Modification of Carbonaceous Materials with Sulfur and Its Impact on Mercury Capture and Sorbent Regeneration

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

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ABSTRACT

Physical activation of oil-sands fluid coke, a dense carbonaceous material, using sulfur dioxide (SO$_2$) was investigated as a means of utilizing a plentiful and inexpensive waste for elemental mercury (Hg) removal. A new model was developed to elucidate physical activation of dense carbonaceous materials. Experiments and model simulations revealed that, during activation with SO$_2$, a sulfur-rich porous layer is formed around the periphery of the coke particles; this porous layer reaches a maximum thickness as a result of diffusion limitations; the maximum porous layer thickness is controlled by activation conditions and determines the maximum achievable specific surface area (SSA). Pre-oxidation in air prior to activation, acid washing after activation and smaller coke particle size all result in higher SSA. The highest SSA achieved was 530 m$^2$/g, the highest yet found for oil-sands fluid coke with physical activation. If present, oxygen out-competed SO$_2$ for carbon during activation. SO$_2$ activation and porous layer formation did not occur until oxygen was depleted. Sulfur added to coke through SO$_2$ activation is mainly in reduced forms which are more thermally stable than elemental sulfur in commercial sulfur-impregnated activated carbons (SIACs). TGA and elemental analyses revealed that only 17% of sulfur was removed at 800°C from SO$_2$-activated coke under inert conditions, compared
with 100% from a commercial SIAC.

The role of sulfuric acid (H$_2$SO$_4$) in vapor Hg capture by activated carbon (AC) was studied due to conflicting findings in the recent literature. In the absence of other oxidizing species, it was found that Hg could be oxidized by oxygen which enhanced vapor Hg adsorption by AC and Hg absorption in H$_2$SO$_4$ solution at room and elevated temperatures. At 200°C, AC treated with 20% H$_2$SO$_4$ reached a Hg loading of more than 500 mg/g, which is among the highest Hg capacities yet reported. When oxygen was not present, S$^{6+}$ in H$_2$SO$_4$ was found to act as an oxidizer of Hg, thus enabling Hg uptake by H$_2$SO$_4$-treated AC at 200°C. Treating the AC with SO$_2$ at 700°C improved the initial rate of Hg uptake, with and without subsequent H$_2$SO$_4$ treatment.
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CHAPTER 1  
OVERVIEW

1.1 MOTIVATION

1.1.1 Oil-sands petroleum coke

Petroleum coke is a by-product of the upgrading of bitumen to synthetic crude oil. In the Athabasca oil-sands region of Alberta, Canada, thousands of tonnes of this material are currently being produced every day. One particular type of oil-sands petroleum coke produced by Syncrude is called fluid coke due to the fact that it is produced in a fluidized bed coking unit. Repeated cycles through the coker result in successive layers of material deposited on each particle, and each particle is likely to complete the cycle more than a dozen times [1]. This results in roughly spherical particles made up of concentric, highly-graphitized layers that are often described as appearing “onion-like.” To maintain the amount of material within the system, part of the coke is removed from the bottom of the burner and sent to be stockpiled [2]. Many years of stockpiling has led to the accumulation of more than 100 million tonnes of fluid coke at the Syncrude upgrading facility.

Due to its high carbon content of 80–85 wt% [3], the coke could conceivably be burned to produce electricity. However, the sulfur content of fluid coke is also quite high (6–7 wt%). Thus, combustion of this material would invariably lead to formation of vast amounts of sulfur dioxide (SO₂). Flue gas desulfurization techniques are widely used and readily available, however they typically deal with SO₂ originating from solid fuel composed of <1 wt% sulfur. Thus, the scale of the control equipment would entail enormous costs which outweigh the potential benefit of burning the coke for fuel. For this reason, there has been considerable push in recent years to find a suitable application for this potentially valuable resource.
1.1.2 Reaction of SO$_2$ with coke

Due to the fact that it is the primary precursor to acid rain, industries face harsh economic penalties for exceeding government mandated limits on SO$_2$ emissions. One possible way of meeting these regulations is through reaction of SO$_2$ with fluid coke to produce elemental sulfur. In addition to removing the gas from the industrial waste stream and preventing its release into the atmosphere, such a system would have the advantage of using an inexpensive and plentiful waste material. Furthermore, the conversion of SO$_2$ to elemental sulfur is an effective way of stabilizing the sulfur in a potentially valuable form. It was previously demonstrated that fluid coke can be used to completely reduce SO$_2$ at a concentration of 15% at 700°C when the gas-solid contact time was greater than 8 seconds [4]. At lower contact times, adding 11% oxygen (O$_2$) enhanced SO$_2$ reduction due to the formation of carbon monoxide (CO), which functioned as an additional reducing agent [5].

Another advantage of reacting SO$_2$ with fluid coke is the fact that it produces an extensive porous network within the coke particles. This porosity increases the specific surface area (SSA) of the reacted coke, creating an activated carbon (AC) in the process. A preliminary study on the use of SO$_2$ in activating fluid coke achieved a SSA of 360 m$^2$/g [6]. The same study found that sulfur content of coke activated with SO$_2$ was greatly enhanced, which, when combined with the inherently high sulfur content of the parent coke, designates the end product as a sulfur-impregnated activated carbon (SIAC). Several studies have demonstrated that SIACs are superior to conventional ACs in the capture of mercury vapor [7–14], which opens up new possibilities for future applications of fluid coke.

Despite this, several unanswered question remain with regards to activation of coke with SO$_2$. SSAs achieved thus far have tended to be somewhat low compared to those of
commercially available ACs. Thus, the conditions necessary for maximizing the SSA of SO$_2$-activated coke needs to be thoroughly investigated. In addition, environmental and economic factors must be taken into consideration. For instance, the ability to activate coke using an industrial flue gas which contains a large amount of SO$_2$ would be greatly beneficial. The activating gas would require no cost of preparation and the reaction would reduce SO$_2$ emissions. However, these flue gases typically contain high concentrations of O$_2$ as well, and therefore its impact on activation of coke with SO$_2$ should be determined. Another economic consideration is the ability to regenerate activated coke once it is spent. The simplest and most common technique for regenerating spent sorbent materials is through heating in an inert atmosphere, but it must be determined if sulfur functional groups added to carbon through reaction with SO$_2$ can withstand this heat treatment. This would indicate whether or not SO$_2$-activated coke may be re-used without losing its enhanced adsorption properties, which would be economically advantageous.

1.1.3 Modeling the physical activation of oil-sands fluid coke

However, physical activation of fluid coke is not well understood at the present time. This is partly due to its unique physical structure, which is vastly different from typical AC precursor materials such as agricultural wastes and low-rank coals. Whereas fluid coke is composed of concentric layers of highly graphitized, virtually non-porous petroleum residue, these materials are quite amorphous and may exhibit a substantial pore structure. The chemical nature of fluid coke also sets it apart from standard AC precursors, which usually contain significant fractions of volatile matter. When these volatiles are removed during the initial carbonization step of the activation process, the internal porous network is enhanced. Oil-sands fluid coke is extensively carbonized as a result of its production in a fluid coker, and thus
contains only ~5.5 wt.% volatiles [3]. Activation of fluid coke therefore presents both engineering and scientific challenges, and modeling the process would provide valuable insights into its optimization and ultimate feasibility.

Models for gas-solid reactions tend to fall into two categories: homogeneous and heterogeneous. Homogeneous models, which are typically used for activation and gasification processes, assume high solid initial permeability and uniform internal reaction. Heterogeneous models use an “outside-in” approach, with the assumption that all reaction takes place on the outer surface of an impermeable reactant core. The most famous of these is the Shrinking Core Model of Yagi and Kunii [15], which assumes a porous product layer that replaces the receding core as the reaction proceeds. Such a model is more suitable for a dense material of low initial porosity like fluid coke. However, recent attempts to activate this material have yielded trends in SSA which are not predicted by the Shrinking Core Model, such as a strong influence of initial particle size on maximum achievable SSA. For this reason, modifications of the existing activation models are needed in order to fine-tune them for dense carbonaceous materials such as oil-sands fluid coke.

1.1.4 Mercury toxicity, transport, and regulation

It is widely known that mercury in the environment can have severe consequences for both wildlife and human health. Metallic mercury, after being converted to methyl mercury by aquatic micro-organisms, is bioconcentrated and accumulates as it moves up the food chain. In the 1950s, this resulted in tragic consequences in Minimata, Japan, where several hundred people died and debilitating birth defects occurred [16, 17]. The presence of methyl mercury in aquatic ecosystems is also thought to carry potential risks to wildlife, in particular those species at higher tropic levels such as large fish and piscivorous birds and mammals [18].
Estimates of the percentage of atmospheric mercury emissions that originate from anthropogenic sources range from 59% [19] to 70% [20]. The primary source, which has consistently contributed over 60% of anthropogenic mercury emissions worldwide, is stationary fossil fuel combustion, particularly that of coal [21, 22]. Numerous studies have demonstrated the ability of anthropogenic mercury to be transported via meteorological patterns over long distances on sub-continental [23–26] and inter-continental [27, 28] scales. Findings such as these, coupled with the potential for biomagnification, has led most jurisdictions to place strict regulations and reduction targets on mercury emissions.

In 2005, the US Environmental Protection Agency (EPA) introduced the Clean Air Mercury Rule (CAMR), a cap-and-trade system which set a limit on mercury emissions from coal-fired power plants across the United States of 38 tons by 2010 and 23 tons by 2018 [29]. Although the CAMR was vacated by the US Court of Appeals in 2008, the EPA is still responsible for standardizing mercury emission regulations according to maximum achievable control technologies [30]. While many states are awaiting these new emission rules, numerous others have opted for their own stringent regulations that will require up to 95% reductions in the short term [31]. Similarly, Canada-Wide Standards were introduced in 2006 in which a 60% overall reduction was required by 2010, and 80% by 2018 [32]. Individual provinces proposed their own mercury emissions caps for coal-fired power generation based on regional factors such as plant configurations, power supply issues, provincial policy commitments, and the range of coals used across the country. Alberta, which is Canada's largest emitter of atmospheric mercury from coal combustion, will require proposals from individual utilities in 2013 to reduce emissions by 80% [33]. Similar strategies have been implemented in Europe, most notably European Directive 96/61/CE [34], although, as of 2009, there were still no legal limits on
atmospheric emissions of mercury from power plants in certain jurisdictions such as Poland [35].

1.1.5 Effects of SO$_3$ and H$_2$SO$_4$ on mercury capture from coal-fired power plants

One of the simplest and most extensively researched Hg control techniques is injection of powdered AC downstream of the boiler [36]. The fast-moving, turbulent gas stream carrying the powdered AC helps to ensure efficient contact between the gas containing Hg and the solid particles, despite their overall residence time being only seconds. Most power plants already use particulate collection devices such as baghouse filters and electrostatic precipitators, thus collection of the spent AC is a relatively simple matter. In recent years, however, the consensus in the industry has been that SO$_2$ and sulfur trioxide (SO$_3$), formed as products of sulfur oxidation reactions during the combustion of coal, seriously hinder attempts to remove Hg through AC injection [36–38].

As possible mechanisms for Hg uptake inhibition by SO$_2$ and SO$_3$, Presto et al. have suggested competitive adsorption, scavenging of oxygen and/or halogen surface groups, and formation of sulfuric acid (H$_2$SO$_4$) leading to pore blockage [39, 40]. Despite these recent findings, an industrial process (Outokumpu Process) has existed since the 1970s for capturing Hg from non-ferrous smelter flue gases using concentrated sulfuric acid (H$_2$SO$_4$) at elevated temperatures [41]. In addition, a patented technique exists for removing Hg from liquid hydrocarbons using AC impregnated with H$_2$SO$_4$, hydrochloric acid (HCl), or phosphoric acid [42]. Some recent studies have even concluded that direct impregnation of H$_2$SO$_4$ on an AC surface has a positive impact on Hg capture [14, 43]. Thus, the exact role played by H$_2$SO$_4$ in Hg uptake to AC in coal-fired utility flue gas is currently a contentious issue which needs additional study.
1.2 OBJECTIVES AND HYPOTHESIS

From a scientific perspective, there were 3 key objectives of this work:

1. Gain a better understanding of the governing factors behind SSA transformations of fluid coke during physical activation with SO$_2$;
2. Determine how O$_2$ affects the reaction of SO$_2$ with coke;
3. Clarify the role of H$_2$SO$_4$ in the uptake of Hg vapor to carbon and sulfur-impregnated carbon surfaces.

Technologically speaking, this work had 3 additional objectives:

1. Determine the conditions for maximizing the SSA of oil-sands fluid coke activated with SO$_2$;
2. Determine how adding sulfur to activated carbon through reaction with SO$_2$ affects performance with regards to Hg uptake;
3. Determine if activated carbon impregnated with sulfur through high temperature reaction with SO$_2$ can be thermally regenerated after loading with Hg vapor.

This study proposed two main hypotheses:

1. The evolution of SSA in dense carbonaceous materials such as oil-sands fluid coke may be described using a modified version of the Shrinking Core Model in which the outer porous layer is considered to be a less reactive form of carbon, rather than an inert product layer;
2. Hg will react with H$_2$SO$_4$ on a carbon surface under the right conditions, but the reaction is limited by kinetics under conditions relevant to most carbon injection systems in coal-fired utilities.
1.3 **Organization of Thesis**

This thesis is composed of 5 separate research papers in addition to one review paper. Chapter 2, the literature review, is largely comprised of a review paper which was published in the *Journal of Sulfur Chemistry* in October of 2010. Chapter 3 describes the development and implementation of a model based on the concept of a constant thickness porous layer which develops during SO$_2$-activation of fluid coke. This chapter investigates Hypothesis #1, and will be submitted to *Carbon* in the very near future. Chapter 4 approaches the activation of coke with SO$_2$ from a technical standpoint in that it explores the application of pre- and post-treatment techniques to optimize SSA. This was recently submitted as a research paper to *Carbon*. In Chapter 5, the chemical transformations occurring on the coke surface during activation with SO$_2$ with and without O$_2$ are discussed in detail. This chapter was published in *Industrial & Engineering Chemistry Research* in November of 2010. Chapter 6 provides a detailed assessment of Hypothesis #2, shown above, and will be submitted to *Environmental Science & Technology* in the near future. Chapter 7 describes the work done to determine the potential for regeneration of SO$_2$-treated activated carbon after it has been loaded with Hg. This chapter is targeted for submission to the *Journal of Hazardous Materials*. Finally, the thesis ends with a collective summary of the major findings from the entire thesis study, as well as suggestions for future work related to these subjects.

Every effort was made to preserve the flow and economy of this document, such as removing redundant figures and descriptions of procedures. Despite this, however, considerable overlap remains between the various papers which make up the main body of this thesis.
CHAPTER 2  
LITERATURE SURVEY

2.1 GAS-SOLID REACTION MODELS

2.1.1 Homogeneous models

In a strictly homogeneous gas-solid reaction model, the solid material is assumed to be initially porous. Thus, for a reacting spherical particle, there is no concentration gradient of reactant gas molecules with respect to particle radius and the reaction proceeds uniformly throughout. Several studies have been conducted to model the transformations in pore structure resulting from such a system and their effect on gas-solid reactivity and SSA. These works have used a variety of approaches, basing their results on experimental work [44], particle density correlations [45], statistical modeling [46], percolation theory [47], and models based on randomized pore networks [48–50].

Of these approaches, those involving randomized networks of pores are most often cited. One of the earliest of these models is that of Petersen [48], which treats the initial porous structure of the solid as being comprised of randomly oriented cylinders of uniform radius. The Petersen model was developed to simulate gasification of graphite rods with CO$_2$, and thus does not account for any solid product formation in the pores. Bhatia and Perlmutter [49] later developed what is known as the random pore model based on cylindrical pores situated in parallel. This model served as an improvement in that it takes into account a distribution in pore size, diffusivity effects related to the formation of product layers surrounding the pores, and effects of overlapping pores. Further models were developed by Ballal and Zygourakis [50], who incorporated effects of bimodal pore size distribution and different pore geometries.
Despite this advancement, the random pore model of Bhatia and Perlmutter continues to be the most widely used. This is perhaps due to the relative simplicity of its application and the fact that it requires parameters that can easily be obtained from measured physical properties of the raw material. Using the random pore model, accurate simulations of reaction rate and pore development have been achieved in the gasification of agricultural wastes [51] and coal chars [52–57].

Previous studies in which homogeneous reaction models such as the random pore model have been successfully applied generally used materials with initially high porosity and low density. This is necessary, since it rationalizes the inherent assumption that pore formation and enlargement occur uniformly throughout the particle. For this reason, homogeneous gas-solid reaction models cannot be directly applied to model the activation of materials which are initially dense and non-porous.

2.1.2 Heterogeneous models

Heterogeneous gas-solid reaction models generally assume a strictly defined reaction front which propagates from the outside of a solid reactant particle towards its center. This reaction front arises due to an initially non-porous solid, which prevents gaseous reactant molecules from diffusing into the particle interior. One of the most widely-known heterogeneous models is the Shrinking Core Model developed by Yagi and Kunii [15] for the combustion of a carbon particle with O₂. This model is based on a gas-solid reaction which produces a solid product that does not participate in further reaction. The product forms a porous layer surrounding the solid reactant core through which gaseous reactant and product molecules diffuse. As the reaction proceeds, the porous product layer becomes thicker until the point at which the solid reactant is exhausted and the entire particle consists of the solid product.
Several modifications have been made over years to improve the Shrinking Core Model by incorporating some degree of homogeneity in the gas-solid reaction. Wen and Ishida [58] proposed a system in which the particle is initially porous, allowing for diffusion of reactant gas molecules into the interior. Although the reaction occurs throughout the particle, it is faster near the exterior, which results in a growing layer of porous solid product. Mantri et al. [59] developed a similar model in which the diffusion of the reacting gas molecules is limited, thus creating a reaction zone of constant thickness. Sohn and Szekely [60] envisaged a solid reactant particle composed of densely packed spherical or plate-like grains around which gas may diffuse. The Shrinking Core Model is then applied individually to all of the grains, with those near the particle exterior experiencing the fastest rate of reaction and becoming exhausted soonest. A similar concept named the crackling core model was developed by Park and Levenspiel [61] which also considers the particle to consist of spherical grains. This model is somewhat different, however, in that the particle is initially non-porous and develops cracks and fissures over time which allow for easy gas penetration. Ramachandran et al. [62] modelled the oxidation of a coke particle by proposing separate mechanisms for hydrogen and carbon oxidation. In the model, the hydrogen oxidation reaction was rapid and occurred at the interface of the solid core, whereas carbon oxidation took place within the diffusion zone left behind by the hydrogen reaction. Pritzker [63] developed a similar but more generalized model and applied it to the reaction of lead sulfate with aqueous sodium carbonate. The primary reaction was assumed to occur at the sharp interface of the unreacted core, while a series of aqueous carbonate reactions occurred homogeneously within the porous product layer.

Some heterogeneous reaction models have taken into account the effect of changing the overall particle size during reaction. Rehmat & Saxena [64] determined the relationship between
particle conversion and reaction time numerically for the cases of shrinking and increasing particle size with a shrinking unreacted core. For shrinking particles in a system controlled by intraparticle diffusion, it was found that conversion was enhanced due to the shorter path length through which reactant gas molecules must diffuse. In the simulation of uranium dioxide fluorination, Homma et al. [65] assumed that an intermediate product layer is formed through a diffusion controlled reaction at the carbon surface, while the product layer itself is consumed through a different chemical reaction; the overall rate of shrinkage was determined by the ratio of the two reaction rates and the diffusion rate of gas through the product layer. This model was not effective beyond the point where the solid core was completely consumed. Braun et al. [66] modelled the growth of a product layer during oxidation of a flat sample of glassy carbon in a similar manner. The model was found to agree with experimental data in that the product layer tended to plateau over time. Furthermore, the magnitude of the maximum thickness and the time needed to achieve it tended to decrease with increased temperature. In a later study, Braun et al. [67] fit a time-dependent equation for surface area to experimentally determined values of BET SSA for glassy carbon particles activated in air at 450°C. An accurate fit was obtained despite the fact that a uniform SSA of 900 m²/g was assumed for the entire porous product layer at all times during the activation. In reality, the porosity of the product layer will vary with respect to particle radius. Furthermore, this model, which predicts that the SSA will asymptotically approach a maximum achievable value, was developed for a material which is essentially pure carbon. Activated carbon is typically produced from different materials such as coal, coke, and agricultural wastes, which contain significant fractions of inorganic ash. This ash may impact the development of SSA over time, therefore similar studies need to be done on other, more conventional, activated carbon precursors.
2.2 REACTIONS OF SULFUR DIOXIDE WITH CARBON

2.2.1 Low-temperature surface interaction

From the perspective of mercury uptake to activated carbons, the interaction of SO$_2$ with the carbon surface and its potential for forming H$_2$SO$_4$ is highly relevant. As mentioned above, H$_2$SO$_4$ has found practical use with regards to capture of mercury [41, 42]. However, H$_2$SO$_4$ is widely regarded as a poison to both Hg$^0$ oxidation and retention via activated carbons.

In studying the enthalpy of adsorption of SO$_2$ on the surface of a graphitized carbon black, Beebe and Dell [68] found that removal of surface oxygen complexes resulted in a sharp decrease in the amount of sulfur dioxide adsorbed at 0°C. Davini [69] came to a similar conclusion, finding that oxygen-containing surface basic groups enhanced SO$_2$ chemisorption at 25°C. Other authors have found contradictory results, however, when the carrier gas used contained O$_2$ and H$_2$O. Using activated carbon fibers, Daley et al. [70] found that the presence of oxygen functional groups decreased SO$_2$ adsorption capacity from a gas mixture containing 5% O$_2$, 7% H$_2$O, and 2500 ppm SO$_2$. Under the same gas conditions, Lizzio and DeBarr [71] obtained similar results using Illinois coal char. These results were explained in terms of a decrease in both pore volume and available surface sites for SO$_2$ adsorption due to the presence of oxygen surface complexes. The authors thus proposed the following adsorption mechanism:

\[
\begin{align*}
\text{SO}_2 \text{ adsorption:} & \quad \text{SO}_2 + C \rightarrow C\text{-SO}_2 \quad (2.1) \\
\text{SO}_2 \text{ oxidation:} & \quad C\text{-SO}_2 + O_2 + C \rightarrow C\text{-SO}_3 + C\text{-O} \quad (2.2) \\
\text{H}_2\text{O adsorption:} & \quad C + H_2O \rightarrow C\text{-H}_2O \quad (2.3) \\
\text{H}_2\text{SO}_4 \text{ formation:} & \quad C\text{-SO}_3 + C\text{-H}_2O \rightarrow C\text{-H}_2\text{SO}_4 + C \quad (2.4)
\end{align*}
\]

This mechanism suggests that adsorbed SO$_2$ is primarily oxidized by vapor-phase oxygen, as opposed to chemisorbed oxygen as is normally assumed. Corroborating evidence has
been found with 5% O₂ and 10% H₂O using activated carbon fibers at 100°C and 1000 ppm SO₂ [72], at 100°C and 3000 ppm SO₂ [73], and at 25°C with 1000 ppm SO₂ [74]. These findings indicate that free O₂ plays a more important role than adsorbed oxygen in oxidizing SO₂ to SO₃ on the carbon surface. However, oxygen surface complexes likely play a minor role as suggested by the results of Beebe and Dell [68] and Davini [69].

Using molecular modeling software, Yang and Yang [75] determined that the only viable route in which H₂SO₄ can be formed from SO₂ on an oxygen-free graphite surface is through a H₂SO₃ precursor. This implies that the order of the oxidation and hydration steps in the mechanism shown above is reversed, with H₂SO₃ being the intermediate as opposed to SO₃. In addition, the authors found that surface oxygen sites can enhance SO₂ adsorption, but only when the oxides are not present on neighboring sites (i.e., when the surface is only sparsely covered with oxygen functional groups). This supports the previous mentioned results in which a decrease in SO₂ capacity with increased surface oxygen was observed in the presence of O₂ and H₂O [70–74].

2.2.2 High-temperature reduction

Abramowitz et al. [76] studied the kinetics of SO₂ reduction to elemental sulfur by carbon black between 780 and 1026°C, and devised a reaction mechanism whereby SO₂ was decomposed to SO and O upon adsorption on the carbon surface. The adsorbed SO subsequently reacts with carbon to form carbonyl sulfide (COS), which then decomposes to carbon monoxide and sulfur. Using both lignite and bituminous coals, Ratcliffe and Pap [77] were able to achieve upwards of 90% conversion of SO₂ to elemental sulfur at 700°C. It was found that reaction of SO₂ with volatile matter occurred within the pores with the lower rank coals, while, in bituminous coal, the volatiles accumulated to form tar which reduced reactivity to SO₂. In a
companion paper [78], the authors argue that this was due to the greater presence of inorganics in the lignite which acted as catalytic sites for SO$_2$ reaction with volatile matter. As previously mentioned, Bejarano et al. [4] achieved complete reduction of SO$_2$ using oil-sands fluid coke at 700°C. The full conversion of SO$_2$ was accompanied by nearly complete elemental sulfur yield, but only when SO$_2$ was in excess supply. Otherwise, secondary gaseous reaction products such as carbon disulfide (CS$_2$) and COS were formed. Raising the temperature above 700°C was found to have a similar impact due to enhanced reduction of product sulfur. Humeres et al. [79] reacted SO$_2$ at 900°C with four different carbon materials: charcoal, graphite, coke with 7.3% ash content, and coke with 11.7% ash content. It was determined that reactivity towards SO$_2$ decreased with increasing crystallinity of the carbon material, with graphite being the least reactive. Coke with high ash content was more reactive than that with low ash, while charcoal was found to be most reactive toward SO$_2$.

2.2.3 Effect of other gases

Comparatively little work has been done on the reduction of SO$_2$ by carbonaceous materials in the presence of other gases. Panagiotidis et al. [80] investigated structural changes of anthracite char resulting from its reaction with SO$_2$ at approximately 30%. The authors observed C-S surface complexes formed along the fissure and pores of the char. When steam was present at levels ranging from 19 to 50%, these structures were continually removed by reaction with (hydrogen) H$_2$ resulting from the interaction of H$_2$O with carbon. Feng & Jia [5] used oil-sands petroleum coke to reduce 18% SO$_2$ in the presence of 0–20% O$_2$ and 0–30% H$_2$O. It was observed that the presence of O$_2$ enhanced SO$_2$ conversion to elemental sulfur due to the production of CO, which also acts as a reducing agent. Similarly, H$_2$O was observed to enhance SO$_2$ conversion via production of H$_2$. The yield of elemental sulfur was also improved,
except when $\text{SO}_2$ was incomplete; in that case, the CO and $\text{H}_2$ formed reacted with elemental sulfur to form COS and hydrogen sulfide ($\text{H}_2\text{S}$), thus reducing the sulfur yield. This result was corroborated by Wang et al. [81], who used microwave plasma to enhance the reduction of $\text{SO}_2$ to sulfur on activated carbon, charcoal, and coke. In this experiment, however, $\text{SO}_2$ was present at only 5,000 ppm (0.5%) and the $\text{O}_2$ concentration was limited to 4%.

2.3 **Sulfur-Impregnated Activated Carbons**

2.3.1 **Production**

SIACs are commonly produced from low-sulfur ACs by depositing elemental sulfur on the surface of the carbon. Otani et al. [7] achieved 13 wt.% by soaking an AC in a solution of sulfur dissolved in CS$_2$. More commonly, elemental sulfur is impregnated by exposing the AC to sulfur vapors at high temperatures [8–12, 82]. Liu et al. [9] exposed Calgon BPL to elemental sulfur vapors at 250–600°C, and found that the total sulfur content decreased and SSA increased with increasing impregnation temperature. At 250°C, the dominant sulfur allotropes are S$_8$, S$_7$, and S$_6$, which are relatively heavy and result in blocked pores. At 600°C, on the other hand, S$_6$ and S$_2$ dominate, leading to improved pore diffusivity and greater SSA compared to the lower impregnation temperature.

Several researchers have also utilized sulfur gases as a means of fixing sulfur to carbon. Sinha and Walker [83] oxidized H$_2$S with O$_2$ in a fluidized bed of carbonized Saran, and achieved 11.8 wt% sulfur. Puri and Hazra [82] and Chang [84] contacted various types of carbon with H$_2$S, CS$_2$, and SO$_2$ at 600°C for 6 hrs, and generally found a higher degree of sulfur addition when SO$_2$ was used. Using a commercial AC, Valenzuela Calahorro et al. [85] came to a similar conclusion when comparing sulfur added by SO$_2$ to that of H$_2$S when temperature was raised to 900°C at 5°C/min. Feng et al. [13] reacted H$_2$S at 3000 ppm with Calgon BPL and AC.
fibers between 400 and 800°C. It was determined that higher reaction temperatures led to more stable sulfur structures due to direct reaction between H₂S and the carbon surface.

2.3.2 Sulfur forms resulting from impregnation with SO₂

Bejarano et al. [86] undertook a cross-sectional analysis of a single particle of oil-sands fluid coke after reaction with 15% SO₂ for 13 hours using scanning electron microscopy with electron dispersive X-ray spectroscopy (SEM-EDX). An accumulation of sulfur was observed in between a mineral-rich ash layer and the unreacted core of the particle, similar to the sulfur-rich layer previously reported by Panagiotidis et al. [80] for the reaction of anthracite char with SO₂. Previous research has found that high temperature reaction of SO₂ with a carbon surface may add sulfur in the form of sulfide [82, 87], disulfide [87], thiol [82], thiolactone [82, 84], thiolactone (defined as a lactone with both oxygen atoms replaced by sulfur) [84], and oxidized forms such as sulfones and sulfoxides [87], but not as elemental sulfur. Moreover, a large portion of the added sulfur was determined to be stable in N₂ at temperatures exceeding 700°C [82, 84], suggesting that thermal regeneration of SIACs produced through reaction with SO₂ might be feasible.

2.3.3 Use in mercury control

There has been extensive research into the potential use of SIAC for the removal and permanent sequestration of vapour-phase mercury. Sinha and Walker [83] determined that carbonized Saran sulfurized with H₂S to a sulfur loading of 1.0 wt% performed better than the original Saran in terms of Hg adsorption at 150°C, but, at 25°C, the opposite was true. The authors thus concluded that physical adsorption of Hg is negligible at the higher temperature, and chemical adsorption (i.e., formation of mercuric sulfide (HgS)) is dominant. This trend was later verified using commercial SIAC by Krishnan et al. [88] and Karatza et al. [89], who found
that Hg adsorbed at 120–150°C existed mainly at sulfur-rich surface sites. In addition, Sinha and Walker [83] found the breakthrough time of Hg decreased substantially when the sulfur loading was increased to 11.8 wt%. This was attributed to the fact that the SSA of this material decreased from 875 to less than 1 m²/g after sulfurisation. In contrast, Otani et al. [7] observed a smaller decrease in SSA from 1250 to 710 m²/g after impregnating a commercial activated carbon to 13.1 wt% with sulfur in a CS₂ solution. Furthermore, the breakthrough time of Hg increased as the sulfur loading increased from 0 to 13.1 wt%.

The effect of the sulfur-impregnation method on Hg uptake is also an active area of study. Korpiel & Vidic [8] heated a bituminous coal-based commercial AC in the presence of elemental sulfur at 600°C and compared the product to a commercially available SIAC in terms of Hg capacity. It was found that the experimental SIAC performed better above the melting point of sulfur, except when the initial Hg concentration was high (684 μg/m³ rather than 55 μg/m³). This trend was attributed to the fact that the sulfur on the commercial SIAC was mostly present on the external surface, and thus agglomerated and became unreactive at high temperature. On the other hand, the sulfur in the experimentally produced SIAC was deeply situated in pores, where a high Hg loading resulted in rapid formation of HgS molecules which prevented further access to the reactive pore structure. Liu et al. [9] performed a similar experiment, except they varied the impregnation temperature and sulfur to carbon ratio. It was observed that the impregnation temperature is of key importance, since the AC impregnated at high temperature (600°C) exhibited the highest Hg adsorption capacity of all other samples analysed. The authors concluded that the form of sulfur, as opposed to the amount of sulfur, is the determining parameter since the predominant form of sulfur is dependent on temperature. At 600°C, sulfur exists mainly as S₂ and S₆, which are more reactive than the S₈ ring structures.
predominant at lower temperatures [90]. Hsi et al. [12] mixed various adsorbent materials (fly ash, coal-derived AC, pistachio shell AC, and zeolites) with elemental sulfur at high temperature to test the Hg adsorption capacity of different sulfur-impregnated adsorbents. All samples except for the zeolites showed improvement in Hg capacity upon impregnation, indicating that the form of sulfur as well as the shape and size of pores may be of critical importance. Lee and Park [91] substantiated this idea, stating that a carbon support material with a large pore size was less prone to blockage by HgS and thus produced better performing SIAC.

2.4 Effects of Sulfur on Mercury Capture from Coal-Fired Utilities

2.4.1 Importance of SO₂ and SO₃ for mercury capture in coal-fired utilities

During the combustion of coal, SO₂ and SO₃ will be formed as products of sulfur oxidation reactions. Depending on the sulfur content of the coal, SO₂ concentrations in the flue gas may exceed 1000 ppm, while SO₃ may be present in amounts ranging from a few to more than 40 ppm. A small percent of SO₂ will be oxidized to SO₃ in the boiler, and more may be oxidized downstream due to the presence of reactive sites on fly ash [92]. There is also considerable evidence to suggest that sulfur in SO₂ is oxidized to S(VI) on carbon surfaces [72–74], which may result in additional gaseous SO₃ when activated carbon is injected for mercury control. In addition, many coal-fired power plants intentionally add SO₃ as a means of reducing the resistivity of fly ash in flue gas so that it may be collected more easily using electrostatic precipitators [36, 37].

Among coal-fired utilities, the consensus in recent years has been that SO₃ in flue gas is a serious detriment to the efficacy of mercury removal via activated carbon injection [36, 38]. Potential mechanisms for the inhibition of mercury adsorption by both SO₂ and SO₃, including competitive adsorption, scavenging of surface oxygen or halogens, and formation of H₂SO₄ with
concomitant blocking of pores, have been suggested by Granite et al. [39, 40]. Yet, an industrial process (Outokumpu Process) was developed in the 1970s for capturing mercury species in non-ferrous smelter flue gases using 80–90% H$_2$SO$_4$ at 150–200°C [41]. While converting Hg species into HgSO$_4$, this process also captures other metal species present in the flue gas.

Although concentrated H$_2$SO$_4$ is a known oxidizer at elevated temperatures, these metal species may make the mechanism of mercury capture more complicated. More recently, a patented technique for removing Hg from liquid hydrocarbons was developed based on activated carbon impregnated with H$_2$SO$_4$, HCl, or H$_3$PO$_4$ [42]. Previous authors took note of these industrial applications [39, 40], but reasons for the difference between these cases and that of coal-combustion flue gas is still unknown. Furthermore, there have been recent studies indicating that H$_2$SO$_4$ has a positive impact on mercury capacity [14, 43].

When activated carbon injection is not used, SO$_2$ and SO$_3$ may still have significant effects on mercury capture. Many utilities rely on catalytic oxidation of Hg$^0$ to Hg$^{2+}$, followed by capture of the oxidized mercury using wet scrubbers. At temperatures exceeding 350°C, SO$_2$ is known to hinder Hg$^0$ oxidation. This may occur through inhibition of other oxidizing species or through competition for the same catalytic surface sites as Hg$^0$, whereupon SO$_2$ is oxidized to SO$_3$ [93].

2.4.2 Impacts of SO$_2$ and SO$_3$ on mercury oxidation state

2.4.2.1 Direct interactions with pure mercury compounds

Zacharewski et al. [94] used Fourier transform infrared spectroscopy to investigate the reaction of solid mercuric oxide (HgO) with SO$_2$ at room temperature. Over a period of weeks, absorption spectra indicating the existence of Hg$_2$SO$_4$ and HgSO$_4$ were observed. The following reactions were proposed to explain the findings:
These reactions suggest a direct participation of SO\textsubscript{2} in the reduction of \( \text{Hg}^{2+} \) to \( \text{Hg}^{0} \). Although the reaction rate was exceedingly slow, it is conceivable that these reactions may proceed at a more significant rate on the surfaces of solid particles such as fly ash or activated carbon at the elevated temperatures associated with coal-fired utility stack gases. Apparently, the authors did not consider the possibility of \( \text{Hg}^{+} \) forming through reaction between \( \text{Hg}^{2+} \) and \( \text{Hg}^{0} \), therefore Reaction 2.6 may be questionable.

2.4.2.2 Homogeneous gas-phase oxidation of mercury

From the perspective of simplifying mercury removal, gas-phase interactions which affect the oxidation state of mercury in flue gas are quite important. Being more water soluble, oxidized mercury compounds can efficiently be removed using existing flue gas desulfurization (FGD) equipment, typically wet scrubbers. For this reason, many researchers have looked at homogeneous reaction mechanisms of mercury in flue gas with the goal of maximizing the proportion of oxidized to elemental mercury.

The effect of SO\textsubscript{2} on homogeneous oxidation of \( \text{Hg}^{0} \) has been observed to be negligible at temperatures ranging from 20 to 900°C [95]. For this reason, studies tend to focus on the effect of SO\textsubscript{2} on other oxidizing species that may be present in typical coal combustion exhausts. Of these, Cl\textsubscript{2} is generally believed to have the greatest potential for oxidizing \( \text{Hg}^{0} \) to \( \text{Hg}^{2+} \). The main source of Cl\textsubscript{2} in flue gas is thought to be through gas-phase reaction of HCl, as per the Deacon Reaction:

\[
4\text{HCl} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Cl}_2
\]
Xie et al. [96] tested the impact of SO$_2$ on the Deacon Reaction by flowing 250 ppm HCl and 0 to 1230 ppm SO$_2$ through a tube furnace at 800°C in a background gas of N$_2$ containing 15% CO$_2$, 0.2% CO, 5% O$_2$, and 5% H$_2$O. The product gases were trapped in a solution of phenol in methylene chloride, which formed chlorinated phenol when contacted with Cl$_2$. It was observed that the amount of chlorinated phenol decreased as the SO$_2$ concentration increased, suggesting that molecular chlorine is rapidly consumed by the following reaction:

$$\text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_3 + 2\text{HCl} \quad (2.9)$$

The feasibility of this reaction is supported by prior pilot-scale studies that looked into reducing emissions of polychlorinated dioxins and furans from municipal waste incinerators by mixing in sulfur-containing coals [97, 98]. Co-combustion of coal produced SO$_2$, which was found to dramatically reduce dioxin and furan generation.

Sterling et al. [99] added Cl$_2$, HCl, and SO$_2$ to a methane combustion gas to simulate the radical pool of a coal flame exhaust. Adding SO$_2$ at 100 and 400 ppm in the presence of 100 ppm HCl had negligible effect on oxidation of Hg$^0$. In contrast, addition of 100 and 400 ppm SO$_2$ to 500 ppm Cl$_2$ inhibited oxidation by approximately 40 and 50%, respectively. Zhou et al. [100] obtained similar results in which addition of 1200 ppm SO$_2$ to a simulated flue gas containing 60 ppm HCl reduced Hg oxidation by roughly 10 to 30% between 400 and 800°C. When HCl was not present, however, increasing SO$_2$ from 0 to 400 ppm resulted in an increase in Hg oxidation of a similar magnitude. The authors postulated that this might be the result of SO$_2$ scavenging Cl reaction intermediates in a manner similar to that shown in Reaction 2.9.

Zhao et al. [101] investigated the impacts of SO$_2$, NO, and Cl$_2$ on Hg$^0$ oxidation and HgCl$_2$ reduction using a horizontal reactor where the temperature varied from 750 to 480°C from inlet to outlet. It was observed that adding 2000 ppm SO$_2$ to a baseline concentration of 13
ppm Cl₂ had no significant effect. However, when 8% H₂O was added along with the 2000 ppm SO₂, Hg⁰ oxidation dropped from more than 40% to approximately 5% across the reactor.

Similarly, the same concentrations of SO₂ and H₂O were found to increase HgCl₂ reduction from ~45 to 80% while SO₂ on its own caused a slight decrease. The authors attributed this behavior to SO₂ and H₂O scavenging Cl and Cl₂ according to Reactions 2.9 and 2.10.

\[
\text{Cl} + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOSO}_2 \tag{2.10}
\]

Results obtained by Agarwal et al. [102] disagree somewhat. By adding 370 ppm SO₂ to a simulated flue gas containing 3.5% O₂, 13.5% CO₂, 2 ppm Cl₂, and 10 μg/m³ elemental mercury, a decrease in mercury oxidation from over 70% to 52% was observed. Furthermore, addition of 13% H₂O did strengthen the inhibitory effect of SO₂, but only very slightly.

A somewhat different explanation for observed inhibition of mercury oxidation due to SO₂ was supported by Krishnakumar and Helble [103] based on the oxidation mechanism proposed by Qiu et al. [104]. The observed results of Sterling et al. [99] were found to correlate quite well with those found using the Qiu mechanism under the same experimental conditions. A sensitivity analysis was thus performed using this mechanism, and it was suggested that SO₂ inhibits Hg⁰ oxidation through scavenging of OH radicals as opposed to Cl species.

\[
\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} \tag{2.11}
\]
\[
\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3 \tag{2.12}
\]
\[
\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 \tag{2.13}
\]

The reaction of HCl with OH, which was determined to be the main pathway for producing Cl atoms, is thus blocked by the addition of SO₂. Lower levels of Cl in the flue gas would result in lower levels of Hg⁰ oxidation. Evidence in support of this conclusion has been observed by Ko et al. [105].

23
No literature could be found describing experiments in which the effect of SO\textsubscript{3} on homogeneous mercury oxidation was studied. It has been speculated, though, that SO\textsubscript{3} may enhance photochemical oxidation of elemental mercury that has been promoted to an excited state by the application of 253 nm ultraviolet light according to Reaction 2.14 [106]:

\[
\text{Hg}^0 + \text{hv} \rightarrow \text{Hg}^* + \text{SO}_3 \rightarrow \text{HgO} + \text{SO}_2
\] (2.14)

In this reaction, Hg\textsuperscript{*} is elemental mercury in the \(6(3P_1)\) excited state. The validity of this reaction needs to be confirmed through experiments.

The overall body of work pertaining to the effect of SO\textsubscript{2} on homogeneous mercury oxidation seems to suggest that it indirectly inhibits the conversion of Hg\textsuperscript{0} to Hg\textsuperscript{2+}. Although SO\textsubscript{2} on its own appears to have little effect in the gas phase, its interactions with oxidizing species such as Cl\textsubscript{2} reduces their availability to react with mercury. In order to understand the situation in a real coal combustion flue gas, however, it is important to incorporate these findings with those of heterogeneous systems.

2.4.2.3 Gas-phase oxidation of mercury in the presence of fly ash

Due to the presence of fly ash in coal combustion flue gas, the effects of sulfur species in these systems may be different than in a homogeneous system. The change in mercury speciation will affect its removal in the existing equipment such as FGD, as previously mentioned.

Using the Ontario Hydro method, Laudal et al. [107] investigated the impact of 1500 ppm SO\textsubscript{2}, 50 ppm HCl, and 10 ppm Cl\textsubscript{2} on the oxidation of Hg\textsuperscript{0} at 20 \(\mu\text{g/m}^3\). Tests were performed in N\textsubscript{2} containing 15\% CO\textsubscript{2}, 4\% O\textsubscript{2}, 10\% H\textsubscript{2}O with and without the gas mixture flowing through a bed of coal fly ash. Results indicated that, without fly ash, SO\textsubscript{2} greatly reduced the ability of Cl\textsubscript{2} to oxidize Hg\textsuperscript{0}, reducing the proportion of oxidized mercury in the
outlet from 84.8 to 1.9%. The addition of fly ash, however, increased the oxidized mercury to 28.5%, confirming its involvement in Hg\textsuperscript{0} oxidation. Fly ash is rich in silica (SiO\textsubscript{2}), lime (CaO), and unburnt carbon, all of which may participate in catalyzing the oxidation of mercury. The alkaline minerals that are present may also help to neutralize acid gases such as SO\textsubscript{2}, which reduces oxidized mercury, and SO\textsubscript{3}, which may combine with H\textsubscript{2}O to form H\textsubscript{2}SO\textsubscript{4} on the ash surface and physically hinder further oxidation [36, 37]. HCl (without Cl\textsubscript{2}) was not observed to have any significant impact on Hg\textsuperscript{0} oxidation, with and without fly ash. Although HCl is not an oxidizer for Hg\textsuperscript{0}, it is believed to be the source of Cl\textsubscript{2} according to the Deacon Reaction. Apparently, under the conditions studied, this reaction did not proceed in any substantial way. In a follow-up study under similar conditions but without Cl\textsubscript{2} in the input stream, the effect of NO\textsubscript{x} on mercury oxidation was investigated [108]. While SO\textsubscript{2} on its own with fly ash was not observed to produce any oxidized mercury, its combination with 20 ppm NO\textsubscript{2} was found to increase Hg\textsuperscript{2+} to 24%. A very similar enhancement was observed when both HCl and NO\textsubscript{2} were added, suggesting that the overall impact of NO\textsubscript{2} in mercury oxidation in the presence of fly ash is greater than that of Cl resulting from HCl via the Deacon Reaction. NO at 300 ppm was found to reduce oxidation under all gas combinations studied.

After studying the data collected from a 100 MW coal-fired boiler, Kellie et al. [109] reported a statistically significant positive relationship between SO\textsubscript{2} concentration in the flue gas and the level of oxidized mercury. The observed enhancing effect of SO\textsubscript{2} was justified with the mechanism described by Frandsen et al. [110]:

\[
\text{HgCl}_2 + \text{SO}_2 + \text{O}_2 \leftrightarrow \text{HgSO}_4 + \text{Cl}_2
\]  

With this reaction, Frandsen et al. indicated that HgSO\textsubscript{4} is more stable than HgCl\textsubscript{2} in an equilibrium system containing the elements C, H, N, O, S and Cl in addition to Hg, but only at
temperatures below approximately 100°C. This is considerably lower than temperatures normally encountered in coal combustion flue gases. Nonetheless, this reaction suggests that, under certain conditions, SO$_2$ along with O$_2$ may liberate Cl$_2$, which is a known oxidant for Hg$^0$. In contrast to Kellie et al., Cao et al. [111] suggested an opposite trend while studying the same 100-MW boiler (Figure 3(b) in [111]). However, a closer inspection of the data revealed that the trend was based on a rather weak correlation that was greatly influenced by a single point at the highest SO$_2$ concentration (~1250 ppm). It should be pointed out that, with O$_2$, the role of SO$_2$ in Hg$^0$ oxidation is very different from that without O$_2$. It is anticipated that the conversion of HgCl$_2$ to HgSO$_4$ according to Reaction 2.15 also depends on the level of O$_2$.

Yang et al. [112] analyzed the coal combustion gases from a 220-MW power plant in China using the Ontario Hydro Method, and observed a negative correlation between sulfur content of coal (which is typically indicative of SO$_2$ and SO$_3$ levels in the stack gas) and Hg oxidation. In contrast, Wang et al. [113] used the same technique to sample flue gases from five Chinese coal-fired power stations and observed a positive correlation between SO$_2$ concentration and Hg oxidation. The conflicting evidence seems to underscore the complicated nature of the effect of sulfur on Hg$^0$ oxidation and the involvement of other active species such as Cl$_2$ and NO$_2$. It should also be noted that mercury speciation in coal-fired power plants is not a simple task that is carried out readily or routinely.

2.4.2.4 Oxidation of Hg on carbon surfaces

Activated carbons are widely used for removal of both Hg$^0$ and Hg$^{2+}$ species from flue gas. The complexity of the carbon surface is thought to enable this relatively indiscriminate adsorptive behavior. Huggins et al. [114] performed X-ray absorption fine structure analyses on a variety of carbonaceous sorbents that had been exposed to simulated flue gases containing Hg$^0$.
and/or HgCl₂ at temperatures below 200°C. The resulting spectra in each case gave no indication of elemental Hg existing on the surface, suggesting that the adsorption process is dominated by chemisorption. Elemental mercury adsorption, it was reasoned, must involve a step where Hg⁰ is oxidized to Hg²⁺ at the surface by anions of Cl, I, S, or O (other possibilities such as Br were not included in the standard spectra).

A model to explain this behavior has been proposed in which the carbon surface has multiple sites which are necessary for effective mercury binding. Firstly, carbenium ion oxidation sites are formed by reaction of HCl with zigzag edge structures. Hg⁰ is then oxidized by NO₂ or other oxidizing gases at these oxidation sites [115]. The oxidized mercury is then bound to similar zigzag structure carbenium ions which act as Lewis basic sites [116]. XPS evidence was found suggesting that NO₂ actively oxidizes sulfur in SO₂ to SO₃, which, when combined with H₂O to form H₂SO₄, then deactivates the basic binding sites which are necessary for retention of Hg²⁺ [117, 118].

2.4.2.5 Catalytic oxidation of mercury

Many coal-fired utilities utilize vanadium-based selective catalytic reduction (SCR) devices in order to reduce NOₓ emissions. These catalysts have been shown to promote oxidation of Hg⁰ to Hg²⁺, and thus provide an attractive means of reducing mercury emissions when combined with FGD [93, 119, 120]. However, the NH₃ injected as a reducing agent may reduce a portion of the oxidized mercury, and vanadium catalysts also promote oxidation of SO₂ to SO₃ with possible undesired effects [36]. Zhuang et al. [121] studied the impacts of adding HCl at 50 ppm, SO₂ at 2000 ppm, and SO₃ at 50 ppm on the oxidation of 13 µg/m³ Hg⁰ across a SCR catalyst at 343°C under 6% O₂, 12% CO₂, 8% H₂O, 600 ppm NO, 18.5 ppm NO₂, and 550 ppm NH₃. Adding SO₂ in addition to HCl was found to reduce oxidation from 71 to 64%. When
both SO₂ and SO₃ were added, oxidation dropped only to 63%, suggesting competition between the sulfur species over catalytic sites. Since SO₃ cannot reduce oxidized mercury, its negative impact on Hg⁰ oxidation is likely an indirect effect on the catalyst.

Several other catalyst materials have been tested at the bench-scale for their ability to oxidize Hg⁰ in flue gas conditions, including gold, palladium, platinum, iridium, and carbon-based catalysts [122–124]. Although these materials displayed great promise for future industrial application, it was suggested that SO₂ could scavenge oxygen or chlorine from the catalyst surface, and that this could have an impact on the rate of mercury oxidation. A similar concern has been raised for titania-based catalysts that may be used in conjunction with photocatalytic oxidation of Hg⁰ [125].

2.4.2.6 Mercury capture using wet FGD scrubbers

It is well understood that, once oxidized to a readily soluble form such as HgCl₂, mercury from coal combustion gases can be efficiently captured using wet FGD scrubbers. However, the presence of SO₂ may yet impact the overall effectiveness of these devices. In order to explain observed increases in Hg⁰ across wet FGDs, Chang and Ghorishi [126] proposed a model by which absorbed mercury in the form of HgCl₂ interacts with sulfite or bisulfite in the scrubbing solution to form Hg-S(IV) complexes. A fraction of these complexes then undergo a series of chain reactions to ultimately produce insoluble Hg⁰.

HgCl₂ + S(IV) → Hg-S(IV) complexes → Hg⁰

Evidence to support this model was observed by Diaz-Somoano et al. [34] using a CaO slurry at 50-60°C with a background gas consisting of 6% O₂, 7% H₂O, and 50 μg/m³ Hg (the Hg⁰:Hg²⁺ ratio was undetermined). As SO₂ concentration increased from 250 to 2000 ppm, a near-linear decrease in mercury removal from approximately 60 to 30% was found. This
observation is consistent with the well-documented reducing nature of SO$_2$ or S(IV) in general.

### 2.4.3 Effects of SO$_2$ and SO$_3$ on uptake of mercury using activated carbons

#### 2.4.3.1 Uptake of mercury to virgin activated carbon

All relevant studies on mercury uptake to virgin activated carbon thus far have focused on SO$_2$. It was shown by Ghorishi & Gullett [127] that SO$_2$ on its own enhanced an activated carbon’s capacity for elemental mercury. Two different commercial activated carbons were tested at 100 and 140°C using 262 μg/m$^3$ Hg$^0$ with and without 1000 ppm SO$_2$. For one of them, a significant increase in Hg uptake capacity was reported while the other was apparently unaffected by the presence of SO$_2$. This finding seems to suggest that the effect of SO$_2$ was not via a homogeneous reaction. The observed difference in SO$_2$ effect between the two carbons was attributed to different levels of calcium (0.13 wt% versus 1.82 wt%), which the authors proposed may act as a catalyst in the formation of active sulfur sites for mercury capture. This explanation has not been verified by other research, however.

In order to more accurately reflect typical industrial stack conditions, most recent studies have incorporated SO$_2$, O$_2$, and H$_2$O (among other components) in Hg sorption experiments. Using a simulated flue gas composed of 6% O$_2$, 12% CO$_2$, 7% H$_2$O, 50 ppm HCl, and 60–70 μg/m$^3$ Hg$^0$ at 135°C, Carey et al. [128] observed a decrease in Hg capacity from 15 to 4 mg Hg/g sorbent with the addition of 100 ppm SO$_2$. Increasing the SO$_2$ concentration up to 3000 ppm resulted in a slight decrease to 2 mg Hg/g sorbent. Using the same sorbent material, Eswaran et al. [129] tested the effect of 369 ppm SO$_2$ and 163 ppm NO on Hg sorption under 3.6% O$_2$, 13.5% CO$_2$, and 10–16 μg/m$^3$ Hg$^0$ at approximately 50 and 92°C. At the lower temperature, SO$_2$ and NO were found to dramatically decrease mercury capacity from ~200 to 10 mg Hg/g sorbent, in agreement with Carey et al. However, this decrease in capacity was not
observed at 92°C. In fact, a 20% increase in initial adsorption rate was found with SO$_2$ and NO at this temperature, which was thought to be due to increased reactive sites on the carbon surface under these conditions. A similar pronounced increase in Hg adsorption efficiency from 0 to 1000 ppm SO$_2$ was observed by Yan et al. [130] using IndoGerman® activated carbon in a simulated flue gas at 90°C. The authors attributed this improvement to the formation of H$_2$SO$_4$ at the surface according to a mechanism similar to that shown in Reactions 2.1–2.4. Granite and Presto [131] tested two commercial activated carbons derived from coal under pure N$_2$ and under N$_2$ containing 16% CO$_2$, 5% O$_2$, 2000 ppm SO$_2$, 500 ppm NO, and 1600 μg/m$^3$ Hg$^0$ at 138°C. In agreement with the findings of Eswaran et al. and Yan et al., both sorbents exhibited approximately an 85% reduction in Hg$^0$ capacity under pure N$_2$. A similar, yet less dramatic result was noted for a third commercial activated carbon at 204°C.

Miller et al. [132] undertook a comprehensive, full-factorial experiment under similar conditions using continuous emission monitoring (CEM) to analyze the individual and combined effects of SO$_2$, HCl, NO, and NO$_2$. The CEM used in this study detected only Hg$^0$. By passing the outlet gases through a reduction cell containing tin(II) chloride prior to quantification, oxidized mercury species were reduced to Hg$^0$. This allowed for the measurement of total Hg, and, by comparison with Hg$^0$, oxidized Hg. It was found that the addition of 1600 ppm SO$_2$ provided a slight enhancement but, nonetheless, resulted in inadequate mercury sorption performance. Addition of 50 ppm HCl and/or 300 ppm NO along with SO$_2$ provided considerable improvement in mercury uptake kinetics as evidenced by enhanced capture efficiency, although slightly less than the cases of HCl and NO alone. On the other hand, adding 20 ppm NO$_2$ in the presence of SO$_2$, even with HCl and/or NO, resulted in rapid breakthrough accompanied by complete oxidation of the mercury. An explanation for this
finding came in a later study in which uptake of HgCl$_2$ and Hg$^0$ onto a fixed bed of lignite activated carbon was monitored under similar baseline and acid gas conditions at 135°C [133]. Combining SO$_2$ with NO$_2$ once again resulted in rapid breakthrough and saturation of the activated carbon. However, this was not observed when H$_2$O was omitted, indicating the formation of H$_2$SO$_4$ via NO$_2$-oxidized SO$_2$, in good agreement with Laumb et al. [117] and Olson et al. [118]. Thus, while NO$_2$ is important for Hg$^0$ oxidation and retention as per the mechanism described by Olson et al. [115, 116], the combination of NO$_2$, SO$_2$, and H$_2$O leads to poisoning of the surface by H$_2$SO$_4$. Furthermore, adding SO$_2$ alone and in combination with NO resulted in reduction of the HgCl$_2$ to Hg$^0$, which could also hinder uptake performance. This effect was counteracted by the addition of NO$_2$ and HCl.

At temperatures typical of coal combustion flue gases, oxidation in the gas phase and on the carbon surface is a critical step in the removal of mercury using activated carbon. However, the formation of H$_2$SO$_4$ on a sorbent under oxidizing conditions can hinder mercury uptake by blocking access to pores and by competing for basic sites with oxidized mercury. It is therefore important to address uptake capacity and oxidation kinetics separately when evaluating the performance of a mercury capture system.

2.4.3.2 Uptake of mercury to chemically impregnated activated carbon

To improve the efficiency of mercury capture, many activated carbons are treated with chemicals such as S, Cl, Br, or I in order to augment the carbon surface with additional reactive sites. It is to be expected that the effect of SO$_2$ and SO$_3$ on mercury uptake will be different when the activated carbon is chemically impregnated. Liu et al. [134] tested the effects of adding SO$_2$ with and without the presence of H$_2$O using Calgon BPL® impregnated with elemental sulfur at 140°C and 55 μg/m$^3$ Hg$^0$. While 1600 ppm SO$_2$ showed no effect at all, increasing H$_2$O
from 0 to 10% was found to hinder Hg uptake, possibly due to increased mass transfer
c resistance. The combination of SO\textsubscript{2} with H\textsubscript{2}O led to results similar to those of H\textsubscript{2}O alone. This
was explained by the low SO\textsubscript{2} concentration: if SO\textsubscript{2} formed a weak acid with H\textsubscript{2}O on the
surface, the concentration was too low to have a noticeable effect. Similarly, Yan et al. [130]
found there to be no significant effect of varying SO\textsubscript{2} from 0 to 2000 ppm in a simulated flue
gas using Waterlink\textsuperscript{®} S-impregnated carbon at 90\textdegree}C. Granite et al. [135] tested two commercial
activated carbons, one impregnated with elemental iodine and potassium iodide and the other
impregnated with elemental sulfur. Although these tests were done in pure argon, they can be
compared to a later study in which the same sorbents were analyzed under N\textsubscript{2} with 16% CO\textsubscript{2},
5% O\textsubscript{2}, 2000 ppm SO\textsubscript{2}, and 500 ppm NO [131]. Under pure Ar at 138\textdegree}C, the S-impregnated
carbon had an adsorption capacity of 3.5 mg/g. This value was seen to decrease to 1.6 mg/g in
the presence of the other gases. The case of the I-promoted carbon was more extreme in that the
capacity decreased from 4.8 to 0.2 mg/g by using the simulated flue gas as opposed to Ar. It
should be noted, however, that the pure Ar test for the I-impregnated sample was performed at a
temperature 50\textdegree}C higher than that of the simulated flue gas.

As mentioned previously, one of the key concerns with SO\textsubscript{2} and SO\textsubscript{3} in flue gas is the
possibility of formation of H\textsubscript{2}SO\textsubscript{4} on the carbon surface, which is widely held to be a poison for
effective mercury removal. However, a number of studies have produced mixed results
concerning the effect of H\textsubscript{2}SO\textsubscript{4}. Olson et al. [136] added 5% H\textsubscript{2}SO\textsubscript{4} to Calgon F-400\textsuperscript{®} and
Centaur\textsuperscript{®}, a catalytic carbon containing nitrogenous edge structures, and subsequently dried
them at 110\textdegree}C. For the catalytic carbon, this treatment was found to increase the 50%
breakthrough time from 8 minutes to 209 and 575 minutes in pure N\textsubscript{2} and air, respectively. For
Calgon F-400\textsuperscript{®} in air, the 50% breakthrough time increased from 1 minute to 171 minutes due to
the acid treatment. The improvement observed in air implied a chemisorption mechanism, however a series of experiments were performed in which Hg adsorption improved slightly with decreasing temperature. This might suggest that the overall process is controlled by an interfacial step, rather than mass transfer which often has a positive temperature dependence.

Werner et al. [14] investigated the effect of different gas mixtures containing SO₂, O₂, and H₂O on uptake of Hg⁰ vapor (1000 μg/m³) at 120°C using a lignite-based activated carbon impregnated with elemental sulfur to 5% by weight. The best performance was seen when all three gases (SO₂, O₂, and H₂O) were present, resulting in what was interpreted as the formation of H₂SO₄ over time along with a relative increase in uptake. This contrasts with the lack of any effect observed under similar conditions by Yan et al. [130] using a Waterlink® S-impregnated carbon, however different treatment methods and sulfur contents may be the reason for this discrepancy. The same uptake enhancement trend was recorded by Werner et al. [14] when H₂O was not present, which was attributed to residual H₂O on the carbon surface. With SO₂ alone, however, the performance was the worst among the conditions studied. The effect of H₂SO₄ on Hg⁰ adsorption was explicitly shown by soaking the virgin activated carbon in 8% H₂SO₄ for 30 seconds, filtering, and drying at 105°C for 4 hours. This treated sample showed no sign of breakthrough after approximately 16 hours of uptake at 90°C, at which point the elemental sulfur impregnated sample had reached ~8% breakthrough. A similar result was found by Uddin et al. [43] using a coconut shell derived activated carbon with 5% O₂, 10% CO₂, 14.7% H₂O, 0–500 ppm SO₂, and 32 μg/m³ Hg⁰. It was observed that O₂ and H₂O were necessary for Hg⁰ removal in the presence of SO₂. Samples pre-treated with SO₂ or 0.2% H₂SO₄ showed excellent Hg⁰ removal capacity, however this enhancement was reduced in the presence of SO₂. The authors suggest that this may be due to reduction of oxidized mercury species (such as HgO) via
reaction with SO$_2$. More direct evidence of mercury binding to sulfate species was provided by Hutson et al. [137] for conventional, Br-impregnated, and Cl-impregnated activated carbon using X-ray absorption spectroscopy. In this study, the sulfate was presumed to originate from the 650 ppm SO$_2$ in the simulated flue gas used while contacting the samples with Hg$^0$.

Several studies, on the other hand, have indicated that H$_2$SO$_4$ originating from either SO$_2$ or SO$_3$ have negative impacts on Hg capture. Using a simulated flue gas containing 5.25% O$_2$, 12.5% CO$_2$, 0–1.5% H$_2$O, 500 ppm NO, 50 ppm HCl, 0–1870 ppm SO$_2$, 0–100 ppm SO$_3$, and 9.3 μg/m$^3$ Hg at 149°C, Presto and Granite [39] tested two commercial activated carbons, one of which was bromine-impregnated. In all cases, SO$_3$ was found to greatly reduce Hg$^0$ uptake (nearly 80% at 20 ppm), while the addition of moisture was also found to decrease uptake when SO$_2$ was present rather than SO$_3$. The authors attribute these findings to competitive adsorption between Hg$^0$ and S(VI) species (i.e., SO$_3$, sulfate, or H$_2$SO$_4$), which was supported by XPS data indicating a dominance of sulfate over other sulfur functional groups. This inhibition of Hg$^0$ capture was more pronounced with the brominated carbon, due to the increase in surface reactivity towards both mercury and sulfur oxides. The raw activated carbon was also impregnated directly with 95% H$_2$SO$_4$ and dried at 110°C, after which it exhibited effectively zero capacity for Hg$^0$. In a companion study using continuous emission monitoring, exposure to SO$_3$ and H$_2$SO$_4$ impregnation were shown to greatly reduce initial mercury removal efficiency in addition to reducing its overall uptake capacity [40]. Sjostrom et al. [37] carried out a full-scale study of the impact of SO$_3$ on Hg adsorption from a 630 MW coal-fired power plant using several varieties of activated carbon. Using Norit Darco Hg-LH®, a commercial brominated carbon, a negative correlation was found between increasing SO$_3$ concentration and Hg removal, in agreement with Presto and Granite. The negative effect of SO$_3$ was reduced when using a
similar sorbent which had also been treated with alkaline materials to neutralize acidic gases.

2.4.3.3 Understanding the effect of $H_2SO_4$ on mercury uptake

Several of the studies described above were performed under conditions in which $H_2SO_4$ could potentially form, and, for some, this was hypothesized to be the reason behind observations of mercury uptake inhibition [39, 40, 133]. On the other hand, it has been suggested by several researchers that the formation of $H_2SO_4$ at the carbon surface was the cause of observed improvements in mercury uptake capacity [14, 130]. To make matters more complicated, different studies in which $H_2SO_4$ was directly impregnated on activated carbon surfaces have given opposite results [14, 43, 136].

This apparent contradiction may be explained by understanding the different mercury uptake conditions used in each case. Considering the experiments in which $H_2SO_4$ was directly impregnated, Presto et al. [39, 40] observed the most negative effects. In this study, 200 mg of sorbent were placed in a cylindrical reactor of 22 mm ID. Assuming a bulk density of 0.5 g/cm$^3$ (typical of activated carbons), this yields a bed height and volume of approximately one mm and 0.4 cm$^3$, respectively. Since the gas flow rate used in that study was 8 L/min, the empty bed residence time (EBRT) was estimated to be only 0.003 s. With such a short residence time, mercury capture is most likely limited by the rate of uptake. Using another $H_2SO_4$-impregnated activated carbon, Werner et al. [14] carried out $Hg^0$ uptake experiments using a sorbent bed made up of 3–6 layers of activated carbon (each approximately 0.5 g) separated by 2 mm layers of quartz wool. With a reactor ID of 30 mm, flow rate of 540 cm$^3$/min, and assuming a bulk density of 0.5 g/cm$^3$, as before, the bed height, bed volume and EBRT are estimated to be 1.0–2.1 cm, 7.2–14.5 cm$^3$ and 0.8–1.6 s, respectively. As previously described, excellent mercury capacity was observed under these conditions. It is possible that the much longer gas-solid
contact time resulted in a system that was not limited by the rate of uptake, consequently allowing the determination of mercury uptake capacity and its dependence on H$_2$SO$_4$-impregnation.

Table 2.1 lists bench-scale studies done under conditions where H$_2$SO$_4$ could conceivably form (H$_2$O with SO$_2$ and an oxidant, O$_2$ and/or NO$_2$), as well as those in which H$_2$SO$_4$ was added directly. The calculated EBRT for each case is shown, along with an indication of the general observed effect of H$_2$SO$_4$ on mercury uptake (regardless of whether or not the acid was in fact formed). The study done by Miller et al. [132] provided inadequate information regarding bed dimensions, so it was not included. Likewise, Carey et al. [128] mixed activated carbon with sand in their study, thereby complicating the comparison. For the remaining studies, it can be seen from Table 2.1 that positive effects of H$_2$SO$_4$ or H$_2$SO$_4$-forming conditions correlate well with higher values of EBRT while negative effects correlate with the lowest EBRTs. Although the EBRT for the study done by Olson et al. [136] was relatively low (0.006 s), it must considered that this is a very rough comparison which does not

\begin{table}[h]
\begin{tabular}{lcccccc}
\hline
Reference & Gas Flow, cm$^3$/min & Fixed Bed Volume, cm$^3$ & EBRT, s & [H$_2$SO$_4$], Vol.% & Effect of H$_2$SO$_4$ \\
\hline
Olson et al. [136] & 3780 & 200$^b$ & 0.006 & 5.0 & positive \\
Yan et al. [130]$^a$ & 300 & 2.1 & 0.42 & N/A & positive \\
Werner et al. [14] & 540 & 1.5–3$^b$ & 0.8–1.6 & 8.0 & positive \\
Presto et al. [39] & 8000 & 0.4$^b$ & 0.003 & 95.0 & negative \\
Uddin et al. [43] & 500 & 0.5 & 0.06 & 0.2 & positive \\
Mibeck et al. [133]$^a$ & 14100 & 0.63 & 0.003 & N/A & negative \\
\hline
\end{tabular}
\end{table}

$^a$ Direct H$_2$SO$_4$ impregnation not used

$^b$ Based on assumed bulk density of 0.5 g/cm$^3$
take into account factors such as temperature, particle size, sorbent characteristics, etc. In a full-scale coal-fired power plant where activated carbon injection is used, the gas-solid contact is likely less efficient than that of bench-scale tests using fixed bed adsorbers. Thus, studies in which the EBRT is very short tend to be more realistic from a practical perspective.

Another factor that may affect the role of H$_2$SO$_4$ is its amount on the carbon surface. For the cases where H$_2$SO$_4$ was directly impregnated, Table 2.1 also indicates the concentration of the aqueous H$_2$SO$_4$ solution used. It is readily seen that positive effects were observed in the experiments where the concentration of H$_2$SO$_4$ was low (0.2–8.0%), while those using a high concentration (95.0%) found detrimental effects. Large amounts of H$_2$SO$_4$ on an activated carbon surface may block access to pores, thus eliminating the vast majority of the surface area on which oxidation and binding of mercury may occur. On the other hand, small amounts of H$_2$SO$_4$ which do not affect mass transfer of mercury into the inner pores may actually improve the adsorption capacity by creating oxidation sites [115, 116]. However, a coal combustion flue gas is at elevated temperature and contains substantial amounts of moisture, oxidants, SO$_2$ and SO$_3$. Thus, it is probable that the amount of H$_2$SO$_4$ on the carbon surface would rapidly exceed the small amount at which enhanced adsorption could occur. The accumulating H$_2$SO$_4$ would first overwhelm the basic binding sites necessary for retention of oxidized mercury, and eventually obstruct the carbon pores.

Overall, the role of H$_2$SO$_4$ in mercury adsorption on activated carbon is not yet fully understood. Carefully designed experiments are needed to quantify the kinetics and capacity of mercury adsorption and to clearly elucidate the capture mechanisms.
CHAPTER 3  A CONSTANT THICKNESS POROUS LAYER MODEL FOR ACTIVATION OF PETROLEUM COKE WITH SULFUR DIOXIDE

3.1 INTRODUCTION

In the modeling of gas-solid reaction systems, there are generally two approaches which have been used: homogeneous models and heterogeneous models. In a strictly homogeneous model, the solid material is assumed to be initially porous. Thus, for a reacting spherical particle, there is no concentration gradient of reactant gas molecules with respect to particle radius and the reaction proceeds uniformly throughout. Of these approaches, the Random Pore Model of Bhatia and Perlmutter [49] is the most widely used despite the development of more refined homogeneous models [50]. This is perhaps due to the relative simplicity of its application and the fact that it requires parameters that can easily be obtained from measured physical properties of the raw material. Using the Random Pore Model, accurate simulations of reaction rate and SSA development have been achieved in the gasification of agricultural wastes [51] and coal chars [52–57].

Heterogeneous gas-solid reaction models generally assume an initially non-porous solid, resulting in a strictly defined reaction front which propagates from the outside of the reactant particle towards its center. One of the most widely-known heterogeneous models is the Shrinking Core Model developed by Yagi and Kunii [15], in which the reaction produces an inert solid product through which gaseous reactant and product molecules diffuse. As the reaction proceeds, the porous product layer becomes thicker until the point at which the solid reactant is exhausted and the entire particle consists of the solid product. Since this case is
highly idealized, several modifications have been made over years by incorporating some
degree of homogeneity in the gas-solid reaction. Different approaches have incorporated limited
diffusion into the solid core to produce a 3-dimensional reaction zone [58, 59] and secondary
reactions occurring within the porous intermediate layer [62, 63], as well as modeling the
particle as a cluster of densely packed grains, to each of which the Shrinking Core Model is
applied as the reactant gas diffuses between them [60, 61].

Relatively few studies have been done on the properties of the porous intermediate layer
and how they may change over time. This is important in activation of dense materials because
the porous layer is expected to comprise the majority of an activated particle’s surface area.
Braun et al. [66] modelled the growth of a product layer during oxidation of a flat sample of
glassy carbon by assuming that an intermediate product layer is formed through a diffusion
controlled reaction at the carbon surface, while the product layer itself is consumed through a
different chemical reaction. The model was found to agree with experimental data in that the
product layer thickness tended to plateau over time. Furthermore, the magnitude of the
maximum thickness and the time needed to achieve it decreased with increased temperature. In
a later study, Braun et al. [67] fit a time-dependent equation for surface area to experimentally
determined values of BET SSA for glassy carbon particles activated in air at 450°C. An accurate
fit was obtained despite the fact that a uniform SSA of 900 m²/g was assumed for the entire
porous product layer at all times during the activation. In reality, the porosity of the product
layer will vary with respect to particle radius. Furthermore, this model, which predicts that the
SSA will asymptotically approach a maximum achievable value, was developed for a material
which is essentially pure carbon. Activated carbon is typically produced from different materials
such as coal, coke, and agricultural wastes, which contain significant fractions of inorganic ash.
This ash may impact the development of SSA over time, therefore similar studies need to be done on other, more conventional, activated carbon precursors.

This study aims to elucidate the mechanisms behind SSA evolution during the activation of oil-sands fluid coke with SO$_2$. Fluid coke is produced through multiple cycles through a fluidized bed coking unit during the upgrading of bitumen. This results in roughly spherical particles consisting of concentric layers of dense, highly graphitized material which is approximately 82% carbon, 7% sulfur, and 6% inorganic ash [3]. Because of its non-porous structure, homogeneous reaction models are not directly applicable to the activation of fluid coke. A heterogeneous model like that of Braun et al. [67] is more appropriate, however, due to the significant ash content and uncertainty with regards to the SSA of the porous layer, a more general approach is needed. In this study, coke particles are modeled as a series of concentric, overlapping shells of uniform thickness, each of which is assumed to react homogeneously with SO$_2$ according to the Random Pore Model. The rates of unreacted core and particle shrinkage are determined experimentally and used to predict SSA evolution, which is then compared to experimentally obtained values of BET SSA. The results obtained are expected to be of practical significance when activating dense carbonaceous materials containing ash.

3.2 MATERIALS AND METHODS

3.2.1 Sample Preparation

Coke used for this work was fluid coke, a particular type of petroleum coke produced in a fluidized bed coker unit. It was obtained directly from an upgrading facility in Alberta, Canada and screened to particle size ranges of 53–106 and 212–300 µm. Prior to activation, the coke was pre-oxidized by spreading approximately 20 g on a watch glass and placing it in a Barnant muffle furnace at 250°C for 18 hours. Air pre-oxidation under similar conditions has been used
previously to enhance pore development during activation of carbonaceous materials [138–144].

The apparatus used for activation of coke samples is shown in Figure 3.1. SO$_2$ (99.95%) and N$_2$ (99.997%) were supplied by cylinders and each set to flow at 100 cm$^3$/min by Aalborg mass flow controllers. Teflon 3-way stopcocks were used both to combine the two gases and to divert flow around the reactor when needed. The reactor was a quartz tube 68 cm in length and 2 cm inner diameter with a porous quartz disc located at the midpoint. Approximately 10 g of coke was placed on this disc, resulting in a cylindrical bed 2.4 cm in height and 7.5 cm$^3$ in volume. The reactor tube was positioned within a Carbolite vertical tube furnace and connected to the gas lines via ball-and-socket joints sealed with high-temperature vacuum grease. The lower connector was an L-shaped Pyrex tube stuffed with aluminum oxide wool, which functioned as a condenser and filter for elemental S produced during the reaction. To ensure integrity of flow, a pressure gauge placed upstream of the reactor and a flowmeter located downstream were monitored throughout the experiment. All gases flowed through a

![Figure 3.1. Schematic diagram of apparatus used in SO$_2$ activation of petroleum coke. 1. Mass flow controllers; 2. 3-way stopcock; 3. Gas sampling port; 4. Pressure gauge; 5. Tube furnace; 6. Coke sample; 7. Sulfur collector; 8. Secondary particulate filter; 9. Flowmeter; 10. NaOH scrubbing solution.](image-url)
concentrated sodium hydroxide (NaOH) scrubbing solution prior to venting.

For all analyses, the reactor was first flushed with pure N\textsubscript{2} for 15 minutes. The furnace was then set to 120°C to drive out moisture for an additional 15 minutes. Gas flow was then diverted around the reactor as SO\textsubscript{2} was introduced. Gas samples were taken from the inlet sampling port and analyzed using gas chromatography until SO\textsubscript{2} was stable at 50 vol% to within ±3 vol%, after which the temperature was increased to 700°C. When this temperature was reached, the 3-way stopcock was turned to introduce the 50 vol% SO\textsubscript{2} gas mixture into the reactor, starting the reaction. At the end of the experiment (1–14 hours), SO\textsubscript{2} was immediately shut off and the reactor allowed to cool under flowing N\textsubscript{2}. The activated coke sample was then weighed to determine sample yield.

3.2.2 Analysis of samples

SSA, pore volume, and pore size distribution were measured by N\textsubscript{2} adsorption at 77 K using a Quantachrome Autosorb-1-C. Forty adsorption points between relative pressures of 0.025 and 0.995 were obtained and analyzed using the quenched solid density functional theory (QSDFT), available as an analysis kernel within the Quantachrome ASiQwin software. It has been shown that QSDFT is the preferred technique for characterizing pore size distribution of amorphous carbons since it takes into account physical and chemical heterogeneity \cite{145}. The specific analysis kernel used assumed slit-shaped micropores (<2 nm) and cylindrical mesopores. Total pore volume was determined using a combination of N\textsubscript{2} adsorption QSDFT and the BJH technique since QSDFT is not valid for pores exceeding 35 nm. SSA was determined with the BET method using three points at relative pressures of 0.025, 0.05, and 0.075. It is uncertain whether points at lower relative pressures might have yielded more accurate results, thus BET SSA is reported as “apparent” BET SSA.
Particle size measurements were obtained with a Malvern Instruments Mastersizer S using the Fraunhofer scattering model. This technique was used to determine average particle radii, $R$, which were then fitted to a linear equation with respect to time, $t$:

$$R = R_0 + \alpha t$$  \hspace{1cm} (3.1)

Where $R_0$ is the initial particle radius and $\alpha$ is the rate of decrease of particle radius.

Cross-sectional samples were obtained by embedding coke particles in one-inch diameter epoxy casts, polishing the surface, and carbon-coating. Images of these casts were obtained using a Hitachi field emission SEM S-4500. The rate of decrease of core radius, $r$, was determined by examining the SEM cross sections at 500× magnification. Four different particles were selected for each activation time with the criteria that they be both relatively round and large. Larger, round particles were deemed more suitable since they were more likely sectioned near the “equator,” and thus more accurately represent the true porous layer thickness. This thickness was measured using a fine ruler at eight equally spaced points around the particle circumference. The porous layer thicknesses were then averaged and subtracted from the particle size data to determine $r$. OriginPro regression analysis software was then utilized to fit the data to an exponential equation of the form:

$$r = y_0 + Ae^{-nt}$$  \hspace{1cm} (3.2)

Where $y_0$, $A$, and $n$ are constants of regression. This analysis was only done for the 53–106 μm series.

### 3.2.3 Theoretical Development

This work proposes a model in which both the solid core and the particle itself shrink at different rates. Initially, the system is controlled by the fast reaction between SO$_2$ and highly
reactive carbon sites at the solid coke surface, producing a porous structure. As the layer of porous carbon becomes thicker and diffusion through it becomes increasingly hindered, the rate-determining step switches to pore diffusion. However, the relatively unreactive carbon comprising the porous layer continues to react at a slower rate, decreasing the particle diameter and increasing the void fraction of this layer. A balance is then established between the fast and slow SO₂-carbon reactions and the diffusion of SO₂ through the porous layer, resulting in a porous layer of constant thickness which migrates toward the particle center at a rate determined by the rate of particle shrinkage. Thus, the volume of the porous layer, which largely governs particle SSA, first increases rapidly then gradually diminishes over time. For the purposes of this study, this model is referred to as the constant thickness porous layer model. Figure 3.2 illustrates the conceptual basis of this model, and compares it with the shrinking core model.

A numerical model was developed to simulate the experimental observations of SSA change with time. This model makes the following simplifying assumptions: 1. All particles are spherical and identical in size; 2. The rate of diffusion through the porous layer diminishes until

![Diagram](image.png)

**Figure 3.2.** (a) Shrinking Core Model vs. (b) the constant thickness porous layer model. SSA is assumed to be directly proportional to porous layer volume. Not drawn to scale.
a maximum porous layer thickness, $\delta_{\text{max}}$, is reached, after which it remains constant; 3. Ash, both loose and within the coke particles, makes an insignificant contribution to overall SSA; 4. The presence of sulfur in coke does not hinder or enhance the porous layer formation in any way.

A grid was set up using Microsoft Excel in which time was varied from 0 to 24 hours in increments of 0.01 hours. For each time step, the porous layer thickness, $\delta$, was determined as the difference between $R$ and $r$. Thus, $\delta$ initially increases as a result of the varying rates of shrinkage between $R$ and $r$. At some point in time, the slopes of Equations 3.1 and 3.2 become equal: this is the point at which $\delta = \delta_{\text{max}}$. From this point on, $r$ decreases at a rate equal to $R$, thus maintaining a constant $\delta$.

In order to take non-uniformity of the porous layer into account, the particle was divided into concentric, spherical shells, each approximately 1 $\mu$m in thickness. A shell becomes “activated” when it is overlapped by the reaction front as it moves inward toward the particle center. The activated portion of that shell expands with the movement of the reaction front until it reaches its maximum thickness of 1 $\mu$m. This activated shell remains at constant thickness and volume until the outer edge of the porous layer (the slow reaction front) coincides with the outer edge of the shell. The activated portion of the shell then shrinks until it is completely consumed. Figure 3.3 illustrates how these spherical shells change with time to form the three regions of a coke particle undergoing activation: the unreacted core, the porous layer, and the wholly consumed outer layers. Although this method was developed independently, a similar approach was used by Mitchell et al. for the combustion of coal char in 6% oxygen [56]. In that work, changes in particle dimensions were calculated analytically, based on an oxygen mass balance, while particle dimensions were measured directly in the current study.
Figure 3.3. A coke particle consisting of 11 spherical shells undergoing activation. Shells 1–3 were once activated, but now entirely consumed. Shell 4 is partly activated, with the activated portion shrinking. Shells 5–7 are within the porous layer, and thus are currently activated. Shell 8 is partly activated, with the activated portion growing. Shells 9–11 are within the unreacted core, and are yet to be activated.

The fractional conversion of carbon within each shell \( i \), \( X_i \), is assumed to increase linearly with time, starting from the point at which the shell is first breached by the porous layer and ending when it is fully consumed. A linear decrease in particle density with burn-off was observed by Hashimoto et al. using coal and coconut shell char [45]. Nevertheless, the small shell thickness used serves to mitigate errors resulting from this assumption, even if it is not entirely accurate.

The surface area per unit volume of porous layer for each section, \( S_i \), is calculated using the Random Pore Model developed by Bhatia & Perlmutter [49]:

\[
S_i = S_0 (1 - X_i) \sqrt{1 - \psi \ln (1 - X_i)}
\]  

(3.3)
Where $S_0$ is the initial surface area per unit volume of the unreacted solid, and $\psi$ is the Random Pore Model parameter:

$$
\psi = \frac{4\pi L_0(1 - \varepsilon_0)}{S_0^2}
$$

(3.4)

Where $\varepsilon_0$ is the porosity of the unreacted coke, determined using the following relationship:

$$
\varepsilon_0 = \frac{V_{p0}}{V_{p0} + \frac{1}{\rho_C}}
$$

(3.5)

Where $\rho_C$ is the unreacted core density, estimated to be 1.5 g/cm$^3$ [2], and $V_{p0}$ is the initial total pore volume. In Equation 3.4, $L_0$ is the length of pores in the unreacted coke, estimated via the QSDFT pore volume distribution function, $V_0(r)$:

$$
L_0 = \frac{1}{\pi V_{p0}} \int_0^\infty \frac{V_0(r)}{r^2} dr
$$

(3.6)

The volume, $V_i$, and mass, $M_i$, for every porous layer section are calculated according to Equations 3.7 and 3.8:

$$
V_i = \frac{4}{3}\pi (R_i^3 - r_i^3)
$$

(3.7)

$$
M_i = V_i \rho_C (1 - X_i)
$$

(3.8)

The single-particle mass, $M_P$, is estimated using Equation 3.9:

$$
M_P = \sum_{i=1}^{n} M_i + \rho_C V_C + 0.06 \rho_C V_{PL}
$$

(3.9)

Where $V_C$ is the volume of the unreacted core and $V_{PL}$ is the total volume of the porous layer. The expression $0.06 \rho_C V_{PL}$ represents the mass of ash in the porous layer, using 6 wt% as an
estimate of the particle ash content [3]. The amount of ash in the particle, $M_{AP}$, was calculated using Equation 3.10:

$$M_{AP} = 0.06\rho_C V_C + 0.06\rho_C V_{PL} \quad (3.10)$$

The total mass, $M_T$, is the mass of the particle at a given time plus the mass of ash it has shed due to particle shrinkage since $t = 0$. The specific surface area, SSA, is then found using the summed surface areas of all porous layer sections and the initial surface area:

$$SSA = \frac{\sum_{i=1}^{n} S_i + S_0 V_C}{M_T} \quad (3.11)$$

As a result of Assumption 1, Equation 3.11 holds for both a single particle and for the bulk material.

Lastly, burn-off is defined as the percent weight loss of sample, including ash:

$$\text{Burn-off} = \frac{M_{P0} - M_T}{M_{P0}} \times 100\% \quad (3.12)$$

Where $M_{P0}$ is the initial particle mass.

### 3.3 RESULTS AND DISCUSSION

Figure 3.4 shows the change in apparent BET SSA with activation time and burn-off for two particle size ranges of petroleum coke activated with $\text{SO}_2$ at 700°C. For both particle sizes, SSA initially increased rapidly, then leveled off and appeared to start decreasing. For the smaller size range, SSA peaked at 447 m$^2$/g at 5 hours (63% burn-off), while the larger size range peaked at 244 m$^2$/g at 9 hours (52% burn-off). Similar observations have recently been made using carbon dioxide and steam activation of petroleum coke. In order to ensure data reliability, the 4 hour activation of 53–106 μm coke was repeated twice and the SSA measured. The
Figure 3.4. Apparent BET SSA versus activation time (left), and coke burn-off (right) for particle size ranges 53–106 µm (◇) and 212–300 µm (●). Error bar at 4 hours based on 3 replicate activation runs.

The resulting standard deviation of 13 m²/g (shown as an error bar in Figure 3.4) is relatively small and therefore demonstrates a high degree of reproducibility with regards to SSA of coke activated under uniform conditions. Moreover, all other SSA measurements shown in Figure 3.4 were obtained through separate experiments. The smoothness of the resulting SSA trends further validates the experimental repeatability.

According to conventional porous layer models such as the shrinking core model, SSA should plateau once the entire particle has become porous and then remain constant. Furthermore, the maximum attainable SSA should not depend on particle size. The Random Pore Model would serve to explain the presence of a surface area maximum, however the peak occurs at a significantly higher burn-off than would normally be expected [49, 52]. These observations suggest that a different mechanism is at work in this system, which led to the development of the conceptual model described in Section 3.2.3.

The results of particle size analyses on activated coke from both size ranges is shown in Figure 3.5. Equation 3.1 was fitted to each data series, and the resulting parameters and
Figure 3.5. Change in average particle size with time for particle size ranges 53–106 µm (◇) and 212–300 µm (●).

Figure 3.6. Cross-sectional SEM images of coke particles after 1–7 hours of SO\(_2\) activation, 53–106 µm initial diameter, 250× magnification.

correlation coefficients are shown alongside the points. In both cases, the decrease in average \( R \) with respect to time follows a linear trend. Despite the lower burn-off, the rate at which \( R \) decreases is somewhat greater for the larger particles. This can be explained as a result of the lower external surface area present with larger particles. A smaller fraction of the SO\(_2\) entering the reactor was able to react due to the lower reactive surface area, thus leading to a higher
average SO$_2$ concentration throughout the bed. Thus, the average rate of reaction at the surface of the larger particles was higher, leading to a faster rate of shrinkage.

Figure 3.6 shows cross-sectional SEM images taken for activated coke in the 53–106 µm size range. Upon visual inspection, it appears as though the porous layer, which appears as a pale outer band surrounding each particle, increases in thickness up to approximately 4 hours of activation. After this point, subsequent changes in $\delta$ are not apparent. Values of $r$ were determined for each activation time based on measurements of $R$ and $\delta$. Within the range of 0–4 hours, these were fitted to Equation 3.2, while those in the range of 4–7 hours were fitted to Equation 3.1 (Figure 3.7). The slope of the linear portion matches closely with that of $R$ in Figure 3.5, which supports the existence of a constant $\delta$. As previously mentioned, $\delta$ was not directly measured for the larger particles. Table 3.1 provides a summary of the important parameters used in this analysis, including those necessary for the Random Pore Model. The constant thickness porous layer simulation was performed for coke particles in the smaller size range ($R_0 = 36.6$ µm) using the parameters for Equations 3.1 and 3.2 given in Table 3.1. Three

![Graph](image_url)

**Figure 3.7.** Change in rate of core shrinkage with activation time for coke of 53–106 µm initial diameter. Averaged measured core radii shown as white squares. 0–4 hours: exponential decay portion; 4–7 hours: linear portion.
Table 3.1. Parameters used in simulation of porous layer and surface area formation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>53–106</th>
<th>212–300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial particle size range, µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_0 ), µm</td>
<td>36.3</td>
<td>110</td>
</tr>
<tr>
<td>( \alpha ), µm hr(^{-1} )</td>
<td>-1.50</td>
<td>-1.90</td>
</tr>
<tr>
<td>( y_0 ), µm</td>
<td>15.6</td>
<td>54.5</td>
</tr>
<tr>
<td>( A ), µm</td>
<td>21.1</td>
<td>48.3</td>
</tr>
<tr>
<td>( n ), hr(^{-1} )</td>
<td>0.486</td>
<td>0.116</td>
</tr>
<tr>
<td>( \delta_{\text{max}} ), µm</td>
<td>12.0</td>
<td>16.0</td>
</tr>
<tr>
<td>( V_{p0} ), cm(^3) g(^{-1} )</td>
<td>1.54 × 10(^{-2} )</td>
<td>6.45 × 10(^{-3} )</td>
</tr>
<tr>
<td>( \varepsilon_0 )</td>
<td>2.26 × 10(^{-2} )</td>
<td>9.58 × 10(^{-3} )</td>
</tr>
<tr>
<td>( S_0 ), cm(^2) cm(^{-3} )</td>
<td>2.87 × 10(^5 )</td>
<td>1.23 × 10(^5 )</td>
</tr>
<tr>
<td>( L_0 ), cm cm(^{-3} )</td>
<td>2.08 × 10(^{13} )</td>
<td>3.22 × 10(^{13} )</td>
</tr>
<tr>
<td>( \psi )</td>
<td>3.10 × 10(^3 )</td>
<td>2.64 × 10(^4 )</td>
</tr>
</tbody>
</table>

Figure 3.8. Comparison between measured SSA and and simulated SSA using constant thickness porous layer model plotted versus activation time (left) and coke burn-off (right), \( R_0 = 36.3 \) µm. LEGEND: apparent BET SSA (◇); simulated SSA for \( \delta_{\text{max}} \) values of 10 (---), 12 (- - - - -), and 14 µm (-----). Point at 24 hours activation, 94% burn-off, based on estimated ash SSA of 10 m\(^2\)/g.
values of $\delta_{\text{max}}$ were tested: 10, 12, and 14 µm. The results of the simulation are shown in Figure 3.8, alongside the measured BET SSA data. The best fit between the model and experimental results is achieved when $\delta_{\text{max}}$ has a value of 12 µm, which agrees well with the direct measurements of porous layer thickness made using the SEM images in Figure 3.6. The right side of Figure 3.8 shows the same simulated results plotted versus coke burn-off. The predicted SSA rapidly drops off after its peak value at approximately 75% burn-off due to the accumulation of mineral matter which has been shed by the reacting particles. Assumption 3 used in this model states that ash does not have any inherent surface area of its own, and thus only acts as additional weight. For the same reason, SSA decreases to zero at a burn-off of 94%, corresponding to the assumed ash content of 6%. The noise observed in the simulated results in Figure 3.8 is due to the spherical shell thickness selected; a shell thickness less than 1 µm would have resulted in a finer grid and, thus, smoother results.

Figure 3.9 shows the results of changing the initial particle diameter on SSA, as predicted by the constant thickness porous layer model. These results were found assuming

![Figure 3.9](image-url)

**Figure 3.9.** Predicted SSA evolution with activation time (left) and coke burn-off (right) over 50 hours of reaction. LEGEND: initial diameter 50 µm ( ), 75 µm ( ), 100 µm ( ), 150 µm ( ), 200 µm ( ), and 250 µm ( ).

53
all particle sizes exhibited structural parameters identical to those found for the 53–106 µm particle size range. Although it is not expected to be the case, this assumption is adequate for illustrative purposes. It is readily seen that a smaller initial particle size results in a higher achievable SSA, as was observed experimentally in Figure 3.4. This result arises due to the limitation in porous layer thickness, which, for larger particles, means a lower porous layer volume to total mass ratio. The limited value of δ also explains the drastic change in the shape of the SSA profile as particle size increases (i.e., less prominent and more trapezoidal). The profile initially plateaus early on as δ_max is reached, then it proceeds to increase gradually as the particle mass diminishes over time. The peak is reached at the point where accumulating ash begins to offset the effect of decreasing particle mass, which is evident from the fact that all particle sizes reach their respective SSA peaks at roughly the same level of burn-off.

It was initially assumed that, due to similar activation conditions, δ_max would be the same regardless of particle size. However, results indicate that this is not the case. The grey lines in Figure 3.10 show the predicted SSA for the 212–300 µm particle size range (R_0 = 110 µm) alongside the apparent BET SSA using δ_max values of 12, 14, and 16 µm. For the case where δ_max is 12 µm, it can be seen that the plateau in the SSA profile is projected to occur at a much lower value than the experimental results. Increasing δ_max from 12 to 16 µm raises the SSA at which this plateau occurs to a level similar to the measured SSA. However, in addition to the maximum porous layer thickness, it would seem the time required to reach that thickness is also extended for larger particles. This is indicated by the fact that the predicted SSA increases at a much faster rate than the BET SSA. For this reason, the parameters of Equation 3.2 were modified so that the time to reach δ_max increased from 4 to 10 hours. The resulting predictions, shown as black lines in Figure 3.10, agree much more closely with the measured data,
Figure 3.10. Comparison between measured SSA and simulated SSA using constant thickness porous layer model plotted versus activation time, $R_0 = 110 \, \mu m$. LEGEND: apparent BET SSA (●); simulated SSA with time to reach $\delta_{\text{max}}$ as 4 hours: $\delta_{\text{max}} = 12 \, \mu m$ (⋯⋯), 14 $\mu m$ (−−−), 16 $\mu m$ (—−−); simulated SSA with time to reach $\delta_{\text{max}}$ extended to 10 hours: $\delta_{\text{max}} = 12 \, \mu m$ (⋯⋯), 14 $\mu m$ (−−−), 16 $\mu m$ (−−−).

The increase in both $\delta_{\text{max}}$ and the time needed to achieve it for the larger particles is thought to be closely related to the increase in particle shrinkage rate shown in Figure 3.5. The time at which $\delta_{\text{max}}$ is reached depends largely on the difference between the fast and slow reaction rates at the unreacted core surface and the outer particle surface, respectively. Assuming the fast reaction rate remains unaffected, it is expected that an accelerated rate of carbon consumption at the outer edge of the porous layer would entail a longer time necessary to reach the point of becoming diffusion limited. A similar argument can be used to explain the larger value of $\delta_{\text{max}}$ obtained. The enhanced rate of reaction between SO$_2$ and the relatively unreactive carbon of the porous layer would also serve to increase its pore volume. This would have the effect of removing some of the obstructions which limit the ability of SO$_2$ to diffuse through the porous layer, thus ensuring that it reaches the unreacted core surface more rapidly and allowing
for a thicker porous layer.

Although the effect of temperature was not studied, it is interesting to speculate its impact on the porous layer. Increasing temperature would have the effect of raising both C-SO$_2$ reaction rate constant as well as the effective diffusion coefficient of SO$_2$ through the pores. The kinetic data of Bejarano et al. suggests that increasing the temperature from 700 to 800°C would increase the rate constant by a factor of approximately 6 [86]. On the other hand, not taking into account tortuosity effects, the diffusion coefficient is expected to increase with $T^{3/2}$. Thus, the increase in reaction rate would be much greater than that of diffusion, resulting in a decreased $\delta_{\text{max}}$ in this diffusion-limited system. Conversely, decreasing temperature would bring about a greater $\delta_{\text{max}}$. Thus, for dense materials which exhibit a constant porous layer thickness during physical activation, a lower temperature is anticipated to produce higher SSA. This was observed experimentally by Braun et al. [66] in the oxidation of flat samples of glassy carbon. Furthermore, preliminary results obtained through activation of petroleum coke with carbon dioxide and steam at different temperatures have also shown this to be the case. In a practical setting, however, the benefits of using lower temperatures would need to be weighed against the longer time needed to achieve maximum SSA.

### 3.4 CONCLUSIONS

A model was developed to explain observed trends in the surface area development of oil-sands petroleum coke activated with SO$_2$ at 700°C. This model was based on the existence of a porous layer which has a maximum thickness due to diffusion limitations. Each particle was divided into several concentric spherical shells in order to accurately simulate both the thickness of the porous layer and variations in porous layer properties with respect to particle radius. The Random Pore Model of Bhatia and Perlmutter [49] was then applied to each volumetric shell to
quantify SSA. The model was able to verify the hypothesis that the evolution of SSA during the activation of coke is governed by the porous layer.

For particles in the size range of 53–106 µm, the model accurately predicts SSA development when a maximum porous layer thickness of 12 µm obtained after 4 hours of activation is used. This finding was substantiated by direct observations of particle cross sections. For larger particles in the range of 212–300 µm, the best fit was obtained when the maximum porous layer thickness was set to 16 µm and the time to reach this thickness was increased to 10 hours. The reason for this difference is believed to be the greater SO$_2$ to external surface area ratio which increases the SO$_2$-carbon reaction rate in the outer porous layer.

The constant thickness porous layer model presented in this paper provides a relatively simple means of estimating the maximum porous layer thickness of dense materials undergoing activation or gasification reactions. The only required measurements are those of particle size, SSA, and pore size distribution, all of which are obtainable through numerous common techniques. This technique provides a welcome alternative to cross-sectional measurements of porous layer thickness, which is laborious, time-consuming, and prone to errors. Future work involving this model would greatly benefit from the application of an optimization algorithm which could accept SSA, particle size, and Random Pore Model parameters as inputs and automatically compute the best fitting porous layer thickness profile.
CHAPTER 4  SULFUR DIOXIDE AS AN ACTIVATING AGENT FOR SULFUR-IMPREGNATED ACTIVATED CARBON PRODUCED FROM DENSE PETROLEUM COKE

4.1 INTRODUCTION

In recent years there has been a considerable motivation to produce activated carbons (ACs) from industrial and agricultural waste products due to increasing economic and environmental constraints. While very high specific surface areas (SSAs) have been achieved through chemical activation \[146–148\], physical activation techniques are desirable due to their relative simplicity and lower material costs. Typically, physical activation consists of a pyrolysis, or carbonization, step, followed by activation with carbon dioxide and/or steam. Pyrolysis is typically utilized to remove volatiles, increase the overall carbon content, and rearrange the carbon atoms into randomized stacks of graphene sheets \[149\]. However, it has been found that highly carbonaceous materials such as coal and coke become somewhat thermoplastic above 400°C, resulting in a transition from isotropic to anisotropic structures \[139\]. This conversion may limit accessibility of activating gases to pre-existing pore structure and reduce the reactivity of the carbon surface to reactive species such as sulfur dioxide (SO\(_2\)) \[79\]. Several studies have investigated the impact of air oxidation at temperatures between 150 and 300°C, observing that it led to increased reactivity and/or porosity development in subsequent treatments \[138–144\]. It is believed that this augmentation was a result of oxygen functional groups which formed on the carbon surface and within the pores, promoting cross-linkages within the carbon matrix. Consequently, the carbon material changes from thermoplastic to thermosetting, imparting a more rigid structure with more accessible pores and
reactive centers at the high temperatures used in activation.

One particular waste material which has been shown to be highly suitable for production of AC is petroleum coke [150]. In the Athabasca oil-sands region of Alberta, Canada, there currently exist vast stockpiles of petroleum coke resulting from the upgrading of bitumen. This highly carbonaceous material is unsuitable for combustion due to its high sulfur content (5–8 wt%), which would necessitate the use of expensive flue gas desulfurization equipment. For this reason, other uses such as AC production are under investigation. One particular type of Alberta oil-sands petroleum coke, which is used in this study, is called fluid coke because it is produced in a fluidized bed coking unit. Fluid coke is unique because of its roughly spherical particle shape and its composition of several, overlapping layers which can be thought of as “onion-like.”

Previous work has shown that oil-sands petroleum coke can be used to efficiently reduce SO$_2$ at 15 vol% to elemental sulfur (S) at temperatures between 600 and 900 °C according to Reaction 4.1 [4]

$$\text{SO}_2 + \text{C} \rightarrow \text{CO}_2 + \frac{1}{2}\text{S}_2 \quad (4.1)$$

In addition to reducing SO$_2$ to S, it has been demonstrated that Reaction 1 increases the BET SSA (up to 360 m$^2$/g [6]) while adding sulfur groups to the coke surface (see Chapter 5). Due to these factors and the high intrinsic sulfur content of fluid coke, an activated carbon produced in this manner would be designated as a sulfur-impregnated activated carbon (SIAC). Due to the favorable chemical interactions, SIACs have been shown in many studies to be highly effective in capturing mercury vapor [7–14]. Furthermore, sulfur added to carbon through high temperature reaction with SO$_2$ has been found to be quite thermally stable [82, 84, 87]. This suggests that SIACs produced in this manner could be thermally regenerated, making their
use in adsorption processes much more economically attractive.

This study aims to determine the treatment steps needed to produce the highest possible SSA attainable through SO$_2$-activation of fluid coke. Specific processes investigated include pyrolysis, air pre-oxidation, and acid washing, but the impact of initial particle size is also analyzed. Further discussion is provided with regards to noteworthy aspects of coke activated with SO$_2$, such as pore size distribution, speciation of added sulfur groups, and their thermal stability.

4.2 Methodology

4.2.1 Sample preparation

Fluid coke used in this study was obtained directly from an upgrading facility in Alberta, Canada and screened to particle size ranges of 53–106 and 212–300 μm. For experiments involving air pre-oxidation, the fluid coke was pre-oxidized by spreading approximately 20 g on a watch glass and placing it in a Barnant muffle furnace at 250°C for 18 hours.

The apparatus used for activation of coke samples is described in detail in Section 3.2.1. SO$_2$ (99.95%) and N$_2$ (99.997%) were supplied by cylinders and each set to flow at 100 cm$^3$/min by Aalborg mass flow controllers. Approximately 10 g of coke was placed within a quartz reactor tube positioned within a vertical tube furnace, resulting in a cylindrical bed 2.4 cm in height and 7.5 cm$^3$ in volume. Gas samples were withdrawn from ports upstream and downstream of the reactor with a gas-tight syringe and analyzed using a Varian 3800 gas chromatograph equipped with a thermal conductivity detector. To separate gas species, a molecular sieve 5A column (0.53 mm × 30 m) was arranged in parallel with a porous divinylbenzene column (0.53 mm × 30 m).

For all analyses, the reactor was first flushed with pure N$_2$ for 15 minutes and then the
furnace was set to 120°C to drive out moisture for an additional 15 minutes. After drying, the
gas flow was diverted around the reactor via a 3-way stopcock as SO₂ was introduced. Gas
samples were taken from the inlet sampling port and analyzed using gas chromatography (GC)
until SO₂ was stable at the desired concentration to within ±5%. At this point, the furnace
temperature was adjusted to that required for the activation. As soon as this temperature was
reached (~12 minutes for 700°C), a 3-way stopcock was turned to introduce the SO₂ gas mixture
into the reactor marking the start of the analysis. Outlet gases was monitored using GC until the
end of the experimental run, at which point SO₂ was immediately shut off and the reactor
allowed to cool under flowing N₂. The activated coke sample was then weighed to determine
sample yield.

The same steps were used to produce pyrolyzed samples, except the activation
temperature was set immediately after the initial N₂ flush. The sample was thus dried under
flowing N₂ while the temperature was ramped. When the desired set point was reached, flow
was diverted around the reactor for 1 hour in order to pyrolyze the sample under stagnant N₂
while the SO₂ concentration stabilized.

Selected samples were further treated to remove ash left behind by the SO₂-coke
reaction. This was done by soaking approximately 0.5 g of activated coke in 100 mL 10 wt%
HCl and placing in a water bath shaker at 45°C overnight. The supernatant was drained and the
remaining slurry filtered and washed with deionized water until the pH of the filtrate was
neutral. The residue was finally dried in an oven overnight at 110°C.

Table 4.1 summarizes the treatment conditions for each series of activated coke
produced. Sample series were named according to their treatment conditions, where “UNT”
denotes untreated, “PYRO” denotes pyrolyzed, “PRE” denotes pre-oxidized, and “AW” denotes
Table 4.1. Conditions used in producing SIACs using fluid coke and SO$_2$ acid-washed. The suffix “(L)” means “large,” referring to the 212–300 µm initial particle size range. All series were produced at a SO$_2$ concentration of 50 vol% unless specified by the suffix “-30,” indicating activation with 30 vol% SO$_2$. Similarly, all samples were activated at 700°C aside from one which was created at 800°C, specified by the suffix “-800.”

4.2.2 Sample analysis

SSA and pore size distribution were measured by N$_2$ adsorption at 77 K using a Quantachrome Autosorb-1-C. Forty adsorption points between relative pressures of 0.025 and 0.995 were obtained and analyzed using the quenched solid density functional theory (QSDFT), which is currently the preferred technique for characterizing pore size distribution of amorphous carbons since it takes into account physical and chemical heterogeneity [145]. The calculation assumed slit-shaped micropores (<2 nm) and cylindrical mesopores. QSDFT is not valid for pores exceeding 35 nm, therefore larger pores were measured using the BJH technique and the
results combined. SSA was determined with the BET method using three points at relative pressures of 0.025, 0.05, and 0.075. It is uncertain whether points at lower relative pressures might have yielded more accurate results, thus BET SSA is reported as “apparent” BET SSA.

Mass percentages of carbon and sulfur were determined using an Exeter Analytical CE-440 elemental analyzer. Cross-sectional samples of activated coke particles were analyzed by scanning electron microscopy (SEM) using a Hitachi S570. Details regarding the production of cross-sectional sample casts has been provided elsewhere (see section 5.2.2).

4.3 RESULTS AND DISCUSSION

4.3.1 Treatment conditions affecting maximum achievable SSA

4.3.1.1 Effect of pyrolysis

Figure 4.1 illustrates the effect of activation time on coke burn-off (or percent weight loss) and apparent BET SSA under different pre-treatment conditions at 700°C. Pyrolysis prior to activation (series PYRO) decreased the resulting burn-off and BET SSA for a particular activation time compared to the untreated coke (series UNT). Above 400°C, it is known that bituminous coal will soften and cause the carbon structure to transition from isotropic to anisotropic [139]. Humeres et al. [79] found that reactivity of carbon materials with SO₂ at 900°C decreased with an increase in anisotropic character. Thus, the reduction in burn-off and SSA could be a result of decreased reactivity between SO₂ and the coke surface due to graphitization of the carbon structure during pyrolysis. GC measurements of SO₂ conversion over 7 hours of activation (Figure 4.2) are consistent with this hypothesis, since conversion for PYRO is consistently lower than that of UNT until about 6 hours of activation. The drop in SO₂ conversion with time is expected as the coke bed is consumed by reaction, but the initial rise observed in some series is thought to be due to equilibration of SO₂ inlet concentration. It is
Figure 4.1. Relationship of apparent BET SSA (left) and burn-off (right) with activation time for series UNT (×), PYRO (△), PRE (□), PRE+PYRO (◆).

Figure 4.2. SO$_2$ conversion for 7 hour activation of UNT (×), PYRO (△), PRE (□), and PRE+PYRO (◆). For 50% SO$_2$ in 200 cm$^3$/min total flow, 0.002 mol/min is roughly equivalent to 50% conversion.

noted that SSA of series PYRO did not show any sign of diminishing after 7 hours of activation, unlike series UNT. It is anticipated that longer activation times would result in a similar plateau and decrease in SSA, but this cannot be verified with the available data.

Figure 4.3 shows the results of pore volume distribution analysis for series UNT, PYRO,
and PRE prior to activation. Although the relative proportions of micropores, mesopores, and macropores did not change significantly, the overall pore volume decreased by approximately 0.0025 cm$^3$/g, or 27%, with one hour of pyrolysis. This can be explained as a result of the coke becoming more plastic at high temperatures, leading to a more ordered structure with fewer accessible pores [139, 143]. A direct consequence of this would be lowered surface reactivity, which is consistent with the diminished SSA and burnoff shown in Figure 4.1.

4.3.1.2 Effect of air pre-oxidation

In contrast to pyrolysis, Figure 4.1 indicates that pre-oxidation in air (series PRE) tended to increase burn-off and SSA relative to series UNT, suggesting an increase in surface reactivity. This is also supported by the higher initial SO$_2$ conversion of series PRE seen in Figure 4.2, although this enhancement appears to have diminished after about 4 hours of activation. Several studies have found that pre-oxidation of carbons under similar conditions led to increased reactivity and/or porosity development in subsequent treatments [138–144]. The general

![Figure 4.3](image)

**Figure 4.3.** Effect of 1-hour pyrolysis and air pre-oxidation on pore size distribution of coke before activation. Micropore volume is shown in black, mesopore volume in grey, and macropore volume in white. Percentage distributions are indicated as numeric values.
consensus is that this enhancement occurs mainly due to the formation of oxygen functional groups such as carboxyl and carbonyl, which are thought to reduce thermoplasticity present at high temperatures by promoting cross-linkages within the carbon matrix. This results in a more rigid material with greater accessibility to existing pores and reactive carbon centers at the high temperatures needed for activation.

Evidence presented in Figure 4.3 suggests that initial pore structure after pre-oxidation may play a role in SSA development as well. Series PRE exhibited a slightly greater (~5%) overall pore volume than did UNT prior to activation, which is primarily due to an increase in micropore volume. Thus, structural changes in the precursor material may also help to explain the enhanced SO₂-coke reactivity observed. The temperature used for air pre-oxidation (250°C) is far below the range typically used in activation/gasification reactions, so it is doubtful that this change is due to pore initiation. It is more likely that additional micropore volume was made accessible through the loss of volatile materials during pre-oxidation. In spite of this evidence, the formation of oxygen functional groups as suggested by previous researchers cannot be ruled out as a major contributing factor.

In Figure 4.1, series PRE+PYRO displayed similar SSA and burn-off to PRE, indicating that air pre-oxidation entirely negated the effect of 1 hour pyrolysis under N₂ at 700°C. However, this effect is only partly apparent from examination of SO₂ conversion shown in Figure 4.2: although conversion was not reduced to the same extent as PYRO, there was no significant enhancement relative to UNT. SO₂ conversion and coke burn-off are expected to be directly proportional according to Equation 4.1. In the case of PRE+PYRO, the burn-off shown in Figure 4.1 includes the mass initially lost due to 1 hour of pyrolysis pre-treatment. A more direct comparison with this initial burn-off excluded would corroborate with the lower SO₂
conversion observed in Figure 4.2. This does not explain the similarity in BET SSA, however, which further suggests that the SSA enhancement seen with air pre-treatment is at least partly due to factors other than improved gas-solid reactivity.

4.3.1.3 Effect of acid washing

Figure 4.4 shows the effect of acid washing after activation on BET SSA (series PRE-AW). This step was done to remove ash from the activated coke as it may block access to existing pore structure. It was observed that, up until the maximum at 5 hours, there was no significant change in SSA resulting from acid washing. After this point, however, SSA was found to increase continuously to 530 m²/g rather than decrease like series PRE. Analysis of both carbon and sulfur content in PRE and PRE+AW (Figure 4.5) indicated an increase in weight percent upon acid washing that was more pronounced at longer activation times. This observation verifies that ash was removed by washing since the increased activation time leads to a greater amount of loose ash in the sample, and that the continual increase in BET SSA was a direct consequence of this.

Figure 4.4. Relationship of apparent BET SSA (left) and coke burn-off (right) with activation time for series PRE (□), PRE(L) (●), and PRE+AW (+).
Figure 4.5. Weight percent of carbon (left) and sulfur (right) for series PRE (□) and PRE+AW (+). Error bars represent standard deviation for 3 replicate analyses.

Ash may reduce apparent SSA either by blocking access to pores or by simply acting as additional weight due to low SSA. The surface area of ash from oil-sands petroleum coke is not currently known, but different studies have measured the SSA of various coal fly ashes to be 1.8 m$^2$/g [151], 3.4 m$^2$/g [152], and from 1 to 15 m$^2$/g [153]. Thus, it is likely safe to assume that ash does not contribute significantly to overall SSA in coke activation. In Chapter 3, SSA was accurately reproduced under the assumptions that raw coke contains 6 wt% ash, and that this ash possessed no inherent SSA. Figure 4.6 shows the results of this model when the weight of loose ash is not factored into the sample weight, which simulates the effect of ash removal by acid washing. The projected SSA is seen to continuously increase more or less in accordance with the measured SSA data. The agreement between this model and the experimental data lends support to the theory that ash reduces overall SSA simply by acting as extra weight with little or no surface area contribution.

It is noteworthy that the model results shown in Figure 4.6 approach 1000 m$^2$/g after 20
hours of activation, effectively doubling the achievable SSA. However, the right side of Figure 4.6 indicates that such a high SSA can only be attained at nearly complete burn-off. For a SSA of 600 m\(^2\)/g, only approximately 10% product yield is obtained. Thus, the practical feasibility of acid washing to enhance SSA of SO\(_2\)-activated coke depends on the relative importance of economics versus performance benefits of greater surface area.

### 4.3.1.4 Effect of initial particle size

The effect of increasing particle size on burn-off and SSA for air pre-oxidized coke is shown in Figure 4.4. For the larger particle size (series PRE(L)), both parameters are greatly reduced for a given activation time. This difference in behavior may arise partially due to a change in SO\(_2\)-carbon reactivity. Figure 4.7 demonstrates that the larger particle size nearly halved SO\(_2\) conversion relative to series PRE, which is explainable by the lower external surface area available for reaction. Another possibility is that the reduction in SSA and burn-off is indicative of porous layer formation. According to the Shrinking Core Model, a particle of larger
Figure 4.7. SO$_2$ conversion for 7 hour activation of PRE (□) and PRE(L) (●).

initial diameter will have a lower porous layer volume to mass ratio at a given reaction time. Since most of the surface area will occur within this porous layer, this leads to lower SSA for a given activation time. However, maximum SSA, which will occur when the particle is completely porous, should be the same irrespective of the initial particle size. This is true whether the difference in SSA profile is due to lower reactivity or lower porous layer volume to mass ratio. In Figure 4.4, it appears as though the cokes in both initial size ranges have reached their maximum SSA values, which indicates that a different porous layer formation mechanism is at work. Work described in Chapter 3 demonstrated that this behavior is due to a constant porous layer thickness resulting from a balance between three competing forces: 1. SO$_2$-carbon reaction at the unreacted core surface; 2. Slower SO$_2$-carbon reaction within the porous layer (leading to overall particle shrinkage); 3. Diffusion of SO$_2$ through the porous layer.

4.3.2 Potential usefulness of SO$_2$-activated coke for mercury capture

The primary goal in the activation of carbonaceous materials is typically the production of an extensive porous network to increase the SSA as much as possible. However, in many
applications, surface chemistry and pore size distribution also play key roles in determining adsorptive capacity and uptake kinetics. SO$_2$-carbon reaction does impart some unique qualities to the activated product that may be more important for particular applications.

In Figure 4.8, cross-sectional SEM pictures of a single particle from Series PYRO(L)-30 reveal a great diversity of pore sizes. The leftmost image shows a large macropore running through the coke particle, which is the gap between two successive layers deposited during its original production in a fluidized coker unit. This gap has become widened after SO$_2$ activation. The photograph on the right shows a section of this macropore at higher magnification, revealing several smaller pores in the mesoporous range (2–50 nm). Also visible on the right are small plate-like structures which are believed to consist of interlinking graphene sheets. The interstitial spaces between these sheets are very narrow and likely function as slit-shaped micropores. The pore size distribution of series PRE after 5 hours of activation with SO$_2$ is presented in Figure 4.9 along with that of Norit Darco Hg, a lignite-based, powdered AC which has been specifically engineered for mercury removal from coal-fired utility flue gases.

Although a recent fixed-bed study has indicated that higher micropore fraction is
Figure 4.9. Pore size distribution of petroleum coke activated with SO$_2$ for 5 hours (PRE-5hrs) compared with a commercial AC engineered for mercury capture (Darco Hg). Micropore volume is shown in black, mesopore volume in grey, and macropore volume in white. Percentage distributions are indicated as numeric values.

Beneficial for mercury capture [154], a positive correlation between mesoporous fraction and mercury uptake was previously reported using a much shorter gas-solid contact time (empty bed residence time = 0.012 s) [9]. Most practical situations involve very short contact times, necessitating rapid transport of mercury into the porous structure and minimal interference to diffusion. For Darco Hg, the relative fractions of macropores and mesopores are considerably larger than most ACs, presumably to enhance mass transfer into the particle. It is notable that the mesopore fraction of PRE-5hrs is quite comparable to that of Darco Hg, suggesting that SO$_2$-activation of petroleum coke produces an appropriate physical structure for rapid uptake of mercury vapor. However, the specific pore volume of PRE-5hrs (0.26 cm$^3$/g) is less than half the total pore volume of Darco Hg (0.56 cm$^3$/g). This is not surprising given the previous finding that the pores are concentrated in an outer layer while the core remains dense and largely non-porous. This may impact the overall mercury capacity of SO$_2$-activated coke, but this remains to be seen.

In addition to physical structure, the surface chemistry of an activated carbon is likely to
play a major role in governing mercury capacity and uptake kinetics. For carbon materials activated with SO$_2$, distribution and speciation of sulfur on the surface become highly important factors. Chapter 5 features SEM-wavelength dispersive X-ray spectroscopy images of particle cross sections from series PYRO(L)-30-800, which included elemental maps of sulfur and carbon (see Figures 5.1 and 5.2). These sulfur and carbon maps reveal the outer porous layer to be rich in sulfur and depleted in carbon relative to the bulk of the particle. A similar sulfur-rich layer was previously described for a similar system by Bejarano et al. [86] and by Panagiotidis et al. [80] in the reaction of SO$_2$ with anthracite char. The nature of the sulfur within this layer was partially resolved by comparing TGA profiles of series PYRO(L)-30-800 with those of Calgon HGR, a bituminous coal-based SIAC (see Figure 5.4). The sulfur on HGR, which was determined by elemental analysis to be $17.3 \pm 0.6\%$, is entirely elemental in nature [155]. HGR experienced weight losses corresponding to the measured sulfur content from 200–450°C in N$_2$ (attributed to sulfur volatilization) and from 250–350°C in air (sulfur combustion). Series PYRO(L)-30-800 did not exhibit weight losses in either temperature range, implying that sulfur added to coke through SO$_2$ activation is not elemental in nature. Further analyses using X-ray photoelectron spectroscopy found that sulfur in the outer porous layer is most likely made up of thiophene from the original coke structure along with similar heterocyclic sulfide and disulfide structures added to the coke through sulfur substitution reactions.

The TGA data in Chapter 5 also provides information pertaining to the thermal stability of sulfur added to coke through activation by SO$_2$. While SIAC produced through deposition of elemental sulfur vapor tends to lose all of its sulfur between 250 and 500°C under N$_2$, the sulfur forms added to coke through reaction with SO$_2$ appeared to be much more thermally stable. Puri and Hazra [82], and Chang [84] found that much of the sulfur added to carbon through high
temperature reaction with SO$_2$ was stable up to at least 700°C. The ability to be heated without losing sulfur functional groups is a valuable characteristic for a SIAC used in mercury capture, potentially allowing for thermal regeneration of the sorbent. The alternative is to send the spent material to landfill, which has obvious economic drawbacks. The thermal regenerability of SIACs produced through reaction with SO$_2$ is therefore a topic worthy of further study.

4.4 CONCLUSIONS

A series of experiments were carried out to determine the impact of various treatment conditions on the SSA of oil sands fluid coke activated using 50% SO$_2$ at 700°C. Pyrolysis in N$_2$ for one hour prior to activation resulted in a significant decrease in SSA which was attributed to thermoplastic behavior of coke at high temperatures. Air pre-oxidation was found to suppress this effect and provided an enhancement over non-pyrolyzed coke, with SSA peaking at 447 m$^2$/g after 5 hours of activation. To date, this is the highest SSA achieved through physical activation of oil-sands fluid coke. Acid washing of air pre-oxidized activated coke in 10% HCl provided a further increase in SSA at high activation times due to removal of low-surface area ash (531 m$^2$/g for coke activated 7 hours). Increasing the particle size range of air pre-oxidized coke from 53–106 µm to 212–300 µm greatly reduced SSA for a given burn-off, with the maximum being 244 m$^2$/g after 9 hours of activation. The formation of a porous layer of constant thickness was responsible for this reduction in maximum achievable SSA.

Aside from the high SSA achieved, petroleum coke activated with SO$_2$ displays some promising physical and chemical characteristics for its potential application as an industrial sorbent, particularly for vapor phase mercury. Approximately 60% by volume of the pores produced are in the mesopore range, which is believed to be highly favourable for mitigating diffusive transport limitations under short gas-solid contact times. The porous structure is
concentrated in a sulfur-rich layer surrounding the particles, which contains reduced sulfur groups in forms that are highly thermally stable compared to elemental sulfur present in a commercial SIAC. This combination of properties presents a unique material which may provide an inexpensive, yet highly effective and regenerable sorbent for use in mitigating industrial emissions of mercury.
CHAPTER 5  EFFECTS OF O₂ ON CHARACTERISTICS OF SULFUR ADDED TO PETROLEUM COKE THROUGH REACTION WITH SO₂

5.1 INTRODUCTION

Oil-sands fluid coke is a type of petroleum coke produced during the upgrading of Alberta oil-sands bitumen. It has high carbon (~85 wt%) and low ash (~5 wt%) contents, giving it a high heating value. However, oil-sands fluid coke is also rich in sulfur (~6 wt%), meaning that combustion to produce electricity would necessitate the use of expensive sulfur dioxide (SO₂) control equipment. For this reason, it is currently being stockpiled on-site at a rate of more than 10 thousand tonnes/day. Efforts to find alternative uses for oil-sands fluid coke are underway, and one of its potential applications is in the reduction of SO₂ to elemental sulfur.

Previous research has shown that oil-sands fluid coke can be used to reduce SO₂ and produce elemental sulfur (S) as a co-product at temperatures up to 1000°C following reaction 5.1 [4]:

\[ C + SO_2 \rightarrow CO_2 + \frac{1}{2}S_2 \] (5.1)

At 700°C, complete SO₂ reduction occurred while elemental S yield peaked at approximately 95%. It was later determined that addition of oxygen (O₂) or water (H₂O) enhance the reduction of SO₂ by up to 15% due to the generation of carbon monoxide (CO) and hydrogen (H₂), which act as secondary reducing gases [5].

Another potential use for oil-sands fluid coke is the production of sulfur-impregnated activated carbon (SIAC). SIACs are typically produced from low-sulfur starting materials by
several methods including direct sulfur deposition [7–12, 82] as well as reaction with sulfur gases such as H₂S [13, 82–85], CS₂ [82, 84], and SO₂ [82, 84, 85]. It has also been found that the same reaction by which petroleum coke reduces SO₂ to elemental S (Reaction (5.1)) also physically activates the coke by producing a porous structure. SIACs of up to 360 m²/g have been produced in this manner [6]. The usefulness of SIACs stems from the fact that carbon-sulfur surface complexes provide effective binding sites for removal of contaminant species. Several studies [7–14] have indicated that SIACs are particularly well-suited for capturing vapor-phase mercury. However, these studies have not addressed the issue of mercury recovery and carbon regeneration after capture – it is typically assumed that the SIAC loaded with mercury will be treated as a hazardous waste and sent to landfill, but this has the obvious drawback of high material and handling costs. The ability to regenerate SIAC would therefore be economically beneficial while reducing its environmental burden. Thermal regeneration is the most commonly used technique for activated carbons, however, in the case of SIACs, the high temperatures used could also destroy the important sulfur sites on the carbon surface. Thus, it is vital that sulfur be impregnated in a way that imparts high temperature stability to the carbon-sulfur groups if thermal regeneration of SIACs is to be done.

Bejarano et al. [86] undertook a cross-sectional analysis of a single particle of oil-sands fluid coke after reaction with 15% SO₂ for 13 hours using scanning electron microscopy with electron dispersive X-ray spectroscopy (SEM-EDX). An accumulation of sulfur was observed in between a mineral-rich ash layer and the unreacted core of the particle, similar to the sulfur-rich layer previously reported by Panagiotidis et al. [80] for the reaction of anthracite char with SO₂. Previous research has found that high temperature reaction of SO₂ with a carbon surface may add sulfur in the form of sulfide [82, 87], disulfide [87], thiol [82], thioketone [82, 84],
thiolactone (defined as a lactone with both oxygen atoms replaced by sulfur) [84], and oxidized forms such as sulfones and sulfoxides [87], but not as elemental sulfur. Moreover, a large portion of the added sulfur was determined to be stable in N₂ at temperatures exceeding 700°C [82, 84], suggesting that thermal regeneration of SIACs produced through reaction with SO₂ might be feasible.

This investigation was intended to improve the current understanding of the reduction of SO₂ using oil-sands petroleum coke through analysis of the speciation and thermal stability of sulfur added to the coke surface through this process. Many real industrial stack gases for which SO₂ is a problem also contain high levels of O₂, therefore it is important to know what effect this has on coke particles if they are to be directly applied for SO₂ control. For this reason, a third goal of this investigation was to analyze how the SO₂-coke reaction is impacted by a large excess of O₂. In carrying out these objectives, a combination of microscopic elemental mapping of particle cross sections and XPS was utilized. Stability of sulfur on the activated coke surface was analyzed using XPS as well as thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

5.2 METHODOLOGY

5.2.1 Sample preparation

Raw fluid coke was obtained directly from an industrial bitumen upgrading facility and sieved to a particle size range of 212–300 μm. The apparatus used is shown in Figure 3.1. Approximately 10 g were weighed and placed on a fritted disc located at the mid-point of a quartz tube reactor 68 cm in length and 2.0 cm inner diameter. This resulted in a cylindrical coke bed with height and volume of 2.4 cm and 7.5 cm³, respectively. The entire reactor was suspended vertically within a tubular furnace (Carbolite) and the inlet and outlet attached to
vinyl tubing via ball-and-socket adapters sealed with vacuum grease. The outlet adapter was a 25 cm tube stuffed with quartz wool which acted as a condenser and filter for elemental sulfur produced in the reactor. Other gaseous products were removed using a sodium hydroxide scrubbing solution prior to venting.

Gases were supplied by cylinders (N₂ and O₂ at 99.995%, SO₂ at 99.3%) and their flow rates controlled by mass flow controllers (Aalborg). Each mass flow controller had previously been calibrated using a bubble flowmeter (Humonics). Gases were mixed to the desired concentrations by combining streams using Teflon 3-way stopcocks. The total gas flowrate used was 200 cm³/min, which is beyond the range in which external mass transfer effects are expected to be significant [86]. A flow of pure N₂ was used to flush out the reactor for at least 15 minutes, and was then maintained as the furnace was heated to the desired reaction temperature. After the temperature stabilized for 10 minutes, N₂ flow was diverted around the reactor using a 3-way stopcock and SO₂ and/or O₂ were introduced. The concentrations of these gases were monitored by taking samples from the inlet sampling port with a gas-tight syringe and analyzing them using a Varian 3800 gas chromatograph (GC). This device was equipped with a molecular sieve 5A capillary column arranged in parallel with a porous divinylbenzene capillary column, both of which were 30 m in length and 0.53 mm inner diameter. After the gas concentrations stabilized, the gas mixture was introduced to the sample in the reactor for a period of three hours. During this time, outlet gases were monitored with GC via the outlet sampling port. In this semi-batch reactor, properties of the coke bed (mass and porous structure) were constantly changing with time as a result of reactions with O₂ and/or SO₂. It is therefore impossible to reach a true steady-state. However, the change in gas composition was observed to be relatively small during the sampling period. At the end of the experiment, SO₂ and/or O₂ were
immediately shut off and N₂ allowed to flow through the reactor until it had cooled sufficiently.

The product coke was not homogeneous due to the inequality in reaction rate from the top to the bottom of the bed, which was evident from the existence of a visible ash layer on the top. To analyze the different regions of the bed separately, coke was removed from the reactor in four roughly equal layers. This was done by means of suction using an aspirator and a narrow glass tube with a fritted glass filter. Care was made to maintain distinct layers, however a some degree of mixing inevitably occurred. These layers were each weighed and then totaled to determine coke burn-off.

Two different samples derived from oil-sands fluid coke were used in this investigation: FC600 and FC800. FC800 was reacted with 30% SO₂ at 800°C for 3 hours, representing conditions under which high SO₂ reduction and sulfur fixation have been achieved in previous experiments. FC600 was made using 3% SO₂ combined with 18% O₂ at 600°C for 3 hours. These gas conditions were chosen to replicate those of a particular non-ferrous metallurgical smelter flue gas, with a somewhat lower temperature to limit burnoff in the presence of O₂.

5.2.2 Sample analysis

Treated particles from the uppermost layer of the coke bed were deposited at the bottom of 25 mm ID polyethylene casts. A cold-curing resin was then prepared and carefully poured over the particles to create a cylindrical cast. A conductive copper resin was initially used for this purpose, but was later changed to a transparent epoxy resin for practical reasons. It is believed that the choice of resin material had insignificant effect on the analytical results. After 24 hours setting time, casts were removed and polished using silicon carbide abrasive discs and 3 μm diamond water. Samples cast in epoxy were then carbon coated prior to being analyzed using a JEOL JXA-8900 SuperProbe electron probe microanalyzer (EPMA). This device used
four different diffracting crystals (thallium acid phthalate (TAP), pentaerythritol (PETH and PETJ, where H and J are specifications used by JEOL), and layered dispersive element (LDE)) and SEM-WDX to produce two-dimensional elemental maps of the coke particle cross sections. No quantitative analysis was performed with EPMA due to a lack of suitable standard materials.

X-ray analyses were performed using a Thermo Scientific K-Alpha XPS spectrometer using a monochromated aluminum X-ray beam and an electron flood gun to avoid charge build-up on the sample surface. The beam width used in all experiments was 400 μm. High resolution scans of the sulfur 2p region were recorded to understand changes in the sulfur electron environment. Using Thermo Avantage software, each spectrum was calibrated with respect to the C 1s peak and the S 2p\textsubscript{1/2} and S 2p\textsubscript{3/2} peaks were separated by exactly 1.18 eV.

TGA and DSC experiments were carried out simultaneously using a TA Instruments SDT Q600. Approximately 20 mg of sample was heated from room temperature to 950°C at 10°C/min. This was done under pure N\textsubscript{2} and air for samples FC600, FC800 and a commercial SIAC, Calgon Carbon HGR\textsuperscript{®}. The exact method of sulfur impregnation for HGR\textsuperscript{®} is proprietary, but it results in a thin, uniform coating of elemental sulfur over the entire exterior and interior surface of a bituminous coal-based activated carbon [155]. This material therefore provides a useful reference in determining the nature and stability of sulfur on the surface of SO\textsubscript{2}-treated fluid coke.

Total sulfur content was determined using an Exeter Analytical CE-440 Elemental Analyzer. It should be noted that this device utilizes a combustion technique, thus some forms of sulfur, such as inorganic sulfates and pyrite, are not accounted for. For this reason, sulfur contents determined using this method are referred to as “combustible sulfur.”
5.3 RESULTS AND DISCUSSION

5.3.1 Characterization of sulfur on coke activated with SO\textsubscript{2}

Figure 5.1 shows a wide-field secondary electron image (SL) and EPMA elemental maps of C, S, O, Si, and Al for a sample from the upper layer FC800. The high background signal for C and O are due to the organic nature of the resin used in casting. This image reveals that particles within the upper layer of the coke bed were highly similar in terms of physical structure in that they all possess outer rings depleted of C but enriched with S, O, Si, and Al.

Upon closer examination, these particles were found to be surrounded by two distinct layers: a sulfur-rich layer around the unreacted core, and an ash layer outside of this enriched with O, Si, and Al. A single particle elemental map from the same sample is shown in Figure 5.2. The outer ash layer is clearly visible as a ring surrounding the particle highly enriched in Al and O. Both C and S were also detected in this outer layer, but in low amounts. Carbon is likely unburned carbon, but may also exist as carbonates. Sulfur in the ash layer is in the form of

![Figure 5.1](image_url). Wide-field WDX cross-sectional map for upper layer of sample FC800. Color bars at right indicate relative signal intensity; concentrations were not quantified.
sulfate bound to calcium or other alkali minerals, as this is the predominant form of sulfate in coals [156, 157]. An ash composition analysis performed by Chung et al. [3] indicates that the ash portion of oil-sands fluid coke initially contains a considerable amount of sulfate (Table 5.1).

In the sulfur-rich layer, both O and Al were slightly enriched compared to their average bulk concentration within the particle. The enrichment of O in this region suggests that sulfur is in a partially oxidized state, possibly due to interactions between SO$_2$ with basic minerals such as calcium oxide, according to Reaction 5.2:

![Figure 5.2. Single particle WDX cross-sectional map for upper layer of sample FC800. Color bars at right indicate relative signal intensity. White lines added as vertical reference for comparison between different elements. C and Al color scales modified to enhance contrast in low concentration areas.](image-url)
Bejarano et al. [86] made similar observations of a sulfur enriched layer for a sample made under similar conditions, attributing the accumulation to carbon surface sulfur complexes.

Figure 5.2 indicates that the S-rich layer is 5–10 μm in thickness, however, which is too thick to be attributed to a single monolayer of surface groups. The only way this would be feasible is if the C-S surface complexes were bound to a highly porous carbon substrate, giving a high sulfur signal over a wide region. Carbon was highly depleted in this layer but still present in low concentrations, which indicate a highly developed porous structure. This scheme could also help to explain how sulfur, which vaporizes at 445°C, could be stabilized during the reaction at 800°C. Measurements of combustible sulfur content before and after the reaction with 30% SO₂

**Table 5.1.** Major ash components of Athabasca oil-sands fluid coke as % by weight of ash [3].

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<td>23.74</td>
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Figure 5.3. XPS S 2p spectrum for sample FC800: petroleum coke treated with 30% SO\textsubscript{2} at 800°C for 3 hours.

indicated an increase of approximately 3.8% (6.6 ± 0.3% initially, 10.4 ± 0.3% after treatment), suggesting a high degree of surface coverage by carbon-sulfur complexes in this region.

The XPS S 2p scan of sample FC800 is shown in Figure 5.3. The 2p binding energies for various sulfur compounds are well-established and have been used in previous works to determine sulfur speciation in petroleum cokes and heavy petroleum residuals [82, 87, 158–161]. Intensity peaks for oxidized sulfur forms appear at higher energy than do peaks for reduced forms, therefore the leftmost peak in Figure 5.3 can be attributed to highly oxidized species such as sulfate. Since electrons detected by XPS originate from the outer 10 nm or so of the sample surface, this peak is most likely a result of sulfate species in the outer ash layer such as CaSO\textsubscript{4} (169.0 eV [162]), while the small signal in the center could be from sulfites such as CaSO\textsubscript{3} (166.7 eV [163]). Using petroleum coke from the same batch as the current study, Cai et al. [158] determined using XPS that sulfur on the raw coke surface was comprised of 5% sulfate.
and 4% sulfoxide. While sulfoxide groups may provide an alternative explanation for the small peak at ~166.4 eV, the presence of sulfate in the original coke lends support to its assignment to the leftmost peak in Figure 5.3.

The rightmost peak indicates reduced sulfur forms, which are expected in the layers beneath the ash. Although the ash layer thickness was observed to be much greater than the effective penetration depth of XPS, it is not expected to surround every particle uniformly, which can be seen in Figure 5.2. Thus, the rightmost peak is attributed to sulfur forms in the S-

![Figure 5.4](image_url)

**Figure 5.4.** (A) TGA under N$_2$, (B) TGA under air, (C) DSC under N$_2$, and (D) DSC under air for FC800 (-----), FC600 (······), and Calgon HGR (—). Temperature profile is shown as a gray line.
rich layer. The placement of this peak at approximately 164.0 eV provides some evidence as to the nature of the S-rich layer. Although this peak coincides well with that expected for elemental S [162], Puri and Hazra [82] demonstrated that elemental sulfur is not likely deposited on a carbon surface through reaction of SO$_2$. Therefore, this peak is attributed to a combination of reduced carbon-sulfur compounds. Cai et al. [158] found that sulfur on the raw petroleum coke surface was comprised of 90% thiophene and/or similar sulfide structures. Therefore thiophene (164.3 eV [162]) from the original coke structure is likely a major contributor to this peak, along with thiophene and similar ring structure sulfides (163.8, thianthrene [164]) produced through carbon-sulfur substitutions during reaction. Carbon-sulfur surface compounds that were likely added include disulfides (164.4 eV, diphenyl disulfide [162]), aliphatic sulfides (163.4 eV, diphenyl sulfide [84]) and thiolactones (163.4 eV, 1,3-dithiolane-2-thione [84]). Thiol (163.1 eV, thiophenol [165]) and thioketone (162.4 eV, thiobenzophenone [164]) may also be present, but evidently in smaller amounts.

Figure 5.4 shows TGA and DSC analyses in N$_2$ and air for FC600 and FC800 (taken from the top portion of the bed) as well as Calgon HGR®, which was determined to have a combustible sulfur content of 17.3 ± 0.6%. From what is known about the sulfur impregnation technique of HGR®, it is assumed that virtually all of this sulfur is elemental. HGR® exhibited a mass decrease of approximately 16% between 200 and 500°C in N$_2$ and 17% between 250 and 350°C in air, both of which correspond well with the measured sulfur content. The loss is therefore attributed to complete volatilization of this sulfur from the surface in N$_2$ and rapid combustion of sulfur at its autoignition temperature of 250°C in air. The TGA profiles for FC800 did not show a similar step, verifying that sulfur in the S-rich layer is not in elemental form.
Figure 5.5. Wide-field WDX cross-sectional map for upper layer of sample FC600. Color bars at right indicate relative signal intensity. Labels in sulfur map: (A) particle with outer S-rich layer; (B) and (C) particles with outer ash layer; (D) and (E) particles converted completely to ash.

5.3.2 Effect of O₂ combined with SO₂ on distribution of S

A wide-field EPMA map of sample FC600 revealed a mixture of different types of particles in the upper layer of the coke bed (Figure 5.5). Some particles showed an outer sulfur layer like those in Figure 5.1 (particle A), some exhibited outer ash layers of varying thicknesses (particles B and C), while others were simply ash (particles D and E). In Figure 5.5, the high carbon background signal from the resin reduces the contrast between ash and unreacted coke, which is why particles B and C appear to have similar carbon concentrations as particles D and E. In addition, particle A appears to have been located within a surface depression of the resin cast,
which may account for its lower observed carbon concentration. The ash particles come from a light-colored region at the top of the bed, and were formed at the upper surface of the coke bed by $O_2$ competitively reacting with carbon. Only after $O_2$ was used up did $SO_2$ react with coke, forming a S-rich layer near the coke surface. Over time, the $O_2$ reaction zone migrated downwards through the coke bed as carbon was spent, consuming the S-rich layer in the process. This process is illustrated in Figure 5.6. $SO_2$ reacts much more slowly than $O_2$, and thus began to break through as the depth of the reactive carbon bed decreased and the reactive residence time of $SO_2$ is reduced. This was observed experimentally using GC to monitor the effluent gases (Figure 5.7). While $O_2$ was completely removed, $SO_2$ broke through the bed after about 30 minutes and its outlet concentration appeared to increase gradually with time. The time needed for inlet gases to flow through the system was calculated as being slightly less than 3 minutes, therefore the delayed appearance of $SO_2$ is not simply a result of space filling. Feng

![Figure 5.6](image-url)

**Figure 5.6.** $SO_2$ and $O_2$ concentrations as a function of fixed bed depth for sample FC600 (a) during initial stages, (b) during later stages of reaction. $SO_2$ initially increases slightly due to combustion of sulfur in coke. Not drawn to scale.
Figure 5.7. GC profile for sample FC600 showing $O_2$ (■), $SO_2$ (▲), and $CO_2$ (◇). Profiles before time = 0 represent stabilization of inlet gas concentrations prior to reaction with coke.

and Jia [5] observed a ~20% increase in $SO_2$ reduction with the addition of 18% $O_2$ at 700°C, which was attributed to generation of CO according to reactions 5.3 and 5.4:

$$2C + O_2 \rightarrow 2CO \quad (5.3)$$

$$2CO + SO_2 \rightarrow \frac{1}{2}S_2 + 2CO_2 \quad (5.4)$$

CO was not detected in the outlet gas stream during the production of sample FC600. Since residual $SO_2$ existed in the outlet gas, reaction 5.3 was likely kinetically limited under the reaction conditions used.

Figure 5.8 provides a closer look at a single particle which is of the same type as particle A in Figure 5.5. It can be seen that the S-rich layer formed under these conditions was similar to that of FC800 in that carbon is depleted but still present, indicating a porous carbon layer. However, unlike with FC800, there is no ash layer surrounding the particle. This is attributed to
the much lower SO\textsubscript{2} concentration that was used, as well as the lower reaction temperature, which led to reduced SO\textsubscript{2}–C reactivity. Less reactive carbon forms which made up the porous carbon structure are not highly susceptible to attack by SO\textsubscript{2} under these conditions and remained intact throughout the reaction, thus precluding the formation of a separate ash layer. It is also evident that some areas of the S-rich layer are oxygen-deficient (upper left edge) while others are oxygen-rich (lower left and right edges). As with sample FC800, this can be attributed to the reaction of SO\textsubscript{2} with basic minerals inherently present in the coke to produce sulfites. Figure 5.8 also shows a particle extracted from the lower portion of the coke bed, which displays a relatively thin layer of sulfur enrichment. This lends further support to the scheme shown in Figure 5.6.

Figure 5.9 shows the XPS S 2p spectra for sample FC600. As with sample FC800, the leftmost peak is located at approximately 169.5 eV and therefore partially attributed to sulfate species such as CaSO\textsubscript{4} which are present in the ash particles. The fact that this peak is substantially larger for sample FC600, however, suggests another source of oxidized sulfur. It is conceivable that residual O\textsubscript{2} may persist into the SO\textsubscript{2} reaction region of the coke bed, which
could oxidize existing carbon-sulfur compounds or produce carbon-oxygen surface complexes which subsequently react with SO₂. In either case, the end result could be oxidized carbon-sulfur compounds like sulfone or sulfonate.

Also similar to FC800, the reduced sulfur peak is positioned at approximately 164.0 eV and can therefore be attributed to a mixture of thiophene and reduced sulfur surface complexes, mainly disulfide, sulfide, and thiolactone. Significant differences between the reduced sulfur forms of FC600 and FC800 could not be detected using XPS. This similarity indicates that their S-rich layers were formed by a similar process despite the different gas conditions. Thus, although O₂ in the reactive gas stream clearly out-competes SO₂ in the reaction with coke, the O₂-carbon and SO₂-carbon reactions seem to occur independently in separate regions of the coke bed as illustrated in Figure 5.6.

Humeres et al. [166] used XPS to analyze a commercial activated carbon reacted with 20% SO₂ at 630°C and detected peaks indicating the presence of S(IV) and S(II), but not S(VI).
A mechanism was thus proposed in which SO$_2$ reacts at the surface to form dioxathiolane (S$^{2+}$) and sultine (S$^{4+}$) surface groups, which coexist alongside their decomposition product, episulfide (S$^{2+}$) [167]. The data presented in Figure 5.9 do not preclude the existence of this mechanism.

5.3.3 Thermal stability of sulfur on oil-sands fluid coke activated with SO$_2$ and O$_2$

Sample FC600 was heated in a stream of pure argon at 800°C for one hour to determine how its sulfur content and speciation change upon heating in an inert atmosphere. Measurements of combustible sulfur content before and after the heating indicated a decrease of approximately 0.5% (9.6 ± 0.1% before heating, 9.1 ± 0.1% after heating), suggesting that the combustible sulfur in the coke treated with SO$_2$ and O$_2$ was relatively stable during heating. Thermal stability is essential to the re-generation of spent SIAC.

The XPS S 2p spectrum for the heat-treated sample is shown in Figure 5.10. The most striking feature of this spectrum upon comparison with that of FC600 is the much smaller oxidized sulfur peak. Since the dominant source of oxidized sulfur in the original sample is thought to be metal sulfates in the ash particles, the lack of this peak indicates that sulfate is reduced upon heating in an inert atmosphere. Although the reduction of sulfate by solid carbon is thermodynamically feasible, the most likely reducer is CO gas which has been identified in the exit gas when fluid coke is heated under inert conditions. As shown in Figure 5.5, FC600 contains particles that were mostly unreacted with only a thin ash layer (particle B). Thus, it is likely that some pyrolysis of unreacted coke did occur. CO reduction of sulfate has been studied previously [168, 169], and the following reaction has been proposed:

\[ \text{CaSO}_4 + 4\text{CO} \rightarrow \text{CaS} + 4\text{CO}_2 \]  

(5.5)
Figure 5.10. XPS S 2p spectrum for sample FC600 after heating in Ar at 800°C for 1 hour. In the presence of catalysts like Fe$_2$O$_3$ [168, 169] and V$_2$O$_5$ [168], reaction 5.5 has been found to be feasible at temperatures as low as 600°C. These transition metal oxides are known to exist in oil-sands fluid coke (see Table 5.1). Figure 5.10 also shows some evidence of metal sulfide species in the small S 2p$_{3/2}$ peak located at approximately 161.4 eV, which agrees well with previously found S 2p$_{3/2}$ binding energy for CaS of 161.0 ± 0.2 eV [170].

As shown in Figure 5.4(A), TGA profiles for samples FC600 and FC800 in N$_2$ did not exhibit the same step decrease in mass attributed to loss of elemental sulfur in the case of HGR$^\circledR$. However, there was an overall weight loss of approximately 15% observed in both samples which gradually accelerated with increasing temperature. In addition to CO pyrolysis of the coke and reduction of oxidized sulfur, the loss of sulfur groups added during reaction with SO$_2$ is also partially responsible.

Figure 5.4(B) shows the TGA profiles in a stream of air. The step decrease attributed to combustion of elemental sulfur at 250°C for HGR$^\circledR$ has a corresponding peak in the HGR$^\circledR$ DSC...
curve (Figure 5.4(D)). This was not observed for FC600 or FC800, however FC800 does exhibit a strongly exothermic reaction feature at ~400°C, which appears just before the carbon combustion peak. This can be explained as the combustion of sulfur which is liberated from the S-rich layer as its porous carbon substrate is consumed. This peak is absent from the FC600 DSC curve; evidently, the FC600 sample which was heated in air contained very few if any particles with an S-rich layer.

The DSC profile for FC800 in N₂ (Figure 5.4(C)) shows a small feature at approximately 575°C which does not have a corresponding feature on the TGA curve. This DSC feature was not observed for FC600 in N₂. In air, however, both FC600 and FC800 exhibited a peak that is highly similar (Figure 5.4(D)). The reason(s) behind these observations are not clear at this stage. A TGA-MS analysis may help find an explanation.

TGA analysis verifies that sulfur added to carbon through high temperature reaction with SO₂ is more thermally stable in both N₂ and air than sulfur added by direct condensation at lower temperatures. Puri and Hazra [82] and Humeres et al. [87] indicated that much of the sulfur added by this technique was in the form of heterocyclic ring structures such as thiophene, and that these structures are highly stable at elevated temperatures (>700°C) under inert conditions. SIACs made using this technique might therefore be economically beneficial to mercury emitting industries, as the active sulfur sites which aid in capturing mercury would not as easily be removed upon heating. This would allow for thermal regeneration of the SIAC to collect the mercury and avoid the costly alternative of shipping the spent carbon to a hazardous waste landfill.

5.4 CONCLUSIONS

1. With SO₂ as the lone oxidizer, the high-temperature (800 °C) SO₂ process was able to
produce SIAC. Although elemental sulfur was the major product of carbothermal reduction of \( \text{SO}_2 \), the high temperature had prevented elemental sulfur from depositing on the coke. However, a substantial amount of sulfur, in forms other than elemental sulfur, was enriched in the activated coke.

2. The enriched sulfur was made up of thiophene from the raw coke plus carbon-sulfur surface complexes from carbon-\( \text{SO}_2 \) reactions. These complexes included mainly heterocyclic sulfide/disulfide, possibly aliphatic sulfide, thiolactone, and thiol. TGA and DSC analyses confirmed that sulfur added to coke via reaction with \( \text{SO}_2 \) was not elemental in nature.

3. When both \( \text{SO}_2 \) (3%) and \( \text{O}_2 \) (18%) were present in the gas phase, the petroleum coke reacted with \( \text{O}_2 \) preferentially. The reaction between the coke and \( \text{O}_2 \) gasified the coke, left behind ash, and prevented the enrichment of sulfur in the coke. Upon depletion of \( \text{O}_2 \), carbothermal reduction of \( \text{SO}_2 \) started and resulted in sulfur enrichment in activated coke. Consequently, the treated coke in the fixed bed reactor was made up of a mixture of particles: completely ashed, partially ashed, sulfur-enriched and unreacted.

4. XPS analysis could not detect significant differences between the sulfur-rich particles produced with and without \( \text{O}_2 \), except for the possible presence of oxidized sulfur forms under high \( \text{O}_2 \) conditions.

5. Analysis with XPS suggested that sulfur in ash was mainly composed of sulfates.

6. In both \( \text{N}_2 \) and air, sulfur added via high-temperature reaction with \( \text{SO}_2 \) was more thermally stable than that of a commercial SIAC sulfurized at lower temperatures. Upon heating (to 800°C) in an inert atmosphere, much (83%) of the sulfur added with \( \text{SO}_2 \) remained in the coke, while virtually all of the impregnated sulfur was lost from the
commercial SIAC. This may have beneficial implications if these SO₂ treated cokes were used to capture mercury from flue gases, since they could be thermally regenerated with minimal loss of active sulfur surface sites, avoiding the costly landfill disposal of mercury containing activated carbon.

This chapter was adapted with permission from: Morris EA, Morita K, Jia CQ. Effects of O₂ on Characteristics of Sulfur Added to Petroleum Coke through Reaction with SO₂. Industrial & Engineering Chemistry Research 2010; 49(24):12709–12717. Copyright 2010 American Chemical Society.
CHAPTER 6  ROLES OF SULFURIC ACID IN ELEMENTAL MERCURY REMOVAL BY ACTIVATED CARBON AND SULFUR-IMPREGNATED ACTIVATED CARBON

6.1 MOTIVATION AND OBJECTIVES

Coal combustion continues to be the dominant source of anthropogenic mercury (Hg) worldwide [22], and, once in the atmosphere, this Hg is capable of being transported across intercontinental distances [27, 28]. For reasons such as these, stringent regulations and emissions targets have been implemented by several governments such as the United States [29], Canada [33], and the European Union [34]. One of the simplest and most extensively researched Hg control techniques is injection of activated carbon (AC) downstream of the boiler [37]. In recent years, however, the consensus in the industry has been that sulfur dioxide (SO$_2$) and sulfur trioxide (SO$_3$), formed as products of sulfur oxidation reactions during the combustion of coal, seriously hinder attempts to remove Hg through AC injection [36–38].

As possible mechanisms for Hg uptake inhibition by SO$_2$ and SO$_3$, Presto et al. have suggested competitive adsorption, scavenging of oxygen and/or halogen surface groups, and formation of sulfuric acid (H$_2$SO$_4$) leading to pore blockage [39, 40]. Despite these recent findings, an industrial process (Outokumpu Process) has existed since the 1970s for capturing Hg from non-ferrous smelter flue gases using concentrated sulfuric acid (H$_2$SO$_4$) at elevated temperatures [41]. In addition, a patented technique exists for removing Hg from liquid hydrocarbons using AC impregnated with H$_2$SO$_4$, hydrochloric acid (HCl), or phosphoric acid [42]. Some recent studies have even concluded that direct impregnation of H$_2$SO$_4$ on an AC surface has a positive impact on Hg capture [14, 43]. Section 2.4.3.3 of this document provides
an analysis of the research regarding the impact of sulfur on Hg capture with ACs. It is concluded that the discrepancy in the available literature can be explained by variability between studies with regards to gas-solid contact time (indicating kinetic limitations to Hg-H₂SO₄ reaction), or to the amount of H₂SO₄ on the surface (indicating pore blockage and swamping of Hg-binding sites).

This study is intended to improve the current understanding of the role played by H₂SO₄ in the complex process of Hg adsorption on AC surfaces. This is carried out by investigating the feasibility of Hg reacting with H₂SO₄ and the impacts of the carbon surface, oxygen (O₂), and sulfur functional groups deposited by reaction of carbon with SO₂ at high temperature. Conditions used are highly idealized and intended to provide fundamental insights as opposed to simulating practical situations in which several competing factors are at work.

6.2 METHODOLOGY

6.2.1 Sample preparation

All samples used in this study were derived from Calgon BPL, a bituminous coal-based activated carbon. BPL was first crushed and sieved to a particle size range of 150–300 μm. To produce SO₂-treated samples (SO₂-BPL), approximately 10 g of BPL was contacted with 50% SO₂ in nitrogen flowing at 200 cm³/min for 20 minutes at 700°C. The apparatus and procedure used for the SO₂ treatment has been described in detail elsewhere (see Section 3.2.1).

Impregnation of samples with H₂SO₄ was done in a fashion similar to that of Presto and Granite [39]. Solutions of H₂SO₄ in deionized water were prepared at concentrations of 5.4 and 20.1 wt%. Approximately 3 g of BPL or SO₂-BPL was placed in a beaker and the desired solution was added to the solid in a ratio of about 1 mL liquid for every 1 g of solid. The resulting slurry was quickly stirred with a glass rod to ensure complete wetting of the particles,
and the mixture was placed in an oven at 110°C overnight for drying. In this way, two samples series were produced: BPL series (BPL, BPL+5%, and BPL+20%) and SO$_2$-BPL series (SO$_2$-BPL, SO$_2$-BPL+5%, and SO$_2$-BPL+20%).

6.2.2 Vapor phase experiments

For each of the two sample series, approximately 0.1 g of each sample was weighed into 3 ceramic crucibles, one for the raw and 2 for the H$_2$SO$_4$-impregnated samples. All 3 crucibles were placed within a 0.7 L glass desiccator flask along with another crucible containing a small drop of liquid Hg. The desiccator was placed within a Barnant muffle furnace set to a temperature of 100, 150, or 200°C. These temperatures were chosen to simulate thermal conditions typically observed downstream of coal-fired utility boilers. As the furnace was heating, the top of the desiccator was left slightly ajar to relieve pressure build-up. When the desired temperature was reached, the lid was sealed using heat-resistant gloves and high-temperature vacuum grease which had been applied beforehand.

Samples were taken at various intervals during the adsorption experiment. The desiccator was taken out of the furnace and the lid removed promptly within a fume-hood. Small amounts of roughly 20 mg were removed from each crucible with a microspatula and placed in borosilicate vials. For the BPL series, this was done after 7, 17, 24, 48, and 72 hours of mercury contact. For the SO$_2$-BPL series, samples were extracted after 6, 24, 48, and 72 hours.

Vapor phase adsorption experiments to be done in the absence of O$_2$ were done by suspending two crucibles (one containing a carbon sample, the other containing a small drop of liquid Hg) within a vertical tube furnace. Pure N$_2$ was flushed through the chamber at 200 cm$^3$/min for 1 hour to purge O$_2$, then the furnace temperature was raised to 200°C. When this temperature was reached, stopcocks were used to seal off the system at the top and bottom. The
sample was removed after 3 days, and no intermediate lengths of time were studied.

6.2.3 Liquid phase experiments

Four 20 mL borosilicate vials were tared and a small drop of Hg weighing approximately 0.1 g was placed in each. Each vial was filled to capacity with a different H₂SO₄ solution: deionized water, 5.4 wt% H₂SO₄, 20.1 wt% H₂SO₄, and reagent grade (~96 wt%) H₂SO₄. If the experiment required the system to be oxygen-deficient, pure N₂ was blown across the surface of each vial for 30 seconds before it was tightly capped. Experiments in which O₂ was required either had the caps left off completely or had pure O₂ bubbled into each solution at approximately 10 cm³/min. O₂ was provided by a cylinder and the flowrate set to 40 cm³/min using an Aalborg mass flow controller. The inlet was split into 4 lines consisting of 1.6 mm ID Teflon tubing. The depth of each branch of tubing within the liquid was carefully adjusted so that a nearly equivalent rate of bubble formation was seen in each vial. This configuration is illustrated in Figure 1. For all experiments, samples were held in their respective conditions for 3 days, after which the H₂SO₄ solution was separated from the Hg by decanting.

For experiments investigating the effect of a carbon, approximately 0.1 g of BPL was first placed in the 20 mL vial, followed by the solution. To facilitate its removal, liquid Hg was placed within an open 2 mL vial completely submerged within the solution, as illustrated in Figure 6.1. For all work using carbons, O₂ was bubbled into the solution.

6.2.4 Sample analysis

Carbon samples from the vapor phase experiments were weighed to approximately 10 mg in 50 mL polypropylene centrifuge tubes. For the liquid phase experiments involving carbon, the entire contents of the 20 mL vials were first transferred into centrifuge tubes and
Figure 6.1. Apparatus used for liquid phase experiments involving BPL. then centrifuged at 1500 rpm for 10 minutes. The liquid portion was decanted and set aside for later use. 10 mL of aqua regia was then added to all samples, which were then swirled and stored in a fume hood overnight with loosened caps. The next day, the caps were tightened and the samples were placed in a water bath shaker at 45°C and 150 rpm for 3 hours. Each sample was then filled to 25 mL with deionized water and centrifuged at 1500 rpm for 5 minutes, after which the liquid portion was decanted into a 250 mL volumetric flask. The remaining sample was rinsed with 25 mL deionized water twice, each time centrifuging and decanting into the 250 mL flask. The liquid portions of the liquid phase samples set aside previously were then added to the appropriate flasks. After adding 5 mL of HCl to every sample, the solutions were diluted to 250 mL with deionized water. Aqueous phase samples not involving carbon were simply diluted to 250 mL after adding 5 mL HCl. All samples were stored in glass test tubes until they were analyzed, at which point they were transferred to 15 mL polypropylene centrifuge tubes.

Total Hg in the samples was measured with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Perkin Elmer Optima 7300. This device was calibrated using standards produced through dilution of a 1000 mg/L certified stock solution. Pore size
distributions were determined using nitrogen adsorption at 77 K with a Quantachrome Autosorb-1-C. Forty adsorption points were determined between relative pressures of 0.025 and 0.995 and analyzed using a combination of quenched solid density functional theory (QSDFT) and the BJH technique. QSDFT was used for pores less than 35 nm in diameter since it is the preferred technique for micropores. Above this size QSDFT is invalid, so BJH was necessary. Specific surface area (SSA) was estimated using the N₂ adsorption BET technique with 3 points at relative pressures of 0.025, 0.05, and 0.075.

6.3 RESULTS AND DISCUSSION

6.3.1 Aqueous phase Hg-H₂SO₄ reaction at room temperature

6.3.1.1 Effect of O₂ and H₂SO₄

Figure 6.2 shows the results of ICP analysis regarding the effect of O₂ on the reaction between Hg and H₂SO₄. It is immediately apparent that bubbling O₂ into the solution greatly increased the amount of mercury detected under all conditions. For the case of pure water, the only conceivable mechanism by which this could occur is through direct oxidation of Hg by O₂:

\[
\text{Hg + } \frac{1}{2}\text{O}_2 \rightarrow \text{HgO} \quad \Delta G^\circ(25^\circ\text{C}) = -58.6 \text{ kJ} \quad (6.1)
\]

At room temperature, Reaction 6.1 is known to occur slowly in the presence of moist air [171]. It is unknown if the surrounding aqueous phase accelerated this reaction. It is likely that HgO only existed on the surface of the Hg droplet, at the site of formation; Figure 6.3 illustrates how this Hg-HgO complex could thereupon be attacked by hydronium ions to form Hg²⁺ in solution. The solubility of HgO in water at 25°C is known to be on the order of 50 mg/L [172], therefore the absorption of Hg²⁺ by the aqueous phase appears to not have been at equilibrium.

It can be seen that Hg uptake by the solution increased with increasing H₂SO₄
Figure 6.2. Dissolved Hg concentrations in water and H$_2$SO$_4$ solutions after 3 days for the cases of O$_2$ limited (black), open top (grey), and O$_2$ bubbled (white).

Figure 6.3. Diagram illustrating mechanism of Hg absorption by water and H$_2$SO$_4$ (aq) and adsorption on AC surfaces. Oxygen functional groups on AC are shown as O*.

correlation is likely due to the formation of mercuric sulfate (HgSO$_4$), formed through Reaction 6.2 [171]:

$$\text{HgO} + \text{H}_2\text{SO}_4 \rightarrow \text{HgSO}_4 + \text{H}_2\text{O} \quad \Delta G^\circ(25^\circ\text{C}) = -37.5 \text{ kJ} \quad (6.2)$$

Reactions 6.1 and 6.2 are used in the Outokumpu process for the removal of Hg from metallurgical smelter flue gas as a solid precipitate of HgSO$_4$, however it is generally carried out
at 150 to 200°C [41]. Thermodynamic simulations using the HSC Chemistry software package indicate that both reactions are feasible at room temperature, but the fact that no precipitate was observed indicates that the solubility limit had not been reached after 3 days.

These results verify that O<sub>2</sub> is a key player in the capture of Hg by H<sub>2</sub>SO<sub>4</sub> at low temperatures. The sample series for which the vials were left open to ambient air without bubbling O<sub>2</sub> showed insignificant change in mercury uptake from the O<sub>2</sub> limited (sealed vial) series. Evidently, passive dissolution of O<sub>2</sub> into the solutions was insufficient to promote oxidation of Hg. In other words, Hg dissolution was hindered by slow kinetics.

6.3.1.2 Effect of AC surfaces

The results of adding small amounts of BPL to the H<sub>2</sub>SO<sub>4</sub> solutions are shown in Figure 6.4 alongside those of the same system with no carbon. In Figure 6.4 the amount of Hg dissolved includes both Hg in the solution as well as Hg adsorbed on the carbon, and is therefore presented as total Hg uptake in mass units. For the case of pure water, it is interesting that adding AC actually decreased the amount of Hg taken up by the system. Activated carbons are
well known for their ability to remove Hg$^{2+}$ from aqueous solution [173]. The reduced Hg dissolution after adding AC was not expected and suggests that the presence of the carbon interfered with Reaction 6.1. One possible mechanism is that the carbon scavenged dissolved O$_2$, as shown in Figure 6.3, thereby limiting its availability for reaction with Hg. Previous studies have shown that aqueous O$_2$ has a strong affinity for carbon surfaces, with the majority of it forming acidic oxygen surface groups rather than being physically adsorbed [174, 175].

However, the same experiment done in 5% H$_2$SO$_4$ yielded the opposite result. BPL had a positive effect on Hg uptake, indicating that the tendency to scavenge O$_2$ was not seen under acidic conditions. The presence of H$_2$SO$_4$ in the solution may have prevented the O$_2$-scavenging effect by preventing the formation of acidic oxygen surface groups on the carbon, thus making O$_2$ available for Reaction 6.1. The net increase observed due to BPL may be attributed to Hg$^{2+}$ adsorption by the carbon, as illustrated in Figure 6.3. Since Hg$^{2+}$ is a product of Reaction 6.2, its removal from the solution should push the reaction forward.

An enhancement in Hg uptake was also observed with BPL for the 20% and 96% H$_2$SO$_4$ systems. In 20% H$_2$SO$_4$, the increase in Hg uptake was much greater than in 5% H$_2$SO$_4$, presumably due to the enhanced solubility of Hg$^{2+}$ in the stronger acid. The greater dissolved concentration of Hg$^{2+}$ led to more Hg being adsorbed to the AC surface, driving the subsequent dissolution of additional Hg$^{2+}$. It is interesting to note that the enhancement observed due to BPL was not as great when 96% H$_2$SO$_4$ was used. This can be attributed to the high acid concentration, since it is generally accepted that binding of oxidized Hg to AC surfaces occurs at Lewis basic sites [115, 116]. The over-abundance of acidic ions in solution may have resulted in competitive adsorption at these sites, thus reducing adsorbed Hg.
6.3.2  Vapor phase Hg-H$_2$SO$_4$ reaction on AC and SIAC surfaces at elevated temperature

6.3.2.1  Effect of temperature

For untreated BPL, it is apparent from Figure 6.5 that very little Hg was adsorbed at 100 and 150°C. This is in good agreement with previous fixed-bed reactor results in which virgin activated carbons were found to have poor Hg capacity at temperatures exceeding 100°C [83, 88, 132]. Increasing the temperature to 200°C, however, increased Hg capture by BPL from 2 to 14 mg/g after 72 hours. This may be explained by the presence of O$_2$ during the experiment. Oxidation of Hg$^0$ is believed to be a necessary step in its capture [115, 116], and O$_2$ should provide this role given enough thermal energy. This observed positive temperature dependence is attributed to a greater rate of Hg supply to the activated carbon due to a higher vapor pressure and a faster mass transport of Hg, although it may also suggest a chemical step that is accelerated at higher temperatures. This chemical step could be the oxidation of Hg in the air and/or on the carbon surface. However, it is not possible to explicitly determine if this effect is due to enhanced rate of reaction or higher Hg concentration in the gas phase. The vapor pressure of Hg is known to increase from roughly 0.02 to 2 kPa as the temperature is increased from 100

![Figure 6.5. Hg loading on BPL at temperatures of 100°C (◇), 150°C (■), and 200°C (△).](image-url)
to 200°C [176]. This translates to an increase in equilibrium Hg vapor concentration from 1.3 to 102 mg/L, which is certain to have had a substantial impact on the amount adsorbed. In addition, the diffusivity always increases with temperature. Despite the increased uptake at 200°C, however, the Hg loading measured for BPL is still quite low compared to that of the H$_2$SO$_4$-treated samples.

The effects of temperature on Hg loading for BPL+5% and BPL+20% are shown in Figures 6.6 and 6.7, respectively. An enhancement due to temperature was observed for both series at 150 and 200°C, which is consistent with an increased rate of reaction. The Outokumpu process (Reactions 6.1 and 6.2) is typically carried out in this temperature range [41], so Hg, O$_2$, and H$_2$SO$_4$ will certainly react to form HgSO$_4$ under these conditions. The maximum amount of Hg loaded was found for BPL+20% after 72 hours at 200°C. The Hg loading was determined to be over 500 mg/g, or half the total sample weight, which is among the highest yet reported. Such a high Hg loading cannot be completely attributed to adsorption on the carbon surface. Absorption of Hg in H$_2$SO$_4$ in pores of H$_2$SO$_4$-treated AC should be a key contributor to the Hg loading capacity.

![Figure 6.6](image)

**Figure 6.6.** Hg loading on BPL+5% at temperatures of 100°C (◇), 150°C (■), and 200°C (△).
6.3.2. Effect of $\text{H}_2\text{SO}_4$ treatment

A better comparison can be made between samples treated with different concentrations of $\text{H}_2\text{SO}_4$ at a given temperature, since Hg vapor concentration and diffusivity are not variables. In Figure 6.8, the effect of increased loading of $\text{H}_2\text{SO}_4$ is shown for 100°C. It is readily apparent that acid treatment improved the ability of BPL to adsorb Hg vapor under these conditions, which is attributed to the formation of HgSO$_4$ within the pores of the carbon. When BPL
was treated with H$_2$SO$_4$ of higher concentrations, more H$_2$SO$_4$ would remain in the pores of BPL after drying. A greater Hg loading is therefore anticipated with the BPL treated with H$_2$SO$_4$ of higher concentrations. As shown in Figure 6.8, however, there was no enhancement seen for BPL+20% relative to BPL+5%, which suggests that the amount of Hg taken up by H$_2$SO$_4$-treated BPL was limited by Hg supply at 100°C.

**Figure 6.9.** Hg loading on BPL (◇), BPL+5% (■), and BPL+20% (△) at 150°C.

**Figure 6.10.** Hg loading on BPL (◇), BPL+5% (■), and BPL+20% (△) at 200°C.
In Figure 6.9 the same comparison is made at 150°C. As with 100°C, Hg uptake was greatly enhanced by treatment with 5% H$_2$SO$_4$, but no further improvement was detected for BPL+20%. Thus, similar to 100°C, the uptake of Hg to H$_2$SO$_4$-treated BPL at 150°C was limited by Hg availability as opposed to the availability of H$_2$SO$_4$ on the carbon. At 200°C (Figure 6.10), the greater availability of H$_2$SO$_4$ on BPL+20% becomes apparent as a result of enhanced Hg supply, confirming the role of H$_2$SO$_4$ in determining Hg loading capacity of H$_2$SO$_4$-treated AC.

![Figure 6.11. QSDFT+BJH pore size distribution with respect to pore volume. Micropore volume is shown in black, mesopore volume is grey, and macropore volume is white. Percent distributions are given as numerical values.](image)

Figure 6.11 shows the pore volume and pore size distributions of BPL, BPL+5%, and BPL+20%. Treatment with H$_2$SO$_4$ reduced the total available pore volume, and this effect increased with increasing concentration. Soaking in 20% H$_2$SO$_4$ resulted in an 80% decrease in pore volume. This was accompanied by an overall decrease in pore volume for all pore size ranges, particularly the microporous range, which is consistent with the filling of pores with liquid, H$_2$SO$_4$ in this case. Considering this substantial loss of available pore space, the remarkable increase in Hg uptake seen in Figure 6.10 after acid treatment could only be due to
absorption of Hg in H$_2$SO$_4$. These results confirm that, under certain conditions, Hg can react with H$_2$SO$_4$ on a carbon surface and that this can greatly improve Hg uptake capacity. Results obtained by Presto et al. [39] indicated that Norit Darco Hg which had been soaked in 95% H$_2$SO$_4$ showed extremely poor Hg removal at 149°C in a simulated flue gas. That study, however, used a fixed bed reactor with a gas stream flowing at 8 L/min, thereby greatly reducing the gas-solid contact time. Thus, reaction kinetics appear to be the limiting factor in the utilization of H$_2$SO$_4$-impregnated sorbents under real flue gas conditions.

6.3.2.3 Effect of oxygen

The liquid phase experiments shown in Figure 6.2 confirmed that O$_2$ is a necessary participant in the capture of Hg by H$_2$SO$_4$ at room temperature. In Figure 6.12, the increase observed for untreated BPL from less than 1 mg/g in the absence of O$_2$ to 14 mg/g in air shows that this is also true at 200°C for carbon surfaces devoid of H$_2$SO$_4$. This evidence further confirms that, in the absence of other oxidizing species, O$_2$ plays a critical role in mercury sorption to carbon surfaces.

As shown in Figure 6.12, the enhancing effect of O$_2$ on Hg uptake was also observed with H$_2$SO$_4$-treated carbon at elevated temperature. The amount of Hg captured by BPL+20% was increased to over 500 mg/g with O$_2$ from 150 mg/g in the absence of O$_2$. However, 150 mg/g was still quite substantial. One possible explanation is that the system wasn’t truly free of oxygen: activated carbons are known to contain a large amount of oxygen in the form of both surface functional groups and adsorbed O$_2$ [174]. It is conceivable that this inherent oxygen content was adequate to support Reaction 6.1, however the lack of Hg capture by BPL without O$_2$ does not support this.

The other possibility is that the temperature was sufficient to allow H$_2$SO$_4$ to act as an
Figure 6.1. Effect of O₂ on Hg loading of BPL (black) and BPL+20% (white) after 72 hours at 200°C.

Figure 6.12. Effect of O₂ on Hg loading of BPL (black) and BPL+20% (white) after 72 hours at 200°C.

oxidizer in the absence of O₂:

\[
\text{Hg + 2H}_2\text{SO}_4 \rightarrow \text{HgSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} \quad \Delta G^\circ(200^\circ\text{C}) = 15.1 \text{ kJ} \quad (6.3)
\]

In Reaction 6.3, S⁶⁺ oxidizes Hg to Hg²⁺ while being reduced to S⁴⁺. Thermodynamic simulation of Reaction 6.3 at 200°C using HSC Chemistry yielded a positive Gibbs free energy change. At temperatures exceeding 260°C, \( \Delta G^\circ \) becomes negative. With a large supply of Hg and H₂SO₄ along with little SO₂ and H₂O in the system, however, a negative \( \Delta G^\circ \) should be feasible, making H₂SO₄ the oxidizing species for Hg at 200°C. Without further study, this remains a hypothesis.

Figure 6.13 provides an illustration of the proposed mechanism for capture of Hg vapor on an AC surface with or without H₂SO₄ present. After being physically sorbed to the surface, Hg is oxidized by either physisorbed O₂ or acidic carbon-oxygen surface functional groups to give adsorbed Hg²⁺. The oxidized Hg then binds to Lewis base surface sites, shown in Figure 6.13 as being either carbon-oxygen or carbon-sulfur functional groups. The Hg may remain in this state, or be absorbed by H₂SO₄ present on the surface. In the absence of O₂ acting as an oxidizer, Hg is oxidized directly by H₂SO₄ (this is shown as a dotted line to indicate a less
6.3.2.4  Effect of sulfur impregnation with SO₂

Inspection of Figure 6.14 shows that SO₂ treatment of BPL brought about an enormous improvement in Hg uptake at 200°C. The literature contains an abundance of studies which concluded that impregnation of sulfur onto a virgin activated carbon greatly enhances its overall performance in Hg capture [7–14], but this is the first time that it has been demonstrated for sulfur impregnation through high-temperature reaction with SO₂. The sulfur groups on the surface are not likely to be in the form of elemental sulfur, but rather as thermally stable surface complexes such as sulfide, disulfide, sulfoxide, and sulfone [82, 84, 87]. Using X-ray absorption near-edge structure spectroscopy, Feng et al. [177] found no correlation between Hg uptake to different sulfur-impregnated ACs and their contents of sulfoxide and sulfone. However, a reasonable correlation was determined for thiophene, which can be considered an aromatic sulfide. This study seems to confirm the ability of organic sulfur groups to bind Hg, however further work needs to be done to confirm the absence of elemental sulfur.
Figure 6.14. Hg loading on BPL (◇) and SO₂-BPL (■) at 200°C.

When SO₂-BPL is treated with 5% H₂SO₄, there is still a substantial improvement in Hg uptake over BPL+5%, as indicated by Figure 6.15. SO₂-BPL+5% appeared to have reached is saturation capacity of approximately 425 mg/g much earlier than BPL+5%, which suggests improved adsorption kinetics resulting from SO₂ treatment. It seems as though the presence of sulfur groups on the surface facilitates the binding of Hg to the surface, whereupon it is converted to HgSO₄ through the action of the acid, which acts as a “reservoir.” Inspection of the early stages of reaction for both samples clearly shows a much faster initial rate of uptake for SO₂-BPL+5%. The same discussion also applies to the comparison between BPL+20% and SO₂-BPL+20% (Figure 6.16). This is interesting because it indicates that the sulfur functional groups imparted by SO₂ treatment are not masked by H₂SO₄ despite the large amount of acid present. These sulfur groups are thus likely concentrated near the outer surface of the carbon particles rather than within the pores which become filled with acid. The SO₂ treated sample appears to have reached saturation at just over 500 mg/g after only 24 hours, similar to SO₂-BPL+5%. BPL+20% achieved a similar Hg loading after 72 hours, but it cannot be determined if that sample had reached saturation.
Figure 6.15. Hg loading on BPL+5% (◇) and SO₂-BPL+5% (■) at 200°C.

Figure 6.16. Hg loading on BPL+20% (◇) and SO₂-BPL+20% (■) at 200°C.

6.3.3 Relevance to Hg capture by powdered AC injection

This study concludes that the reaction of Hg with H₂SO₄ on an AC surface is feasible and dramatically improves overall Hg uptake capacity, particularly with the presence of O₂. However, in a practical setting such as powder AC injection in a coal-fired utility flue gas where the AC-gas contact time is on the order of seconds, the relatively slow kinetics of Hg absorption may result in H₂SO₄ being an impediment to effective Hg capture. The reported hindering effect
of SO$_3$ and/or H$_2$SO$_4$ on Hg capture during powder AC injection was likely due to slow kinetics. As a rough comparison of Hg adsorption under the conditions of the present study to that in powdered AC injection, we can look at the flux of Hg to AC and the mass transfer coefficients involved in each situation. Flux is calculated according to Equation 6.1:

$$N = k_m (C_A - C_{AC}^*)$$  \hspace{1cm} \text{Eq. 6.1}

Where $N$ is the flux (mg/s·m$^2$), $k_m$ is the mass transfer coefficient (m/s), $C_A$ is the gas concentration of Hg (mg/m$^3$), and $C_{AC}^*$ is the gas concentration of Hg at the AC surface (mg/m$^3$), which is calculated according to Equation 6.2:

$$C_{AC}^* = C_{AC} K_{A/AC} = C_{AC} \left( \frac{C_A}{C_{AC}} \right)_{eq}$$  \hspace{1cm} \text{Eq. 6.2}

Where $C_{AC}$ is the concentration of Hg on the AC surface (mg/m$^2$) and $K_{A/AC}$ is the air-AC partition coefficient at equilibrium. Under equilibrium conditions, $C_{AC}$ is expected to be much greater than $C_A$ in magnitude, and thus $K_{A/AC}$ approaches zero. Equation 6.1 can therefore be rearranged to form Equation 6.3:

$$k_m = \frac{N}{C_A}$$  \hspace{1cm} \text{Eq. 6.3}

For BPL and SO$_2$-BPL at 200°C, the flux, $N$, is estimated using the slope of the line connecting the first data point with the origin in Figures 10 and 16, respectively, and dividing by the measured BET SSA in m$^2$/g. For powdered AC injection, $N$ is estimated by assuming typical operating parameters [36]: 90% removal in a gas stream containing 10 μg/m$^3$ Hg, AC injection rate of 5 lbs/MMacf (80 mg/m$^3$), flow rate of $1.4 \times 10^6$ scfm (661 m$^3$/s), and a gas-solid contact time of 5 seconds. Powdered AC SSA is assumed to be 1000 m$^2$/g, which was measured for
Table 6.1. Comparison of some operating parameters encountered in the present study for BPL+20% and SO$_2$-BPL+20% at 200°C with those used in typical Hg capture through powdered AC injection.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BPL+20%</th>
<th>SO$_2$-BPL+20%</th>
<th>Powdered AC injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_A$, mg/m$^3$</td>
<td>$10^5$</td>
<td>$10^5$</td>
<td>0.01</td>
</tr>
<tr>
<td>SSA, m$^2$/g</td>
<td>177</td>
<td>177</td>
<td>$10^3$</td>
</tr>
<tr>
<td>$N$, mg/s·m$^2$</td>
<td>$3.03\times10^{-5}$</td>
<td>$1.21\times10^{-4}$</td>
<td>$2.25\times10^{-5}$</td>
</tr>
<tr>
<td>$k_m$, m/s</td>
<td>$3.03\times10^{-10}$</td>
<td>$1.21\times10^{-9}$</td>
<td>$2.25\times10^{-3}$</td>
</tr>
</tbody>
</table>

Calgon BPL in this study. $C_A$ for BPL and SO$_2$-BPL is estimated using vapor pressure data for Hg at 200°C [176]. Table 6.1 summarizes the findings for the 3 different situations.

The mass transfer coefficients for the present study are vastly reduced from that estimated for powdered AC injection, which is expected due to the stagnant gas conditions used. However, due to the much higher Hg concentration, the overall flux of Hg to the AC surface for BPL treated with 20% H$_2$SO$_4$ was very similar to that of the practical case. Adding sulfur to the BPL surface via reaction with SO$_2$ at 700°C followed by treatment with 20% H$_2$SO$_4$ increased the flux by one order of magnitude. Thus, despite the fact that the operating conditions used in this study were greatly different from those seen in real powdered AC injection in coal-fired utility flue gases, the results obtained are still relevant and warrant further research. Subsequent studies should be performed under fixed bed conditions so that gas-solid contact time and Hg concentration can be carefully controlled. More experiments are needed to experimentally validate the improved kinetics brought about by SO$_2$ treatment, with and without impregnation by H$_2$SO$_4$. 
CHAPTER 7 THERMAL STABILITY OF MERCURY AND ITS BINDING SITES ON CHEMICALLY TREATED ACTIVATED CARBON

7.1 MOTIVATION AND OBJECTIVES

One of the key obstacles facing the widespread implementation of activated carbon injection for removal of vapor mercury (Hg) from coal-fired utility stack gases is the lack of data with regards to its regeneration. Few studies have investigated the thermal desorption of Hg species from carbon surfaces, but fewer still have looked at the ability of thermally treated carbon to re-adsorb Hg. One of the key issues in this case, particularly with chemically-impregnated activated carbons, is the loss of active surface sites which play a vital role in Hg uptake.

Using activated carbons doped with Co$_3$O$_4$, MnO$_2$, and CuCoO$_4$, Mei et al. [178] performed three successive mercury desorbing and re-loading cycles, where the desorption was done at 450°C for 10 hours. While all three samples lost varying degrees of Hg loading capacity after the first regeneration (losses ranged from 6 to 60%), subsequent regeneration cycles had very little impact. Okwadha et al. [179] tested the Hg adsorption capacity of Norit Darco Hg-LH, a bromine-impregnated powdered activated carbon, after thermal regeneration for 2 hours at 371, 427, 538, and 593°C. For all 4 temperatures studied, the loss of Hg removal efficiency dropped by 20–45% over one hour of Hg adsorption. The authors concluded that this degree of loss was acceptable, so long as the regenerated carbon was mixed with fresh carbon before reuse.

The current study is intended to determine the capability of activated carbon treated with
sulfur dioxide (SO$_2$) at high temperature to be regenerated after loading with Hg vapor. Special focus is given to the loss of surface functionality at different heat treatment temperatures. The regenerability of Hg binding sites added through SO$_2$ treatment is compared with that of binding sites added through soaking in a solution of bromine (Br), since Br-impregnated activated carbons are currently the state of the art in vapor Hg sorption.

7.2 METHODOLOGY

7.2.1 Sample preparation

CSAC (Fisher) was pulverized and sieved to a particle size range of 53–106 μm. SO$_2$ treated CSAC (SO$_2$-CSAC) was produced by reacting approximately 10 g of CSAC with 50% SO$_2$ in nitrogen flowing at 200 cm$^3$/min for 20 minutes at 700°C. The apparatus used for the SO$_2$ treatment has been described in detail elsewhere (see Section 3.2.1). Br treated CSAC (Br-CSAC) was produced by thoroughly drying about 10 g of CSAC in an oven overnight at 110°C. After weighing, the dried CSAC was immersed in 1 L of 15 wt% Br in water. This mixture tightly stoppered and agitated with a magnetic stir-bar overnight. The Br-CSAC was separated from the liquid by vacuum filtration through a paper filter, ensuring that the suction gas passed through an Erlenmeyer flask containing ethanol to scrub Br vapors. The filter paper containing the sample was then dried at 110°C overnight, after which Br-CSAC was physically removed and weighed to determine the amount of Br added.

7.2.2 Hg loading and sorbent regeneration

Approximately 0.2 g of CSAC, SO$_2$-CSAC, and Br-CSAC were weighed into 3 ceramic crucibles. All 3 crucibles were placed within a 0.7 L glass desiccator flask along with another crucible containing a small drop of liquid Hg. The desiccator was placed within a Barnant
muffle furnace set to a temperature of 200°C in order to simulate thermal conditions typically observed downstream of coal-fired utility boilers. As the furnace was heating, the top of the desiccator was left slightly ajar to relieve pressure build-up. When the desired temperature was reached, the lid was sealed using heat-resistant gloves and high-temperature vacuum grease which had been applied beforehand.

Approximately one quarter of the Hg loaded sample was set aside for future analysis, while the rest was placed into the quartz tube reactor used to produce SO₂-CSAC. The reactor was flushed with pure N₂ flowing at 100 cm³/min for 30 minutes, and then the furnace temperature was set to 290, 315, or 500°C. These temperatures were chosen based on known thermal decomposition temperatures of different mercury-sulfur species. After one hour of heat treatment at the desired temperature under N₂ flow, the furnace was allowed to cool.

About one third of each heat treated sample was then placed in crucibles and re-loaded with Hg at 200°C for 72 hours in the same manner as before. The end result was 27 samples: CSAC, SO₂-CSAC, and Br-CSAC at 3 stages of treatment (Hg loaded, Hg desorbed, Hg re-loaded), heat treated at 3 different temperatures (290, 315, 500°C).

### 7.2.3 Sample analysis

All samples were prepared for ICP analysis through a process of aqua regia digestion identical to that described for vapor phase experiments in Section 6.2.4. Total Hg in the samples was measured with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Perkin Elmer Optima 7300. This device was calibrated using standards produced through dilution of a 1000 mg/L certified stock solution. Pore size distributions were determined using nitrogen adsorption at 77 K with a Quantachrome Autosorb-1-C. Forty adsorption points were determined between relative pressures of 0.025 and 0.995 and analyzed using a combination of
quenched solid density functional theory (QSDFT) and the BJH technique. QSDFT was used for pores less than 35 nm in diameter since it is the preferred technique for micropores. Above this size QSDFT is invalid, so BJH was necessary. Weight percentages of sulfur were measured using an Exeter Analytical CE440 elemental analyzer.

7.3 **RESULTS AND DISCUSSION**

7.3.1 **Characterization of samples**

Figure 7.1 shows the pore size distribution with respect to volume for samples CSAC, Br-CSAC, and SO$_2$-CSAC. It can be seen that both treatment techniques had only a slight effect on the overall pore volume. Soaking in Br overnight appears to have filled some of the micropores, which is evident from the decrease in total pore volume and increase in mesopore fraction. The amount of Br added to the AC was determined by weight difference to be 1.1 g, giving a Br content of 12.3 wt%. This added bromine was not likely to be in liquid form within the pores, since the drying temperature was far above its normal boiling point of 59°C. Rather,

![Figure 7.1. QSDFT+BJH pore size distribution with respect to pore volume. Micropore volume is shown in black, mesopore volume is grey, and macropore volume is white. Percent distributions are given as numerical values.](image)

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Br is expected to have reacted with the carbon surface forming stable functional groups. Treatment of CSAC with SO$_2$ at 700°C also resulted in an increase in mesoporous fraction. However, the increase in overall pore volume indicates that this was not due to pore filling, but rather widening of micropores through reaction of carbon with SO$_2$. Elemental analyses done before and after SO$_2$ treatment indicated an increase of more than 10% sulfur from 2.3 ± 0.2 to 12.7 ± 0.4 wt%. Despite the large amount of sulfur added, access to pores appears not to have been impeded.

### 7.3.2 Thermal stability of mercury

ICP results for Hg loaded samples thermally treated at 500, 315, and 290°C are given in Figures 7.2, 7.3, and 7.4, respectively. Both Br-CSAC and SO$_2$-CSAC showed considerably improved initial Hg loading after 72 hours at 200°C, which is easily attributable to the presence of chemically active surface sites for Hg binding. It is not expected that the minor modifications to pore volume shown in Figure 7.1 would have such a significant impact on Hg sorption over long time periods.

Not visible in Figure 7.2 is the Hg loading for thermally desorbed samples. The treatment temperature of 500°C was high enough that virtually complete removal of Hg occurred after 1 hour. This was not the case when the samples were heat treated at 315°C (Figure 7.3) and 290°C (Figure 7.4), as a small amount of residual Hg was detected for Br-CSAC. It has been demonstrated that mercury(II) bromide (HgBr$_2$) will decompose at approximately 110°C under inert atmosphere [180]. Because the initial Hg loading was done at 200°C, it is unlikely that any of the adsorbed Hg is in this form. Mercury(I) bromide (Hg$_2$Br$_2$) is a more plausible candidate species, because its sublimation point has been stated as 340–350°C [178]. Evidence provided here suggests that decomposition of Hg$_2$Br$_2$ begins at significantly
lower temperatures. Very small amounts of mercury were detected on CSAC and SO$_2$-CSAC treated at 290°C. The appearance of Hg at this desorption temperature provides a clue as to its form when bound to SO$_2$-CSAC. Two candidate sulfur compounds are mercury (I) sulfate (Hg$_2$SO$_4$), which decomposes near 280°C, and mercury(II) sulfide (HgS), which decomposes at

Figure 7.2. ICP-AES measurements of total Hg after initial Hg loading (black) and thermal treatment at 500°C (grey). Hg on thermally regenerated samples was below the detection limit, and is therefore not visible at this scale.

Figure 7.3. ICP-AES measurements of total Hg after initial Hg loading (black) and thermal treatment at 315°C (grey).
Figure 7.4. ICP-AES measurements of total Hg after initial Hg loading (black) and thermal treatment at 290°C (grey).

around 310°C [181]. It is unclear at this point which form of mercury would remain stable on the surface of CSAC at this temperature.

It is important to realize that, under all the heat treatment temperatures studied, the amount of Hg left over on the surface is very small. In light of this, it can be concluded that efficient removal of Hg from all three carbons is achievable with one hour of thermal desorption at moderately low temperatures. However, if the sorbent is being placed under heat treatment for regeneration purposes, the stability of active sites on the carbon surface are equally important to that of Hg.

7.3.3 Thermal stability of mercury binding sites and reuse of thermally treated carbons

Figures 7.5, 7.6, and 7.7 show the amount of Hg re-loaded on each sample after thermal desorption. In all cases, the amount that could be re-loaded was reduced from the initial loading. This indicates that important reactive centers were lost from the carbon surface during thermal desorption of Hg. In order to quantitatively compare the degree to which surface functionality was lost at all three heat treatment temperatures, the reduction in 3-day Hg loading capacity is
expressed as a percent loss in Table 7.1.

For CSAC, the total percent loss was significantly less than that of Br-CSAC and SO$_2$-CSAC at every temperature studied, which shows that a smaller proportion of the surface sites responsible for Hg binding were lost. It is expected that, on CSAC at 200°C, Hg will primarily be bound to oxygen-containing surface functional groups. The lower percent loss strongly

![Figure 7.5. ICP-AES measurements of total Hg after initial Hg loading (black) and Hg re-loading after thermal treatment at 500°C (white).](image)

![Figure 7.6. ICP-AES measurements of total Hg after initial Hg loading (black) and Hg re-loading after thermal treatment at 315°C (white).](image)
Figure 7.7. ICP-AES measurements of total Hg after initial Hg loading (black) and Hg re-loading after thermal treatment at 290°C (white).

suggests that much of these functional groups are thermally stable and can be considered the innate loading capacity of CSAC and its derivatives for a particular temperature. Those binding sites that are removed from CSAC through heat treatment are believed to be volatile surface groups formed through passive oxidation of the carbon surface over time.

For Br-CSAC and SO₂-CSAC, percent loss is expressed in Table 7.1 as both a total percent loss and as “Added” percent loss, which is defined as the percent loss of Hg loading over and above that of CSAC:

\[
\% \text{ Loss, Added} = \left(1 - \frac{[\text{Hg}]_f - [\text{Hg}]_{\text{CSAC},f}}{[\text{Hg}]_i - [\text{Hg}]_{\text{CSAC},i}}\right) \times 100\% 
\]

Where \([\text{Hg}]_f\) is the amount of Hg re-loaded after thermal treatment on Br-CSAC or SO₂-CSAC, \([\text{Hg}]_i\) is the initial amount of Hg loaded on Br-CSAC or SO₂-CSAC, and \([\text{Hg}]_{\text{CSAC},f}\) and \([\text{Hg}]_{\text{CSAC},i}\) are the same quantities but specifically for CSAC. Added percent loss is useful because it emphasizes the change made through chemical modification of CSAC. For the case of Br-CSAC at 290 and 315°C, approximately 70% of the added surface functionality towards
Table 7.1. Percent loss of Hg loading capacity at 200°C following thermal desorption at different temperatures.

<table>
<thead>
<tr>
<th>Thermal Treatment Temperature, °C</th>
<th>CSAC</th>
<th>Br-CSAC</th>
<th>Br-CSAC, Added</th>
<th>SO2-CSAC</th>
<th>SO2-CSAC, Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td>26.8</td>
<td>62.8</td>
<td>71.5</td>
<td>63.8</td>
<td>74.8</td>
</tr>
<tr>
<td>315</td>
<td>20.1</td>
<td>59.7</td>
<td>69.4</td>
<td>74.0</td>
<td>88.9</td>
</tr>
<tr>
<td>500</td>
<td>37.7</td>
<td>80.6</td>
<td>91.9</td>
<td>74.1</td>
<td>85.3</td>
</tr>
</tbody>
</table>

Hg was lost. Thus, much of the Br surface groups responsible for binding Hg decompose between the initial binding temperature of 200°C and 290°C. Heat treatment at 500°C removed more than 90% of the added Hg loading capacity resulting from Br treatment.

SO2-CSAC lost 75% of its added functionality towards Hg after heat treatment at 290°C, similar to Br-CSAC. Raising the thermal desorption temperature to 315°C resulted in an additional 10% loss, but this amount did not increase upon heat treatment at 500°C, which indicates that all of the unstable surface functional groups were lost by 315°C. Figure 7.8 shows direct measurements of added sulfur content for SO2-CSAC after undergoing heat treatment at all three temperatures. Two important observations are made: 1. The loss of added sulfur after heating at 290 and 315°C is approximately 25%, much less than the loss of Hg loading upon re-adsorption following thermal desorption; 2. Increasing the thermal desorption temperature from 315 to 500°C resulted in a decrease in sulfur content, but this loss of sulfur did not appear to impact the ability of SO2-CSAC to be re-loaded with Hg. These observations suggest that the most important Hg binding sites added to CSAC through SO2 treatment are only a fraction of the total sulfur added. These sites might be comprised of particular sulfur functional groups which have a high affinity for mercury, yet are not as thermally stable as the less active sulfur.
Figure 7.8. Impact of thermal desorption at 290°C (regen290), 315°C (regen315), and 500°C (regen500) on added sulfur content of SO$_2$-CSAC. The amount of sulfur measured for CSAC (2.3%) has been subtracted from the weight percentages originally measured.

groups. Feng et al. [177] found reasonable correlations between elemental sulfur, thiophene, and sulfate content of carbon sorbents and their relative affinities to mercury. Elemental sulfur was found to have the strongest affinity, followed by thiophene and then sulfate. Although it was demonstrated in Chapter 5 that sulfur added to fluid coke through activation with SO$_2$ at 700°C is not elemental, CSAC is a greatly different material. It is conceivable that, due to its high micropore fraction (see Figure 7.1), some elemental sulfur could have been trapped within the pore structure during treatment with SO$_2$. This could explain both the reduction in mercury capacity and the accompanying loss of sulfur after thermal treatment. The 60–75% of the sulfur added to CSAC which remained after heat treatment apparently did possess some capacity for binding Hg, since it provided an additional 10–15 mg/g of Hg loading over and above that of heat treated CSAC. This sulfur may have been in the form of thiophene, since Feng et al. found it to possess some affinity for mercury and it has a relatively high thermal stability (see Chapter 5).
Another possibility, however, is that the apparent loss of mercury capacity has more to do with the accessibility of sulfur to mercury, as opposed to its chemical form. Being highly microporous, it is possible that much of the internal pore space of CSAC is inaccessible to large molecules such as mercury, despite the high diffusivity expected at 200°C. These steric hindrances would only be exacerbated by the addition of sulfur groups to the internal pore walls through reaction with SO$_2$. Much of the added sulfur in SO$_2$-CSAC could be located deep within narrow pores which subsequently became choked off as more sulfur was added. If this is the case, then the loss of sulfur after heat treatment shown in Figure 7.8 must be closely related to the thermal desorption of mercury. In other words, sulfur which binds with mercury during the adsorption stage is liberated from the carbon during heat treatment as a result of thermal decomposition of the mercury-sulfur compound. Further research must be completed in order to ascertain whether mercury uptake is more closely related to sulfur type or sulfur accessibility, or both.

**7.4 CONCLUSIONS**

Sulfur-impregnated activated carbon was produced through high temperature reaction of SO$_2$ and a coconut shell-derived activated carbon. The ability of this SO$_2$ treated carbon to be thermally regenerated following loading with Hg was compared with that of the same carbon treated with Br. Br-impregnated activated carbon is the current state of the art in the capture of Hg vapor from industrial sources.

After exposure to Hg vapor at 200°C for 3 days, both SO$_2$ and Br treated carbons showed initial Hg loading capacities much greater than that of the virgin activated carbon. Thermal desorption at 500°C resulted in total loss of Hg from all samples, but very small amounts remained after desorption at 290 and 315°C. Hg bound to Br-treated carbon under
these conditions is believed to be in the form of Hg\(_2\)Br\(_2\), while that of SO\(_2\)-treated carbon is likely HgS or Hg\(_2\)SO\(_4\). Approximately 70\% and 90\% of added Hg functionality was lost from Br-treated carbon after thermal desorption of Hg at 315 and 500°C, respectively, indicating significant loss of Br surface sites. 85–90\% of added Hg functionality was lost from SO\(_2\) treated carbon after desorption above 315°C, which was attributed to the loss of thermally unstable sulfur functional groups. About 60–75\% of added sulfur was highly stable and effectively doubled Hg loading compared to untreated activated carbon after thermal desorption at 500°C.

This study illustrates the challenge of modifying the activated carbon surface in order to enhance its affinity to Hg while allowing it to be thermally regenerated. Further studies are needed to examine the regenerability of other activated carbon materials treated with SO\(_2\), as the inherent surface chemistry of the carbonaceous precursor may play a significant role. Subsequent research should also extend the number of thermal desorption and Hg re-loading cycles to determine if regenerability of Br- and SO\(_2\)-treated Hg sorbents deteriorates further upon repeated exposure to high temperatures.
CHAPTER 8 MAJOR CONCLUSIONS

The following overall conclusions were drawn from this study.

1. In the SO\textsubscript{2}-activation of dense, non-porous, carbonaceous materials, such as fluid coke, a sulfur-rich porous layer is formed around the outer periphery of the particles. The thickness of this porous layer reaches a maximum value due to diffusion limitations of SO\textsubscript{2} within the layer. The maximum porous layer thickness is governed by the conditions of activation, and determines the maximum achievable SSA. For fluid coke of initial diameter 53–106 μm activated with 50% SO\textsubscript{2} at 700°C, the maximum porous layer thickness was approximately 12 μm.

2. When activating fluid coke with SO\textsubscript{2}, greater SSA values are attainable by air pre-oxidation, use of optimal particle size, and washing with dilute HCl after activation. The highest SSA achieved was 530 m\textsuperscript{2}/g for pre-oxidized coke of 53–106 μm initial diameter activated 5 hours and washed with 10% HCl.

3. When O\textsubscript{2} is present during SO\textsubscript{2} activation of a carbonaceous material, O\textsubscript{2} competitively reacts with the carbon. As a result, SO\textsubscript{2} does not react and a sulfur rich porous layer is not formed until O\textsubscript{2} is depleted.

4. Sulfur added to fluid coke as a result of SO\textsubscript{2}-activation exists mainly as reduced sulfur forms which are more thermally stable than elemental sulfur present on commercial sulfur-impregnated ACs. After 1 hour of thermal treatment at 500°C, 26% of Hg sorption capacity remained for a commercial AC treated with 50% SO\textsubscript{2} at 700°C.

5. In the absence of other, stronger oxidizing agents, O\textsubscript{2} was able to oxidize Hg and enhance vapor Hg adsorption by AC at 200°C and Hg absorption in H\textsubscript{2}SO\textsubscript{4} solution at room
temperature as well as at 200°C. Using a commercial AC treated with 20% H$_2$SO$_4$, a Hg loading of more than 500 mg/g was achieved, which is one of the highest yet reported. Treating the AC with 50% SO$_2$ at 700°C greatly improved the Hg uptake kinetics, even after the AC had been treated with 20% H$_2$SO$_4$.

6. When O$_2$ was not available, S$^{6+}$ in H$_2$SO$_4$ was capable of acting as an oxidizer of Hg and enabled Hg uptake by H$_2$SO$_4$-treated AC at 200°C. The Hg loading achieved in the absence of O$_2$ after 3 days was 150 mg/g.
Recommendations for Future Work

1. Future work involving the constant thickness porous layer model developed in Chapter 3 should implement the system of equations into an optimization algorithm using MATLAB, or another similar mathematical suite. Ideally, this program would accept SSA, particle size, and Random Pore Model parameters as inputs and automatically compute the maximum porous layer thickness.

2. The impact of different SO$_2$ activation temperatures on porous layer thickness should be addressed. Ideally, a series of cross-sectional SEM images similar to that shown in Figure 3.6 should be produced, as this could directly confirm or refute the hypothesis that lower activation temperatures will lead to thicker porous layers.

3. A systematic study of the effect of H$_2$SO$_4$ impregnation of activated carbon on Hg uptake should be performed under flowing gas conditions in which the contact time is very short. Such a study could explicitly demonstrate whether or not Hg uptake to H$_2$SO$_4$ is limited by chemical reaction kinetics. Furthermore, since the Hg concentration can effectively be controlled in a flow system, the real impact of temperature on Hg adsorption to carbons impregnated with H$_2$SO$_4$ can be elucidated.

4. The thermal regenerability of SO$_2$-activated coke and SO$_2$-treated activated carbons other than that derived from coconut shell should be investigated. Since activated carbon from different carbonaceous precursors will have different physical structures and chemical compositions, the thermal stability of Hg binding sites could very well be affected.

5. Future studies on thermal regenerability of different activated carbon materials after loading with Hg should look into the effect of thermal treatment time. It may be possible
to decrease the length of time spent at high temperature and still achieve complete Hg removal while retaining more of the active surface sites. In addition, the effect of multiple thermal desorption and Hg re-loading cycles should be determined, since repeated thermal treatment may diminish the regenerability more and more each time.
References


[94] Zacharewski TR, Chreniak EA, Schroeder WH. FTIR investigation of the heterogeneous reaction of HgO(s) with SO₂(g) at ambient temperature. Atmos Environ 1987; 21(11):2327–2332.


[159] Kelemen SR, George GN, Gorbaty ML. Direct Determination and Quantification of
Sulphur Forms in Heavy Petroleum and Coals. I. The X-ray Photoelectron Spectroscopy

[160] Jiménez Mateos JM, Fierro JLG. X-ray Photoelectron Spectroscopic Study of Petroleum


[163] Siriwardane RV. Interaction of SO$_2$ and O$_2$ Mixtures with CaO (100) and Sodium

[164] Brauman SK. Chemiluminescence Studies of the Low Temperature Thermooxidation of

[165] Roberts JT, Friend CM. Spectroscopic Identification of Surface Phenyl Thiolate and

[166] Humeres E, Peruch MGB, Moreira RFPM, Schreiner W. Reduction of Sulfur Dioxide on

[167] Humeres E, de Castro KM, Moreira RFPM, Peruch MGB, Schreiner WH, Aliev AE,
Canle M, Santaballa JA, Fernández I. Reactivity of the Thermally Stable Intermediates of
the Reduction of SO$_2$ on Carbons and Mechanisms of Insertion of Organic Moieties in the

[168] Zadick TW, Zavaleta R, McCandless FP. Catalytic Reduction of Calcium Sulfate to
11(2):283–287.

[169] Li H, Zhuang Y. Catalytic Reduction of Calcium Sulfate to Calcium Sulfide by Carbon


581.


