samples that had already adsorbed H₂S were used in gas phase regeneration experiments. A 2–5 g sample of sulfided sample was thermally desorbed to 925°C in N₂ to determine if the added sulfur would be released simply by adding heat. Thermal desorption and all gas phase regeneration experiments were performed with the quartz reactor experimental set-up described in part I of this series [1]. A mass spectrometer (MS) monitored the reactor effluent gas for most regeneration experiments. Regeneration experiments with 2–5 g of sulfided sample were also performed with O₂ in N₂. O₂ concentration was varied between 3 and 20%, temperature was varied between 200 and 400°C, and gas flow rate was varied between 100 and 500 cm³/min. The concentration of SO₂ released was measured by the MS. Regeneration experiments with 50% steam (in N₂) and 50% steam (in

N₂) with 6% O₂ were also performed. Total sulfur was measured to determine how much sulfur was removed.

The final method for sulfided activated carbon regeneration used gaseous H₂ to regenerate the sorbents. The experimental set-up was the same as for the previously described adsorption experiments, except that H₂ was the only influent gas [1,2]. A temperature programmed desorption (TPD) in H₂ was performed to determine the temperature at which the greatest concentration of H₂S was released from the sulfided sample. A previously sulfided sample in the quartz reactor was heated at 5°C/min to 850°C and the outlet gas concentration was monitored by the MS. H₂ regeneration experiments were performed using 2–5 g of sulfided activated carbon with varied heating rates, temperatures held constant at 400–850°C, and H₂ flow rates varied between 100 and 500 cm³/min. Samples were again tested for total sulfur content after regeneration.

2.4. Multiple cycle adsorption/regeneration experiments

Multiple cycle adsorption/regeneration experiments were performed during this study. H₂S was adsorbed by an activated carbon sorbent, as in previous adsorption experiments, regenerated with H₂, and then the samples were subjected to another H₂S adsorption cycle. The first adsorption experiment was performed using the same experimental procedures as in previous experiments (0.5% H₂S, 50% CO₂, 49.5% N₂, 1 atm, 550°C). The outlet H₂S was measured by the MS. Once a predetermined breakthrough concentration was reached, the experiment was stopped and a small portion of the sample was removed for total sulfur testing. The remaining sample was regenerated in H₂ as previously described and a small portion of the sample was again removed for total sulfur testing. The second cycle was performed using the same method as in the first cycle, with the H₂S outlet concentration being measured by the MS. After the second cycle, the sample was analyzed for total sulfur. The breakthrough curves were normalized to a SV of about 1700 h⁻¹, due to the sample bed becoming shorter after a portion was removed for sulfur testing.

3. Results and discussion

3.1. Breakthrough curve experiments

The H₂S adsorption breakthrough curves were obtained using the same methods as outlined in part I of this series. As stated previously, *breakthrough time* is the time required to reach 200 ppmv H₂S outlet concentration, which is a common standard at IGCC plants. In the breakthrough figures, all gas compositions are in percent by volume, *S* represents steam activated, *O* represents

HNO₃ oxidized, and *D* represents thermally desorbed in N₂ at 925°C. Lines representing H₂S outlet concentration versus time in breakthrough plots were smoothed once using graphing software.

3.2. Effect of total gas pressure on H₂S adsorption

Since commercial IGCC plants operate at total pressures of up to 20 atm, some activated carbon samples were tested under pressurized conditions at the Research Triangle Institute (RTI). Activated carbon samples were run at RTI at pressures of 1 and 10 atm and a reaction temperature of 550°C using a simulated coal gas stream containing 0.55% H₂S, 12% H₂, 5% H₂O, 18% CO, 6% CO₂, and balance N₂. SV for experiments at RTI was 2000 h⁻¹, which was slightly greater than 1700 h⁻¹ typically used for adsorption experiments at the Illinois State Geological Survey (ISGS) [1,2]. Although high pressure experiments were performed at 10 atm rather than 15–20 atm, which is the gas pressure that most sorbents operate at an IGCC plant, most of the effect of increase in pressure is found in the first 10 atm [3]. In general, activated carbon samples adsorbed more H₂S before breakthrough under high pressure conditions. These results are encouraging for carbon-based sorbent applications at IGCC plants.

All seven types of sorbents tested at RTI clearly performed better at 10 atm than 1 atm. Steam-activated carbon samples and HNO₃-oxidized samples did not perform well at RTI (Fig. 1). Steam-activated carbon at 10 atm had the longest breakthrough time at 44 min. A surprising result of the tests at RTI was the poor per-

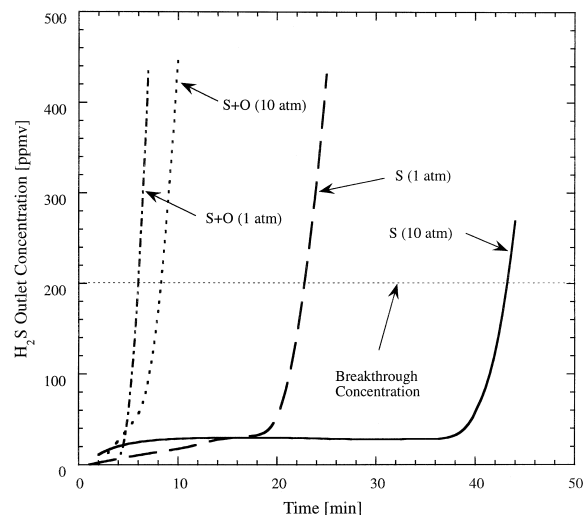


Fig. 1. Effect of pressure on H₂S breakthrough time of steam-activated and oxidized activated carbons. Gas composition: 0.55% H₂S, 12% H₂, 5% H₂O, 18% CO, 6% CO₂, balance N₂. *T* = 550°C; *P* = 1 and 10 atm.

formance of HNO_3 -oxidized samples. Results from experiments at ISGS consistently showed HNO_3 -oxidized samples performing better than steam-activated carbons, but the opposite was true for the experiments at RTI [1,2]. This result is currently not fully understood, but it may be because the gas composition for the RTI tests differed from the ISGS tests. As shown in part I of this series, high temperature adsorption of H_2S on carbon can vary greatly depending on the gas composition.

Metal-impregnated carbon-based sorbents tested at RTI exhibited longer breakthrough times during simulated coal gas H_2S adsorption experiments (Fig. 2). Zn-impregnated samples performed better than Cu-impregnated carbon. These samples clearly performed better at 10 atm than at 1 atm. H_2S breakthrough time for the Zn-treated carbon sample was 90 min at 1 atm and 150 min at 10 atm, which is an increase of about 60%. Similarly, the copper-treated carbon sample had a breakthrough of 80 min at 1 atm and 125 min at 10 atm, for an increase of about 50%. Sulfur deposited to these samples during H_2S adsorption under simulated coal gasification conditions ranged from 3.43 to 5.16% sulfur by weight. The best performing sample (S+O+0.83 wt.% Zn) adsorbed 5.16% sulfur by weight, which meets the 5% level of sulfur removal required at Tampa Electric's IGCC facility [4]. This percentage can be compared to a zinc titanate, which typically adsorbs about 15% sulfur by weight at 550–600°C [5].

ZnCl_2 chemically activated carbons were also tested for H_2S adsorption at RTI (Fig. 3). Two formulations of ZnCl_2 samples, using coal to ZnCl_2 weight ratios of 1:0.5 and 1:1, were tested at 1 atm and 10 atm. Different ZnCl_2

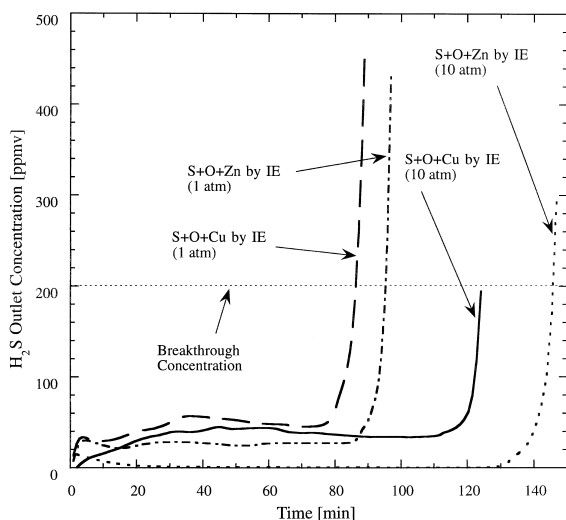


Fig. 2. Effect of pressure on H_2S breakthrough time of copper and zinc-impregnated activated carbons. Gas composition: 0.55% H_2S , 12% H_2 , 5% H_2O , 18% CO , 6% CO_2 , balance N_2 . $T=550^\circ\text{C}$; $P=1$ and 10 atm.

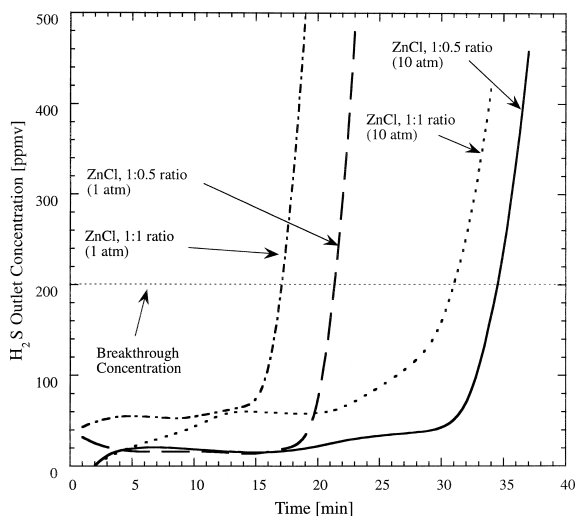


Fig. 3. Effect of pressure on breakthrough time of ZnCl_2 chemically activated carbon. Gas composition: 0.55% H_2S , 12% H_2 , 5% H_2O , 18% CO , 6% CO_2 , balance N_2 . $T=550^\circ\text{C}$; $P=1$ and 10 atm.

ratios had a minimal impact on H_2S breakthrough time. ZnCl_2 chemically activated carbons had a relatively poor H_2S breakthrough time with the best sample having a breakthrough time of 35 min (Fig. 3). Again, samples performed significantly better at 10 atm than at 1 atm. Preparation techniques for ZnCl_2 chemically activated samples had not been refined and only 0.52% Zn by weight was retained on the carbon after chemical activation. Refining the preparation of ZnCl_2 activated carbon may increase H_2S breakthrough time.

3.3. Effect of temperature on H_2S adsorption

Due to recent interest in lower temperature (350–500°C) applications for hot gas clean-up sorbents, the effect of temperature on H_2S adsorption was studied [4,6]. H_2S adsorption experiments were performed using the same batch of Zn-impregnated (by IE) carbon at ISGS (Fig. 4). Five experiments were performed with the temperature varying between 400 and 600°C using a simulated coal gas stream. Temperature variation had virtually no effect on breakthrough time. All breakthrough times were between 76 and 82 min. Consistent breakthrough times at varied temperatures can be explained by principles of chemical adsorption, i.e. an activation energy is required for chemical adsorption to occur and once that energy is supplied, the reaction proceeds. Physical adsorption of H_2S at ambient temperature is widely known to occur. H_2S adsorption performance remaining constant at lower temperatures (<550°C) is a positive result because of the probable application for H_2S sorbents at lower tempera-

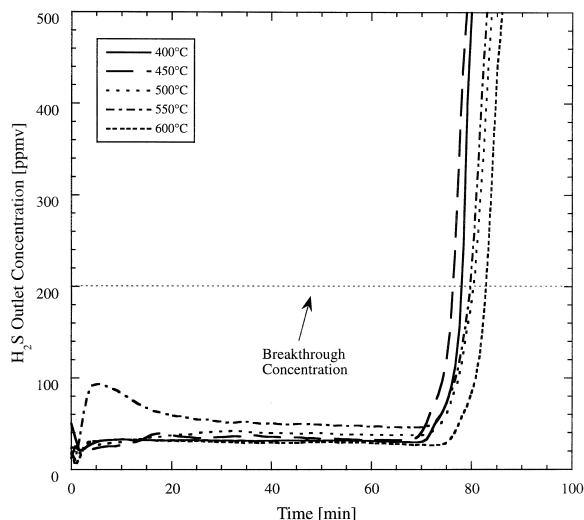
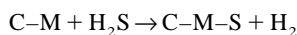
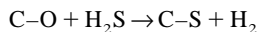
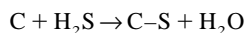


Fig. 4. Effect of temperature on breakthrough time of zinc-impregnated activated carbon. Gas composition: 0.5% H₂S, 13% H₂, 8.5% H₂O, 21% CO, 7.5% CO₂, balance N₂. *T* = 550°C; *P* = 1 and 10 atm.

tures (350–500°C). The performance of metal-based sorbents for H₂S adsorption greatly deteriorates as reaction temperature decreases (<500°C).

3.4. H₂S adsorption mechanisms

One advantage of carbon-based sorbents is that there are several mechanisms by which H₂S can be adsorbed. Firstly, sulfur can be adsorbed by carbon in an addition reaction involving sulfur and active carbon sites. Other researchers have shown evidence of this reaction and during this study H₂S adsorption by oxygen desorbed carbons illustrates this reaction [7–9]. Secondly, sulfur can be adsorbed by carbon–oxygen sites in a substitution reaction involving sulfur replacing oxygen in the carbon–oxygen bond. The more oxygen on the carbon, the greater the chance that this substitution reaction will occur. This substitution reaction has been noted by the authors and also by other researchers [1,2,7–9]. Thirdly, sulfur can be adsorbed by metals in a favorable addition reaction where sulfur bonds to an active metal (M). Reaction of H₂S is very favorable with some metals, so if more metal is present on an activated carbon, then more H₂S can be removed. An advantage of carbon-based sorbents over metal-based sorbents is that the carbon support matrix actively adsorbs H₂S, whereas metal sorbents such as zinc titanate have titanate as an inert support matrix. Having an active support matrix may provide a more mass efficient sorbent. In summary, the three major reaction mechanisms for H₂S removal by carbon-based sorbents are:



3.5. Sample regeneration

Regeneration of hot gas clean-up sorbents is necessary so that sorbents can be reused for repeated H₂S adsorption. Sulfur, in the form of solid sulfur or H₂SO₄, should be recovered as a useful product. According to feasibility studies, sorbents should be able to be used for hundreds of adsorption/regeneration cycles [4]. Regeneration of carbon-based sorbents is more challenging than that of metal-based sorbents, most of which will easily react with O₂ to produce a high concentration SO₂ stream. SO₂ or H₂S can be produced during regeneration and then converted to elemental sulfur or H₂SO₄. If a high concentration of SO₂ is produced during regeneration, a sulfuric acid plant may be used in conjunction with an IGCC plant. Conversion of a concentrated H₂S gas stream to elemental sulfur via the Claus reaction is also possible [10]. The carbon–sulfur bond is very stable and researchers have been trying for years to remove sulfur from coal so that high sulfur coal could be burned cleaner [7–9,11,12]. During the course of this research, numerous regeneration experiments were performed in the liquid and gas phase, to attempt to recover sulfur in a useful form after it had adsorbed to the carbon-based sorbents. Our regeneration experiments are summarized in Table 1.

Initial regeneration experiments were attempted with gaseous O₂ in gaseous N₂. Several temperatures, gas flow rates, and O₂ concentrations were used. While some of the sulfur was released as SO₂ (up to 5000 ppmv SO₂), only 5% of the adsorbed sulfur was removed from the carbon and the SO₂ outlet concentration did not rise to desired levels. Regeneration of carbon-based sorbents was performed with an inlet gas containing only N₂ in a reactor heated at temperatures up to 925°C. Regeneration/desorption in N₂ to 925°C removed 24.8% of the adsorbed sulfur. Adsorbed sulfur was released as SO₂, H₂S, and COS.

Regeneration experiments were performed in aqueous solutions containing H₂O₂, HNO₃, or KOH. The goal of this type of regeneration was to substitute the sulfur with oxygen, which would produce a regenerated, oxidized activated carbon. KOH and HNO₃ regeneration showed limited potential, removed 0.0 and 26.8% by weight of the adsorbed sulfur, respectively. Regeneration with H₂O₂ proved to be a more effective method. Up to 71.7% adsorbed sulfur was removed with repeated H₂O₂ treatment. One problem noticed with H₂O₂ regeneration was the reduction of activated carbon particle size after 1 h of H₂O₂ treatment. While H₂O₂ regeneration showed promise, the treatment appeared to be too harsh for the carbon sorbent. Pelletized carbon sorbents regenerated with H₂O₂ would break apart into a particle size similar to that of powdered activated carbon.

Table 1
Summary of sorbent regeneration experiments

Regeneration method	Phase (wt.%)	Maximum temp. (°C)	Starting sample type	Sulfur added by H ₂ S adsorption (wt.%)	Sulfur removed by regeneration (wt.%)	Sulfur removed (%)	Regeneration time (min)
3% O ₂ in N ₂	Gas	275	S	6.1	0.39	6.4	140
N ₂	Gas	925	S	10.5	2.6	24.8	190
30% H ₂ O ₂	Liquid	60	S+O	10.8	4.6	42.2	60
1.3 M KOH	Liquid	25	S+O	10.8	0.0	0.0	60
70% HNO ₃	Liquid	70	S+O	10.8	2.9	26.8	90
30% H ₂ O ₂	Liquid	70	S+O+D	6.5	4.6	71.7	90
100% H ₂	Gas	800	S	5.3	4.1	77.2	180
100% H ₂	Gas	850	ZnCl ₂ , ratio 1:1.5	19.4	17.6	90.7	180
100% H ₂	Gas	850	ZnCl ₂ , ratio 1:0.5	10.7	12.3	100	260
100% H ₂	Gas	800	S+O+Zn	10.5	7.6	72.5	200

Of the regeneration methods examined in this study, the most promising method was with gaseous H₂. Several H₂ regeneration experiments were performed at various temperatures and gas flow rates. H₂ regeneration removed between 72 and 100% of adsorbed sulfur (Table 1). In one experiment, 19.4% by weight sulfur was added to the carbon during adsorption and 90.7% of the added sulfur was removed by H₂ regeneration. Another experiment removed 100% of H₂S adsorbed sulfur and plus some of the initial sulfur in the coal. A chemically activated ZnCl₂ sample, had a sulfur content of 3.6% by weight before H₂S adsorption, 23% after H₂S adsorption, and 1.95% after H₂ regeneration. A profile of H₂S released during the regeneration of a ZnCl₂ chemically activated carbon is shown in Fig. 5. This illustrates that H₂ regeneration of sulfided activated carbon can be very effective.

Sulfur was released in a high concentration of H₂S

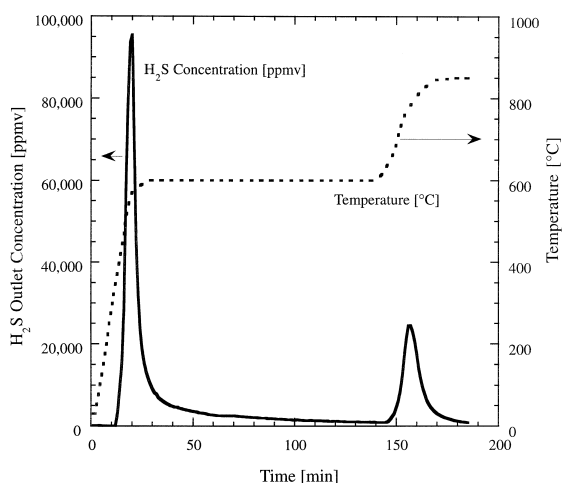


Fig. 5. Regeneration of sulfided ZnCl₂ chemically activated carbon with H₂.

during H₂ regeneration. After adsorbing 0.5% H₂S by volume from a simulated coal gas stream, H₂ regeneration produced H₂S at up to 10% H₂S by volume. An advantage of H₂ regeneration is that the largest amount of sulfur was released at a temperature at or below the adsorption temperature (550°C). High concentrations of H₂S can be converted to elemental sulfur via the direct sulfur recovery process (DSRP) [10]. One possible drawback of using H₂ regeneration at an IGCC plant is H₂'s low compressibility ratio, which could require very large H₂ storage capability on site. H₂ is also expensive and is a valuable byproduct of coal gasification. Only preliminary H₂ regeneration experiments were performed, so improvements to the H₂ regeneration procedure are possible.

Multiple cycle adsorption experiments were performed during this study. Two initial experiments were performed to determine whether prepared carbon-based samples would adsorb additional amounts of H₂S after one adsorption cycle followed by H₂ regeneration. Multiple cycle adsorption experiments used the same experimental set-up and inlet gases as the H₂S adsorption experiments [1]. One experiment had a second cycle breakthrough time of less than 30 min, but the other experiment with a ZnCl₂ chemically activated carbon had a fairly significant second cycle breakthrough time of about 80 min.

A multiple cycle experiment is shown in Fig. 6. After an H₂S adsorption experiment, the ZnCl₂ chemically activated sample was regenerated using H₂, and then adsorbed H₂S again. While the breakthrough time dropped from 150 to 75 min from the first to second cycle, 75 min was still a significant breakthrough time and showed progress. SV for the test were linearly normalized to 1700 h⁻¹ since the sample used during the second cycle had a significantly higher SV due to a portion of the sample being removed for sulfur content testing between cycles. It should be noted that preparation of ZnCl₂-activated carbon has not been refined, H₂ regeneration is still in its early stages, and these were initial multiple cycle tests. Considering this, we anticipate better results when the procedure is refined.

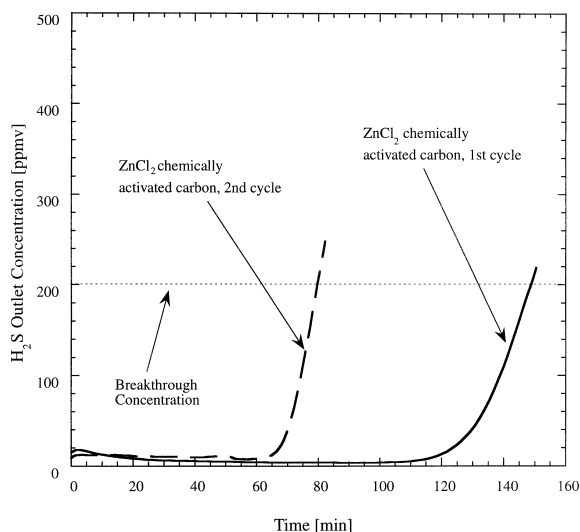


Fig. 6. Multiple cycle H_2S adsorption with $ZnCl_2$ chemical activated carbon. Gas composition: 0.5% H_2S , 50% CO_2 , balance N_2 . $T=550^\circ C$; $P=1$ atm.

4. Summary and conclusions

Activated carbon samples used for H_2S adsorption were produced from bituminous coal using several techniques, including steam activation, thermal and nitric acid oxidation, and metal addition. In part II of this study, the effects of adsorption temperature, and total gas pressure on H_2S adsorption were examined. To determine the extent of regenerability of these carbon-based sorbents, several types of liquid and gas-phase regeneration experiments were carried out. Multiple cycle adsorption/regeneration experiments were also performed with selected activated carbon samples.

Since hot gas clean-up systems in an IGCC system operate at 15–20 atm, H_2S adsorption experiments were performed at 10 atm to determine the effect of total gas pressure. Breakthrough time for a steam-activated, HNO_3 -oxidized, Zn-impregnated sample (RTI-7) was 140 min at 10 atm with simulated coal gas. This sample adsorbed 5.16% by weight sulfur, which meets the 5% sulfur removal requirement set at one of the DOE's IGCC plants. Breakthrough time did not change as temperature was varied from $400^\circ C$ to $600^\circ C$.

Gaseous H_2 regeneration was found to be the most effective method of sorbent regeneration. Sulfur was removed by H_2 and evolved as high concentration H_2S (10,000 ppmv). One sulfided sorbent was completely regenerated using H_2 . H_2S present at high concentrations can be converted to saleable elemental sulfur or used by an adjacent sulfuric acid plant. Multiple cycle H_2S adsorption experiments showed that samples continue to adsorb sulfur after one H_2S adsorption and one H_2 regeneration cycle.

Breakthrough time decreased approximately by half for the second cycle.

Carbon-based sorbents have shown potential as high-temperature H_2S sorbents, but several issues should be further addressed to evaluate their potential use as sorbents in IGCC systems. Sorbent regeneration is a very important issue that should be refined and further investigated, and the feasibility of using H_2 for regeneration at an IGCC facility needs to be addressed. Sorbent attrition resistance for multiple cycles is another important issue that needs to be studied. Optimizing Zn-impregnation techniques and $ZnCl_2$ chemical activation may greatly improve H_2S adsorption performance. And finally, a thermodynamic analysis would be useful to better understand the complex gas and solid phase chemical reactions.

Acknowledgements

The authors would like to acknowledge the Illinois Clean Coal Institute and the University of Illinois Research Board for funding this research project. The authors would also like to thank Dr. Mark Rood of the University of Illinois at Urbana-Champaign, and Dr. John Lytle and Gwen Donnals of the Illinois State Geological Survey for their technical assistance.

References

- [1] Cal MP, Strickler BW, Lizzio AA. High temperature hydrogen sulfide adsorption on activated carbon. I. Effects of gas composition and metal addition. Carbon, this issue.
- [2] Strickler BW. High temperature removal of hydrogen sulfide from coal gasification streams with carbon-based sorbents, Urbana-Champaign: University of Illinois, 1998, M.S. thesis.
- [3] Gangwal SK. Personal communication. Research Triangle Institute, 1997.
- [4] Jothimurugesan K, Gangwal S, Gupta R, Turk BS. Advanced hot-gas desulfurization sorbents. In: Advanced coal-based power and environmental system '97 conference, July 22–24, Pittsburgh, PA: US Department of Energy/Federal Energy Technology Center, 1997.
- [5] Swisher JH, Yang J, Gupta RP. Attrition-resistant zinc titanate sorbent for sulfur. Ind Eng Chem Res 1995;34(4):4463–71.
- [6] Ayala RE, Venkataramani VS, Chuck TL. Hot gas desulfurization using moving-bed reactor. In: Advanced coal-based power and environmental system '97 conference, July 22–24, Pittsburgh, PA: US Department of Energy/Federal Energy Technology Center, 1997.
- [7] Puri BR, Jain CM, Hazra RS. Studies in formulation and properties of carbon-sulphur surface complexes. Part II. Stability of carbon-sulphur complexes formed on charcoal. J Indian Chem Soc 1966;43(8):554–7.

- [8] Puri BR. In: Walker PL, editor, Chemistry and physics of carbon, vol. 6, New York: Dekker, 1970, pp. 191–282.
- [9] Puri BR, Hazra RS. Carbon–sulphur surface complexes on charcoal. *Carbon* 1971;9:123–34.
- [10] Gangwal SK, McMichael WJ, Dorchak TP. The direct sulfur recovery process. *Environ Progress* 1991;10(3):186–91.
- [11] Wibaut JP. In: Proceedings of the third international conference on bituminous coal, 1932, p. 657.
- [12] Palmer SR, Hippo EJ. Chemical cleaning using selective oxidation. In: Final technical report to the Illinois Clean Coal Institute, 1991.