High temperature hydrogen sulfide adsorption on activated carbon
I. Effects of gas composition and metal addition

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Abstract

Various types of activated carbon sorbents were evaluated for their ability to remove H_2S from a simulated coal gas stream at a temperature of 550°C. The ability of activated carbon to remove H_2S at elevated temperature was examined as a function of carbon surface chemistry (oxidation, thermal desorption, and metal addition), and gas composition. A sorbent prepared by steam activation, HNO_3 oxidation and impregnated with Zn, and tested in a gas stream containing 0.5% H_2S, 50% CO_2 and 49.5% N_2, had the greatest H_2S adsorption capacity. Addition of H_2, CO, and H_2O to the inlet gas stream reduced H_2S breakthrough time and H_2S adsorption capacity. A Zn impregnated activated carbon, when tested using a simulated coal gas containing 0.5% H_2S, 49.5% N_2, 13% H_2, 8.5% H_2O, 21% CO, and 7.5% CO_2, had a breakthrough time of 75 min, which was less than 25 percent of the length of breakthrough for screening experiments performed with a simplified gas mixture of 0.5% H_2S, 50% CO_2, and 49.5% N_2. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

While coal gasification has been around for many years, the interest in coal gasification for commercial power generation has just recently been revived. The current interest in coal gasification predominately concerns the application of coal gasification to the Integrated Gasification Combined Cycle (IGCC) process. Over the past 15 years, the coal gasification combined cycle method of power generation has progressed from the research laboratory to the threshold of widespread commercial application [1].

Rather than burning coal directly, as in a traditional coal-fired power plant, the gasification process begins by converting coal into a combustible gas. In the gasification process, coal reacts with steam and oxygen (O_2) or air.

The gas mixture produced is predominately hydrogen (H_2) and carbon monoxide (CO), both of which have a high heating value. In addition to the high heating value gases produced during gasification, there are numerous other gases that are produced, including carbon dioxide (CO_2), methane (CH_4), hydrogen sulfide (H_2S), carbonyl sulfide (COS), and water (H_2O). Commercial gasifiers are generally classified as one of two types: Oxygen-blown or air-blown. Typical gas compositions of an O_2-blown gasifier are (in vol %) 27.7% H_2, 39.4% CO, 13.1% CO_2, 18.4% H_2O, 1.1% H_2S, and 0.0% N_2 [2]. Typical gas compositions of an air-blown gasifier are (in vol %) 14.2% H_2, 23.1% CO, 5.8% CO_2, 6.6% H_2O, 0.5% H_2S, and 49.8% N_2 [3].

One advantage of coal gasification over other forms of electric power generation is the large supply of coal available within the United States. Coal currently supplies 56% of the electricity in the U.S. and remaining coal reserves could power the U.S. for hundreds of more years [1]. Environmental benefits of coal gasification compared

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to other means of power generation are extremely important considering the increasing concern with CO_2 as a greenhouse gas and increasingly stringent nitrogen oxides (NO_x) and sulfur dioxide (SO_2) regulations. Environmental advantages of the IGCC process compared to traditional coal-fired combustion include very low NO_x and SO_2 emissions and lower CO_2 emissions.

The IGCC process is an innovative electric power generation technology that combines modern coal gasification with gas turbine and steam turbine power generation technologies; hence, the name *combined cycle*. Hot fuel gas produced by gasifying coal is cleaned and then burned in a gas turbine to produce electric power. Heat recovered from the gas turbine's exhaust produces steam that turns the steam turbine to produce more electricity. Requirements for coal gas cleaning systems are based upon erosion and corrosion protection for turbines and environmental emission limits. Particulate material must be removed to prevent erosion of the blades of the gas turbine. Sulfur products that must be removed from the coal gas include H_2S, CS_2, and COS, but H_2S is the greatest corrosion concern.

In the past, the typical method for sulfur removal in IGCC systems was cold gas cleanup at temperatures of 100–150°C. Cold gas cleanup typically uses wet scrubbing or acid gas treatment to remove sulfur. If H_2S can be removed while the gas is still hot (400–650°C), then there is a gain in overall process thermal efficiency (~3%). Current IGCC plants operate with an efficiency of about 43% compared to a maximum of 35% for conventional coal-fired power plants. With improved gas turbine technology and high temperature coal gas cleanup, efficiencies exceeding 50% are possible [4].

Much research has been devoted to developing regenerable metal-based sorbents to efficiently remove H_2S from coal gasification streams at high temperature, but until recently no one has examined the use of carbon-based sorbents for the same purpose. The use of activated carbon as a hot gas cleanup sorbent in an IGCC system is a novel research area and it was the focus of this study. The overall objective of this study was to evaluate the potential of carbon-based sorbents to remove H_2S from hot coal gasification gas streams.

2. Materials

2.1. Preparation of steam activated carbon sorbents

All samples in this study were prepared from Illinois No. 2 coal. The coal was from a stockpile named IBC-102, which is part of the Illinois Basin Sample Program [5], and IBC-102 is a bituminous coal from a mine in western Illinois. On a weight percentage basis, IBC-102 consists of 39.9% volatile material, 53.2% fixed carbon, 8.6% oxygen,

2.1% pyritic sulfur, 1.1% organic sulfur, and 6.7% high temperature ash.

IBC-102 was ground and sieved to a particle size of 48×100-mesh (0.147–0.295 mm) and then steam activated. Activated carbon samples were prepared from the size-graded (48×100-mesh) IBC-102 coal. Most sorbents prepared for this study were prepared using a steam activation method. The steps of steam or physical activation were preoxidation, pyrolysis, and then steam activation in a 5 cm diameter fluidized-bed reactor (FBR) at Illinois State Geological Survey (ISGS) facilities. The FBR is 55 cm long, type 304 stainless steel pipe with a porous hastalloy gas distributor plate located 15 cm from the bottom of the reactor. The FBR was heated by a 7.5 cm diameter, 2260 W split-tube furnace controlled by a PID controller. Sample temperature was monitored with a type-K thermocouple placed in the middle of the sample bed [6].

During the first step of steam activation, a batch of 150 g of coal was preoxidized with air at 225°C for 2 h in the FBR at a total gas flow rate of 4 l/min. Initially, during preoxidation, air was periodically diluted in half using N_2. Reducing the oxygen concentration was necessary to prevent a temperature increase due to an exothermic reaction between oxygen and coal. Preoxidation was performed to minimize coal caking and agglomeration during pyrolysis. Next, the sample was pyrolyzed at 425°C for 1 h in 4 l/min N_2. Pyrolysis continued for about 30 min while temperature was increased to 825°C. Once the temperature leveled at 825°C, the coal was activated using steam by replacing the N_2 flow with a 50% H_2O/50% N_2 mixture. H_2O for the steam mixture was supplied either by bubbling N_2 through a flask containing unfiltered H_2O at 82°C or by adding H_2O to a heated N_2 stream with a peristaltic pump (Cole Palmer model # 7553-60). Steam activation at 825°C continued in the FBR for 4 h. The sample was cooled to room temperature (23°C) in N_2. About 70 g of activated carbon was typically produced from the original 150 g coal, for a yield of 45%. Surface areas were measured after the production of each batch of activated carbon to confirm proper activation.

2.2. Chemical activation

A small number of samples were prepared by chemical activation with zinc chloride ($ZnCl_2$). Typically, 25–100 g $ZnCl_2$ was dissolved in a beaker of 0.2–0.4 l H_2O. About 50 g of 48×100-mesh coal was added to the beaker, for a $ZnCl_2$ to coal mass ratio of 0.5–2.0. The solution was continuously stirred and heated at 70–90°C until all liquid evaporated. After physical mixing and cooling, the sample was oven dried at 120°C for approximately 16 h. The sample was then placed in a tube furnace for pyrolysis-activation. Samples were heated in a tube furnace (Lindberg type 59344) at 600–800°C for 1–3 h in 2 l/min N_2. After cooling in N_2 to 30°C, the sample was washed with

deionized H_2O to remove any excess chloride and the pH of the rinse solution was verified to be about neutral. Resulting sample surface areas were checked to determine degree of activation. Several researchers have more extensively studied $ZnCl_2$ activation and the reader is referred to the literature for more information [7–9].

2.3. Oxidation of carbon sorbents

After steam activation, most samples were oxidized with aqueous nitric acid (HNO_3) treatment. Typically, 35 g of steam activated sample was added to 0.35 l 45% HNO_3 by mass solution and heated to 90°C for 2.5 h. A reflux column was used to prevent excessive HNO_3 loss. The reason for oxidizing the steam activated carbon samples with HNO_3 was to create more carbon–oxygen (C–O) complexes. In some cases, oxidized samples were thermally desorbed of C–O complexes in N_2 to 925°C or metals were added to oxidized samples. When a highly oxidized activated carbon sample is thermally desorbed, the number of active carbon sites is greatly increased, which may enhance H_2S adsorption. Other researchers have more extensively studied oxidation of coal-derived activated carbons [10].

2.4. Metal addition to carbon sorbents

After HNO_3 oxidation, a portion of the steam activated sorbents was impregnated with selected metals to improve H_2S adsorption performance. Metal (Zn, or Cu) acetate was used as the source of metal in all cases. Metals were added to the carbon surface by an aqueous ion-exchange (IE) process. Typically for IE, 20.5 g of zinc acetate [$Zn(C_2H_3O_2)_2$] was added to 0.5 l deionized H_2O and mixed. About 10 g of oxidized carbon sample were added and the mixture was continuously stirred for 1.5 h at 23°C. The sample was filtered once and rinsed with deionized H_2O, and then air dried.

3. Experimental

3.1. Measurement of H_2S breakthrough curves at ambient pressure

H_2S adsorption experiments were performed at the ISGS using a 1.2 cm inner diameter quartz reactor with a fritted plate. Teflon fittings and tubing were used at lower temperatures where fittings were required to insure an inert experimental system. Periodically, blank adsorption experiments were performed at actual experimental conditions using an empty quartz reactor. Outlet concentrations from the empty quartz reactor were compared to outlet concentrations from a bypass line. This experiment confirmed that the experimental system was inert with respect to H_2S.

Compressed gas cylinders provided the inlet gases,

which were controlled by Tylan mass flow controllers (MFC). Gas cylinders used were technical grade CO_2, ultra high purity (UHP) N_2, and 1% H_2S by volume in N_2. Calibrations for the MFCs were performed for all gases used.

The experimental apparatus used for H_2S adsorption experiments consisted of a quartz reactor fixed-bed adsorption unit followed by a quadrupole mass spectrometer (MS). During a typical breakthrough curve experiment, 5.5 g of activated carbon was loaded into the fixed-bed quartz reactor, which created a bed length of approximately 5.5 cm. Samples were dried while being heated in N_2 at 120°C for 30 min with the bottom of the reactor open to allow moisture to escape. Samples were heated in 200 cm^3/min N_2 until a constant temperature (usually 550°C) was maintained.

Reactant gases were added to the quartz reactor using compressed gas cylinders, or in the case of H_2O, a syringe pump (Cole-Parmer 74900) was used to inject liquid H_2O into a preheated gas stream. Once the gas stream, containing varying amounts of H_2, CO, CO_2, H_2O, H_2S, and N_2, was adjusted to desired concentrations, an H_2S adsorption experiment was started. The MS measured the concentration of H_2S in the effluent gas exiting the fixed-bed reactor, and recorded a signal every minute. By measuring the influent and effluent H_2S gas concentration, the gas flow rate, and breakthrough time, the mass of H_2S removed (adsorbed) can be calculated from the H_2S breakthrough curve. Reactor temperature was held constant at 550°C for most experiments and total gas flow rate was 200 cm^3/min. The space velocity (SV), which is defined as volumetric gas flow rate divided by volume of sample bed, for all adsorption experiments was 1700–2000 h^{-1}.

The composition (vol %) of the simulated coal gas stream was 0.5% H_2S, 50% N_2, 13% H_2, 8.5% H_2O, 21% CO, and 7.5% CO_2 This mixture corresponds to a typical coal gas generated at an air blown IGCC plant. Several adsorption experiments were performed with different permutations of the gas mixtures to determine the effect of each gas on the H_2S adsorption capacity and breakthrough time. The outlet gas concentration was again measured using the MS and total sulfur adsorbed on the carbon-based sorbents was measured after each adsorption experiment.

3.2. Measurement of physical and chemical properties of prepared sorbents

Single-point BET surface areas for prepared activated carbon samples were measured using N_2 at 77 K and a Monosorb flow apparatus (Quantachrome Corporation). Each sample was measured twice, and the accuracy of the Quantachrome Monosorb was checked periodically with standard materials. The surface areas for some of the samples were also determined using a five-point isotherm

Quantachrome adsorption apparatus, and then compared to the single-point measurements.

Temperature programmed desorption (TPD) was used to quantify the oxygen content of the oxidized samples. Typically, 0.6 g of a HNO_3 oxidized sample was placed in a 2.5 cm diameter, type 304 stainless steel reactor with a hastalloy porous plate. Samples were heated in 0.5 l/min N_2 from 25°C to 925°C at a rate of 10°C/min. Chemically bound oxygen evolved as CO and CO_2, and were continuously monitored with a steady-state infrared analyzer (Rosemount Model 880). Surface oxygen content was calculated based upon the amount of CO and CO_2 released. Quantification of sample oxygen content was necessary to correlate surface oxygen content with H_2S adsorption capacity.

Metal content of zinc and copper impregnated carbon-based sorbents (by IE method) and zinc chloride activated carbon samples was determined using atomic absorption (AA) spectrometry. Carbon-based samples were dissolved in hydrofluoric acid aqua regia before analysis. Measurements were made using atomic absorption spectrophotometer (Perkin-Elmer Model 306) using the settings recommended by the manufacturer. Calibration curves were calculated for each set of analyses using standard solutions. Practical determination limits were 5 ppm Cu and 2.5 ppm Zn by mass.

After adsorption and regeneration experiments, total adsorbed sulfur was determined by elemental analysis of the activated carbon using a solid-state infrared detector (LECO SC-32). Samples were combusted in an oxygen atmosphere where the sulfur oxidized to SO_2 and was then measured with a solid-state infrared detector. Measured SO_2 was then converted to total percentage of sulfur. Sulfur content of samples before and after H_2S adsorption experiments was measured in order to calculate the total sulfur adsorbed and was then compared to the calculated value for the adsorbed sulfur from the breakthrough curves. Samples were analyzed for sulfur before and after regeneration experiments to determine the effectiveness of different regeneration methods.

4. Results and discussion

4.1. Prepared activated carbon samples

Physical and chemical properties of most prepared activated carbon samples were characterized before the samples were used for H_2S adsorption experiments. Activated carbon samples were analyzed for surface area, oxygen, and metal content so that properties of the samples before H_2S adsorption experiments could be correlated to their adsorption performance [11]. N_2-BET surface areas for most prepared samples were measured using N_2 at 77 K. Surface areas of steam activated samples (*S*) were in the range of 460 to 700 m^2/g, metal impregnated carbon

samples ranged from 250 to 510 m^2/g, and $ZnCl_2$ chemically activated samples ranged from 400 to 1030 m^2/g. Sample surface areas were tested before and after H_2S adsorption and results showed surface areas remaining constant (within ~5%), except for some metal impregnated chars. Ion exchange (IE) metal impregnation did not significantly change the surface areas for most samples, and as long as the samples had a surface area greater than about 100 m^2/g, H_2S adsorption performance did not appear to be dependent on sorbent surface area.

Temperature programmed desorption (TPD) was used to quantify the oxygen content of HNO_3 oxidized carbon-based sorbents. TPD results showed that HNO_3 oxidized samples had a surface oxygen content between 10 and 15% by weight, and steam activated samples had a surface oxygen content between 2 and 4% by weight.

Metal content of Zn- and Cu-impregnated activated carbon samples (by IE) and $ZnCl_2$ activated samples was determined using atomic absorption (AA) spectrometry. Zn content of the impregnated sorbents (by IE) was found to be between 0.83 and 3.23% by weight. The 3.23% Zn by weight sample had a Zn content of 0.03% by weight after heating to 925°C in N_2. Cu content of the Cu-impregnated carbon-based sample (by IE) was found to be 1.03% by weight. Zn content of the chemically $ZnCl_2$ activated carbon samples was found to be between 0.5 and 0.7% by weight. After completing H_2S adsorption experiments for various samples, the treatment and impregnation techniques were compared and then altered to improve H_2S adsorption. Characterizations for a few examples of representative activated carbon samples before H_2S adsorption are shown in Table 1.

4.2. H_2S adsorption experiments with $H_2S/N_2/CO_2$ inlet gas stream

Initial H_2S (screening) adsorption experiments were performed to narrow the large number of prepared carbon-based sorbents down to two or three of the best performing sorbents. Part of the goal of these experiments was to understand H_2S adsorption with carbon-based sorbents and to examine the effects of sample surface oxygen and metal addition on H_2S adsorption.

A few notational definitions need to be clarified for the breakthrough curve experiments and sample identification. All inlet and outlet gas concentrations are in percent by volume. The term *breakthrough* is used throughout this paper and refers to a predetermined H_2S outlet condition when a certain concentration of H_2S has not been removed by the carbon bed or H_2S has *broken through*. *Breakthrough* in all H_2S adsorption experiments is defined as 200 ppmv H_2S outlet concentration, which is a common standard at IGCC plants. *Breakthrough time* is the time that the outlet gas H_2S concentration reaches 200 ppmv. In the breakthrough figures, *S* represents steam activated, *O* represents HNO_3 oxidized, and *D* represents thermally

Table 1
Representative activated carbon sample characterization for H_2S adsorption experiments[a]

Activated carbon sample description	Oxygen [wt %]	Metal [wt %]	Surface area [m²/g]
S	~4	~0	600
S + O	14.7	~0	470
S + O + D	~0	~0	570
S + O +Cu by IE	10–14	1.03	130
S + O +Zn by IE	10.1	3.23	510
ZnCl, 1.0 coal:0.5 ZnCl₂ weight ratio before activation	~2	0.52	400

[a] Note: *S* = steam activated, *O* = HNO_3 oxidized, *D* = thermally desorbed in N_2 at 925°C, IE = metal added by ion-exchange.

desorbed in N_2 at 925°C. Lines representing H_2S outlet concentration versus time in breakthrough plots were smoothed once using graphing software.

4.3. Effect of sorbent oxygen content on H_2S adsorption

Experiments were performed with carbon samples of controlled surface oxygen contents ranging from 0 to 15% oxygen by weight (Fig. 1). As suggested from previous literature and our initial experimental results, the more oxygen present on a sample's surface, the greater the sorbent's capacity for H_2S [11,12]. This agrees with the theory that sulfur atoms react in a substitution reaction with C–O surface complexes to form C–S complexes. Although the thermally desorbed sorbent ($S + O + D$) had a relatively fast breakthrough time, the desorbed sample did adsorb some sulfur, which indicated adsorption by unsaturated bonds or active sites on the carbon surface. A steam activated sample (*S*) performed almost as well as a HNO_3 oxidized carbon (*S + O*), but did not polish the H_2S

outlet gas concentration down to very low levels (<20 ppmv).

A few H_2S adsorption experiments were performed with varied amounts of CO_2 present in the inlet gas stream. All three breakthrough experiments shown in Fig. 2 were performed with steam activated carbons using the same experimental conditions. Breakthrough time decreased from 260 min to 90 min and then to 40 min as the inlet CO_2 concentration decreased from 50% to 10% and then to 0% by volume, respectively. These results suggest that interaction between the CO_2 gas and solid C sites enhances H_2S adsorption. One possible explanation of this phenomenon is that CO_2 partially gasifies C sites and forms C–O complexes. This reaction is an intermediate step of gasification of carbon which is known to occur above 800°C [13]. It was determined, by monitoring the concentrations of outlet gas compounds during H_2S adsorption experiments, that CO or CO_2 reacted with H_2S in the gas phase in the presence of activated carbon to form gaseous COS. COS was only formed when the carbon was nearly
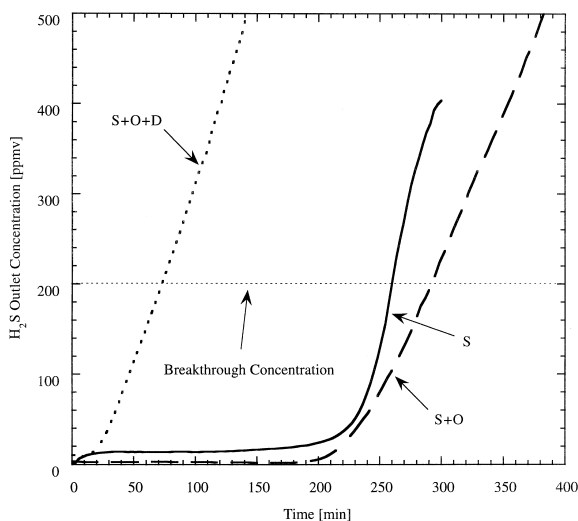

Fig. 1. Effect of sample oxygen content on H_2S breakthrough time. Gas composition: 0.5% H_2S, 50% CO_2, balance N_2. T = 550°C. P = 1 atm.
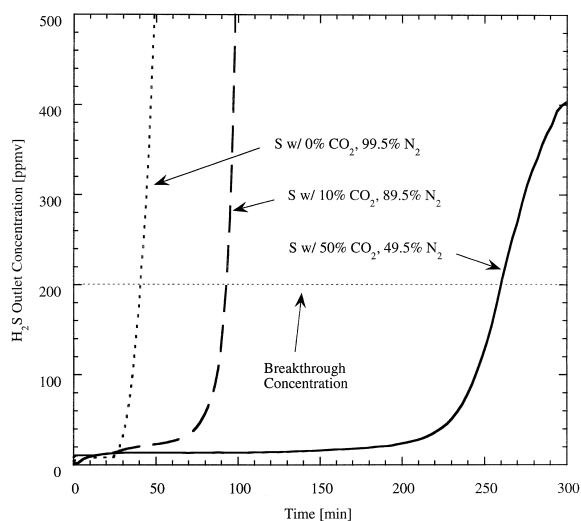

Fig. 2. Effect of CO_2 inlet gas concentration on H_2S breakthrough time. Gas composition: 0.5% H_2S, 0–50% CO_2, balance N_2. T = 550°C. P = 1 atm.

saturated with H$_2$S, and COS was not formed in blank runs when a carbon sorbent was not present.

Zn and Cu, which are metals known to chemically adsorb appreciable amounts of H$_2$S, were added to the carbon-based sorbents using IE impregnation, and chemical activation. Breakthrough curves for four metal-impregnated carbon sorbents at the same experimental conditions are shown in Fig. 3. Activated carbon impregnated with Zn by IE performed the best with a breakthrough time of 380 min. The good performance of the Zn-impregnated sorbent can be partially attributed to the sample having a Zn content over 3% by weight. A Cu-impregnated sorbent also performed well. The ZnCl$_2$ chemically activated sorbent performed reasonably well considering that the ZnCl$_2$ chemical activation technique was rather crude and was not as thoroughly investigated as the other metal addition techniques.

H$_2$S adsorption screening experiments with the quartz reactor system are summarized in Fig. 4 and Table 2. Adding Zn to HNO$_3$ oxidized activated carbon ($S + O + $ Zn) improved the H$_2$S adsorption performance. Steam activated (S) and HNO$_3$ oxidized ($S + O$) samples did not perform as well as Zn-impregnated ($S + O + $Zn), but did have good breakthrough times compared to Calgon Carbon Centaur™. Centaur™ is a commercial sorbent with catalytic properties and it is used for H$_2$S removal at ambient temperatures, but did not perform well in our tests at 550°C. A steam activated (S) sample prepared in this study had a breakthrough time more than six times that of Centaur™.

Table 2 displays the sulfur contents for the four samples with breakthrough curves shown in Fig. 4. Sulfur testing after H$_2$S adsorption experiments is another method to
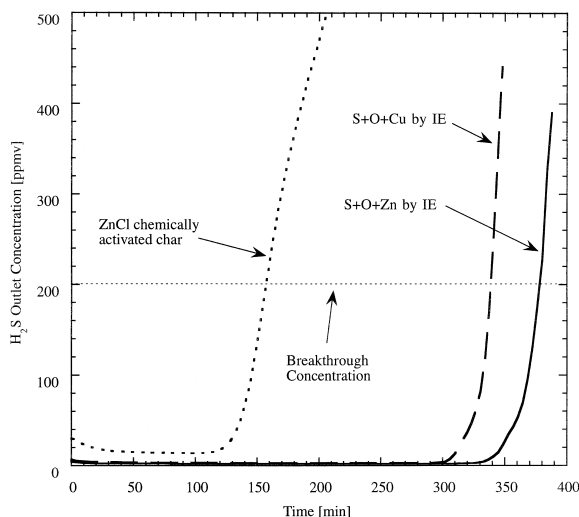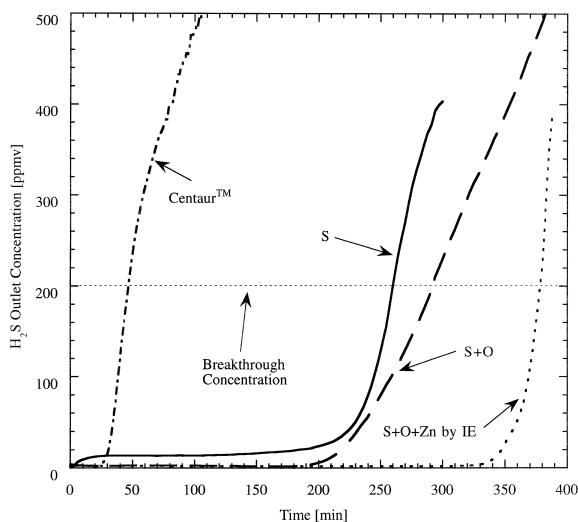

Fig. 4. H$_2$S breakthrough times for various screening experiments. Gas composition: 0.5% H$_2$S, 50% CO$_2$, balance N$_2$. $T = 550$°C. $P = 1$ atm.

analyze the performance of carbon-based samples. It is important to know how much sulfur a sorbent will remove before reaching breakthrough (200 ppmv outlet H$_2$S). Adsorption capacity of hot gas cleanup sorbents determines how much sorbent is needed at an IGCC plant, which is an important design and economic consideration. Zn-impregnated activated carbon ($S + O + $Zn) adsorbed approximately 10% sulfur by weight at 200 ppmv breakthrough, and a steam activated sample (S) adsorbed about 5.3% sulfur by weight after 260 min at 200 ppmv breakthrough, and 6.1% sulfur after 300 min. It should be noted that these sulfur loadings were for screening experiments with a simplified inlet gas and did not use a complete simulated coal gas. The amount of sulfur adsorbed can also be calculated using a mass balance on the inlet and outlet H$_2$S concentrations. Results of sulfur content measurements, using the combustion technique described in Section 3.2, typically differed from the results of sulfur content calculated from the breakthrough curves by 10–25%. Measured sulfur contents were consistently higher than the calculated sulfur contents. It is unknown why this consistent error occurred.

4.4. Effect of CO$_2$, CO, H$_2$, and H$_2$O in inlet gas stream on H$_2$S adsorption

By varying the inlet gas composition, effects of individual gases on H$_2$S adsorption with carbon-based sorbents can be determined. For simplicity, initial adsorption experiments used inlet gas streams consisting of only H$_2$S, CO$_2$, and N$_2$. Since coal gasification streams also contain CO, H$_2$, and H$_2$O, it was important to examine the effects of these gases. Concentrations of gases

Fig. 3. H$_2$S breakthrough times for activated carbon samples after metal addition (Cu and Zn). Gas composition: 0.5% H$_2$S, 50% CO$_2$, balance N$_2$. $T = 550$°C. $P = 1$ atm.

Table 2
Amount of sulfur added to selected carbon-based sorbent samples during H_2S breakthrough experiments[a]

Sample description	% Sulfur added [wt%]	Total adsorption time [min]	Breakthrough time to 200 ppmv [min]
S	6.1	300	260
S + O	12.7	610	290
S + O +Zn	10.4	390	380
Calgon Carbon Centaur™	3.2	120	40

[a] Note: *S* = steam activated, *O* = HNO_3 oxidized, Zn added to sample by ion-exchange.

used for this set of experiments were similar to those found at an air-blown IGCC plant. It is important to note that the same batch of steam activated, HNO_3 oxidized, Zn-impregnated (by IE) activated carbon was used for all gas effect experiments. By using the same activated carbon for all experiments, the only variable was the inlet gas. Information gained in these parametric gas studies may lead to useful information that could be used to design better activated carbons for high temperature H_2S adsorption.

4.4.1. Addition of CO_2 to inlet gas stream

As seen with the steam activated carbon (Fig. 2), decreasing the concentration of CO_2 had a negative impact on breakthrough time of the Zn-impregnated sample (Fig. 5). The *S + O* +Zn sorbent, with 0% CO_2 in the inlet gas, still had a significant breakthrough time of 160 min compared to 40 min for the steam activated carbon (*S*) with 0% CO_2 in Fig. 2. This shows the effect of oxygen and Zn on H_2S adsorption. Addition of 7.5% CO_2 increased breakthrough time to 200 min on the *S + O* +Zn
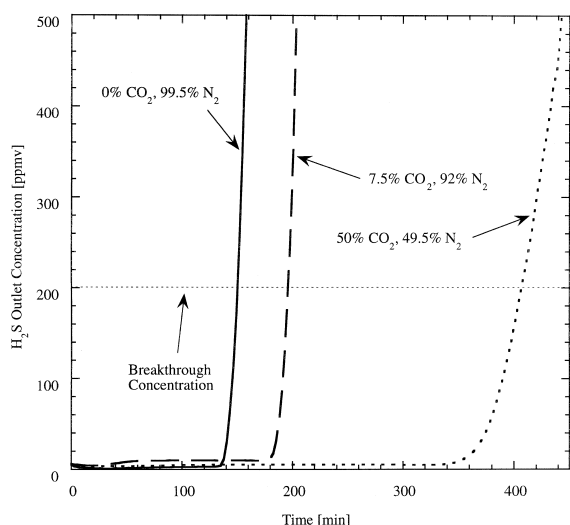
sorbent, but that time was only half of the breakthrough time for the experiment with 50% CO_2.

4.4.2. Addition of CO to inlet gas stream

Addition of CO to the inlet gas stream had a detrimental effect on breakthrough time (Fig. 6). Adding CO to the inlet gas decreased breakthrough time from 160 min for an inlet gas of just 0.5% H_2S and 99.5% N_2 to 100 min for an inlet gas of 0.5% H_2S, 20% CO, and 79.5% N_2. The negative effects of CO addition may be because CO reduces oxidized sites on the carbon surface, forming CO_2, and thereby limiting H_2S adsorption, but further study is needed to confirm this hypothesis. Despite the positive effects of having CO_2 in the inlet gas as shown in previous experiments, the addition of 7.5% CO_2 to the 20% CO mixture did not change the 100 min breakthrough time. Adding H_2 to the inlet gas decreased breakthrough time further from 100 min for an inlet gas of 0.5% H_2S, 20% CO, and 79.5% N_2 to 60 min for an inlet gas of 0.5% H_2S, 20% CO, 13% H_2, and 66.5% N_2. The initial elevation in H_2S concentration seen in Fig. 6 for the gas stream

Fig. 5. Effect of CO_2 on H_2S breakthrough time of zinc impregnated (*S + O* +Zn by IE) activated carbons. Gas composition: 0.5% H_2S, 0–50% CO_2, balance N_2. *T* = 550°C. *P* = 1 atm.
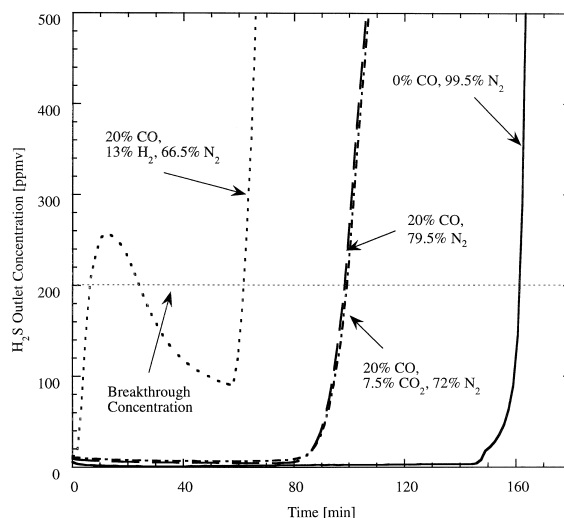

Fig. 6. Effect of CO inlet gas concentration on H_2S breakthrough time of zinc impregnated (*S + O* +Zn by IE) activated carbons. Gas composition: 0.5% H_2S, 0–20% CO, 0–7.5% CO_2, 0–13% H_2, balance N_2. *T* = 550°C. *P* = 1 atm.

containing H_2 is believed to be caused by the introduction of H_2 into the system and is discussed in more detail in Section 4.4.3.

4.4.3. Addition of H_2 to inlet gas stream

Addition of H_2 to the inlet gas stream was found to have the most negative effect of all inlet gases on breakthrough time (Fig. 7). Breakthrough time decreased from 160 min for an inlet gas of 0.5% H_2S and 99.5% N_2 to about 65 min for an inlet gas of 0.5% H_2S, 13% H_2, and 86.5% N_2. Adding 7.5% CO_2 or 20% CO had almost no effect on breakthrough time. This shows that the effects of H_2 dominate over the effects of CO_2 and CO for H_2S adsorption with carbon-based sorbents at the concentrations tested in these experiments. An initial increase in the H_2S outlet concentration shown in Fig. 7 is believed to be caused by introduction of H_2 into the system, which caused a small amount of preexisting sulfur (<1% of sulfur by weight) on the activated carbon sample to be removed as H_2S. This initial phenomenon was seen in other experiments and was not considered true breakthrough.

4.4.4. Addition of H_2O to inlet gas stream

Addition of H_2O to the inlet gas had a negative effect on breakthrough time, but the effect was not as severe as it was for CO or H_2 addition (Fig. 8). Breakthrough time for Zn-impregnated samples with an inlet gas of 0.5% H_2S, 50% CO_2, and 49.5% N_2 was 400 min, but decreased to 200 min for the experiment with an inlet gas of 0.46% H_2S, 7.5% H_2O, 46% CO_2, and 46% N_2. It should be noted that the experiments analyzing the effects of H_2O on
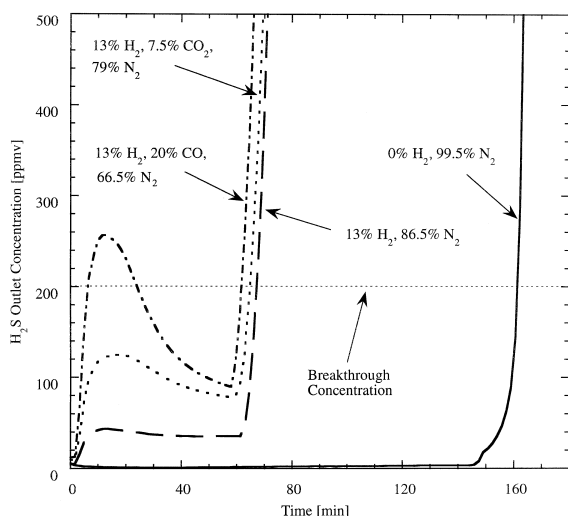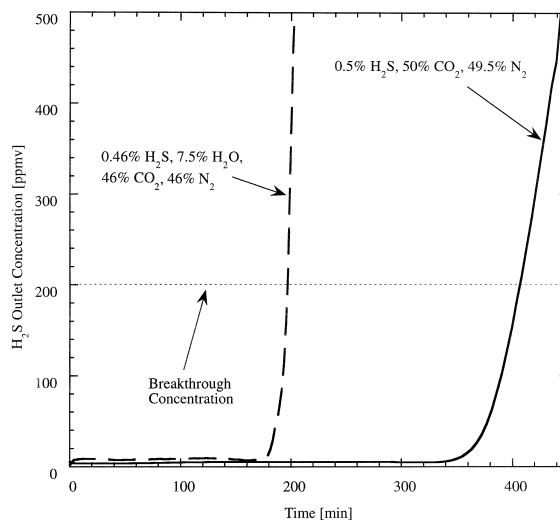
Fig. 8. Effect of H_2O inlet gas concentration on H_2S breakthrough time of zinc impregnated ($S + O + Zn$ by IE) activated carbons. Gas composition: 0.46–0.5% H_2S, 0–50% CO_2, 0–7.5% H_2O, balance N_2. $T = 550°C$. $P = 1$ atm.

H_2S adsorption had excess CO_2 (~50%) present in the inlet gas, whereas the other gas effects experiments did not have excess CO_2.

4.5. H_2S adsorption with $H_2S/H_2/CO/CO_2/H_2O/N_2$ in inlet gas stream

H_2S adsorption experiments with simulated coal gas streams were performed. Gas composition used to simulate an O_2 blown IGCC plant was 0.5% H_2S, 13% H_2, 21% CO, 7.5% CO_2, 8.5% H_2O, and 49.5% N_2 by volume. Effect on H_2S adsorption of the simulated coal gas versus the simple mixture used for screening experiments is shown in Fig. 9. All three experiments shown in Fig. 9 were performed with Zn-impregnated carbon (by IE). Breakthrough time decreased from 400 min for the screening gas mixture to 70–95 min for the complete coal gas mixture.

5. Summary and conclusions

Carbon-based sorbents made from bituminous coal were examined for their ability to adsorb H_2S from high-temperature simulated coal gas streams. Currently, the leading sorbents for this application are metal-based sorbents, such as zinc titanate and copper and manganese oxides. These metal-based sorbents, while effective at temperatures around 550°C, lose much activity when the gas reaction temperature is lowered much below 550°C. Metal-based sorbents are also expensive, costing between $15 and 30/kg. Carbon-based sorbents have the potential to be a

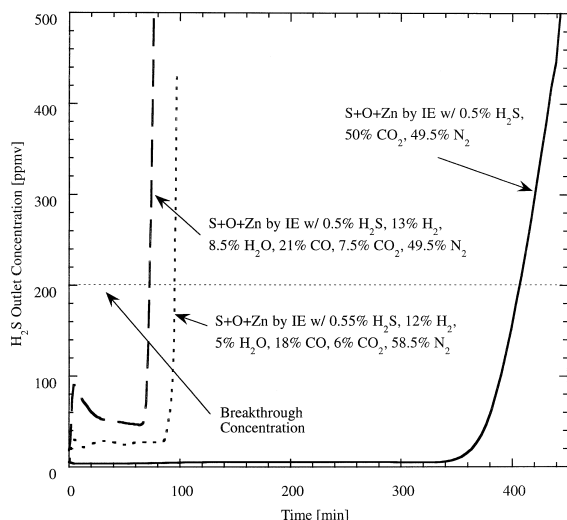Fig. 7. Effect of H_2 inlet gas concentration on H_2S breakthrough time of zinc impregnated ($S + O + Zn$ by IE) activated carbons. Gas composition: 0.5% H_2S, 0–20% CO, 0–7.5% CO_2, 0–13% H_2, balance N_2. $T = 550°C$. $P = 1$ atm.

Fig. 9. Comparison of H_2S breakthrough time for zinc impregnated ($S + O + Zn$ by IE) activated carbons with different inlet gas compositions. Gas composition: 0.5% H_2S, 0–21% CO, 0–7.5% CO_2, 0–13% H_2, 0–8.5% H_2O, balance N_2. $T = 550°C$. $P = 1$ atm.

less expensive hot gas cleanup sorbent and they retain their activity as the reaction temperature is lowered. While more research still needs to be done to determine the viability of carbon-based sorbents for hot gas cleanup, zinc-impregnated carbon sorbents show much promise and have breakthrough times approaching those of the best metal-based sorbents. Part II of this study will examine the effects of gas temperature and gas pressure on H_2S adsorption capacity and it examines methods of sorbent regeneration.

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