

**SULFUR IMPREGNATION OF ACTIVATED CARBON
THROUGH
HYDROGEN SULFIDE OXIDATION**

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Activated carbon adsorption is a most promising technology for reducing mercury emissions from coal-fired power plants (CFPPs) because of its high efficiency to remove gas-phase mercury, especially when activated carbon is impregnated with elemental sulfur.

The present study provides preliminary information about activated carbon impregnation with sulfur through H_2S oxidation. Impregnation conducted in the temperature range of 20-200°C showed that the maximum sulfur loading can be achieved at 100°C (up to 27% after 10 minutes), but the reaction at room temperature achieved 13% sulfur loading, which is also considered sufficient for enhanced mercury uptake. Sulfur loading increased with prolonged reaction time in the range from 5 to 30 minutes. 10 minutes was found to be sufficient to achieve substantial sulfur deposition using 25% H_2S in the influent. The presence of excess oxygen is essential to promote the reaction and can increase sulfur loading up to 3 times at room temperature. Furthermore, sulfur content of impregnated carbon increased with the increase in H_2S concentration from 2.5% to 25%. However, impregnation with low H_2S concentration (2.5%) resulted in more efficient conversion.

Carbons impregnated under all experimental conditions investigated in this study exhibited high thermal stability below 210°C, which demonstrates the potential of these sorbents to be applied for mercury adsorption under realistic process conditions. Sulfur deposited on activated carbon through H₂S oxidation can be completely removed by heat treatment above 400°C.

Hydrogen treatment was found to substantially remove acidic functional groups from BPL carbon surface and inhibit active sites from catalyzing H₂S oxidation at room temperature. Other surface modifications such as oxidation and acid washing showed limited impact on H₂S oxidation.

Performances of five virgin carbons tested in this study (BPL, PCB, F400, BD, and Centaur) varied greatly with the highest sulfur loading at room temperature achieved by Centaur (above 40%) and the lowest by BD (below 5%). No direct relationship was found between sulfur loading and surface properties, such as total acidity, functional group types, basicity, and total surface area.

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1.0 INTRODUCTION

On December 14th 2000, EPA announced its determination to propose regulations for mercury emissions from power plants by December 2003. Extensive mercury emission studies identified coal-fired power plants (CFPPs) as the largest single source of anthropogenic Hg emissions in the United States, not only because they account for about one-third of total anthropogenic emissions, but also because mercury exists mainly in the metallic form in these flue gas streams. Existing control technologies, such as wet scrubbers, fabric filters, and electrostatic precipitators are not effective in removing metallic mercury. Therefore, there is a need of highly efficient mercury control technologies in order to meet the more stringent regulations expected in the near future.

Activated carbon based adsorption has been intensively studied and proven to be a promising technology to effectively remove gas-phase mercury from CFPPs. Powdered activated carbon (PAC) injection as well as granular activated carbon (GAC) fluidized bed systems have been evaluated in pilot-scale studies.

Activated carbon impregnated with sulfur through H₂S oxidation is of particular interest in this research, because hydrogen sulfide is also a hazardous air pollutant (HAP) emitted from a number of industries, such as: natural gas processing facilities, oil refineries, and sulfur recovery

plants. Currently applied H₂S control devices include: amine process system and scrubbers. However, tail gas after these devices can still cause environmental problems if it is directly discharged or incompletely flared. In recent years, activated carbon has also been used in these industries as tail-gas sorbent or pretreatment filter material to remove H₂S and other constituents.

Studies on H₂S oxidation over activated carbon surface have revealed that chemisorption can enhance the capacity of activated carbon to adsorb hydrogen sulfide. Furthermore, carbon performance for H₂S uptake is dependent on impregnation conditions and is also influenced by carbon base material and surface properties.

The purpose of this study was to evaluate the impacts of reaction conditions on H₂S oxidation catalyzed by activated carbon surface. Reaction temperature and time, H₂S concentration, O₂ concentration and particle size have been varied to compose an experimental matrix to investigate the influence of each factor. Sulfur content and thermal stability were measured for carbons impregnated under different conditions. The effects of hydrogen treatment, nitric acid treatment, and acid washing were studied for BPL carbon. Furthermore, impacts of surface properties such as: surface functional groups, ash content, and total surface area were also investigated using several commercially available carbons.

2.0 LITERATURE REVIEW

2.1 Activated Carbon Based Mercury Control Technologies

2.1.1 Mercury Emissions

Mercury is of particular importance as a result of the Clean Air Act Amendments of 1990 (CAAA). Mercury and mercury compounds are included in the Title III list of hazardous air pollutants (HAPs) and will be subject to standards established under Section 112 [b][1], including maximum achievable control technology (MACT). Most concerns for the lack of balance in the global mercury cycle are related to anthropogenic emissions. The total nationwide anthropogenic mercury emissions were estimated at 140 Mg (154 tons) per year from major sources⁽¹⁾. According to *EPA 1997 Mercury Report Study To Congress*⁽²⁾, approximately 87% of anthropogenic mercury emission is from combustion point sources, 10% is from manufacturing point sources, 2% is from area sources, and 1% is from miscellaneous sources. Four major categories of combustion sources are: utility boilers (33%), municipal waste combustion (19%), commercial/industrial boilers (18%), and medical waste incinerators (10%).

Prior to 1995, municipal waste combustors (MWCs) and medical waste incinerators (MWIs) were the largest identifiable sources of mercury emissions to the atmosphere. Several studies reported that the flue gases from municipal waste combustors have 1 to 3 orders of magnitude higher mercury concentrations ($100\text{-}1000\mu\text{g}/\text{m}^3$ of mercury at $177\text{-}299^\circ\text{C}$) than those from coal-fired power plants (CFPPs), which usually contain $1\text{-}10\mu\text{g}/\text{m}^3$ of mercury at $121\text{-}177^\circ\text{C}$ ⁽³⁻⁶⁾. Final regulations for MWCs and MWIs, when fully implemented, will reduce emissions by 90% when compared to year 1995's levels.

Current emission estimates indicate that utility boilers are the single largest emission source (51.8 tons/yr). About 81% of the total energy consumption in utility boilers resulted from coal combustion (51.6 tons/yr)⁽²⁾. Almost all of the coal burned in the U.S. (95%) are bituminous and sub-bituminous coals⁽⁷⁾. Although mercury is present in very small quantities in coal (0.02 to 0.25 ppm with an average of 0.09 ppm)⁽²⁾, large volume of flue gas generated by coal-fired power plants can contain an unacceptable amount of mercury.

The primary source of mercury from CFPPs is the combustion stack. Because the combustion zone in boilers operates at temperatures above 1000°C (2000°F), mercury in the coal is vaporized and emitted as a gas. Some of the gas may cool and condense as it passes through the boiler and the air pollution control devices (APCDs). The current understanding is that, Hg⁰ is not so well collected in PM or SO₂ control systems, while Hg²⁺ is collected to a greater or lesser degree depending on the characteristics of each control device⁽⁸⁾.

Future trends in mercury emissions from coal combustion sources are largely dependent on both the nation's future energy needs and the fuel chosen to meet those needs. Another factor is the nature of actions the utility industry may take in the future to meet other air quality requirements under the Clean Air Act. On December 14th, 2000, the EPA announced that it intends to develop mercury regulations for CFPPs under the Section 112. A proposal of emission standards will be completed before December 15th of 2003, with promulgation launched before December 15th of 2004 and full compliance expected by 2007^(9, 10).

2.1.2 Mercury Control Technologies

The primary types of control devices used for coal-fired utility boilers include electrostatic precipitators (ESPs), wet scrubbers, fabric filters (FFs) or bag houses. Mercury removal efficiencies of these APCDs without activated carbon injection are shown in Figure 2.1⁽³⁾.

ESPs are the most widely used particulate control device by the fossil fuel-fired electric utility industry. Because mercury in electric utility flue gas is predominantly in the vapor phase⁽¹¹⁾ with only about 5% to 15% in the fly ash⁽¹²⁾, ESPs are relatively ineffective at removing mercury compounds from flue gases. Cold-side ESPs (CS-ESPs), located after the air preheater have a median removal efficiency of 14.7% and a maximum removal efficiency of 82.4%.

Fabric filters are more effective than ESPs at collecting fine particles. This performance may be important in achieving better mercury removal. Also, the mercury may adsorb onto the fly ash cake that is collected on the fabric and allow more residence time for mercury removal. FFs have a median mercury removal efficiency of 8%, with a range from no control (zero percent removal) to 73%.

Scrubbers or flue gas desulfurization (FGD) units for coal-fired plants are generally used as devices for the removal of acid gases (mainly SO₂ emissions). Most utility boilers have an ESP or a FF before the wet FGD units to collect the majority of PM. FGD units have a median mercury removal efficiency of about 22.6%, with a maximum of 61.7% removal.

A spray dryer adsorber (SDA) is a dry scrubbing system followed by a particulate control device. A lime/water slurry is sprayed into the flue gas stream and the resulting dried solids are collected by an ESP or a FF. Tests conducted on a SDA/FF system had a median mercury removal efficiency of 24%, with a maximum of 55% removal.

Mechanical collectors typically have very low PM collection efficiencies, often lower than 20% for particles less than or equal to 1 μ m in size. Venturi scrubbers can be effective for particulate control, but require high pressure drops (more than 50 or 60 inches of water) for small particles. These two devices are not expected to provide effective mercury removal, especially for those mercury compounds concentrated in the sub-micron PM fractions and in the vapor phase.

As can be observed in Figure 2.1, none of the APCDs described above are able to achieve a median mercury removal efficiency of more than 30 percent. In 1999, the APCDs installed on existing units captured 43% of the mercury in these as-burned fuels and 43 tons of mercury was emitted to the atmosphere from coal-fired utility power plants⁽¹³⁾.

2.1.3 Fixed-Bed GAC Adsorber and PAC Injection

Fixed-bed GAC adsorption has been widely used for the control of vapor phase emissions from a variety of industrial processes. Several advantages of this approach for mercury control are worth mentioning: (1) nearly no loss of activated carbon will occur in the adsorber; (2) it allows the mercury-contaminated activated carbon to be isolated from the fly ash waste stream,

which increases the potential for by-product utilization programs instigated by many CFPPs; (3) it also permits carbon regeneration and mercury recovery from the carbon; (4) the carbon utilization is maximized since the fixed-bed adsorber is located downstream of other air pollution control devices; and (5) the fixed-bed adsorber results in a longer reaction time between the mercury and carbon relative to PAC injection. However, fixed-bed adsorption also has major disadvantage due to significant pressure loss across the adsorption bed.

On the other hand, PAC injection process involves direct injection of activated carbon into the plant's flue gas stream. Activated carbon captures vapor-phase mercury and is collected in the downstream particulate control equipment, such as a fabric filter or ESP. However, Young et al.⁽¹⁴⁾, Lowe and St. John⁽¹⁵⁾ suggested that PAC injection applied to a CFPP with an inlet mercury concentration of $20\mu\text{g}/\text{m}^3$ would only contribute 5% to the overall mercury removal by air pollution control devices. The authors also indicated that PAC injection will not provide significant mercury control for the flue gas conditions representative of CFPPs.

The effectiveness of PAC injection in removing trace levels of mercury from flue gases at various coal-fired power plant facilities can vary considerably depending on the following factors: flue gas composition and temperature, coal type, mercury speciation, activated carbon properties, injection rate, and other plant operating conditions⁽⁷⁾. Besides, PAC injection has some disadvantages such as: it can decrease ESP performance, reduce ash salability due to excess carbon and mercury contamination, and can also cause waste disposal problems because mercury may volatilize from the landfills where saturated activated carbon is deposited.

According to a technical memorandum released by EPA⁽¹³⁾, annualized costs of mercury control using powdered activated carbon injection will be high only for the plants using hot-side ESPs (HS-ESPs). This document also suggested that the costs of mercury control will dramatically diminish if retrofit hardware and sorbents are employed for the control of other pollutants, such as: NO_x, SO₂, or fine particulates. Despite the disadvantages and varied efficiency of PAC injection, it is still the most commonly applied technology for mercury containing tail gas clean up because of its operational simplicity.

Recent study⁽¹⁶⁾ of powder sorbent injection approach utilized fixed-bed adsorption data in a predictive model to estimate performance of sorbent injection for mercury removal. It was found that the difference between the laboratory and field results can be attributed to differences in the flue gas compositions and operating conditions. It was also suggested that the laboratory measurements may be well suited to simulate field results if direct field tests and sufficient information on flue gas components can be obtained.

2.1.4 Sulfur Impregnated Carbon Adsorbents

2.1.4.1 Advantage over Virgin Activated Carbon.

Virgin PAC injection is much more effective in removing oxidized mercury forms than elemental mercury. MWC tests using PAC injection showed that although the mercury speciation was 67% oxidized and 33% elemental upstream of the baghouse, the mercury discharged from the stack was 100% elemental mercury⁽¹⁷⁾. This test result suggests that injection of virgin PAC would not be effective in removing mercury from the flue gases of coal-

fired power plants which tend to have larger fractions of elemental mercury than MWCs. Sinha and Walker⁽¹⁸⁾ showed that virgin carbon adsorb significantly less mercury at ambient temperature compared with sulfur impregnated carbon. A previous study on comparison of BPL virgin carbon and sulfur impregnated carbon also found that BPL carbon displayed significantly less ability to remove mercury, either in terms of the adsorption kinetics or the overall mercury uptake⁽¹⁹⁾. Sulfur impregnated GAC showed much greater elemental mercury adsorption, especially in the temperature range of 25-90°C. This effectiveness of sulfur impregnated carbon is due to the enhanced chemisorption involving mercury reaction with elemental sulfur to form nearly non-soluble mercuric sulfide⁽²⁰⁾.

2.1.4.2 Impregnation of Activated Carbon with Elemental Sulfur.

Mercury adsorption performance of HGR (commercial available sulfur impregnated carbon, Calgon Carbon corporation, Pittsburgh, PA) and BPL-S (lab-produced elemental sulfur impregnated carbon) were compared by Korpiel and Vidic⁽²¹⁾. These two carbons had similar sulfur loads and BET surface area, but HGR showed lower mercury removal at higher reaction temperature. Such behavior was explained with hypothesis that BPL-S has more reactive S₂ chains, which not only have stronger bonding to the carbon matrix, but also are also less voluminous and located deeper inside the carbon particles. On the other hand, S₈ is the predominant sulfur form in HGR, which is mainly located on the external surface and its ring structure makes it less reactive. Furthermore, pore size distribution and available surface area are also essential for effective mercury capture on activated carbon⁽²²⁾. Based on further kinetic studies with these two carbons⁽²³⁾, it was concluded that BPL-S is more suitable for direct

powdered activated carbon injection in CFPPs because of favorable kinetics and better performance at higher temperatures. On the other hand, HGR would be a better choice for fixed-bed activated carbon application or for removing higher mercury concentrations, which are typically found in MWCs.

2.1.4.3 Impregnation of Activated Carbon through H₂S Oxidation.

Preliminary studies showed that sulfur deposition on the surface of activated carbon can be accomplished through H₂S oxidation by oxygen⁽²⁴⁾. Thermogravimetric analysis showed that this method of sulfur impregnation resulted in lower thermal stability of sulfur deposits when compared with impregnation with elemental sulfur. However, the latter sorbent was produced at 600°C while the former utilized reaction temperature of 150°C.

Impregnation with elemental sulfur requires elemental sulfur as the raw material and also requires more energy input because of higher impregnation temperature. On the other hand, H₂S is commonly found in numerous industrial waste streams. Utilizing H₂S from these streams will be beneficial to reduce the total sulfur emissions from these industries and could also lower the cost of producing effective mercury adsorbents.

2.2 Hydrogen Sulfide Emissions

2.2.1 Hydrogen Sulfide Emission Sources

Hydrogen sulfide is produced in nature primarily through anaerobic decomposition of proteinaceous material by bacteria. It also occurs as a constituent of natural gas, petroleum, sulfur deposits, and numerous volcanic gases and sulfur springs. Background air concentrations of hydrogen sulfide due to the natural sources have been estimated between 0.15-0.46 $\mu\text{g}/\text{m}^3$, which is well below the threshold odor levels and the concentrations at which deleterious effects are known to occur⁽²⁵⁾.

The major H_2S emission point sources include: natural gas processing, petroleum refineries, petrochemical plant complexes, kraft mills, and coke ovens⁽²⁵⁻²⁷⁾. The H_2S emissions related to coal burning are relatively insignificant and incineration usually converts these H_2S to SO_2 , which is vented directly to the atmosphere. Production of sour natural gas and the refining of higher sulfur-content crude oil are the major concerns for H_2S emissions in the world today. H_2S contents in the gas streams (including raw gas and waste gas streams) of these facilities vary from 0-60% by volume, while some facilities with even higher hydrogen sulfide contents have also been reported⁽²⁷⁾. Possible H_2S emission sources (industries and processes), concentrations and flue gas characteristics are summarized in Table 2.1^(26, 28-33). Figure 2.2 and 2.3 illustrate some of these processes and possible sulfur impregnation points⁽²⁹⁻³³⁾.

The need to reduce H_2S and SO_2 from these sources and the economical potential of recovered sulfur compounds lead to various sulfur recovery technologies. The most commonly applied sulfur recovery technology is the Claus process, which has been successfully serving

these industries for over 100 years due to its relatively high recovery efficiency⁽²⁸⁾. However, with the more stringent regulations promulgated in recent years, the Claus process is considered to be a potential major air polluter, since the process typically recovers only 95-97% of the hydrogen sulfide fed to it. Tail gas clean-up processes are required to treat the exhaustion of the Claus process to achieve the overall sulfur recovery up to 99%.

2.2.1.1 Natural Gas Processing.

The average H₂S concentration in raw natural gas has a range of 0.055-4% by volume in different Air Quality Control Regions. However, it is also recorded that H₂S contents of some deposits can reach as high as 23% in Wyoming, 63% in Michigan⁽²⁹⁾, and 50% in Alberta, Canada⁽²⁵⁾. According to the regulation promulgated by the Department for Natural Resources, hydrogen sulfide emission from any combustion process including natural gas burning, should not exceed 165 ppm by volume⁽³⁴⁾.

Sweetening with amine is used to remove H₂S⁽³⁵⁾ from raw natural gas followed by the recovery of H₂S. The recovered H₂S undergoes the following treatments: (1) vented, (2) flared in waste gas flares or modern smokeless flares, (3) incinerated, or (4) utilized for the production of elemental sulfur or sulfuric acid. Emissions will result from gas sweetening plants only if the acid waste gas from the amine process is flared or incinerated⁽²⁹⁾. Otherwise, the acid waste gas is used as feedstock in nearby sulfur recovery plants or sulfuric acid plants. The emission of sulfur recovery plants will be introduced in the following sessions.

2.2.1.2 Petroleum Refining.

At an average level, approximately 50 tons of hydrogen sulfide is formed for each 20,000 barrels of crude oil with high sulfur content processed⁽³⁰⁾. The main sources of H₂S emissions in refineries are untreated gas stream leaks, vapors from crude oil and raw distillates, and condensate sewers.

One of the major operations in a refinery to produce H₂S is the atmospheric distillation process, which separates the crude oil into its various boiling point fractions. After initial distillation, light non-condensable fuel gas (hydrocarbons such as: CH₄) with hydrogen sulfide and ammonia are typically sent back as furnace fuel to heat the distillation system. Temperature of this mixture gas discharged from distillation column is up to 400°C⁽³⁰⁾. Air emissions of hydrocarbons, CO₂, H₂S, SO₂, and other constituents during atmospheric distillation arise from the combustion of fuels in the distillation furnace, process vents and fugitive emissions. The quantity of these emissions depends on the size of the unit, the type of the feedstock, and the cooling water temperature.

Other process units that release hydrogen sulfide include: vacuum distillation, thermal cracking, coking, and catalytic hydrocracking. The catalytic hydrocracking process is designed to make different products (for instance: gasoline), in which hydrogen is used to break heavy distillates produced from the atmospheric distillation process into lighter hydrocarbons. However, impurities such as sulfur and nitrogen bonded with hydrocarbons will be released to form hydrogen sulfide and ammonia, which not only cause poisoning of the catalysts but also

lead to hydrogen sulfide and ammonia emissions. Usually, feedstock of hydrocracking process need to be hydrogenated first to remove sulfur and nitrogen, and is then sent to the catalytic bed.

2.2.1.3 Sulfur Recovery.

There are several applications of Claus processes in sulfur recovery plants that were classified according to the H₂S concentrations in the feedstock. These concentrations have ranges of <10%, <20%, 20-50% and >50% as recorded in EPA documents⁽³⁶⁾. Usually, H₂S concentration below 20% is not suitable for the Claus process because the furnace cannot be self-sustained under such condition^(37, 38).

In the Claus process, one third of the H₂S feedstock is combusted with oxygen or air in the furnace to produce SO₂ at temperature up to 980-1540°C. The rest two third of the H₂S feedstock is sent to the thermal zone (temperature is about 650°C) to react with the SO₂ produced in the furnace. Approximately 70% H₂S can be converted to elemental sulfur and removed as sulfur liquid without scrubbing system. The remaining sour gases can further go through a series of re-heating, catalytic conversion and cooling/condensing steps to yield an overall recovery of up to 95-97%, depending upon the number of catalytic reaction stages and the type of reheat methods used. Temperature of this catalytic reaction is about 200-315°C. Usually 2 to 3 stages (or 2 to 3 beds) will be installed to ensure high sulfur recovery efficiency, which is normally as high as 96-97.5%. A schematic layout of the Claus process is illustrated in Figure 2.3⁽³⁶⁾.

In addition to main reactions (i.e., oxidation of H₂S to SO₂ and the reaction of SO₂ with H₂S in the reaction furnace), many other side reactions occur to form other compounds, such as: COS, CS₂, and CO₂. Typical tail gas from the Claus plant still contains 0.8% to 1.5% total sulfur, including 0.22% H₂S. Other constituents in the tail gas may also include: N₂, CO₂, Argon, and H₂. An existing New Source Performance Standard (NSPS) limits sulfur emissions from some Claus sulfur recovery plants at below 0.025% by volume⁽³⁸⁾. Accordingly, technologies are required to reduce H₂S emission from the Claus process tail gas, which involve one or more of the following processes: (1) extending the number of reaction stages, (2) adding scrubbing processes or, (3) incineration.

2.2.1.4 Kraft Pulping.

Hydrogen sulfide and organic sulfides are produced and released to the atmosphere from kraft mills in a number of locations. These emissions impart the characteristic odor in the vicinity of kraft paper mills and has been the cause of considerable air pollution problems. The major sources of hydrogen sulfide emission in kraft mills are the stack gases from the recovery furnace, the stack gases from the lime kilns, the non-condensables from the digester relief, the blow tank, and the multi-effect evaporator⁽²⁵⁾. H₂S concentration from these sources ranges from 0-0.11% by volume (up to 1080ppm). The current control technology is to reduce H₂S by process modifications and improved operating conditions. Several new mills have incorporated recovery systems (Table 2.1) that replace the conventional direct-contact evaporators so that H₂S emission can be reduced by more than 99%⁽³¹⁾.

2.2.1.5 Coke Production.

The sulfur emissions in coke production can occur in the form of hydrogen sulfide and carbon disulfide. Hydrogen sulfide is produced in the coking operation at the rate of about 6.7 pounds per ton of coal charged. H₂S concentration is about 4-13ppm in non-purified gas, 1-4ppm in partially desulfurized gas, and 0 ppm in municipal gas or pipeline gas⁽²⁵⁾. The recovery of coal chemicals is an economical necessity for modern coke ovens as they equal approximately 35% of the value of the coal. After the removal of water vapor, tar, light oils, particulate, and carbon compounds, the coke oven coal gas goes through a series of recovery processes, where ammonia, part of the light oils, and hydrogen sulfide are separated. In this case, H₂S recovery is normally done in a scrubbing tower containing a solution of ethanolamine⁽³²⁾.

2.2.1.6 Minor Sources.

H₂S emissions can also be found in other sources, such as: coal mining, chemical processing industries, dye manufacturers, viscose rayon manufacturers, sulfur productions, manufacturers of sulfur-containing chemicals, iron and metal smelters, food processing plants, and tanneries⁽²⁵⁻²⁷⁾. Sour gases produced in some of these industries (e.g., sulfur production) may have very high H₂S content. However, these sour gases are usually sent to sulfur recovery plants for further treatment. Some sulfuric acid plants burn spent acid and hydrogen sulfide as raw materials, where H₂S can be completely converted to SO₃ in the oxidation process. Hydrogen sulfide emissions from these plants are usually negligible⁽³³⁾.

Table 2.1 H₂S Emission Sources^(26, 28-33)

Emission Source	H₂S Concentration (%)	Temperature (°C)	Other Constituents	Type of Control
Vented gas from natural gas processing	N/A (very low)	Ambient	SO ₂ , and hydrocarbons	Untreated
Tail gas from natural gas sweetening	N/A	Ambient	SO ₂ and hydrocarbons	Flared
Off-gas from refinery distillator	N/A	400	Light hydrocarbons and NH ₃	Flared or fed back to distillation furnace
Off-gas from refinery sour gas sweetening	N/A	Ambient		Flared or reused
Off-gas from refinery hydro-cracking	N/A (high)	N/A	H ₂ , hydrocarbons and NH ₃	Sent to sour gas treatment unit: sweetening process
Tail gas from coking production	0-13ppm	Ambient	Coke oven gas	N/A
Tail gas from kraft pulping evaporator	0-0.11% (6 kg/ton pulp)	N/A	Steam and CH ₃ SH	Untreated, Venturi scrubber, ESP, or Auxiliary Scrubber
Tail gas from kraft pulping condenser	0-0.11%	Ambient	CH ₃ SH, CH ₃ SCH ₃ , and non-condensables	Untreated

Table 2.1 (Continued)

Emission Source	H₂S Concentration (%)	Temperature (°C)	Other Constituents	Type of Control
Stack gas from kraft pulping	0-0.11%	N/A	CH ₃ SH, CH ₃ SCH ₃ , and higher compounds	Untreated
Tail gas from Claus plant	0.22	200-315	SO ₂ , sulfur vapor, N ₂ , CO ₂ , Ar, H ₂ , COS, SO ₂ , and CS ₂	Extended scrubbing process, or incineration
Exhaust gas from incomplete flaring	N/A	N/A	CO ₂ , PM, SO ₂ , NO ₂ , and steam	Untreated

N/A: Information is not available.

2.2.2 Hydrogen Sulfide Control Technologies

Generally, if the H₂S concentration in a stream is fairly low, it is usually vented or incinerated. Hydrogen sulfide in H₂S-emitting industries (natural gas processing, oil refineries, coke ovens, and pulp factories) is removed as a waste by sweetening process or other tail gas clean-up devices. If recoverable, this formerly wasted H₂S is sent to H₂S-consuming industries (sulfur recovery or chemical production) as a raw material. A number of control technologies have been applied for H₂S emissions, such as: amine process, scrubbers, and incineration.

2.2.2.1 Amine Process.

Since 1930', attention has been turned to approaches that not only remove waste stream H₂S, but also recover sulfur for commercial use. The first was the Girbotol process⁽³⁵⁾, which has become the most widely used for removing H₂S even in the present time. Girbotol process is the major step of sour gas sweetening and its principle is also adopted by several H₂S scrubbing systems. This process is based on the fact that the amines can react with hydrogen sulfide at low temperatures to form salts, which dissociate readily upon heating.



Where: R = mono, di, or tri-ethanol

The hydrogen sulfide-bearing gas enters the base of the contacting tower or absorber and flows up through the tower countercurrent to the absorbing solution. The purified gas leaves at the top of the tower. Then the adsorbed solution rich in hydrogen sulfide enters the reactivator where the solution is heated and stripped of hydrogen sulfide by steam. Regenerated H₂S is sent to a condenser where the water is removed from the gas and returned to the system or discarded. The hydrogen sulfide-rich gas is then available for further use.

A disadvantage of the Girbotol process has been the inability of amines to adsorb H₂S in the presence of other impurities, such as: tars and oxygen. Numbers of improvements in the use of amines for gas purification have been made to improve the performance of this process, including the use of different amine combinations, super-atmospheric pressure, or split flow.

These improvements not only avoid process difficulties caused by impurities, but also increase the removal efficiency.

2.2.2.2 Incineration and Flaring.

Most H₂S emission related plants employ elevated smokeless flares or tail gas incinerators for complete combustion of all waste gas constituents, including virtually 100 percent conversion of H₂S to SO₂. However, some plants still use older and less efficient waste gas flares which usually operate at temperatures lower than necessary for complete combustion (in order to properly remove the sulfur, incinerators must operate at a temperature of 650°C or higher to ensure 100% H₂S conversion). As a result, larger emissions of H₂S, hydrocarbons and particulates may occur⁽³⁹⁾. Although the estimate of these emissions is not readily available, the disadvantages of flaring and incineration include considerable H₂S emission, especially for large capacity plants.

2.2.2.3 Scrubbing Process.

The current available scrubbing processes include two alternatives: oxidation type (converting total sulfur to SO₂) and reduction type⁽³⁶⁾. Reduction type of scrubbing process involves hydrogenation of total sulfur to H₂S, cooling and removal of moisture, and then followed by scrubbing processes. There are at least four reduction scrubbing processes developed for sulfur removal from the tail-gas of the Claus process: Beavon, MDEA, SCOT and ARCO. In the Beavon process, H₂S is converted to sulfur outside the Claus units undergoing a

lean H₂S-to-sulfur reaction. The other three processes utilize conventional amine scrubbing and regeneration to recycle H₂S back to the Claus process.

2.2.2.4 Other Technologies.

Other H₂S removal technologies include: (1) caustic soda adsorption and the Seaboard process which uses sodium carbonate, (2) the Shell phosphate process and phenolate process, and (3) the Thylox process⁽³⁵⁾.

Dry processes for removing hydrogen sulfide include: iron oxide and activated carbon adsorption. The former process is based on direct contact and reaction between iron oxides and hydrogen sulfide to form non-soluble sulfides. However, the use of this process on the large industrial scale is not looked upon favorably because of its slow kinetics and higher operational cost⁽⁴⁰⁾.

Activated carbon adsorption has great advantages in several applications, such as deodorization of air, removal of traces of organic impurities, purification of carbon dioxide, and the filtration of gas streams to remove sulfur compounds. Although this process is not usually utilized in refining industries, numerous studies have been carried out to investigate the nature of H₂S adsorption over activated carbons under conditions that are similar to refining waste streams (Section 2.3). Moreover, it was shown that activated carbons have the potential to remove H₂S from sewer gases⁽⁴¹⁾.

2.2.3 Possible Applications of Carbon Impregnation Using Waste Stream H₂S

Based on the above summary, it seems that there are two types of H₂S streams that can be used to impregnate activated carbon for the purpose of producing mercury adsorbents (possible application points are illustrated in Figures 2.2 and 2.3). The first application can be for the tail gases containing H₂S, such as vents from natural gas processing, coking production scrubber tail gas, the Claus plant tail gas, and the gas from kraft mill stacks, condensers and evaporators. As shown in Table 2.1, these streams also contain SO₂, hydrocarbons, inert gases, and steam. The Claus plant emissions even contain sulfur vapor, which could serve to increase the sulfur loading on the carbon. Temperature of these streams may vary from ambient temperature to 100°C, and above 300°C for the Claus plant. Hydrogen sulfide concentration is very low in these cases (*e.g.*, 1% in the tail gas from the reduction scrubbers in the Claus plants). The advantage of adsorbing low H₂S streams is that activated carbon may help to achieve complete removal of H₂S, given sufficient bed depth and reasonable flow rate.

The other possible application is to utilize H₂S produced during several unit processes. For example, the gases from refinery hydrocracking and coking processes contain H₂S and H₂ at a temperature up to 400°C, which may be suitable for physical adsorption of H₂S by carbon. Because the H₂S concentration in this gas stream is not very high, physical adsorption may be sufficient for complete removal. Also, coke oven foul gas after removing other impurities can be used for activated carbon impregnation. The problem for this application is that the stream contains a certain amount of light oil, which may foul activated carbon and prevent efficient H₂S adsorption. Therefore, more effective pretreatment of oil constituent or several stages of carbon bed may be required. Sour natural gas that is to be directly distributed to chemical plants and the

raw gas from coal gasifiers⁽⁴²⁾ in coal conversion plants can also be utilized for carbon impregnation. Moreover, activated carbon beds can be installed before any flares and incinerators to adsorb H₂S. However, interference by particulates, SO₂ and NO_x may need to be considered in these cases.

2.3 Activated Carbon Adsorption of Hydrogen Sulfide

Activated carbon is known to be suitable for the removal of hydrogen sulfide from natural, synthesis or other product gases⁽⁴³⁾. The performance of activated carbon is dependent on the physical properties of base materials and the methods of activation. Other factors which have a considerable influence on the adsorption process include the following: flue gas velocity and pressure, temperature, concentration of the adsorbates, concentration of other gas constituents, moisture content, carbon grain size and bed depth⁽⁴⁰⁾.

2.3.1 Physical and Chemical Adsorption of Hydrogen Sulfide

Physical adsorption is the adsorption process in which activated carbon adsorbs H₂S predominantly by Van der Waals forces, while chemical reaction with the adsorbate is negligible. Although activated carbon has significant amount of total surface area, the available active sites that can effectively capture H₂S from the gas stream are limited. Moreover, the H₂S bound to these sites can readily desorb upon temperature increase. These facts result in the relatively slow kinetics and low sulfur loadings on the carbon when only physical adsorption occurs. Mikhalovsky and Zaitsev⁽⁴⁴⁾ revealed that the carbon achieved a sulfur content of only up to 6% at steady state in a static system under inert atmosphere (Argon). When air was used instead of Argon, sulfur loading of the same carbon increased to 95%. Bandosz⁽⁴⁵⁾ stated that the capacities obtained in physical sorption tests are much less than chemical sorption capacities. The highest sulfur content in H₂S chemical sorption with air can be as high as 120% by weight⁽⁴³⁾.

Many studies^(43, 46-48) have suggested the possible mechanisms of H₂S chemical sorption over activated carbon in the presence of oxygen. The common knowledge of this process can be summarized as follows: first, H₂S and O₂ diffuse to the internal surface of the catalyst particle; O₂ is then chemically adsorbed and dissociated into atoms while H₂S adsorption is physical in nature; the reaction between these two adsorbed molecules is the next step; sulfur is formed and adsorbed at the internal surface leading to self-poisoning of the catalyst thereby influencing the reaction course. The key factors for this reaction involves partial pressure of both O₂ and H₂S, reaction temperature and the sulfur loading⁽⁴³⁾.

2.3.2 Kinetics of Hydrogen Sulfide Chemical Adsorption

The major reaction in hydrogen sulfide chemical adsorption involves the H₂S oxidation by oxygen to form elemental sulfur and water:



An investigation of H₂S oxidation rate has been provided by Klein and Henning⁽⁴⁷⁾. It was summarized that the rate varies from 0-1 and from 0.5-1 in terms of O₂ and H₂S respectively at relatively low H₂S concentrations. The existence of a steady state was found by Sreeramamurthy and Menon⁽⁴⁹⁾, who reported that the molten sulfur flows down the catalyst bed at temperatures above 120°C and the catalyst can remain active for days or weeks if the molten sulfur is removed from the system. Ghosh and Tollefson⁽⁴⁸⁾ agreed with the above finding and the authors also pointed out that one must consider the vaporization of sulfur from the pores, pore size distribution and pore geometry in order to predict the rate of reaction at steady state.

Blayden and Patrick⁽⁵⁰⁾ studied the impact of increasing reaction temperature on H₂S adsorption. They found that lower sulfurisation temperature resulted in higher sulfur retention, while the sulfur retained on activated carbon rarely exceeded 5% at temperature from 300-500°C. However, the carbons sulfurized at low temperature tended to be desorbed more readily than that produced at higher temperatures. On the other hand, Coskun and Tollefson⁽⁴³⁾ showed that sulfur loading increased with the increase in reaction temperature from 24°C to 152°C.

Sreeramamurthy and Menon⁽⁴⁹⁾ found that bed temperature usually rises about 10°C due to H₂S oxidation process. Using more carbon and higher H₂S concentration can increase the bed temperature to about 250% of the originally set temperature. Tests were also carried out using 6.25% H₂S and furnace temperature was set to 65-100°C, in which bed temperature increased from 23% to 34%. Both reaction rate and the maximum bed temperature appeared at about 8-10 minutes from the starting point. And the carbon bed cooled back to the original temperatures only after two hours or even longer time.

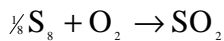
The impact of H₂S pressure in the stream was studied by Lee and Reucroft⁽⁵¹⁾. They showed that the sulfur loading increased with increasing H₂S relative pressure. However, this study was carried out only for H₂S concentrations below 2%. However, it was also found that the degree of temperature increase was independent of the preset temperature level.

Since the substantial sulfur build-up can reduce the surface area and the number of active sites on the carbon, some studies suggested that further reaction might be catalyzed by the reaction product other than active sites. Steijns and Mars⁽⁵²⁾ showed that hydrogen sulfide

oxidation was catalyzed by molten sulfur at low rates at temperatures above 130°C (sulfur melting point is 119°C). This result is in perfect agreement with that of Iwasawa and Ogasawara⁽⁵³⁾. On the other hand, Sreeramamurthy and Menon⁽⁴⁹⁾ found out that sulfur has no catalytic effect at temperature between 65°C and 100°C and that no SO₂ formed under these conditions. Other studies investigated possible H₂S conversion catalyzed by ^(43, 49, 54) and it was concluded that sulfur deposited in the carbon pores has no catalytic ability below 115°C.

2.3.3 Side Reactions and By-Products

Several side reactions also occur on the carbon surface during H₂S oxidation, which produce sulfur compounds other than elemental sulfur⁽⁴⁷⁾:



Ghosh and Tollefson⁽⁴⁸⁾ suggested that the predominant reaction: $\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S}$ can be carried out completely in the presence of activated carbon at temperatures below 200°C, while SO₂ and SO_x will be produced substantially at the reaction temperatures above 200°C. According to Mikhalovsky and Zaitsev⁽⁴⁴⁾, about 1% SO_x was produced at 102°C, 5% SO_x was produced at 152°C, and 10% SO_x was produced at 177°C. It was also concluded that high oxygen/hydrogen sulfide ratio improved the formation of SO_x. Moreover, Walker et al.⁽⁵⁵⁾

revealed that chemisorption of SO₂, and/or its dissociation products, was small between 50-300°C (amounting to about 1% of the total surface area).

Bandosz⁽⁴⁵⁾ suggested that at temperatures below 100°C, where most water can be retained, H₂S can be converted to SO₂ and further to H₂SO₄ in the water film. H₂S impregnated carbon was found to have a pH value of 2, which the author suggested was due to the acidity of sulfuric acid formed. On the other hand, Mikhalovsky and Zaitsev⁽⁴⁴⁾ found that no acidic products were formed when 15% H₂S in argon was adsorbed on carbon at 20°C. Sulfur was measured through photoelectron spectra as S⁰, S^{IV} and S^{VI}, which the authors attributed to the formation of elemental sulfur, C=S, C-S-H and C-S-C. Moreover, Blayden and Patrick⁽⁵⁰⁾ concluded that sulphurization by heating a carbon in the presence of H₂S vapor favors the formation of surface complexes through surface reactions only at temperatures above 300°C.

2.3.4 Impact of Surface Chemistry

2.3.4.1 Acidic Oxygen-Containing Functional Groups.

Long-term exposure to air or heating in oxygen leads to the formation of acidic oxygen-containing functional groups on activated carbon. Boehm et al.^(56, 57) and Coughlin and Ezra⁽⁵⁸⁾ concluded that the “Free valences” at the edges of graphitic layer planes of microcrystalline carbon are very reactive and can form compounds with any suitable foreign atoms present. Therefore, functional groups or surface compounds can be expected almost exclusively at the layer edges. Coughlin and Ezra⁽⁵⁸⁾ also suggested that foreign atoms and molecules which do not

covalently bound to the graphite edges can only be weakly bounded to the basal faces by means of graphitic π electron system.

The effect of acidic functional groups in carbon adsorption was reported differently when different adsorbates were taken into concern. Vidic et al.⁽⁵⁹⁾ concluded that the presence of acidic surface functional groups hindered the ability of activated carbon to adsorb phenolic compounds. This result was also reported in another study on the adsorption of phenol and nitrobenzene molecules from aqueous solution⁽⁵⁸⁾. On the other hand, it seems that the functional groups tend to enhance gas phase H₂S adsorption. Bandosz et al.^(45, 60) concluded that carbon with large number of acidic sites (including all types of functional groups) has better performance in H₂S adsorption. However, this better performance of carbon as indicated by the author is not the result of single influence of functional groups. Other factors such as: water uptake, basic groups and large number of pores larger than 30Å also have their roles in the reaction. Cariaso and Walker⁽⁴⁶⁾ also suggested that chemisorption is strongly sensitive to the geometry of the carbon surface and that activation in O₂ at 300°C creates a template susceptible to subsequent oxygen chemisorption. In their study, the oxidation rate was significantly higher for the O₂-activated carbon than for the CO₂-activated carbon (CO₂ activation was conducted at 900°C). Furthermore, Mikhalovsky and Zaitsev⁽⁴⁴⁾ pointed out that both pre-sorbed oxygen and oxygen from the feed gas are involved in the H₂S oxidation and carbon surface functional groups contributed significantly to the formation of SO_x.

Boehm et al.^(56, 57) utilized an acid/base titration method to classify acidic functional groups into four major groups which include: carboxyl, lactonic, phenol, and carbonyl groups.

These groups can evolve as CO or CO₂ from the carbon surface upon heating to different temperatures. The decomposition temperatures for these groups are as follows: carboxyl groups (200-400°C)⁽⁶⁰⁾ < lactonic groups (250-600°C)⁽⁵⁹⁾ < hydroxyl groups (500-600°C)⁽⁵⁹⁾ < phenol and carbonyl groups (500-900°C)^(59, 61). It was also suggested by Papirer et al.⁽⁶²⁾ that carboxyl, lactonic and phenol groups can be broken at 400°C to form ether-type structures while carbonyl groups resists pyrolysis.

Quantitative measurement of these four groups (as well as basic groups) by Boehm titration^(56, 57) is based on the fact that each type has different acidity that can be neutralized by different basic groups. However, as was also pointed out by the authors, the functional groups detected by this method account for only 50% of the analytically determined oxygen content. Moreover, acid/base titration technique does not differentiate between acidic groups and other acidic impurities, nor does it differentiate between basic functional groups and delocalized electrons.

Radovic et al.^(63, 64) suggested that H₂ treatment at elevated temperatures stabilizes carbon surface and maintains the carbon basicity, because H₂ not only removes most of the acidic functional groups from carbon surface sites but also stabilizes these sites to avoid re-adsorption of oxygen. This behavior is due to the formation of stable C-H bonds. It is also possible that increasing the basicity can increase the hydrophobicity of the carbon surface and increase electron-withdrawing ability of the constituents on the aromatic ring.

2.3.4.2 Metal, Metal Oxides and Promoters.

All the virgin activated carbons contain certain amount of metals and metal oxides that originally existed in the base materials or were formed during the activation processes. Some of these impurities are believed to promote the adsorption efficiency of the carbon. It was reported that the presence of promoters (impurities or additional catalysts) can reduce the activation energy of H₂S oxidation reaction by 12-20 kJ/mol⁽⁴⁷⁾.

It has been already known that oxides of iron, zinc, and copper are used in industry as absorbents or catalysts for H₂S removal from different gaseous media at 20-200°C. The H₂S removal at low temperatures mainly occurs due to gas-solid reactions in a thin hydrated lattice of metal oxides, which leads to the formation of sulfides. Carbonates of calcium and magnesium also have high affinity for H₂S adsorption in wet condition due to neutralization reactions⁽⁴¹⁾. According to Bandosz et al.⁽⁴¹⁾, sludge-derived adsorbents which are rich in Fe, Zn, Cu, and aluminum oxides that have weight losses between 20-30% after acid washing also have much better performances for H₂S removal.

Other promoters such as: sodium and iron⁽⁴⁶⁾, potassium iodide, silver iodide, steam at temperatures below 100°C⁽⁴⁷⁾, vanadium-grafted catalyst at sulfur melting point⁽⁴⁴⁾, and caustic soda⁽⁶¹⁾, have also been proven to improve the carbon performance for H₂S uptake.

2.3.5 Impact of Surface Texture and Particle Size

Surface texture of activated carbon includes several aspects, such as: total surface area, pore size distribution, and pore geometry. These properties are mainly governed by the carbon base material and activation process.

Lee and Reucroft⁽⁵¹⁾ compared H₂S uptake by coal-based (activated with KOH) and wood-based (activated with H₃PO₄) carbons at low pressure range (<2%) and found that coal-based carbon achieved over 12% sulfur loading compared to less than 7% for wood-based carbon. Activated carbons with lower surface area generally adsorbed more H₂S than those with higher surface area when H₂S pressure was below 1%. The authors concluded that the degree of surface area development and the limiting micropore volume generally control the adsorption process in the high relative pressure range through the micropore filling mechanism. This conclusion is consistent with results of Bandosz⁽⁴⁵⁾, which showed that predominantly microporous materials with high surface areas does not necessarily give better performance. The author suggested that because H₂S is a small molecule (diameter = 4.2 Å), microporous materials should be favorable for physical adsorption due to the enhancement of the adsorption potential. On the other hand, adsorbents with large portions of macropores and relatively small surface area may favor the creation of water film that can facilitate H₂S chemisorption and higher sulfur deposition⁽⁴⁵⁾.

Cariaso and Walker⁽⁴⁶⁾ showed that mass transport resistance within the carbon particles has a negligible effect on reaction rate when carbon particle size was reduced from 28×48 mesh

to 150×250 mesh. The authors suggested that particle size reduction to 150×250 mesh size would not be sufficient to reduce average micropore length.

2.3.6 Impact of Water Vapor

As mentioned before, steam promotes the formation of sulfuric acid at temperatures below 100°C. Kaliva and Smith⁽⁶⁵⁾ observed that humidity promotes H₂S oxidation at room temperature: the oxidation rate increased by a factor of 6 for an increase in relative humidity by a factor of 3. Badosz⁽⁴⁵⁾ suggested that H₂S breakthrough capacity is dependent on water uptake. On the other hand, Ghosh and Tollefson⁽⁴⁸⁾ showed that the sorption of water is negligible at 125-200°C. Moreover, Steijns and Mars⁽⁵²⁾ observed a significant decrease in H₂S conversion at 200°C when water vapor was added to the feed stream at the level twice that produced by H₂S oxidation.

The mostly commonly cited mechanism for the impact of water vapor on the reaction is through the formation of a water film on the internal carbon surface at low temperatures that facilitates the dissociation of O₂ and H₂S⁽⁶¹⁾. The presence of oxygen-containing groups is favorable for water sorption through hydrogen bonds with water at the edge of carbon crystallites. Water molecules tend to adsorb firstly on oxygen-containing groups and then on the water which was already adsorbed to finally become water clusters (condensation or water film)⁽⁵⁸⁾.

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Reaction Gases

Gases that were used to study H₂S oxidation reaction are listed in Table 3.1 together with information about manufacturers and purities.

Table 3.1 Reaction Gases

Reaction Gases	Manufacturer	Purity
H ₂ S	Matheson Gas Products, Pittsburgh, PA	99.99%
H ₂ S (in N ₂)	Praxair, Inc., Los Angeles, CA	5%±2%
N ₂	Praxair, Inc., Pittsburgh PA	99%
O ₂	Praxair, Inc., Pittsburgh PA	99.99%

3.1.2 Virgin Carbons

Five virgin activated carbons: BPL, F400, PCB, BD, and Centaur (Calgon Carbon Corporation, Pittsburgh, PA) were used in this study as received. Two uniform particle sizes, namely 10×16 (16×20 for Centaur) and 170×200 U.S. mesh size, were obtained by grinding and sieving the granular carbons. All the virgin carbon samples were thoroughly washed to remove fines and dried in an oven at 120°C. Dried carbons were stored in a dessicator until use. The research designation, base material, manufacturer, trade name, and particle size for each carbon sample are given in Table 3.2.

Table 3.2 Virgin and Modified Activated Carbons

Research Designation	Base Material	Manufacturer	Particle Size (U.S. Mesh)
BPL	Bituminous Coal	Calgon	10×16 170×200
BPL-a ^a	Bituminous Coal	–	10×16
BPL-h ^b	Bituminous Coal	–	10×16
BPL-w ^c	Bituminous Coal	–	10×16
F400	Bituminous Coal	Calgon	10×16
Centaur	Bituminous Coal	Calgon	16×20
PCB	Coconut Shell	Calgon	10×16
BD	Wood	Calgon	10×16

^a Nitric acid treated BPL carbon.

^b Hydrogen treated BPL carbon.

^c Sulfuric acid washed BPL carbon.

Preparation of these modified carbons is related in Section 3.1.3

3.1.3 Modified BPL Carbons

Oxidation, reduction and acid washing were performed to modify carbon surface characteristics. In oxidation treatment, BPL virgin carbon (10×16) was soaked in 15N nitric acid (EM Industries, Inc., Gibbstown, NJ) at a ratio of 5ml/g carbon, for 24 hours with continuous stirring at room temperature. Treated BPL carbon was washed with water till stable pH was obtained, and dried at 120°C. This nitric acid treated carbon was designated as BPL-a.

The reduction treatment was conducted under 99.99% pure hydrogen (Praxair, Inc., Pittsburgh, PA) atmosphere in a Lindberg Hevi-Duty furnace (Lindberg, Watertown WI) fitted

with a mullite tube. BPL virgin carbon (10×16) in the sealed mullite tube was flashed with 99% nitrogen for 30 minutes at room temperature to remove air. Nitrogen was then replaced by pure hydrogen with a flow rate of 0.2L/min. The carbon was then heated at a rate of 200°C/hr to a maximum temperature of 900°C, followed by outgassing the sample at the maximum temperature for another 10 hours before cooling back to room temperature at a rate of 200°C/hr. The carbon was used immediately after preparation to reduce oxygen chemical adsorption which normally occurs during storage. This carbon was designated as BPL-h.

BPL virgin carbon (10×16) was also treated with 10N sulfuric acid (Aldrich Chemical Company, Milwaukee, WI) at a ratio of 5mL/g carbon to remove metal and metal oxides from the carbon surface. This treatment was carried out for 24 hours with continuous stirring. The carbon was then washed and dried in the same way as BPL-a sample. This sulfuric acid washed BPL carbon was designated as BPL-w.

3.1.4 Deionized Water

The water used in experiments has been purified using reverse osmosis (RO Pure LP, Sybron/Barnstead Inc., Boston, MA) and deionization (Nanopure II, Sybron Barnstead Inc., Boston, MA).

3.2 Methods

3.2.1 Sulfur Impregnation

3.2.1.1 Experimental Set-Up.

Figure 3.1 illustrates the experimental setup of sulfur impregnation through hydrogen sulfide oxidation over carbon catalyst. Pure N₂ served as an inert carrier gas and was mixed with O₂ and H₂S entering the carbon bed. Flow rate of each gas stream was controlled by a needle valve. A total gas flowrate of 0.2L/min was maintained for all the experimental runs. The reaction was carried out in a ¾-inch inner diameter stainless steel reaction column charged with 1g of activated carbon sample. A 200 U.S. Mesh size stainless steel sieve was placed downstream in the column to support the carbon sample. The column was placed in a laboratory oven (Cole Palmer Model 05015, Cole Parmer Instrument Co., Niles, IL) in order to maintain stable temperature during the reaction. Exhaust gases were sent to a sodium chloride (NaCl) solution to remove the remaining hydrogen sulfide and then were vented into the fume hood.

3.2.1.2 Selection of Impregnation Conditions.

Bench-scale fixed-bed H₂S oxidation over activated carbons was previously investigated in some research^(45-48, 50, 52) in which different H₂S impregnation procedures and parameters were chosen to study the nature of this reaction. The following is a brief summary of experimental parameters that have been utilized in these studies:

- Total gas flow rate: 0.2-0.5L/min
- Carbon particle size: Granular, 20×40⁽⁴³⁾, 70×90, and 150×250⁽⁴⁶⁾ U.S.

mesh size

- Carbon sample weight: 0.05g⁽⁵⁰⁾, 0.4-1.2g⁽⁴³⁾, 2cc⁽⁴⁴⁾
- H₂S concentration: 0.3%-6.0%⁽⁴³⁻⁴⁶⁾, 15%⁽⁴⁴⁾, 2%-23%⁽⁵⁰⁾
- Reaction temperature: room temperature^(44, 45), 200°C^(43, 46, 48), 300°C, 500°C, 600°C and <600°C⁽⁵⁰⁾

Generally, temperatures of waste H₂S streams rarely exceed 200°C and many are close to ambient temperatures. Therefore, reaction temperature in this research was varied from room temperature to 200°C. H₂S concentration of 0%, 2.5%, 10%, and 25% were used in order to represent the range of H₂S concentration in the waste streams. Although typical H₂S concentration could be lower than 1.0 % H₂S in waste streams, higher concentrations of up to 25% can also be found in some processes (Section 2.2.1). Because of easy control and high relative accuracy, 25% H₂S composition was applied for many experiments in this research.

3.2.1.3 H₂S Impregnation Procedure.

Carbon sample of 1 gram was weighed and loaded into the stainless steel reaction column. The depths of adsorption columns for different carbons were similar (less than 0.5cm), except for BD carbon, which was almost twice as large compared to other columns due to its low density. After preheating the column to a desired reaction temperature, nitrogen with a flow rate of 0.2L/min was sent through the column for 10 minutes in order to remove air from the system. Then the reaction gases: H₂S and O₂ were added into the feed stream at predetermined flow rates. After a desired reaction time, H₂S and O₂ were turned off immediately, while N₂ was

continuously purged through the carbon bed for another 10 minutes to remove unreacted gases. Then the impregnated sample was collected from the reaction column and cooled down to room temperature, followed by immediate sulfur content measurement and thermogravimetric analysis (TGA). Carbon impregnation under each set of reaction condition was conducted at least 3 times and the average value of experimental results is reported in all cases.

3.2.2 Sulfur Content Determination

Sulfur content of impregnated samples was determined using a Leco Model SC-132 Sulfur Determinator (Leco Co., St. Joseph, MI). After preheating the furnace of the determinator to a temperature of 1200°C, a ceramic boat containing about 100mg of sample was placed inside the furnace. Sulfur in the carbon sample is oxidized with oxygen (Praxair Inc., Pittsburgh, PA) to sulfur dioxide and the evolved SO₂ is measured by an infrared (IR) detector. Calculated results are displayed in terms of percent sulfur. Standard sample (Leco Co., St. Joseph, MI) of known sulfur content (3.87%±0.06%) was used for the calibration of the sulfur determinator.

In order to define the linear range of sulfur measurement, a series of samples composed of sand and a known amount of sulfur were measured using sulfur determinator. Experimentally measured sulfur content of these samples as a function of theoretical sulfur content is displayed in Figure 3.2. The results revealed that sulfur measurement has good linear relationship within a range of 0-7%, suggesting that a sample with sulfur content higher than 7% needs proper dilution in order to be measured accurately. Therefore, samples with high sulfur content were accurately weighed, ground if they were granular carbons, and mixed with sand (sulfur content of the sand

is less than 0.005%) in order to dilute actual sample concentration into a linear instrument range. Each sample was measured at least 3 times and the average sulfur content was reported in all cases.

3.2.3 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was conducted using a Thermogravimetric Analyzer TGA7 (Perkin-Elmer Corporation, Norwalk, CT) to investigate thermal stability of carbon samples. Each sample was first heated from room temperature to 120°C at a rate of 10°C/min, where it was kept for 10 minutes to remove moisture. Then the temperature was raised to 460°C at a rate of 17°C/min, where it remained for another 10 minutes to remove sulfur (sulfur boiling point is 445°C). The sample weight was measured during the whole heating process and was reported as a percent of the initial sample weight.

Prior to thermogravimetric analysis, both weight and temperature calibrations of TGA7 were conducted to ensure data reliability. Weight calibration was accomplished within a range of 0-100mg using a 100mg standard provided by the manufacturer (Perkin-Elmer Corporation, Norwalk, CT). Temperature calibration was conducted within a range of 20-900°C. (The actual sample weight used in this study was from 20-30mg and the actual temperature was from 20-460°C.)

Differential Thermogravimetric Analysis (DTA), was also performed on several samples by calculating differential sample weight loss as a function of time. Similar initial sample

weights were used for different samples and differential weight loss of these samples was divided by the initial sample weights to give DTA profiles for better comparison among these samples:

$$\text{DTA (min}^{-1}\text{)} = \text{Differential Weight Loss (mg/min)} \div \text{initial sample weight (mg)}$$

3.2.4 Surface Functional Group Measurement

To classify and quantify oxygen-containing acidic functional groups (acidic groups) and basic groups existing on the carbon surface, Boehm titration^(56, 57) was performed on several carbon samples. Targeted functional groups and related reaction agents are listed in Table 3.3. Standard methods (Method 2310B and 2320B)⁽⁶⁶⁾ were used to measure the original concentrations of prepared basic and acidic reaction agents: 0.25N and 0.05N NaOH, 0.05N NaHCO₃, 0.05N Na₂CO₃, and 0.05N HCl. Standardization of 0.05N NaOH solution was conducted using 0.05N Potassium Hydrogen Phthalate (KHP) solution by titrating the solution to pH 4.5. The standardized NaOH solution was then used to determine the concentration of 0.05N HCl by titrating the solution to pH 7. The standardized HCl was then used to measure other carbonate solutions by titrating these solutions to pH 7 also.

3.2.4.1 Acidic Functional Groups.

Two grams of carbon sample was accurately weighed and soaked in 100ml of appropriate solutions in 160 mL glass vials. Teflon stoppers and aluminum caps were used to seal the vials in

order to prevent interference of carbon dioxide in the air. The vials were placed in a rotator and rotated end over end for 24 hours. The reaction solution was separated by filtration through a 0.45 μm nylon membrane and titrated to determine the remaining acid or base. Reaction solutions without carbon sample were also treated and titrated using the same procedure to provide control blanks.

After removing carbon from the solution, the amount of remaining base was titrated to pH 7 using 0.05N HCl solution. Base consumed by the acidic functional groups on the carbon surface was calculated as the difference between the amount of acid required to titrate the remaining base in the filtrate and the amount of acid required to titrate the control blank to the same endpoint (pH 7). The amount of acidic sites for a specific group were calculated under the assumption that 0.25N NaOH neutralizes total acidity; 0.05N NaOH neutralizes carboxyl, phenolic, and lactonic groups; Na_2CO_3 neutralizes phenolic and lactonic groups; and NaHCO_3 only reacts with phenolic groups.

The phenolic group content on the carbon surface was determined as the amount of 0.05N NaHCO_3 consumed by the carbon sample. Lactonic group content was calculated as the difference between the amounts of 0.05N Na_2CO_3 and 0.05N NaHCO_3 consumed by the carbon. Carboxyl group content was obtained by subtracting the amount of 0.05N Na_2CO_3 consumed by the carbon from the amount of 0.05N NaOH consumed. Finally, carbonyl group content was calculated as the difference between the amounts of 0.25N NaOH and 0.05N NaOH reacted with the carbon.

**Table 3.3 Targeted Functional Groups
and Reaction Solutions Used in Boehm Titration**

Functional group to be neutralized	Reaction solution
Total acidic groups ^a	0.25N NaOH
Carboxyl, lactonic and phenolic groups	0.05N NaOH
Lactonic and phenolic groups	0.05N Na ₂ CO ₃
Phenolic groups	0.05N NaHCO ₃
Basic groups	0.05N HCl

a. Total acidic groups include: carbonyl, carboxyl, lactonic and phenolic groups

3.2.4.2 Basic Functional Group.

Basic group content was evaluated by reacting the carbon in 0.05N HCl solution using the similar procedure as that for acidic groups. At equilibrium, the filtrate was separated from carbon and was titrated to pH 7 using 0.05N NaOH solution. The basic group content was calculated as the additional NaOH required to reach the endpoint for the filtrate as compared to the control blank.

3.2.5 pH Measurement

The pH of the carbon sample was measured by placing two grams of carbon in 100ml de-ionized water (DI water). After the sample was rotated for 24 hours, the filtrate pH was measured using a pH meter (Accument pH meter 25, Fisher Scientific, Pittsburgh, PA).

3.2.6 Ash Content Measurement

Ash content was determined by combusting the carbon sample in a muffle furnace (Type F62730, Barnstead/Thermolyne, Dubuque, IA). After preheating the furnace to 500°C, tare-weighted crucibles with known amount of carbon samples were placed in the furnace and the furnace temperature was maintained at 500°C for 10 hours before the samples were cooled down to room temperature and transferred to a desiccator. The sample residuals were carefully weighed and calculated in terms of percent ash content. Each sample was measured at least 3 times and the average ash content value is presented in this report.

3.2.7 Carbon Bed Temperature Measurement

A K type thermocouple (nickel-chromium vs. nickel-aluminum) was installed to measure the actual temperature changes in the carbon bed. As illustrated in Figure 3.3, the tip of the thermocouple was inserted into the carbon sample from the effluent side through the supporting screen and the thermocouple signal was measured by a digital thermometer (Type 2168A, Omega Engineering, Inc., Stamford, CT).

3.2.8 Leakage Tests in the System

A soap bubble test on joints in the H₂S impregnation system was conducted regularly to ensure that no leaks developed during the experiments. Inlet and outlet flow rates of the feeding gas were measured using a rotameter and showed no detectable difference.

4.0 RESULTS AND DISCUSSIONS

4.1 Impact of Reaction Temperature

The impact of reaction temperature on H₂S oxidation with 25% O₂ in the feed stream can be observed from Figure 4.1. Generally, at temperatures below 100°C, sulfur content increases with an increase in temperature. The change in sulfur deposition from room temperature to 100°C tends to increase when higher H₂S concentrations are applied. This behavior indicates that temperature change of the system may have more impact for higher H₂S concentrations than for the lower.

Almost all the samples exhibited slight decrease in sulfur loading when the reaction temperature increased from 100°C to 200°C. The reason for this deactivation can be attributed to the generation of sulfur oxides, which usually occurs when oxygen reacts with H₂S or elemental sulfur at higher reaction temperature. It was already demonstrated that the reaction:



can be carried out to completion at temperatures below 200°C^(43, 49). On the other hand, at reaction temperatures above 200°C, SO₂ and SO_x will be produced at a significant rate. Michalovsky and Zaitsev⁽⁴⁴⁾ observed that 1% SO_x can be produced at 102°C, 5% at 152°C and 10% at 177°C. Moreover, Walker et al.⁽⁵⁵⁾ found that SO₂ adsorption on activated carbon decreases sharply from 3% to 0.3% with an increase in temperature from 50°C to 150°C, and that SO₂ adsorption is negligible above 250°C. Therefore, the decrease in sulfur content above

100°C on Figure 4.1 is due to some H₂S or sulfur being converted to SO_x that can not be retained on the carbon surface.

Previous study showed that high oxygen to hydrogen sulfide ratio favors the production of SO_x⁽⁴⁶⁾, which could be one of the reasons for low sulfur deposition in experiments with low H₂S concentrations when oxygen pressure remained at excess level (25%).

Since the H₂S oxidation is a highly exothermic reaction with heat generation of up to 53 kcal/mole, it is important to investigate the actual temperature of the reaction bed during H₂S oxidation with 25% O₂. Tests with 25% and 2.5% H₂S in the feed stream were conducted at room temperature and the actual temperature measurement as a function of time is shown in Figure 4.2. When comparing reactions with high and low H₂S concentrations in the feed stream, it is clear that the high H₂S concentration reacts more dramatically. The maximum bed temperature reached above 70°C at 8-11 minutes and then dropped to about 45-50°C, where it remained throughout the rest of the experiment. Sharp and early temperature increase observed for 25% H₂S stream is due to fast H₂S transfer through the pore structure and the heat release that subsequently accelerates further H₂S oxidation. This result is in agreement with conclusion of Sreeramamurthy and Menon⁽⁴⁹⁾ that the catalytic activity has the same trend as the temperature of the catalyst with both of them showing a steep maximum within a short period of time from the start of the reaction. Reaction conducted using 2.5% H₂S in the feed stream, on the other hand, is limited by relatively low mass transfer rate. Mild temperature increase from 19-24°C may be too small to overcome the effect of low diffusion in order to accelerate the reaction to a higher rate.

Ghosh and Tollefson⁽⁴⁸⁾ also reported that actual bed temperature usually increases about 10°C above the “set temperature”. Sreeramamurthy and Menon⁽⁴⁹⁾ observed a 250% temperature increase when pure H₂S stream was treated at 100°C using a 10g carbon bed. Temperature increase is high in the present study (approximately 250% increase using 1g carbon) probably because the reaction was conducted at low temperature 20°C, where the same energy generated by the reaction would cause a dramatic temperature increase. It is also possible to deduce that when the “set temperature” is high, other reactions, such as: SO₂ generation (which is endothermic and requires high energy for initiation), the evaporation of sulfur, water and/or gaseous by-products, can also consume part of the reaction-produced heat. Thus, less bed temperature increase is more likely to be observed at high initial temperature conditions. Since the degree of temperature increase is directly dependent on H₂S concentration, initial temperature, and the carbon weight, the combined effects of these parameters should be taken into consideration in order to utilize reaction heat and provide operation safety in large-scale applications.

4.2 Impact of H₂S Concentration and Reaction Time

Figure 4.1 also shows the impact of H₂S concentration on sulfur loading. In general, sulfur loading increases with an increase in H₂S concentration. This increasing trend is easy to understand because H₂S oxidation initiates from the physical sorption of H₂S. Therefore, more H₂S in the feed gas means more reactant specie can be transferred onto the carbon inner surface so that higher amount of sulfur will be formed.

Sulfur loading and sulfur conversion ratio (sulfur loading/sulfur input) as the function of reaction time are illustrated in Figure 4.3. It can be observed that sulfur loading increases with prolonged reaction time for both high and low H₂S concentrations. Previous work⁽²⁴⁾ showed that over 50% sulfur loading can be achieved by reacting H₂S with oxygen over carbon catalyst for about 2 hours at 150°C. In the present study with higher H₂S concentration (25%) impregnation, 10 minutes reaction time was found to be sufficient to accomplish 13% sulfur loading at room temperature.

It can also be seen in Figure 4.3 that the conversion ratio (sulfur loading/sulfur input) decreases after the sulfur loading reaches a certain level. In addition, conversion ratio is much lower for high H₂S concentration than that for low H₂S concentration, although the former conditions resulted in much higher sulfur loading for the same time period. These results indicate that the activity of carbon catalyst is dependent on the sulfur coverage because the reaction may be hindered after available active sites were partially blocked by elemental sulfur. As can be seen from Figure 4.3, higher sulfur deposit results in lower conversion rate. Direct comparison of these two cases shows that the conversion ratio for high H₂S concentration starts to decrease when sulfur content reaches as high as 27%, while for the low H₂S concentration conversion ratio declines from the early stages of the reaction when the sulfur content is below 5%. Nevertheless, lower influent H₂S concentrations would be more desirable for practical applications because they would result in lower sulfur emission from this type of air pollution control system.

According to Iwasawa and Ogasawara⁽⁵³⁾, first deposition of sulfur tends to fill mesopores with radii ranging from 40-150Å. Further deposition tends to fill pores ranging from 7Å to 25Å, which represent the major part of the total pore volume. Jankowska et al.⁽⁶⁷⁾ suggested that deposited sulfur will also form new porous structure (transient pores), thereby converting mesopores into numerous micropores. High H₂S concentration may help to quickly reach the point when most of the porosity is present in the form of micropores that facilitates condensation of sulfur and its effective deposition. However, diffusion of H₂S into small pores becomes slower, which causes the reaction rate to decrease. On the other hand, low H₂S concentration never makes a big impact on the apparent pore size distribution but the low driving force for sulfur diffusion prevents significant sulfur conversion inside carbon particles.

As can be seen on Figure 4.2, the heat produced in the case of low H₂S concentration is too small to have an impact on the kinetics of the reaction, while high temperature increase in the case of the high H₂S concentration certainly improves the reaction rate. In their investigation of the conversion of low H₂S concentration (0-2%) by activated carbon, Lee and Reucroft⁽⁵¹⁾ concluded that the key factors appeared to be the surface chemistry and/or micropore size.

4.3 Impact of Oxygen Input

Figure 4.4 compares sulfur content of BPL carbon exposed to 25% H₂S in the feed gas in the presence and absence of oxygen. It is apparent that sulfur content increases dramatically throughout the whole temperature range by adding 25% oxygen into the feed stream. Addition of oxygen increases carbon capacity from 4% to 13% even at room temperature because H₂S is

more readily oxidized to sulfur in the presence of sufficient electron acceptor (oxygen). On the other hand, the reactions with no oxygen in the feed stream still achieved a little sulfur loading from 2% to 4%. This sulfur may be a result of H₂S physisorption as well as chemisorption involving oxygen-containing functional groups.

Differential weight loss represents the rate of weight loss as a function of time. Normalization of the differential weight loss profiles is accomplished by dividing differential weight loss with initial sample weight so that reactions performed with different sample sizes can be compared. Figure 4.5 compares derivative weight losses of pure sulfur (in sand) and carbons exposed to 25% H₂S at 100°C and without oxygen in the feed stream. Carbon produced with 25% oxygen in the feed stream has 27.1% sulfur and it exhibited initiation of the weight loss at the same temperature (200°C) as the sample containing 3.4% of pure sulfur mixed with sand. This similar thermal stability indicates that pores of the impregnated carbon are saturated with pure sulfur that is most likely located close to the external surface of the carbon particles.

It can also be observed from Figure 4.5 that the carbon impregnated without oxygen input started weight loss at higher temperature than pure sulfur sample, although both have similar sulfur content (3.05% vs. 3.4%). The higher thermal stability of this impregnated carbon is most likely due to the fact that the sulfur is deposited deeper inside the carbon pores, which results in slower diffusion of sulfur vapor out of the pore structure and requires higher energy to facilitate the process. This result also suggests that the acidic oxygen-containing functional groups on the carbon surface can serve as electron acceptors for H₂S oxidation.

It is also seen in Figure 4.5 that the carbon exposed to H₂S in the absence of oxygen exhibited significant weight loss below 100°C where no measurable weight loss was observed for the carbon impregnated with sulfur in the presence of oxygen. This weight loss at temperature below 100°C can be attributed to physically adsorbed H₂S because humidity build-up is negligible at the reaction temperature (100°C). Therefore, it seems that H₂S chemisorption is the predominant process on the activated carbon in the presence of excess oxygen.

4.4 Impact of Particle Size

Figure 4.6 shows the sulfur contents of PAC and GAC carbons when the reactions were conducted at 100°C. It can be seen that GAC showed higher adsorption capacity than PAC for all reaction times evaluated in this study.

Particle size decrease from 4×10 to 170×200 mesh size increases the external area by only 0.05m²/g, which is a tiny number compared with the original total surface area of 1050-1150m²/g (GAC, type BPL 4×10, Calgon Corporation, Pittsburgh, PA). Furthermore, the diameter of PAC particle is at least 4 orders of magnitude larger than micropores. Therefore, breaking particles to 170×200 mesh size is not sufficient to destroy micropores and affect the total surface area. Moreover, no significant difference in carbon bed depth was found between these two carbons, which indicates that Empty Bed Contact Time (EBCT) is similar for GAC and PAC. Therefore, it seems that neither the total surface area nor the EBCT is the key reason to cause the low capacity of PAC.

One possibility is that the destruction of large particles can affect pore structures, namely the presence of long transport pores. These pores have wide openings connected to the particle surface, and are winding into the particle to connect with micropores. When destroyed, these pores may fail to facilitate diffusion of the reacting species into micropores where most adsorption and reaction is believed to occur. Since the number of available micropores is essential for the carbon capacity, reducing the access to these micropores may eventually reduce the sulfur loading.

4.5 Thermal Stability of H₂S Impregnated Activated Carbons

The sulfur content of impregnated carbon was measured by a Leco Sulfur Analyzer. Sulfur content and TGA weight loss obtained for BPL carbons impregnated at different reaction temperatures are compared in Figure 4.7. It is obvious that weight losses of all the samples caused by heating in TGA apparatus are in agreement with the amount of sulfur measured by Leco analyzer. It is also important to note that in all cases, all of the sulfur was removed from the carbon surface upon heating to 400°C. Further increase in temperature to 460°C resulted in negligible weight change of these samples.

One major concern about the application of activated carbons impregnated with elemental sulfur through H₂S oxidation for mercury control will be the thermal stability of these adsorbents. According to Chang and Offen⁽⁷⁾, typical Hg containing flue gas from a coal-fired power plant has the temperature from 121-177°C. Energy & Environmental Research Center (University of North Dakota) also reported that most mercury control devices would not

significantly change the flue gas temperature⁽¹⁰⁾. The only exception is the hot-side ESP, whose operational temperature can reach 250-400°C. Therefore, the derivative weight losses of impregnated carbons from room temperature to the sulfur dew point (20-460°C) were measured and compared in Figure 4.8. Similar results were found for the samples produced at different reaction temperatures. All three samples experienced weight loss at temperatures above 210°C, which is higher than the realistic process temperatures. Therefore, nearly no sulfur loss from these adsorbents would occur in full-scale applications even if they were produced through low temperature impregnation processes.

4.6 Impact of Surface Modification of BPL Carbon

4.6.1 Hydrogen Gas Treatment

Three surface treatments were applied to BPL virgin carbon in order to evaluate the impact of total acidity, basicity and ash contents of the carbon on the uptake of H₂S. Because the ability of acidic functional groups to influence adsorption by activated carbon was demonstrated in some cases^(41, 45, 68), it is important to find out their impact on H₂S adsorption. Therefore, BPL virgin carbon was treated in H₂ gas at 900°C for 10 hours and this BPL carbon is denoted as BPL-h. Surface properties of BPL-h carbon are shown in Table 4.1.

As can be seen in Table 4.1, hydrogen treatment at 900°C is capable of eliminating most of the acidic groups from the carbon surface. Measurement of specific types of surface functional groups shows that no carboxyl or lactonic groups were left after hydrogen treatment because

these types of surface groups decompose at lower temperature when compared to other acidic groups.

Table 4.1 Surface Properties of Virgin and Modified BPL Carbons

Carbons	Total Acidity ^a ($\mu\text{eq/g}$)	Basicity ($\mu\text{eq/g}$)	PH	Ash (%)
BPL	249	456	6.6	6.83
BPL-h	54	507	9.3	7.2
BPL-a	1317	141	3.2	6.28
BPL-w	425	385	7.2	4.37

Performance of BPL-h carbon for H_2S sorption is shown in Figure 4.9. It is clear that BPL-h achieved much lower sulfur content when compared to BPL. H_2 treatment not only reduces the number of functional groups, but also terminates most reactive edge sites resulting in deactivation of carbon surface for further catalysis. The mechanism of deactivation of surface sites is due to the reaction between highly active carbon atoms with H_2 to form C-H bonds, which fixes the free electrons⁽⁶⁵⁾.

However, BPL-h carbon gradually regained its capacity to promote H_2S oxidation as the reaction temperature increased from 20°C to 200°C . This finding is in agreement with Radovic et al.⁽⁶³⁾, who showed that re-adsorption of oxygen takes place at a high rate at 150°C , but is negligible at room temperature. Therefore, it seems that some of the inhibited surface sites on BPL-h carbon can be reactivated at elevated temperature. As a consequence, the impact of H_2 treatment diminished for the higher H_2S oxidation temperatures.

4.6.2 Nitric Acid Treatment

It appears from the above discussion that acidic surface functional groups have a positive impact on the ability of activated carbon to promote H₂S oxidation. As can be seen in Table 4.1, the total acidic surface functional group content increased almost 5 times when compared to virgin BPL as a result of nitric acid treatment. However, as can be observed in Figure 4.9, sulfur loading of BPL-a is similar with that of BPL carbon at 100°C and 200°C, but is surprisingly lower at 20°C (only 3.3% sulfur content).

Figure 4.10 illustrates the derivative weight losses of BPL and modified BPL carbons. It is clearly shown that more weight loss can be detected on BPL-a below 100°C (may be caused mostly by water) and above 300°C (may caused by by-products or surface functional groups). It is very likely that the functionalities removed during a TGA experiment are by-products of nitric acid oxidation, which are normally very acidic. This may be the reason that pH of BPL-a is as low as 3.2, which can not be attributed solely to a larger number of functional groups because these groups are very weak acids. Therefore, it would be reasonable to expect that these by-products will remain and occupy substantial amount of active sites on carbon surface at room temperature, and would prevent H₂S from being adsorbed. Reactions at higher temperatures would likely lead to the removal of these by-products, thereby rendering carbon surface more active to catalyze H₂S oxidation. Another possible mechanism that could interfere with the target reaction is that these by-products would create strong acidic environment, which hinders the dissolution of H₂S in the adsorbed water. Bandosz et al.⁽⁶¹⁾ suggested that H₂S adsorption on activated carbon has a pH threshold below which the reaction will be suppressed.

Moreover, the weight loss for BPL-a above 300°C can also be attributed to the decomposition of functional groups. A number of literature references^(59, 61, 69) reported that carboxylic acids and lactonic groups decompose above 200°C, especially when carbon was oxidized at 20-150°C. Substantial amount of acidic groups produced in nitric acid treatment could block active sites for H₂S catalysis at room temperature, or completely occupy micropores where most of the adsorption is supposed to take place.

4.6.3 Acid Washing

As shown in Table 4.1, acid washing in diluted sulfuric acid reduced the ash content of BPL carbon by 36% compared with the original BPL. However, this acid washed BPL carbon (BPL-w) did not show any significant changes in terms of sulfur loading when compared with BPL-a except of low impregnation temperature (Figure 4.9). This indicates that the ash content of BPL carbon could play an important part in promoting the H₂S oxidation only at low temperature while it does not contribute to catalytic properties of activated carbon at higher temperatures. Based on all the results shown in Figure 4.9, it can be concluded that while the presence of acidic groups and surface metals (ash) may be important for catalytic properties of the carbon at room temperature, they become less relevant at higher reaction temperatures.

4.7 Performances of Different Commercial Available Virgin Carbons

Several commercially available virgin carbons were also tested for their surface properties and the results are listed in Table 4.2. Capacity of these carbons to adsorb H₂S after 10 minutes of reaction time at different reaction temperatures are shown in Figure 4.11.

Table 4.2 Surface Properties of Virgin Carbons

Carbon	I ^a ($\mu\text{eq/g}$)	II ^b ($\mu\text{eq/g}$)	III ^c ($\mu\text{eq/g}$)	IV ^d ($\mu\text{eq/g}$)	Total Acidity ($\mu\text{eq/g}$)	Basicity ($\mu\text{eq/g}$)	Ash (%)	Surface Area(m^2/g)
BPL	8	25	125	91	249	456	6.83	1020 ⁽²⁴⁾
PCB	0	0	143	10	153	531	2.46	1124 ⁽⁷⁰⁾
F400	45	284	0	26	355	411	6.82	1224 ⁽⁷⁰⁾
BD	62	67	48	83	260	305	0.37	510 ⁽⁷⁰⁾
Centaur	25.9	58	17.1	131	232	521	4.23	632 ⁽⁶⁸⁾

a. Carboxyl groups; b. Lactonic groups; c. Phenolic groups; d. Carbonyl groups

As can be observed in Figure 4.11, almost all the carbons showed the highest capacity at 100°C, except for Centaur, which exhibited the highest sulfur loading at room temperature. Sulfur loading of these carbons varies from 5-40% at 20°C, while it has smaller ranges of 26-34% at 100°C and 20-31% at 200°C. It is possible that the reaction mostly depends on the base material or surface properties at room temperature, since the impact of reaction kinetics may be insignificant under such condition. On the other hand, higher reaction temperatures lead to faster reaction rate, which may overshadow carbon-related factors and result in similar adsorption performances of these carbons.

The impacts of total acidity, basicity, and ash content of the carbons on H₂S adsorption are shown in Figure 4.12, 4.13, and 4.14. No direct relationship can be found between these surface properties and sulfur loading obtained. This may be attributed to the fact that the amounts of total acidity, basicity and ash content are fairly small on these virgin carbons and that their impacts may be shadowed by substantial sulfur build-up during the impregnation using 25% H₂S

in the influent. Furthermore, no relevance was found when each of the acidic groups was compared with sulfur loading (data not shown).

Figure 4.15 shows the relationship between sulfur loading and surface area of the carbons used in this study. As can be observed, sulfur loading increases with surface area at room temperature while it decreases at 200°C. The only exception to this trend is the Centaur carbon that was produced using a proprietary process to enhance its catalytic ability at room temperature. When reaction was conducted at 100°C, sulfur content seems more independent of surface area. These trends may be due to the fact that most sulfur deposits on the carbon surface may be in the liquid form at 100°C, which may alter the pore structure and change the adsorption behavior of these carbons.

As shown in Figure 4.11, Centaur has the highest potential to catalyze H₂S conversion at room temperature (40% sulfur by weight). The reason for this better performance is not obvious, because surface properties of Centaur are within the range of these observed for other carbons used in this study. One possible explanation can be that the micropore volume of Centaur is high (83% of its total pore volume as reported by Bandosz et al.⁽⁶⁸⁾) which effectively adsorbs H₂S and retains more sulfur. Despite of its larger fraction of micropores, Centaur has a relatively small surface area among all the carbons used (632 m²/g as shown in Table 4.2). It seems that pore size distribution or pore geometry is much more important for H₂S uptake than total surface area. Unfortunately, the pore size distributions of other carbons are not available to compare with that of Centaur. Therefore, it is not possible to fully explain the significance of pore size distribution on this reaction.

5.0 SUMMARY AND CONCLUSIONS

5.1 Summary

For higher H₂S concentrations in the feed stream, it appears that, room temperature is sufficient to achieve high sulfur loading. On the other hand, slight heating along with prolonged reaction time should be used for low H₂S concentrations in the feed streams. However, temperatures above 100°C are not desirable since they will cause other pollutants, such as SO_x and SO₂, to form and will reduce sulfur loading on the carbon surface. Actual catalyst bed temperature increases during the reaction and the degree of increase varies with different H₂S concentrations in the influent gases. This behavior should be taken into account when considering practical applications.

In general, reaction time and H₂S concentration in the feed stream that are needed to achieve sufficient sulfur content approximately of 10%, which was shown to be adequate for mercury removal, can be broadly classified as follows: 10 minutes reaction time is enough when high H₂S concentration (*e.g.*, 25%) is applied, while low H₂S concentrations (*e.g.*, 2.5%) require longer time, but no more than 30 minutes. In terms of H₂S conversion rate, the activated carbon is more effective in removing low H₂S concentrations than the highly concentrated streams.

Mechanisms of H₂S oxidation under different H₂S pressures differ for high and low H₂S concentrations. It seems that high H₂S concentration in the feed stream initiates the reaction quickly by providing large driving force for faster diffusion to inner pores. As a result, sulfur loading increases quickly and is accompanied with significant heat generation. This generated heat, in turn, will accelerate the degree of reaction rate until some degree of pore saturation is

achieved. Although, the sulfur loading may still increase after significant micropore saturation is accomplished, the rate of sulfur conversion decreases to the point that it makes the sorbent unattractive for practical applications.

On the other hand, reaction with low H_2S concentration in the feed stream starts slowly and generates insufficient heat to improve the rate of reaction. As the reaction proceeds, small amount of sulfur is formed steadily and the initial pore structure is altered by deposited sulfur. This conversion of the pore structure towards micropores reduces the rate of mass transfer and reduces the reaction rate. Heat generated by the reaction is fairly small to cause appreciable temperature change in the reactor. Pore filling with deposited sulfur causes similar effect to that already discussed for high H_2S concentrations in the feed stream. However, it will take much longer to reduce the reaction rate than with high H_2S concentration because the carbon is still far from saturation. By using longer EBCT or lower H_2S concentration in the feed gas, conversion rate would be maintained at higher level for a longer period of time

Surface oxygen that exist on the carbon surface in the form of acidic groups can react with H_2S to form elemental sulfur, but the sulfur loading will be limited to below 4%. Sulfur loading can be greatly increased even at room temperature by adding excess oxygen to the influent. Because the surface oxygen is located in the inner pores of the carbon particle, the sulfur produced by this reaction has high thermal stability since steric blockage will prevent it from easily diffusing out of the carbon particle. H_2S oxidation without oxygen would result only in physical sorption of H_2S and low sulfur conversion that is not desirable for real applications.

Performance of PAC for the conversion of H_2S was observed in the present study to be somewhat below that of a GAC. Surface area change from GAC to PAC is not very significant and its influence was addressed in this study. Modified pore structure resulting in the increase of transport pores could be the most possible reason for the lower capacity of PAC and further study of the impact of pore size distribution is needed to fully explain these results.

Activated carbons impregnated with sulfur under all experimental conditions possess good thermal stability. Even adsorbents produced at room temperatures will not lose sulfur at temperatures below 210°C . Due to the existence of impurities and different sulfur molecular structures, impregnated sulfur evaporates at temperature below the sulfur boiling point. Information on the major sulfur structures or impurities could be helpful to better understand more about sulfur reaction with activated carbon surface. This information can be perhaps obtained using more sophisticated surface science techniques like Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM).

Sulfur deposited on carbon in impregnation below 200°C can be removed by heating the sorbents to more than 400°C .

Hydrogenation of activated carbon surface is effective in reducing or even eliminating acidic functional groups on the surface because it deactivates surface sites. As a result, the ability of the carbon surface to convert H_2S to sulfur is diminished. Nitric acid treatment causes total acidity of the surface to increase greatly but it does not facilitate better performance in H_2S conversion, especially at room temperature. This ineffectiveness can be attributed to the

combined effects of excess functional groups and acidic impurities. Unfortunately, the single effect of acidic groups cannot be determined at this stage. Acid washing can cause the ash content to decrease in BPL carbon. This treatment exerts the impact on the ability of activated carbon to catalyze H₂S oxidation only at room temperature.

The present study was not successful in identifying those surface properties that are chiefly responsible for H₂S oxidation to elemental sulfur in the presence of oxygen. This is not so surprising because the catalytic surface used in this study is that of activated carbon, which is known to possess multitude of properties, both chemical and morphological, that can catalyze numerous reactions. In such situation, it is almost impossible to separate any single property and evaluate its impact on a given reaction. To accomplish this goal, one would have to start with a surface with much simpler chemical and morphological properties, such as highly oriented pyrolytic graphite.

5.2 Conclusions

- Reaction conditions that achieve sufficient sulfur loading on BPL carbon for enhanced mercury control (sulfur content is approximate 10%) are summarized in Table 5.1. In terms of H₂S conversion rate, activated carbon is more effective in removing H₂S from low-level waste streams than from highly concentrated streams. Actual catalyst bed temperature increases during the reaction and the degree of increase varies with influent H₂S concentration. This behavior should be taken into account when considering practical applications.

Table 5.1 Summary of Reaction Conditions

H ₂ S%	Reaction Temperature	Reaction Time	O ₂ %	Sulfur Conversion	Bed Temperature
High 25%	Room Temperature	10min	25%	Low (up to 40%)	High (250%)
Low 2.5%	<100°C	Up to 30min	25%	High (up to 67%)	Low (31%)

- High hydrogen sulfide concentration is more suitable for the impregnation process, if the goal is to obtain high sulfur loading on activated carbon. On the other hand, higher conversion rate can be achieved by using lower H₂S concentration or longer EBCT (Empty Bed Contact Time).
- H₂S oxidation in the absence of oxygen is not desirable not only because it results in low sulfur content on the carbon (below 4%), but also because physically adsorbed H₂S can be re-emitted from the sorbent during handling. Addition of oxygen in the feed gas can greatly increase sulfur loading on BPL carbon.
- Activated carbons impregnated with sulfur under all experimental conditions are suitable for enhanced mercury control under realistic process temperatures because of the thermal stability of sulfur deposits. Sulfur deposited on activated carbon can only be removed by heating the adsorbents to more than 400°C.
- Surface modifications (*i.e.*, reduction, oxidation, acid washing) do not have much practical relevance because their impact on the ability of activated carbon to catalyze H₂S oxidation is minimal.

- Sulfur loading on activated carbons is not related to base material or surface properties, such as total acidity, individual acidic functional group type, basicity, ash content, and total surface area. Centaur is the best sorbent to achieve the highest sulfur loading at room temperature.

6.0 SUGGESTIONS FOR FUTURE WORK

- Mercury removal needs to be studied using H₂S impregnated carbons produced under different conditions to investigate the impact of different impregnation procedure on mercury up-take.
- Because most H₂S waste streams also contain a great amount of other constituents, such as moisture, CO₂, SO₂, H₂, N₂, NH₃, hydrocarbons, light oil or particulates, impacts of these impurities on H₂S oxidation over activated carbon surface are worth studying when considering industrial application of this process.
- Impact of oxygen feeding scheme (*i.e.*, continuous vs. pulsed) on reaction kinetics, sulfur loading and bed temperature changes.
- To scale up impregnation system, some considerations have to be studied such as: carbon load for maximum treatability, flow pattern of the feed gases, heat generation, and pressure drop, in order to design reactors to achieve both high H₂S conversion and sufficient sulfur loading.
- Influence of carbon pore size distribution and pore structure on reaction kinetics to choose better particle size, base material and carbon activation method.
- Sulfur speciation deposited on carbon should be studied to better understand kinetics, impact of side reactions and effect of surface functional groups in catalyzing H₂S oxidation.

APPENDIX

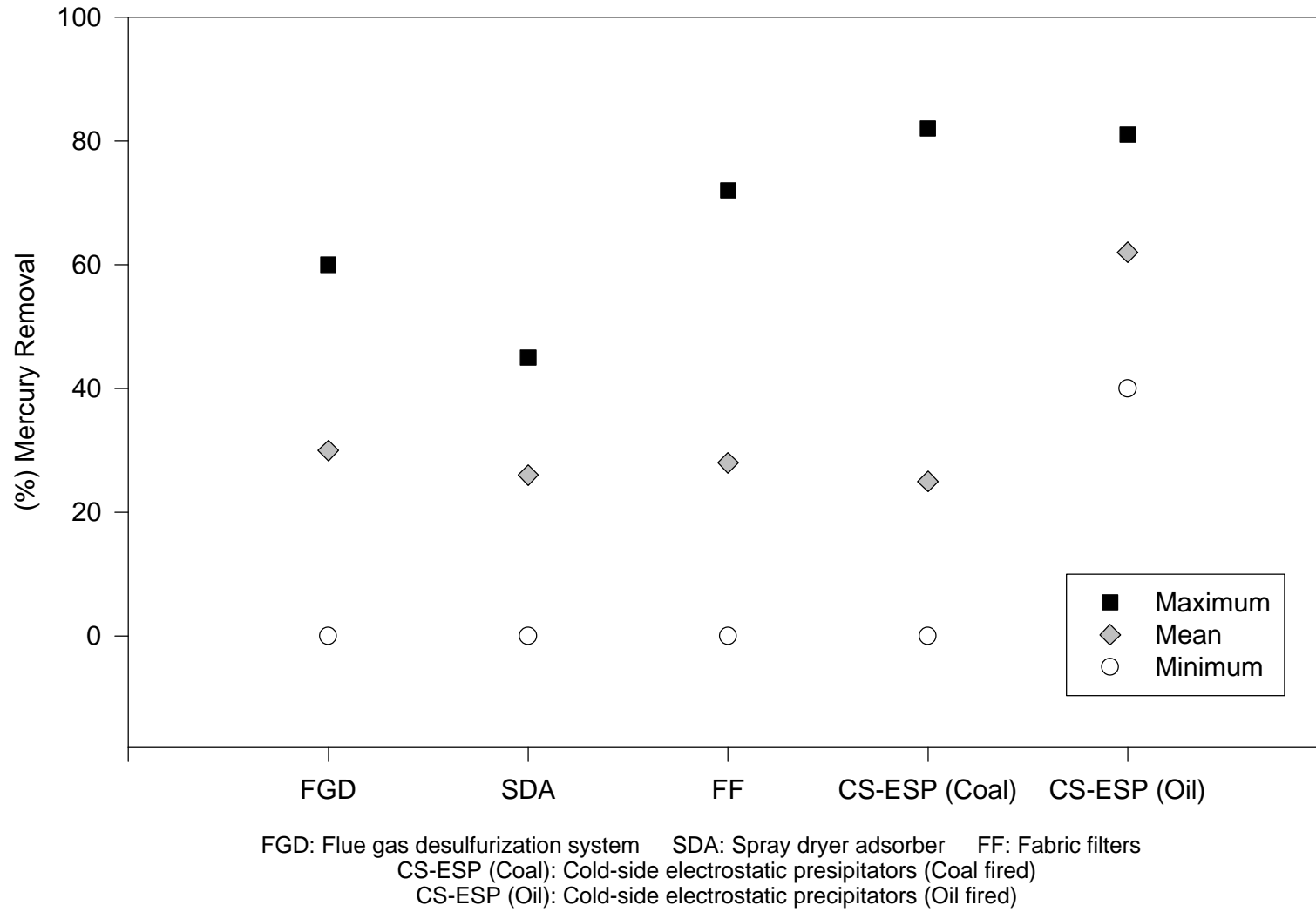


Figure 2.1 Comparison of Mercury Removal Efficiencies of Conventional APCDs⁽⁴⁾

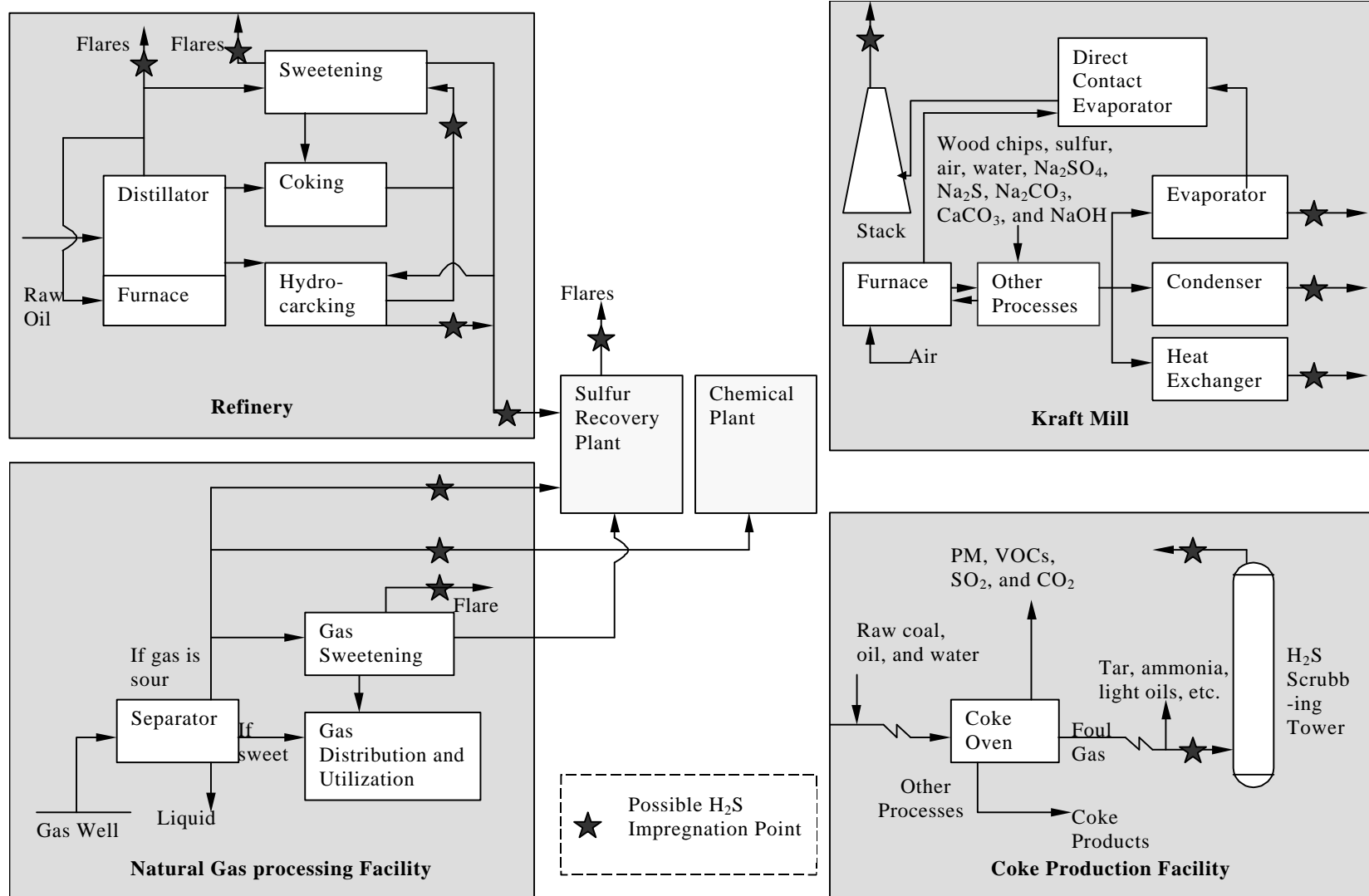


Figure 2.2 Possible H_2S Emissions and Impregnation Points in Several Industrial Processes⁽³⁰⁻³⁴⁾

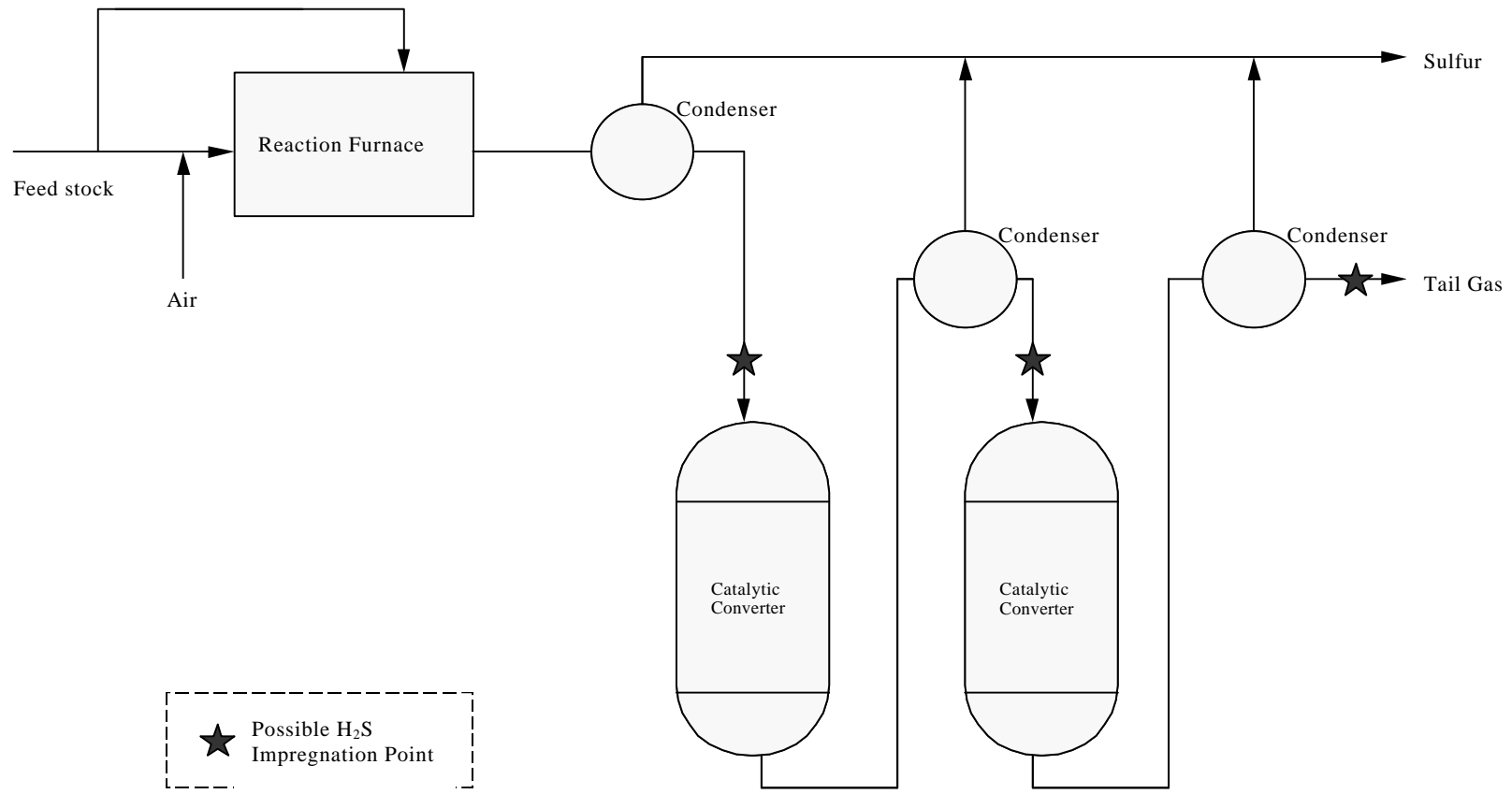


Figure 2.3 Typical Claus Sulfur Recovery Units⁽³⁷⁾

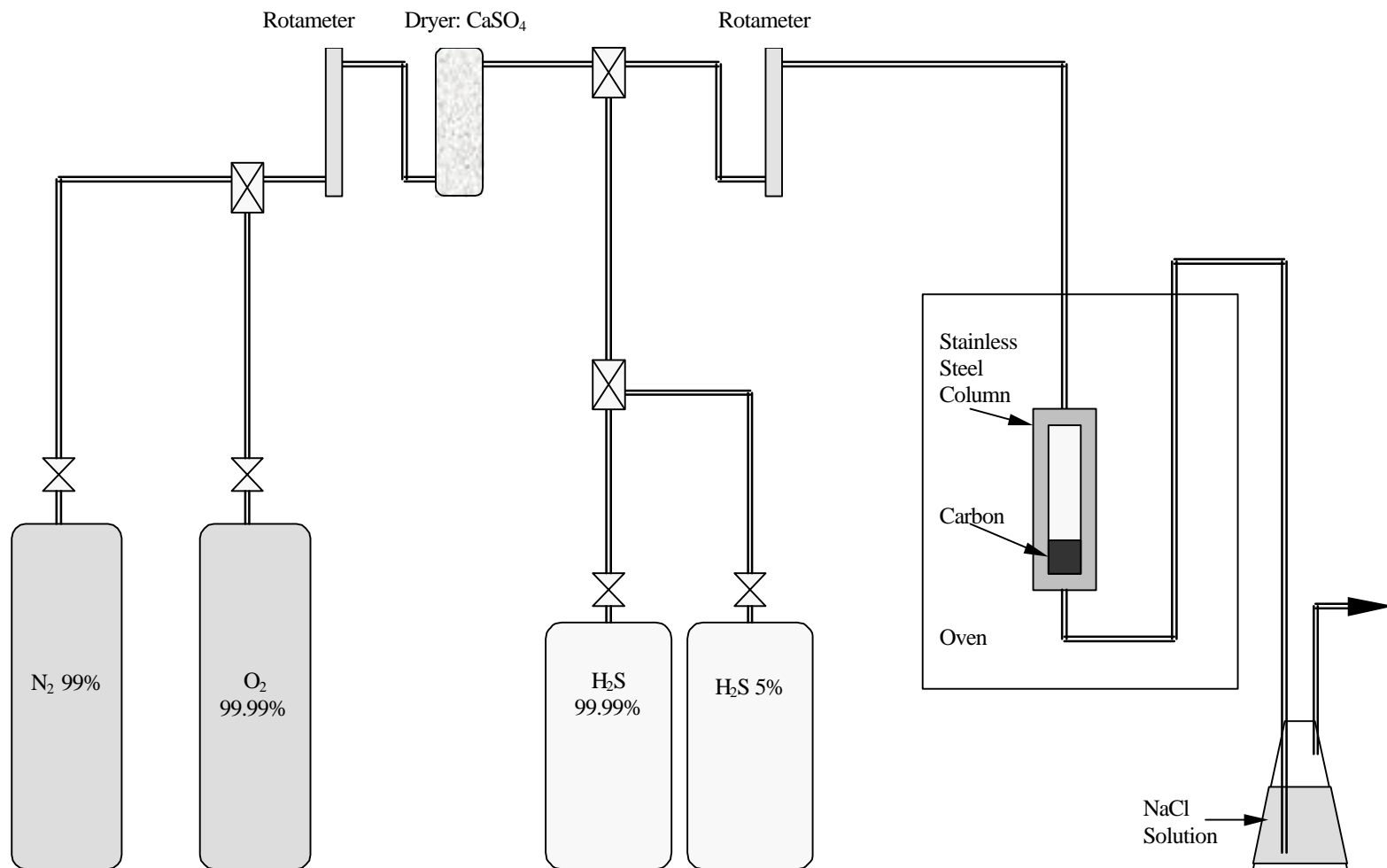


Figure 3.1 H₂S Oxidation Experimental Set-Up

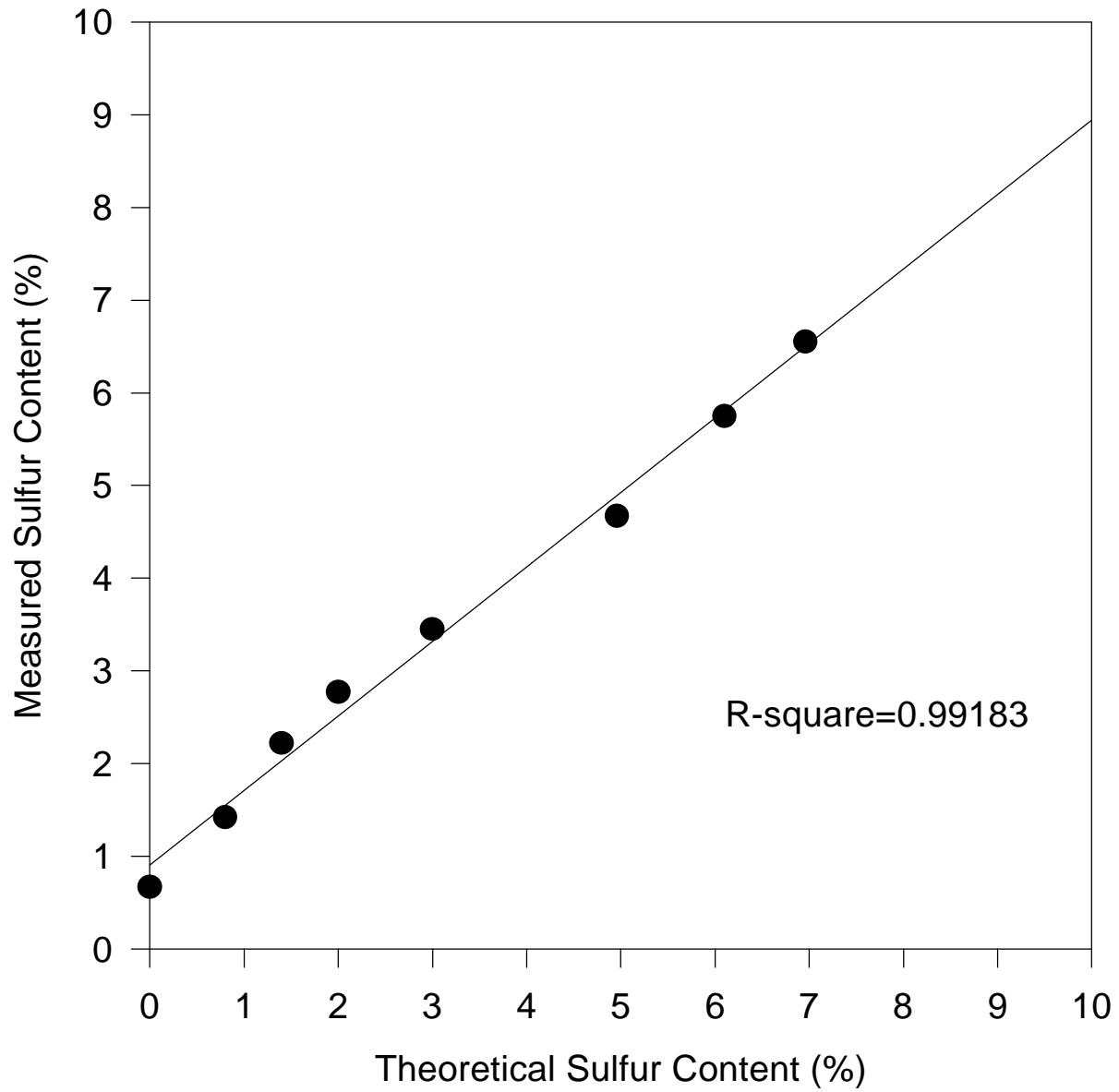


Figure 3.2 Linear Range of Sulfur Determinator

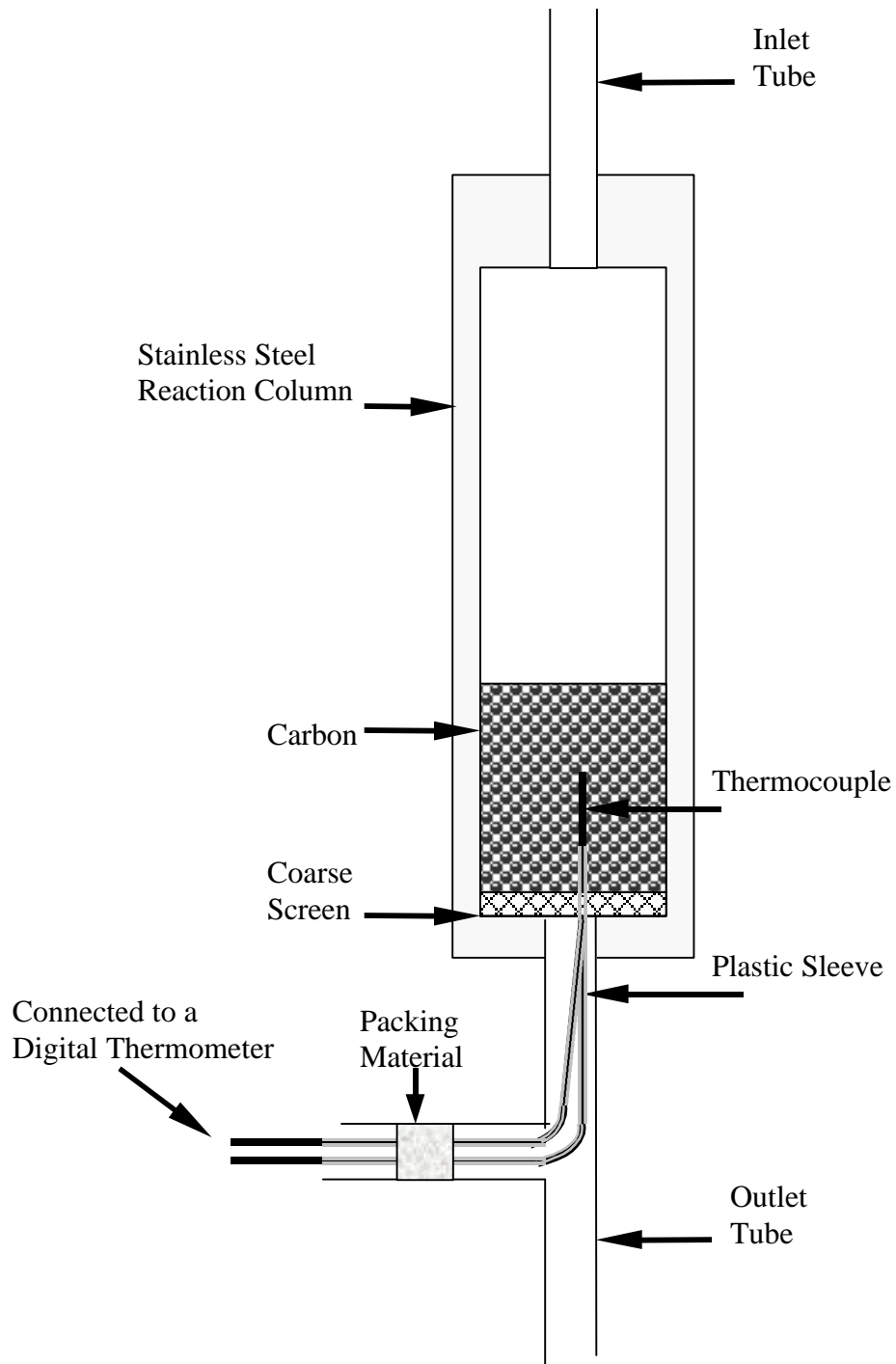


Figure 3.3 Carbon Bed Temperature Measurement

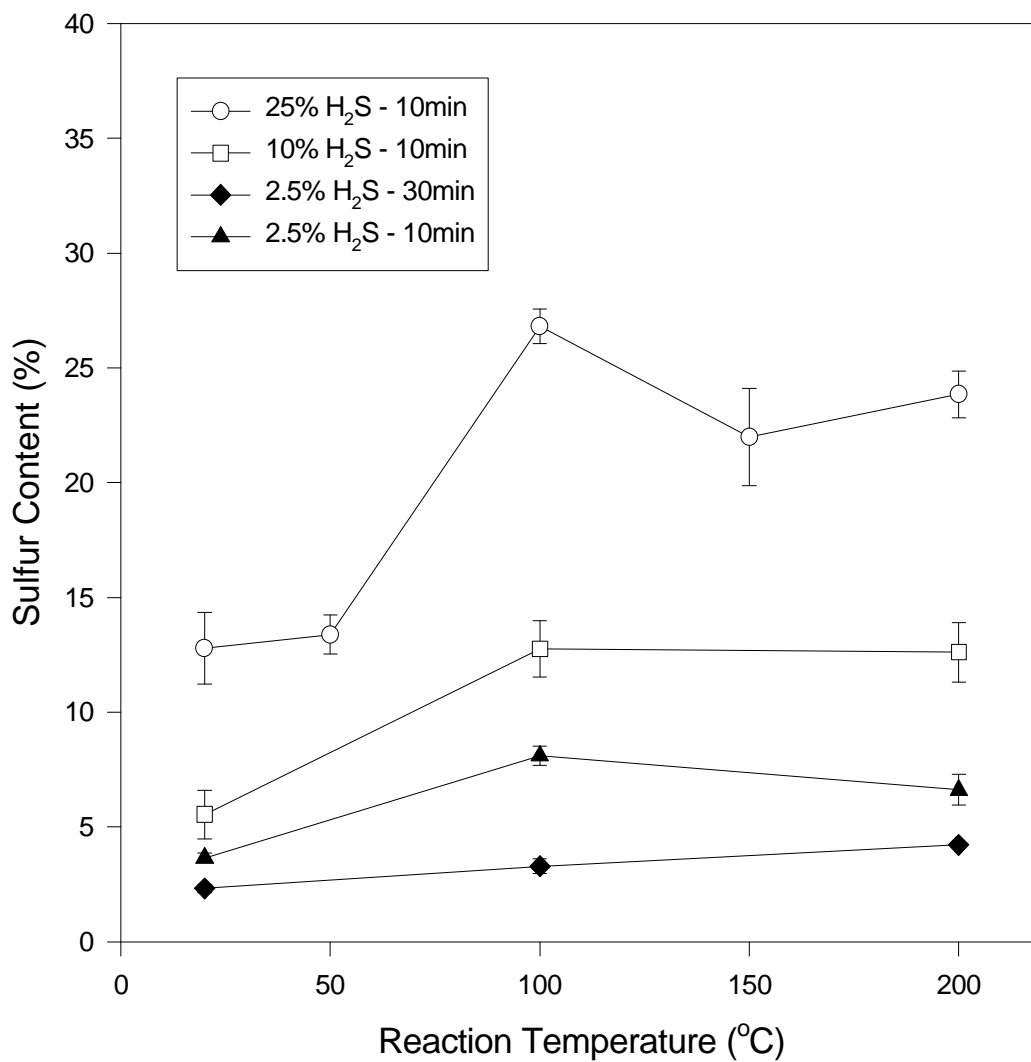


Figure 4.1 Impact of Reaction Temperature and Time on Sulfur Loading through H₂S Oxidation in the Presence of 25% O₂

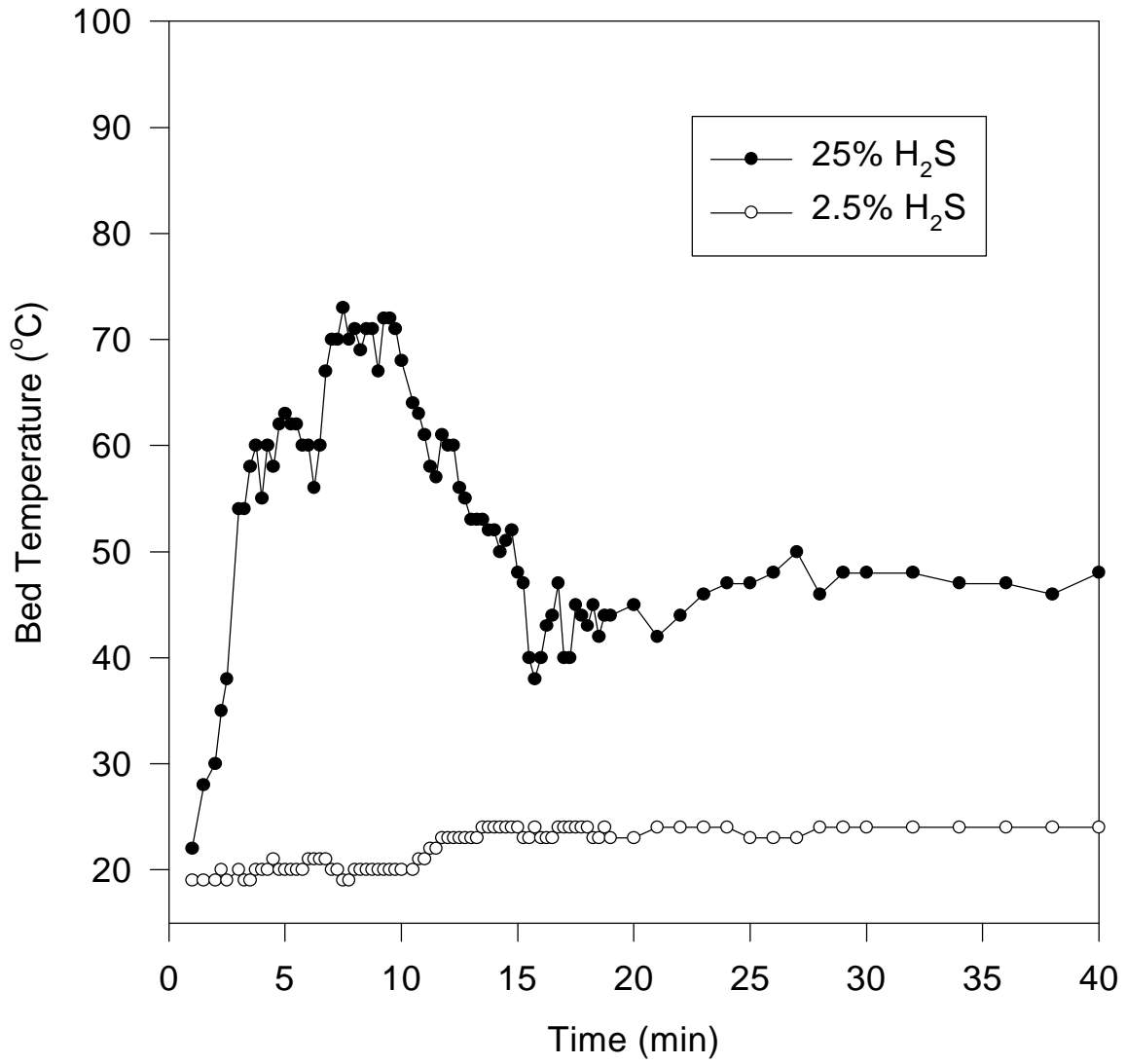


Figure 4.2 Actual Bed Temperature for Impregnation Using Different H₂S Concentrations (25% O₂ in the influent, set temperature = 20°C)

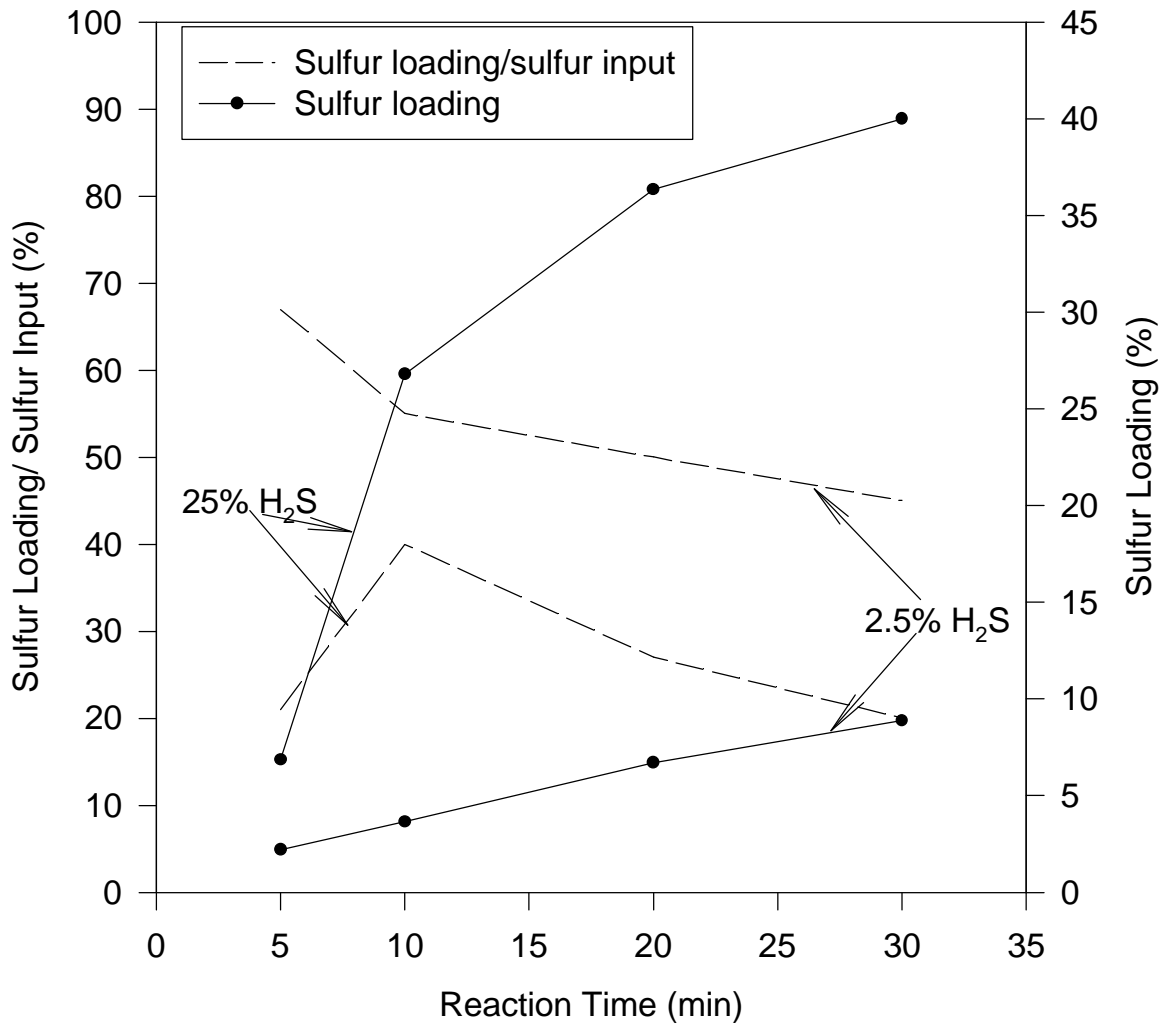


Figure 4.3 Impact of H₂S Concentration and Reaction Time on Sulfur Loading and H₂S Conversion (reaction temperature = 100°C)

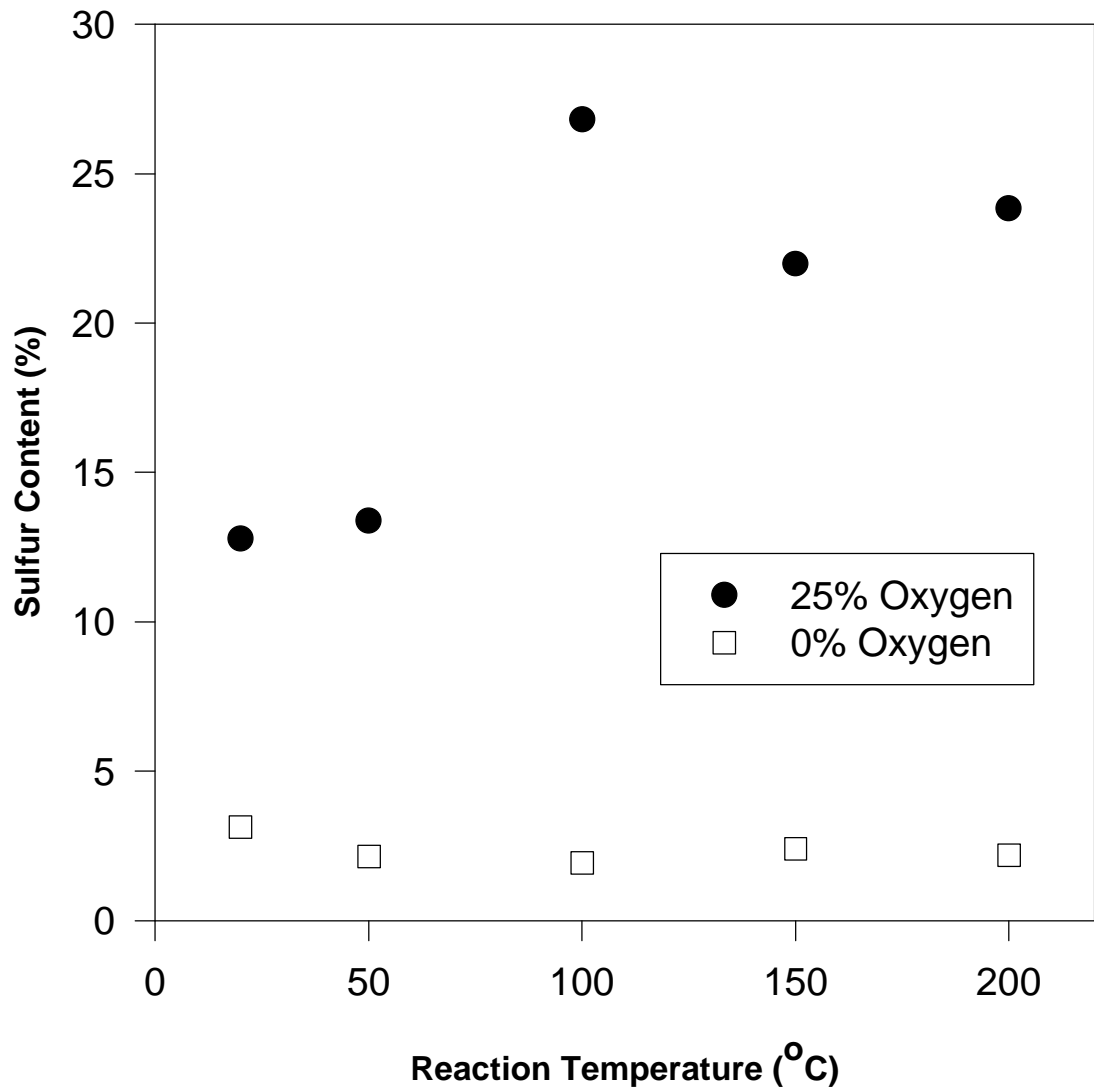


Figure 4.4 Impact of Oxygen Concentration on Sulfur Loading through H₂S Oxidation (reaction time = 10 min)

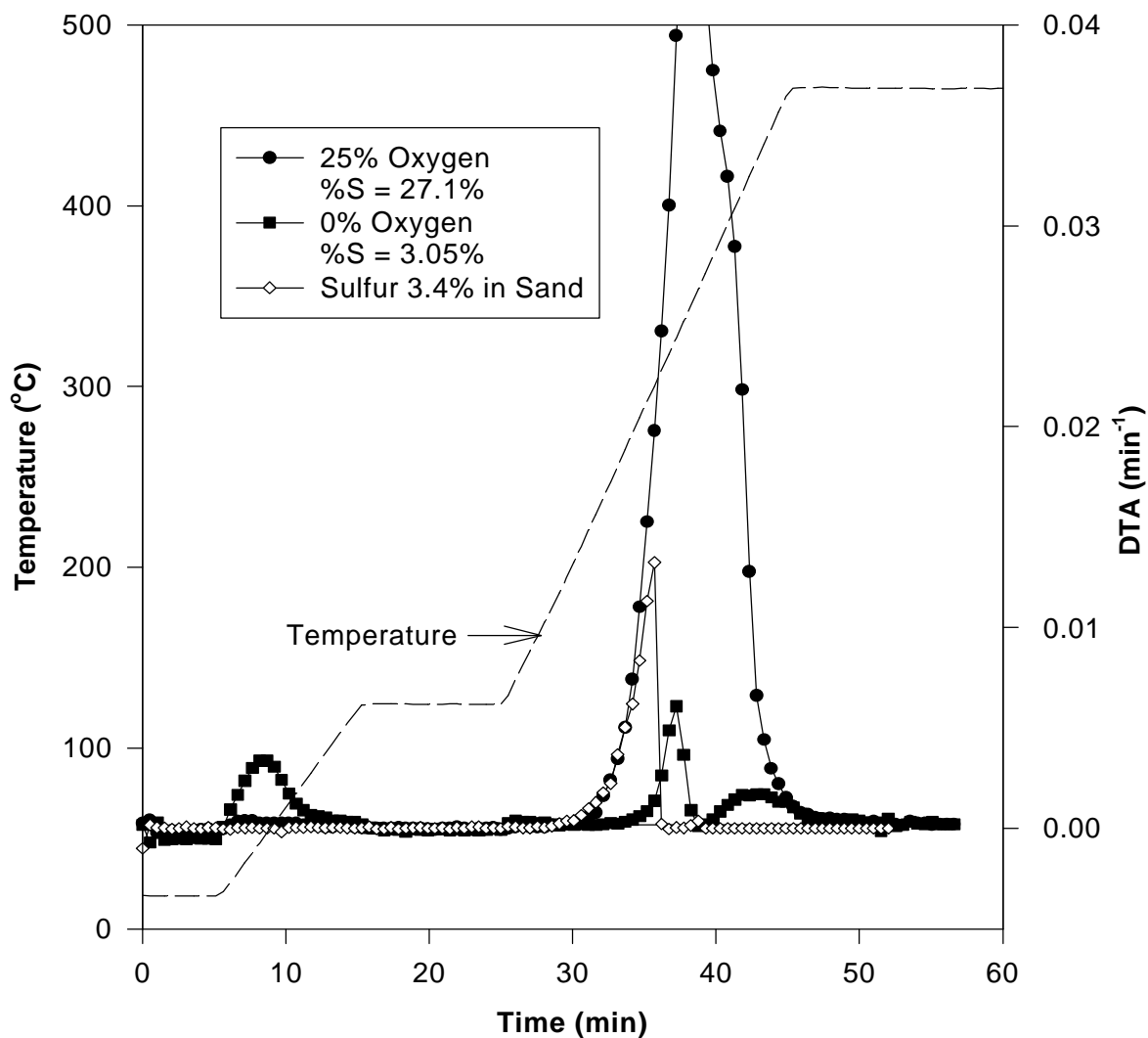


Figure 4.5 DTA Profile for Pure Sulfur and Carbon Impregnated with Sulfur in the Presence and Absence of Oxygen (25% H₂S in the influent, reaction temperature = 100°C)

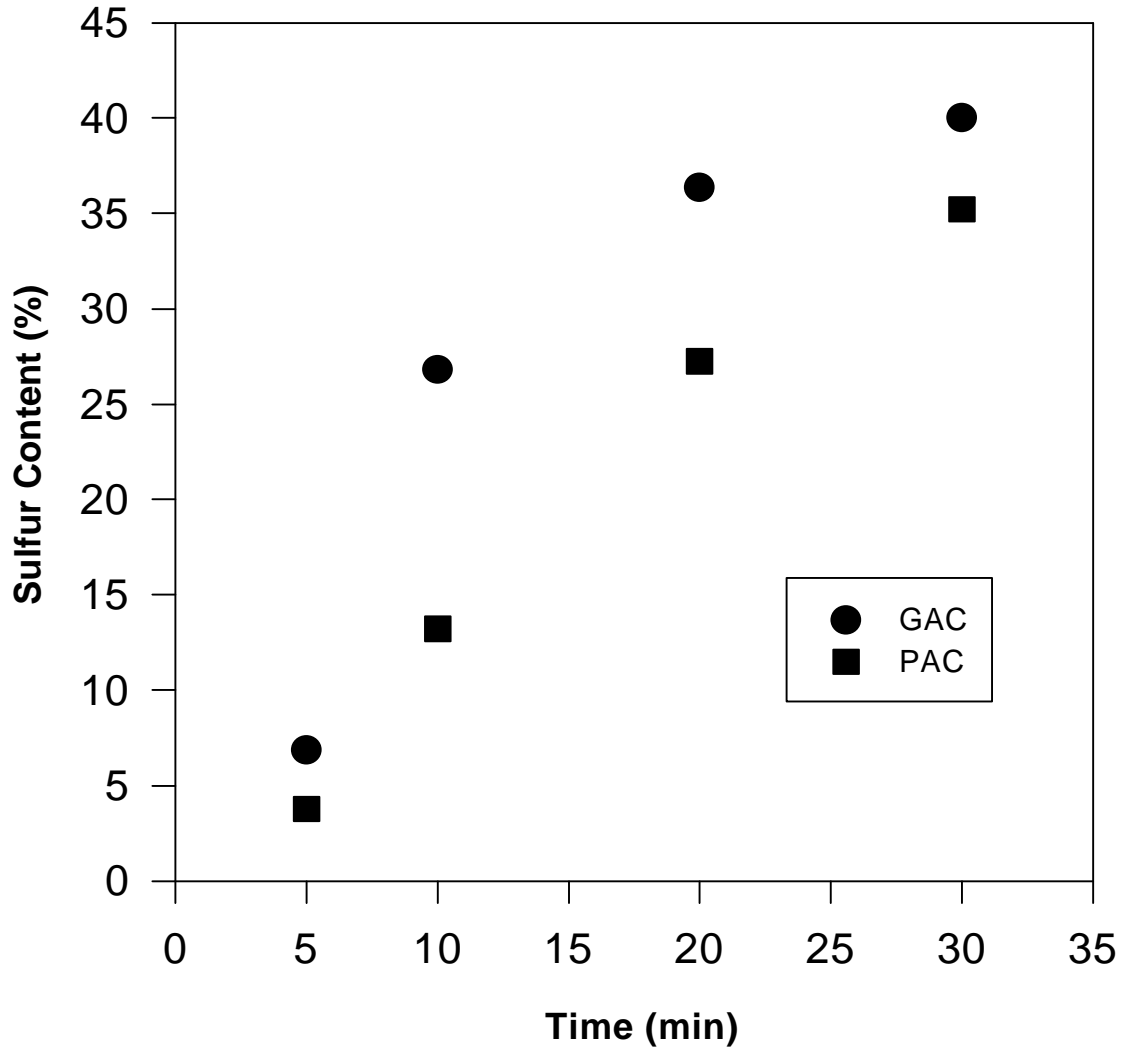


Figure 4.6 Impact of Particle Size on Sulfur Loading (25% H₂S and 25% O₂ in the influent, impregnation temperature = 100°C)

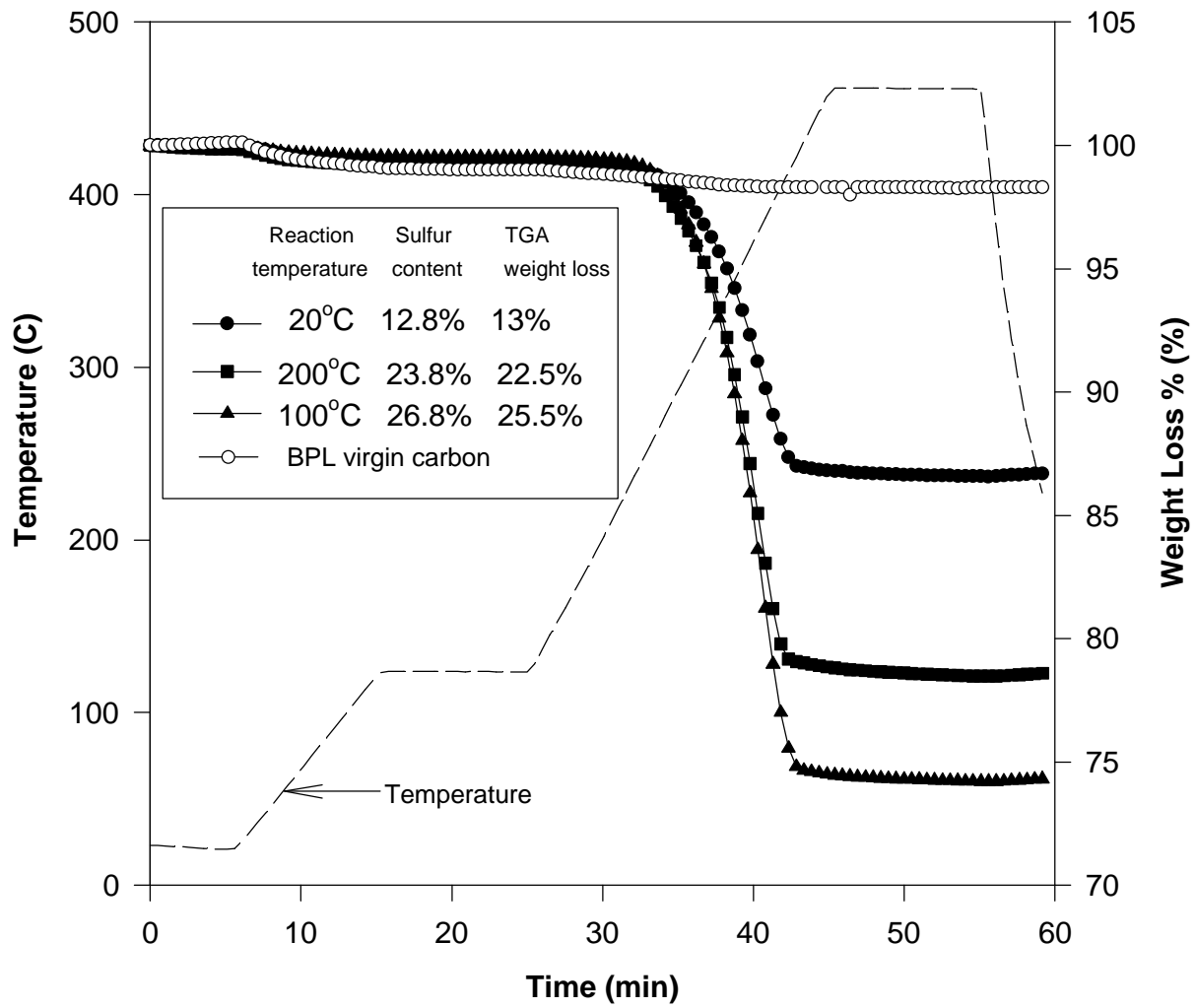


Figure 4.7 Comparison of TGA and Sulfur Measurement for Carbons Impregnated with Sulfur at Different Temperatures (25% H₂S and 25% O₂ in the influent)

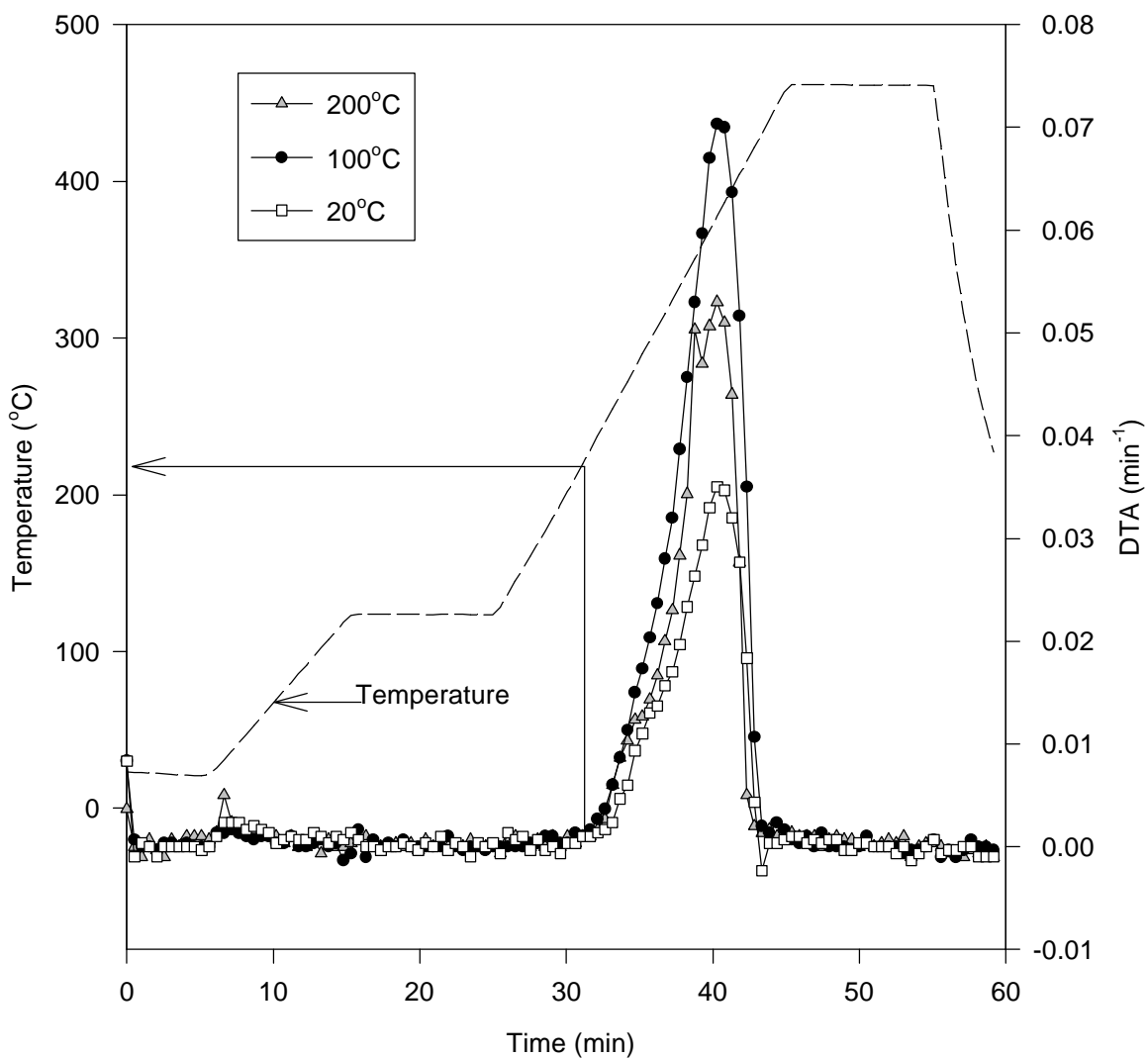


Figure 4.8 Thermal Stability of H₂S Impregnated Carbons (25% H₂S and 25% O₂ in the influent, reaction time = 10 min)

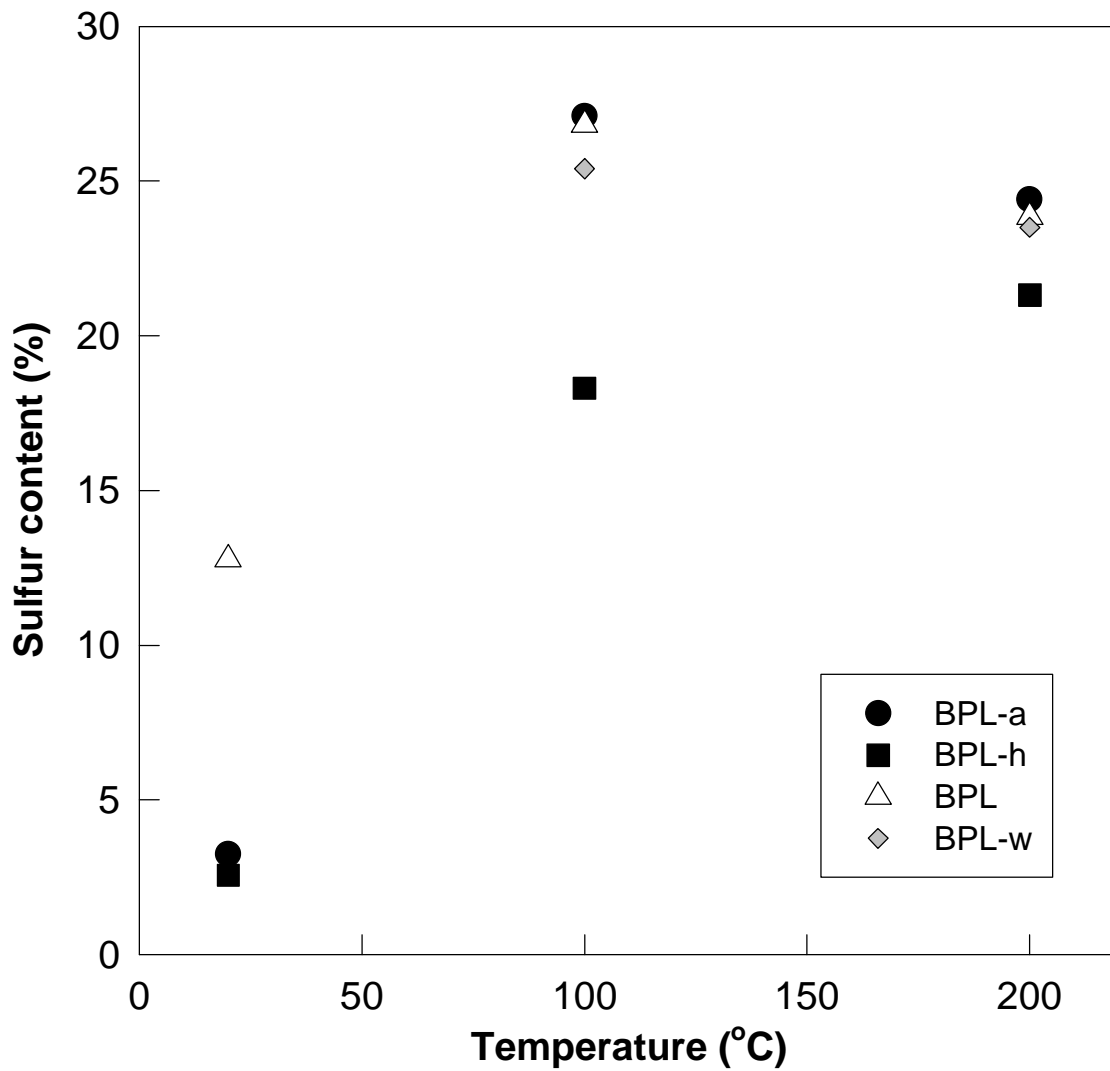


Figure 4.9 Impact of Surface Modification on BPL Performance in H₂S Impregnation (25% H₂S and 25% O₂ in the influent, reaction time = 10min)

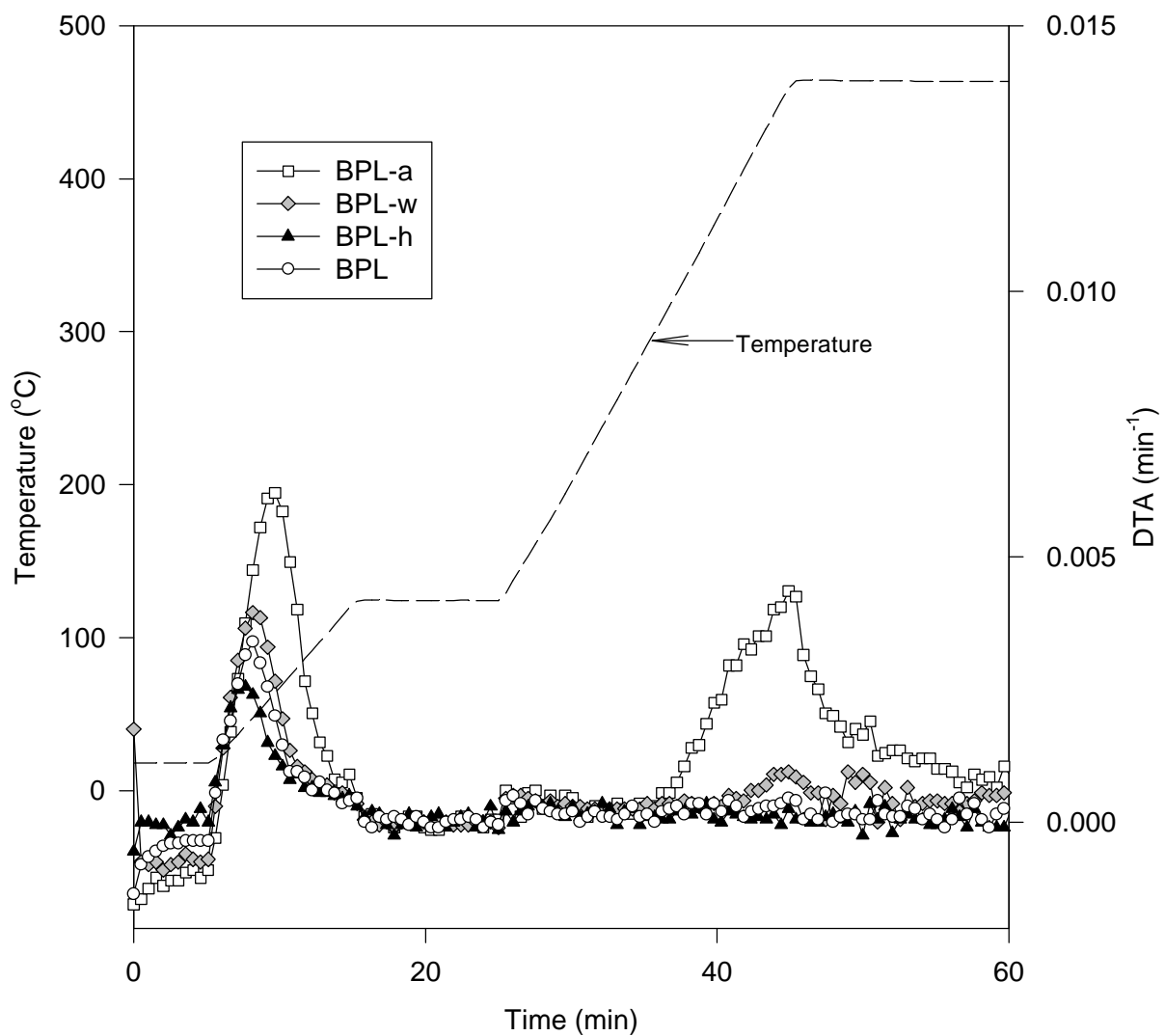


Figure 4.10 DTA Profiles for Virgin and Modified Carbons

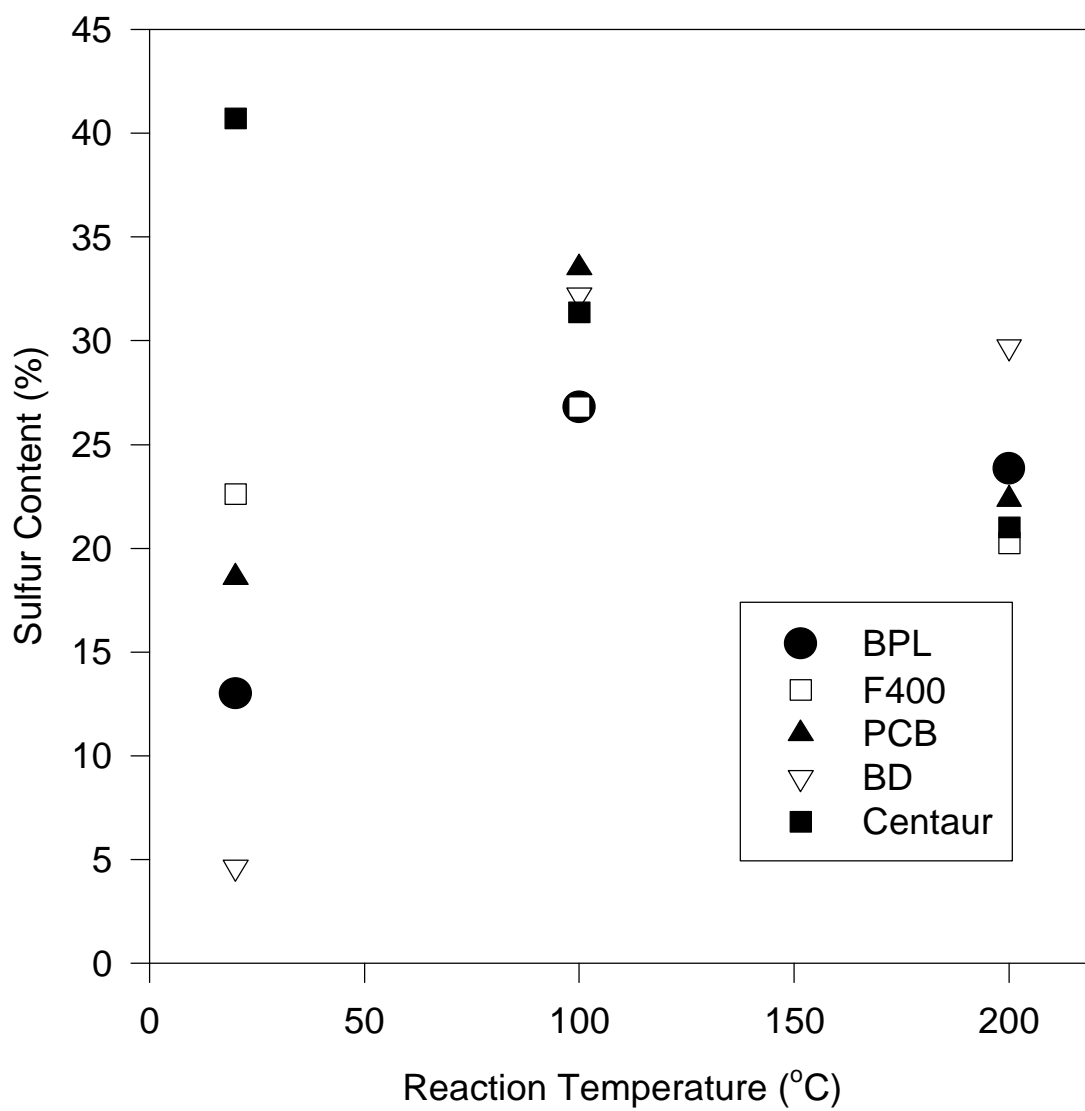
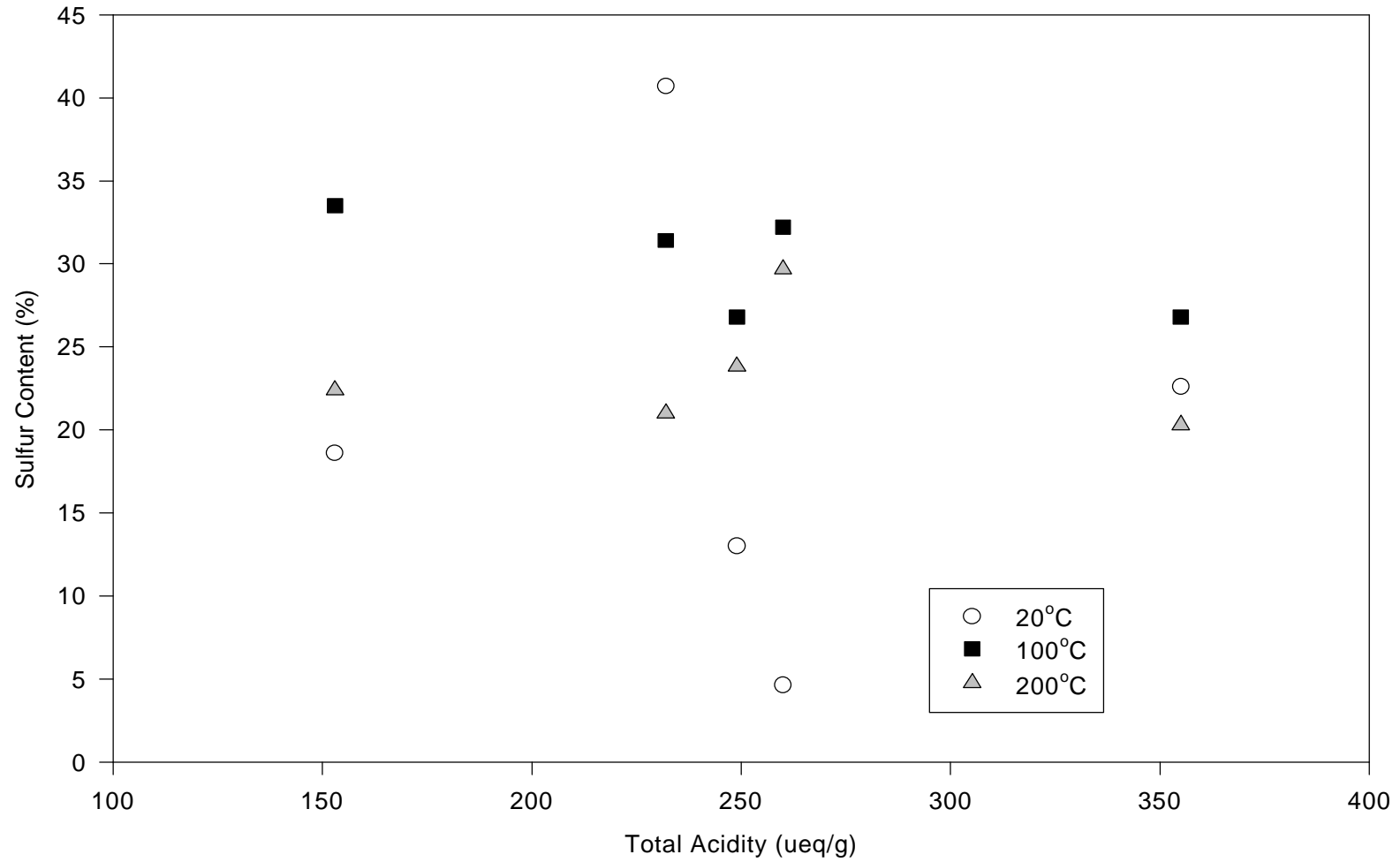
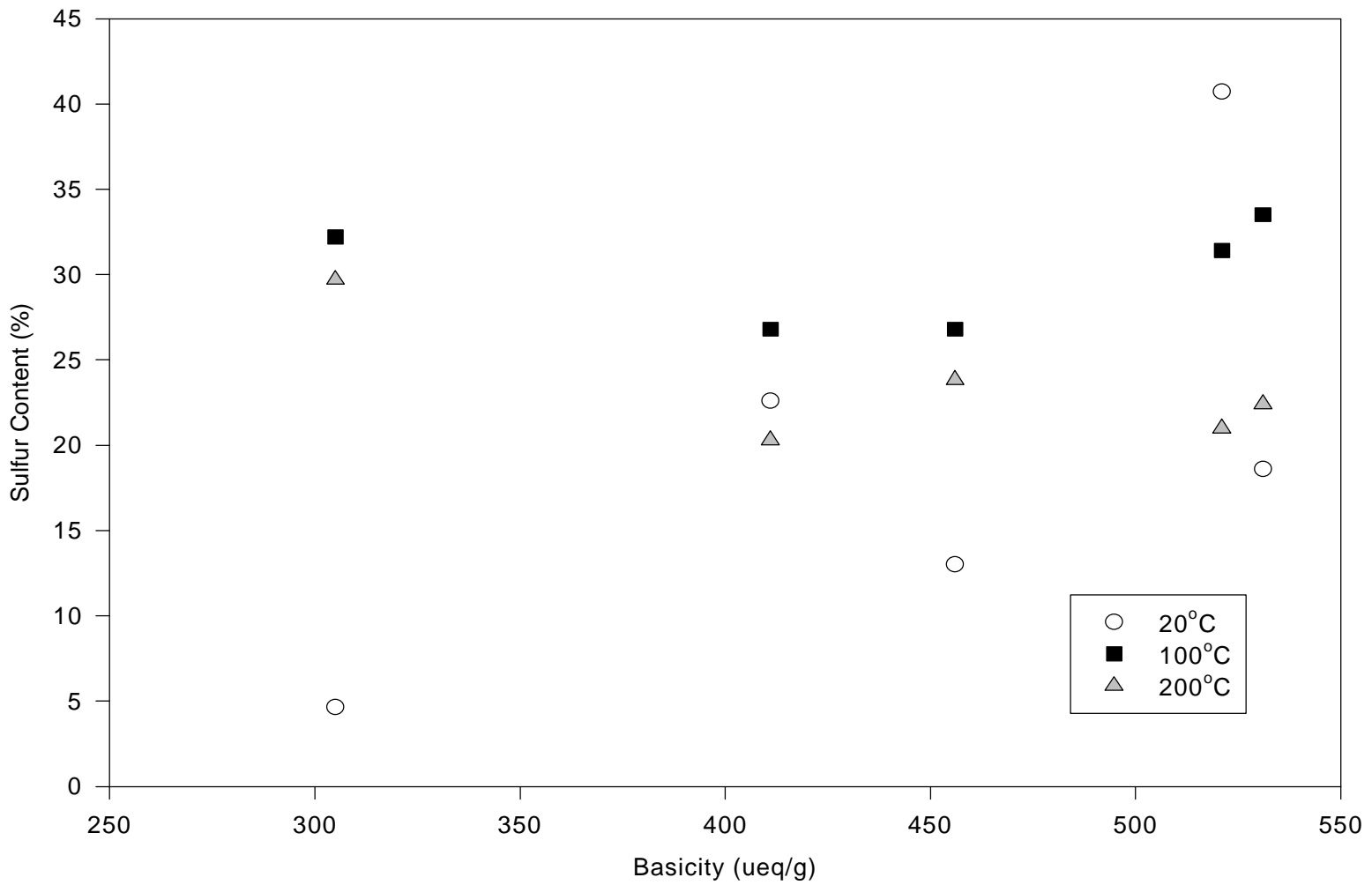


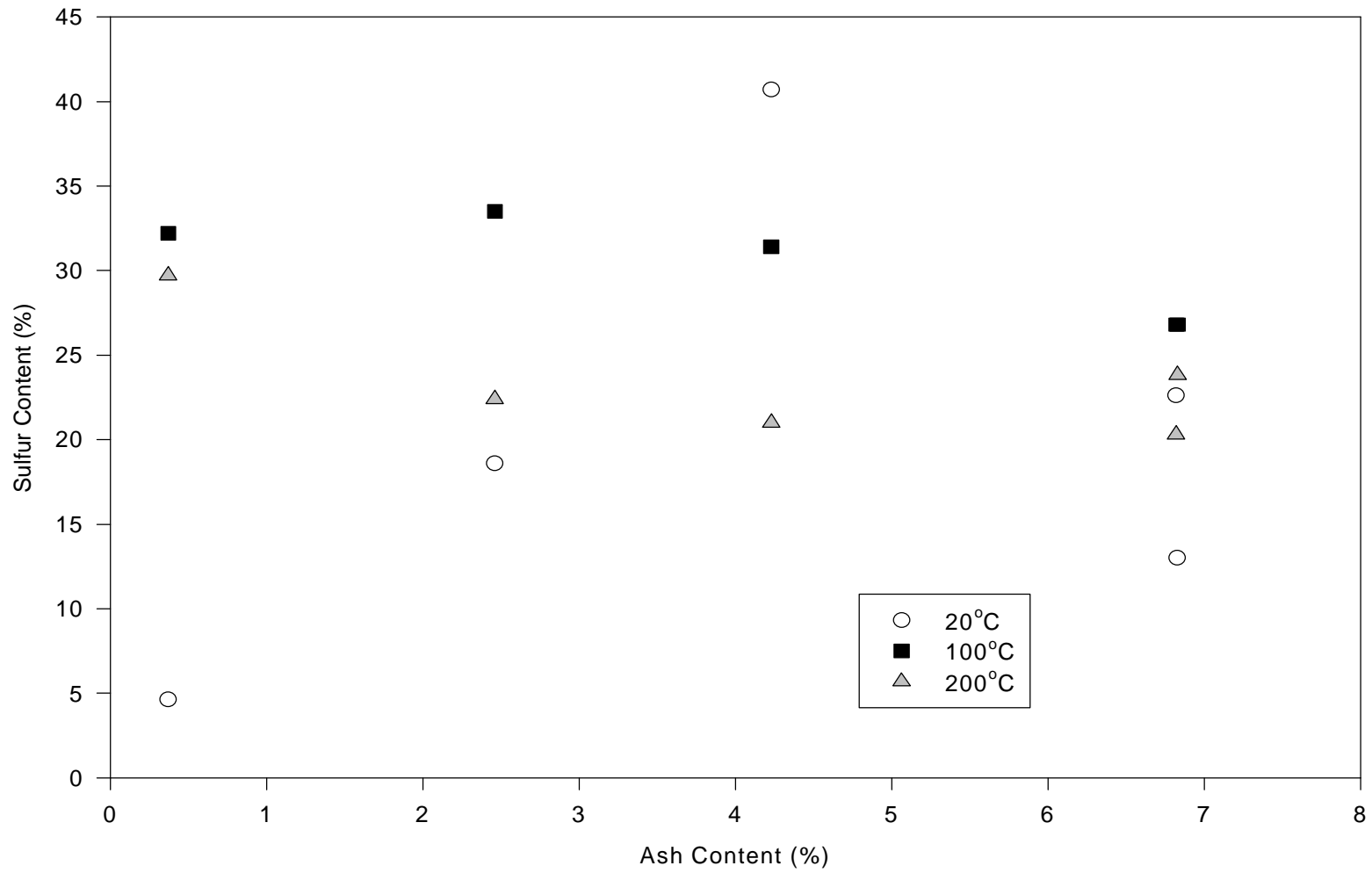
Figure 4.11 Performances of Different Virgin Carbons in H₂S Impregnation (25% H₂S and 25% O₂ in the influent, reaction time = 10 min)



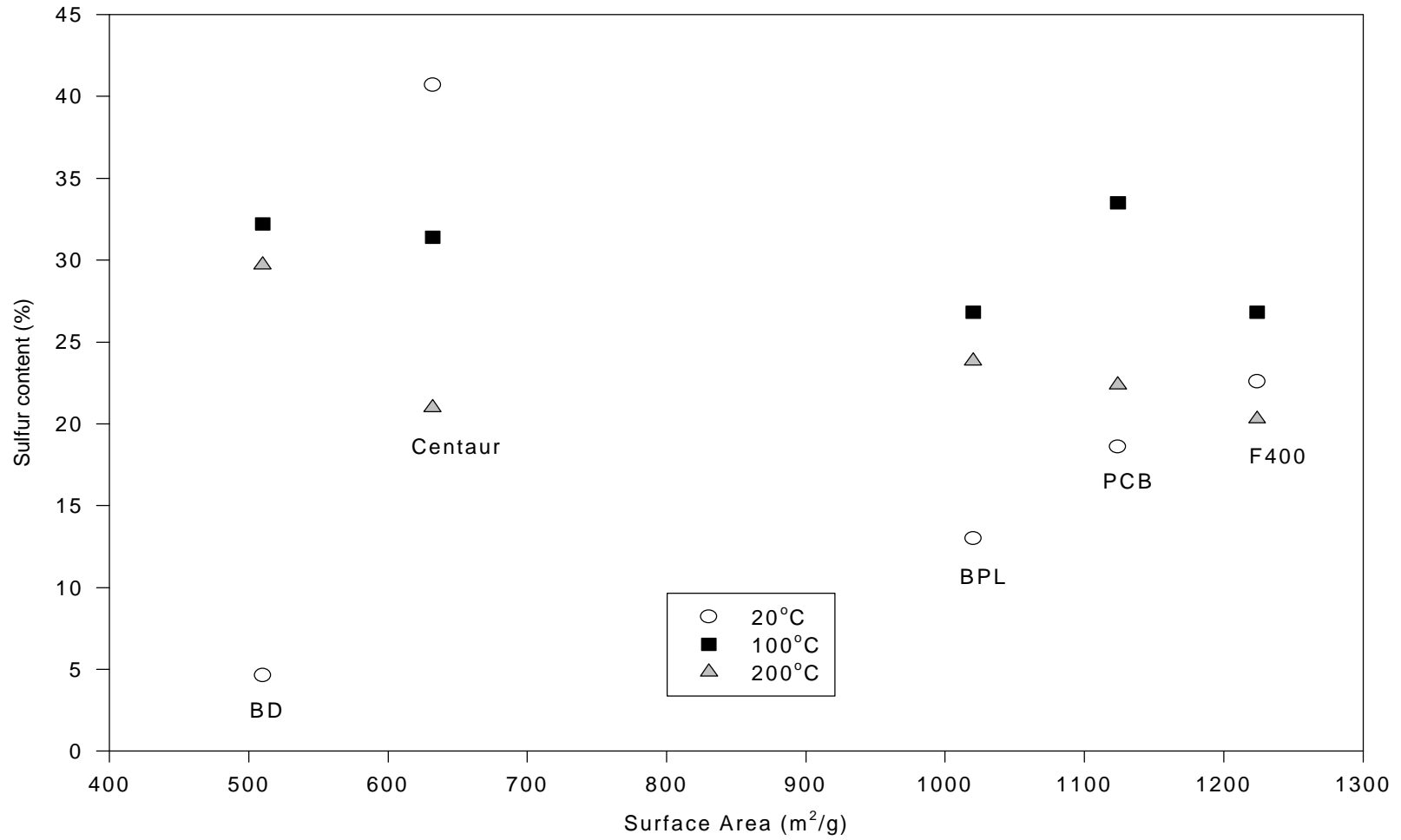
**Figure 4.12 Impact of Total Acidity on H₂S Impregnation
(25% H₂S and 25% O₂ in the influent)**



**Figure 4.13 Impact of Basicity on H₂S Impregnation
(25% H₂S and 25% O₂ in the influent)**



**Figure 4.14 Impact of Ash Content on H₂S Impregnation
(25% H₂S and 25% O₂ in the influent)**



**4.15 Impact of Surface Area on H₂S Impregnation
(25% H₂S and 25% O₂ in the influent)**

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