Sulfur-Impregnated Activated Carbon – Surface Interactions with Elemental Mercury and Its Wettability

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Chemical Engineering and Applied Chemistry
University of Toronto

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Mater of Applied Science
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Abstract

This work addresses the effects of oxygen (O₂) and sulfuric acid (H₂SO₄) on the performance of sulfur-impregnated activated carbon (SIAC) in elemental mercury (Hg⁰) uptake and the wettability of SIAC. O₂ significantly enhances the uptake via Hg⁰ oxidation and the subsequent physisorption of Hg⁰ onto chemically adsorbed Hg. H₂SO₄ and its dilution form has a hindering effect on Hg⁰ adsorption due to pore blockage. Absorption of Hg⁰ in H₂SO₄ is not a significant contributor to Hg uptake when Hg⁰ concentration is low. The wettability study shows that graphite basal surface is intrinsically hydrophilic with a water contact angle (WCA) of 61.6°, while the side surface is even more hydrophilic (intrinsic WCA most likely < 40°). Sulfurization and oxidation make the graphite surface more hydrophilic. Considering the great roughness of pore wall and the presence of high-energy edge carbon and sulfur species, SIAC internal surfaces are expected to be highly hydrophilic.
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Nomenclature

\( a_{H_2SO_4} \) activity of \( H_2SO_4 \)

\( a_{HgSO_4} \) activity of \( HgSO_4 \) in \( H_2SO_4 \)

\( C \) Outlet concentration (\( \mu g/m^3 \))

\( C_{in} \) inlet \( Hg^0 \) concentration (\( \mu g/m^3 \))

\( C_{out} \) outlet \( Hg^0 \) concentration (\( \mu g/m^3 \))

\( C_{out,des} \) real-time outlet \( Hg^0 \) concentration in desorption (\( \mu g/m^3 \))

\( F \) flow rate of the carrier gas in adsorption (mL/min)

\( F_{des} \) flow rate of the carrier gas in desorption (mL/min)

\( m \) adsorbent sample mass (g)

\( m_{AC} \) mass of the packed AC in the reactor tube (\( \mu g \))

\( m_{Hg} \) Hg uptake per gram of AC at 90% breakthrough (\( \mu g/g \))

\( m_{Hg,des} \) Hg desorption amount per gram of AC (\( \mu g/g \))

\( k_{Th} \) Thomas rate constant (L/\( \mu g/min \))

\( k_Y \) Yan rate constant (L/\( \mu g/min \))

\( K_{eq} \) reaction equilibrium constant

\( K_{eq}' \) constant defined in Equation 4

\( p_{H_2O} \) partial pressure of water vapor
\( p_{\text{Hg}^0} \)  partial pressure of Hg\(^0\) vapor

\( P_{O_2} \)  partial pressure of oxygen

\( q_{th} \)  predicted equilibrium uptake (\( \mu g/g \))

\( q_{Y} \)  predicted equilibrium uptake (\( \mu g/g \))

\( q_{exp} \)  Hg\(^0\) uptake in experiments at 90\% breakthrough (\( \mu g/g \))

\( R_a \)  average roughness

\( R_q \)  root mean square roughness

\( R_w \)  surface area ratio

\( t \)  time (min)

\( t_{90\%} \)  time after 90\% breakthrough is completed (min)

\( t_d \)  time after \( C_{out} \) reaches the detection limit (min)

**Greek letters**

\( \theta_{app} \)  apparent WCA

\( \theta_Y \)  Young WCA
Abbreviations

AC               activated carbon
ACF              activated carbon fibers
AFM              atomic force microscopy
BET              Brunauer–Emmett–Teller adsorption theory
DFT              density functional theory
HOPG             highly oriented pyrolytic graphite
MGG              multi-grain graphite
SIAC             sulfur-impregnated activated carbon
SIAC-CSA         concentrated sulfuric acid treated SIAC
SIAC-DSA         diluted sulfuric acid treated SIAC
SSA              specific surface area
SPV              specific pore volume
PSD              pore size distribution
WCA              water contact angle
XPS              X-ray photoelectron spectroscopy
XRD              X-ray diffraction
Preface

I. Composition of the thesis and their connections

This thesis is based on two journal papers ready for submission. Part I investigates the effects of oxygen and sulfuric acid on Hg vapor adsorption by sulfur-impregnated activated carbon (SIAC) under dynamic conditions, and Part II studies the wettability of graphitic carbon and its dependence on crystal structure and surface chemistry.

The two parts of the research are different in subject yet connected. In the course of the first study, as requested by a third party company, received activated carbon (AC) products were treated in a similar manner to the SIAC samples in Part I. The samples were treated to improve the mercury uptake performance in both gaseous and aqueous phases. However, despite the better adsorption performances achieved in flue gases, the results of tests with wastewater were unsatisfactory. It was hypothesized that the poor performance of the treated AC in aqueous phases was due to the blockage of pores by sulfur formed during the treatment and/or the change in the wettability of pore wall and hence the pore accessibility after the treatment. To test this hypothesis, the change in porosity after the treatment was examined with BET and DFT methods, which yield specific surface area (SSA), specific pore volume (SPV) and pore size distribution (PSD). It was found that the treatment with SO₂ had enlarged mesopores, created more micropores and increased SSA of the AC, suggesting that SO₂ treatment didn’t result in pore blockage. These positive results didn’t explain the poor performance of the treated AC in water and led us to the second part of this research – to answer the questions such as what is the intrinsic wettability of graphitic carbon and how does the sulfur treatment affect the wettability
of ACs? Given the graphitic nature of ACs, crystalline graphite was selected as a “base-line” material for the study on wettability. Subsequent literature review (see Chapter 5) revealed substantial discrepancies in the wettability of graphite. The scope of the study was then extended to include both multi-grain graphite (MGG) and highly oriented pyrolytic graphite (HOPG) and to understand the effects of crystal structures, roughness, and surface chemistry on the wettability of graphite.

II. Objectives and hypotheses

This work had six key objectives:

For Part I,

1. Clarify the effect of O\textsubscript{2} on Hg uptake by SIAC and its mechanism;
2. Gain a better understanding of roles of H\textsubscript{2}SO\textsubscript{4} in Hg uptake kinetics under dynamic conditions and associated mechanisms;
3. Quantify the reversibility of Hg adsorption and better understand the roles of physisorption and chemisorption in Hg uptake by SIAC;

For Part II,

1. Determine the effect of crystal orientations on the wettability of graphitic materials, which include the determination of the intrinsic wettability of HOPG’s basal and side surfaces and the estimation of the wettability of MGG;
2. Verify the Wenzel model and understand the effect of roughness on the wettability of graphitic carbons;
3. Investigate the effects of surface chemistry, particularly sulfur and oxygen groups, on the wettability of graphitic carbons.
This study tested three main hypotheses:

1. The enhancing effect of O\textsubscript{2} on Hg uptake can be attributed to the additional contribution of subsequent physisorption of Hg\textsuperscript{0} onto HgO that forms on the AC surface via oxidation;
2. Under dynamic conditions, the interactions of Hg species with H\textsubscript{2}SO\textsubscript{4} are limited by the low concentration of Hg\textsuperscript{0};
3. The effect of roughness can be described by the Wenzel Model, and MGG, like HOPG, is also hydrophilic despite of its difference in crystal orientation.

III. Organization of the thesis

As previously mentioned, this thesis is composed of two separate research papers. Part I is comprised of Chapters 1 to 4, and Part II includes Chapters 5 to 8.

Chapter 1 introduces the motivation of Part I – the discrepancies in the roles of H\textsubscript{2}SO\textsubscript{4} during Hg removal by AC in the literature.

Chapter 2 describes the procedures of preparing samples and the experimental set-up for Hg uptake under dynamic conditions, as well as of the procedures for quantifying physisorption and chemisorption.

Chapter 3 documents and discusses the effects of O\textsubscript{2}, concentrated and diluted H\textsubscript{2}SO\textsubscript{4} on the adsorption of Hg\textsuperscript{0} on the SIAC surfaces. In this chapter, physical and chemical mechanisms of these effects were proposed and the reversibility of Hg adsorption was quantified.

Chapter 4 summarizes the major findings in Part I and recommends future studies.

In Part II, Chapter 5 summarizes the current understanding and discrepancies of the wettability of graphitic materials and proposes the objective of this study.
In Chapter 6, a variety of methods used for sample preparation and treatments, as well as the various characterization techniques used for surface and bulk analyses are introduced. A detailed description of the wettability measurement is also presented.

In Chapter 7, intrinsic water contact angles are reported for HOPG basal and side surfaces and corrected contact angle is estimated for MGG samples. The factors that can alter the surface wettability, including roughness and surface chemistry (contamination, surface oxidation, sulfurization etc.) are also investigated.

Chapter 8 summarizes the main conclusions drawn in Part II and the recommendations for further studies.
PART I

Effects of $O_2$ and $H_2SO_4$ on Hg Vapor Adsorption by Sulfur-Impregnated Activated Carbon under Dynamic Conditions
Chapter 1  Introduction

1.1  Hg and its removal from flue gases

The fossil fuels (primarily coal) burned by power plants are still the largest single source of anthropogenic gaseous mercury (Hg) emissions worldwide [1, 2], and the release of Hg into the environment has caused increased environmental and health concern among the public [3, 4]. To protect human health and the environment from anthropogenic emissions of mercury and its compounds, the Minamata Convention on Mercury initiated by the United Nations Environment Programme (UNEP) has been adopted in October 2013 and is open for signature. The convention includes compulsory and voluntary measures to control or limit supply and trade of mercury, manufacturing and mining processes that use or release mercury compounds etc [5]. Apart from the human factors, the environment also participates in the global transport of mercury in the atmosphere. In a recent study conducted in the Arctic, researchers discovered that the open sea-ice leads induced shallow convection recovers the concentrations of elemental mercury (Hg$^0$) and ozone on the ice, making this a potential source of additional Hg$^0$ and O$_3$ to the atmospheric surface layer and a threat to the Arctic biota [6].

Among the Hg species in flue gases, i.e. elemental mercury (Hg$^0$), oxidized mercury (Hg$^{2+}$), and particulate mercury (Hg$_p$), Hg$^0$ is the most difficult to remove efficiently [7]. While powder activated carbon (AC) injection has been widely considered the leading technology for removing gaseous Hg$^0$, the consensus in the industry has been that sulfur-impregnated activated carbon (SIAC) can greatly enhance mercury uptake from flue gases [7-10].
1.2 Formation of H$_2$SO$_4$ and its effect on Hg removal

Sulfur dioxide (SO$_2$) and sulfur trioxide (SO$_3$) in flue gases can form sulfuric acid (H$_2$SO$_4$) on the AC surfaces in the presence of oxygen (O$_2$), nitrogen dioxide (NO$_2$), and moisture during AC injection [11-13]. XPS analysis by Presto et al. suggested that sulfate is the primary form of sulfur species on AC surfaces when sulfur components are present in flue gases, making H$_2$SO$_4$ an inevitable factor that may affect Hg removal efficiency of AC injection [11]. Both enhancing and hindering effects of H$_2$SO$_4$ on Hg removal from flue gases have been reported in the literature. H$_2$SO$_4$ was impregnated into AC and used to scrub Hg from liquid hydrocarbons [14] and to effectively remove Hg from a stream of nitrogen [15, 16]. H$_2$SO$_4$-impregnated AC has shown Hg$^0$ removal activities in the absence of SO$_2$ [17]. The acid treated AC was also reported to remove mercury from smelter gases [18]. On the other hand, there were reports on the hindering effect of H$_2$SO$_4$ on Hg adsorption, which was often attributed to poisoning of and competition for active sites as well as pore blockage [11, 16, 19]. These discrepancies found in the literature, however, have not been fully understood and require further investigation [17, 20].

More recently, Morris et al. summarized the discrepancies on the effect of H$_2$SO$_4$ (see Table 1.1) [19], and demonstrated that the acid would greatly increase the Hg uptake capacity of AC in the presence of air under static conditions [21]. In Morris’ study, a pool of liquid Hg$^0$ and H$_2$SO$_4$-impregnated commercial AC samples (H$_2$SO$_4$-BPL) were placed in a desiccator which was heated to 100-200°C. H$_2$SO$_4$-impregnated AC samples were withdrawn from the desiccator periodically and analyzed for adsorbed Hg. Hg concentrations in the AC were as high as 500 mg/g after 3 days of exposure to saturated Hg vapor at 200°C. However, these conditions are significantly different from the actual ones in power plants, particularly in Hg vapor
concentrations in flue gases (up to 50 μg/m³ vs. 1.3-102 mg/L, or 1.3×10⁶-1.02×10⁸ μg/m³ under the static condition used in their study). Thus, the mechanism of the interactions between H₂SO₄ and low concentrations of Hg⁰ on the AC surfaces under dynamic conditions is still not completely clear. Understanding the behavior and mechanisms of H₂SO₄-Hg interactions and the availability of active sites after the formation of H₂SO₄ on AC surfaces would help improve the effectiveness and efficiency of Hg removal by AC powder injection in power plants.

**Table 1.1.** Discrepancy on the effect of H₂SO₄ in the available literature [19].

<table>
<thead>
<tr>
<th>Reference</th>
<th>Gas Flow, cm³/min</th>
<th>Fixed Bed Volume, cm³</th>
<th>Empty Bed Residence Time, s</th>
<th>H₂SO₄ (l), vol. %</th>
<th>Effect of H₂SO₄</th>
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</thead>
<tbody>
<tr>
<td>Olson et al.</td>
<td>3780</td>
<td>200</td>
<td>0.06</td>
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<td>Yue et al.</td>
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<td>0.8-1.6</td>
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</tr>
<tr>
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<td>Uddine et al.</td>
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<td>0.2</td>
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<td>Mibeck at al.</td>
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<td>0.003</td>
<td>N/A</td>
<td>Negative</td>
</tr>
</tbody>
</table>

**1.3 Objective of this study**

The objective of this work was to better understand the effect of the presence of H₂SO₄ on Hg adsorption by SIAC under dynamic conditions. Hg adsorption experiments were conducted with
low-concentration Hg\textsuperscript{0} (~ 25 μg/m\textsuperscript{3}) in nitrogen (N\textsubscript{2}) or air, using a semi-continuous flow fixed-bed reactor kept at 120 or 180 °C. The low-concentration Hg\textsuperscript{0} and the dynamic conditions used in this study are a better representation of the actual Hg\textsuperscript{0} capture conditions in coal-fired utilities. The work focused on Hg adsorption capacity, reversibility and mechanisms.
Chapter 2 Materials and Methods

2.1 Sample preparation

2.1.1 Sulfur Impregnated Activated Carbon - SIAC

All the samples were chemically modified from petroleum fluid coke, a carbon by-product of the bitumen upgrading process in the oil sands industry in Alberta, Canada. Raw petroleum fluid coke samples are black solid particles with various particle sizes, as shown in Figure 2.1. Fluid coke samples were first crushed and sieved to 53-106 μm, and then pre-oxidized with air at 200°C overnight at high temperatures. The samples were then activated in a fixed-bed system by exposure to a flow of 50% SO₂ in N₂ at 700°C for 5h to impregnate sulfur and increase the porosity [22]. Readers are referred to Appendix A for details of the apparatus setup and treatment procedures. The activated product was designated as sulfur impregnated activated carbon (SIAC).

Figure 2.1. Raw petroleum fluid coke.

2.1.2 Samples treated with concentrated H₂SO₄ (SIAC-CSA)

SIAC-CSA samples were made by exposing SIAC to H₂SO₄ vapor in a closed desiccator at high temperature. First, approximately 0.2 g dried SIAC sample was uniformly placed on a clean and
dry watch glass: using such a small amount of carbon is to make sure that the sample forms a layer which is thin enough to have full contact with H$_2$SO$_4$ vapor from top to bottom. At the same time, about 10 g of concentrated H$_2$SO$_4$ solution (98 wt%) was placed in a crucible. Next, the watch glass and the crucible were placed and sealed into a desiccator (with desiccant). The desiccator was then put into a muffle furnace at 200°C to maintain a high vapor pressure of H$_2$SO$_4$. The samples were extracted after 3, 4, and 12 h of H$_2$SO$_4$ contact. The mass increases of the samples after acid vapor treatment were measured and the H$_2$SO$_4$/SIAC mass ratios in percentage were calculated. A series of the SIAC-CSA samples impregnated with different amounts of H$_2$SO$_4$ were therefore obtained: SIAC-CSA-14%, SIAC-CSA-20%, and SIAC-CSA-30%.

2.1.3 **Samples treated with diluted H$_2$SO$_4$ (SIAC-DSA)**

SIAC-DSA samples were prepared to simulate the condition under which the H$_2$SO$_4$ formed becomes diluted due to the moisture in flue gases. 1 g of the SIAC sample was weighed and placed in a beaker. At the same time, different amounts of 20 wt% H$_2$SO$_4$ was used to prepare SIAC-DSA with 5, 10, 15 and 20 wt% of acid. For example, the sample with 5 wt% acid was obtained by adding approximately 0.25 g 20 wt% H$_2$SO$_4$ solution into 1 g of SIAC. To keep the solid/liquid ratio constant, the acid was further diluted with deionized water to 1 mL before it was added to the solid SIAC. The acid-SIAC mixture was stirred quickly with a glass rod for 15 minutes. The slurry was placed in an oven at 100°C overnight first and a muffle furnace at 200°C for 2 hours to reduce water content. A series of the SIAC-DSA samples were therefore obtained: SIAC-DSA-5%, SIAC-DSA-10%, SIAC-DSA-15%, and SIAC-DSA-20%, where the value of % is weight percentage of H$_2$SO$_4$ in SIAC on a dry basis. It should be pointed out that removing
water from diluted H\textsubscript{2}SO\textsubscript{4} is extremely difficult. Consequently, theses samples were just partially dried after discharged from the muffle furnace.

### 2.2 Hg adsorption and desorption experiments

#### 2.2.1 Experimental setup

![Schematic diagram of the semi-continuous flow fixed-bed reaction system](image)

**Figure 2.2.** Schematic diagram of the semi-continuous flow fixed-bed reaction system. Legend:
1. Gas cylinders; 2. Three-way stopcock; 3. Mass flow controllers; 4. Oil bath for the Hg\textsuperscript{0} generation device (in U-tube); 5. Pressure gauge; 6. Inlet Hg\textsuperscript{0} sampling port; 7. Fixed-bed reactor; 8. SIAC sample; 9. Pyrex glass reaction tube; 10. Outlet Hg\textsuperscript{0} sampling port; 11. Hg\textsuperscript{0} scrubbing solution; 12. Mercury analyzer; 13. Computer.

The Hg adsorption experiments were conducted in a semi-continuous flow fixed-bed reaction system, shown in Figure 2.2. Hg\textsuperscript{0} vapor was generated from a Hg\textsuperscript{0} permeation device (VICI Metronics Inc., USA). Secured in a U-tube within an oil bath, the device supplied a constant amount of Hg\textsuperscript{0} vapor per unit time at a given temperature. Either nitrogen or air at 300 mL/min worked as a carrier gas and then carried the Hg\textsuperscript{0} vapor to the Pyrex glass reaction tube, which is
packed with a known quantity of original or treated SIAC. The working temperature was maintained at 120°C, which is consistent with the temperature in coal-fired flue gases. The inlet and outlet Hg$^0$ vapor concentrations (\(C_{in}\) and \(C_{out}\)) of the tube furnace were then sampled from the sampling ports (6 and 10) and measured with the 2600 CVAFS Mercury Analysis System (Tekran, USA). At last, the Hg$^0$ vapor concentration data was collected and analyzed by the vendor software.

### 2.2.2 Hg adsorption and desorption calculations

A breakthrough curve is typically used to quantify the adsorption process in terms of equilibrium uptake and kinetics, which can be obtained by plotting \(C_{out}\) versus time. A typical breakthrough curve is shown in Figure 2.3. The amount of Hg uptake per unit mass is calculated by integrating

![Figure 2.3. A typical mercury adsorption breakthrough curve.](image)

the area between the \(C_{in}\) line and the \(C_{out}\) breakthrough curve along the time axis and then following Equation 2.1,
\[ m_{Hg} = \frac{t_{90\%}}{m_{AC}} \int_0^{t_{90\%}} (C_{in} - C_{out}) \times dt \times F \]  

(2.1)

where \( m_{Hg} \) (\( \mu g/g \)) is the Hg uptake per gram of AC at 90% breakthrough (\( C_{out}/C_{in} \times 100\% = 90\% \)), \( t_{90\%} \) (min) is the time when 90% breakthrough is obtained, \( C_{in} \) (\( \mu g/m^3 \)) is the average inlet mercury concentration, \( C_{out} \) (\( \mu g/m^3 \)) is the real-time outlet Hg concentration, \( F \) (mL/min) is the flow rate of the carrier gas, and \( m_{AC} \) (\( \mu g \)) is the mass of the packed AC in the reactor tube.

To investigate the contributions of physisorption and chemisorption and further understand the adsorption behavior and mechanisms, desorption experiments were also conducted once the adsorption experiments were assumed to be completed (>90% breakthrough). Pure \( N_2 \) (200 mL/min) was introduced into the fixed bed reactor at 120°C, and \( C_{out} \) was analyzed and plotted versus time. A typical desorption curve is shown in Figure 2.4. The area below the desorption

![Figure 2.4. A typical mercury desorption concentration curve.](image-url)
concentration curve was integrated along the time axis, and Equation 2.2 was used to determine the amount of Hg desorbed from a unit amount of SIAC.

\[
m_{\text{Hg,des}} = \frac{t_d}{m_{\text{AC}}} \int_0^{t_d} C_{\text{out,des}} \, dt \times F_{\text{des}}
\]

(2.2)

where \( m_{\text{Hg,des}} \) (μg/g) is the Hg desorption amount per gram of AC, \( t_d \) (min) is the time when \( C_{\text{out,des}} \) reaches the detection limit (about 0.5 μg/m\(^3\)), \( C_{\text{out,des}} \) (μg/m\(^3\)) is the real-time outlet mercury concentration in desorption, \( F_{\text{des}} \) (mL/min) is the flow rate of the carrier gas in desorption, and \( m_{\text{AC}} \) (μg) is the mass of the packed AC in the reactor tube.

Given that chemically adsorbed Hg\(^0\) is bound to the heteroatoms on the SIAC surface, it is assumed that chemisorption is not reversible under the tested condition. Please note that the term “chemisorption” may refer to not only chemical adsorption but also the potential chemical absorption for H\(_2\)SO\(_4\) impregnated SIAC samples. The contribution of the absorption process will be discussed in detail in Section 3.2.3. The desorbed Hg, on the other hand, is attributed to physisorption, which is reversible and governed by the partitioning law. This law describes the equilibrium concentrations of a compound in two different phases at a given temperature, and in this case, it leads to Hg\(^0\) desorption into the nitrogen gas phase until the depletion of physically adsorbed Hg\(^0\) on the SIAC surface.
2.3 Analytical methods and data quality

2.3.1 Hg\(^0\) vapor concentration

The Hg\(^0\) vapor generated from the permeation tube remains in a constant concentration at a given temperature. Due to the nonlinear correlation between the temperature and the concentration, the oil bath is always kept at the same temperature (±0.5°C) unless needed for higher or lower Hg\(^0\) concentrations. At the same time, the mercury analyzer was maintained regularly and calibrated every time before use. Readers are referred to Appendix B for details in the calibration method. In general, the mercury analyzer can measure the Hg\(^0\) concentration with an accuracy of ±3%.

In most cases, Hg inlet concentration \(C_{in}\) was kept at around 25 μg/m\(^3\) and the adsorption experiments were terminated at around 90% breakthrough. To fairly compare the results of different samples, \(C_{in} = 25 \ \text{μg/m}^3\) and 90% breakthrough were thus set as a benchmark for the data that need slight adjustment. Ho et al. proposed that Henry’s Law applies to Hg adsorption isotherm when \(C_{in}\) is extremely low (<500 μg/m\(^3\)) [23], thus when \(C_{in}\) slightly deviated from 25 μg/m\(^3\), the linear approach of Henry’s law was applied to estimate the equivalent mercury uptake at the same level of \(C_{in}\) (25 μg/m\(^3\)) and completion (90%).

2.3.2 Sulfur in SIAC

The sulfur and other elemental compositions in SIAC and raw petroleum coke were determined by the EAI CE-440 Elemental Analyzer (Exeter Analytical Inc., UK) and shown in Table 2.1. It is seen from the table that the sulfur content is doubled for SIAC compared with that of the raw
coke, while the carbon content decreases by almost 30%, indicating that SIAC is well activated and containing sufficient amount of sulfur.

Table 2.1. Elemental compositions of the raw petroleum coke and SIAC.

<table>
<thead>
<tr>
<th>Samples</th>
<th>C%</th>
<th>S%</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Petroleum Coke</td>
<td>81.0 ± 0.7</td>
<td>7.1 ± 0.3</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>SIAC</td>
<td>51.9 ± 2.9</td>
<td>15.9 ± 0.5</td>
<td>1.8 ± 0.2</td>
</tr>
</tbody>
</table>

2.3.3 Porosity of SIAC

To quantify the porosity of SIAC samples, specific surface area (SSA) and specific pore volume (SPV) were measured by N₂ adsorption at 77 K using a Quantachrome Autosorb-1-C. The BET (Brunauer–Emmett–Teller) method was applied to calculate SSA and SPV, and the results were shown in Table 2.2. It is observed from the table that SO₂ activation significantly increased the porosity of the raw coke, creating huge surface area and pore volume inside the coke samples from the negligible level. This makes the SIAC a sulfur-containing sorbent ready for mercury uptake.

Table 2.2. The porosity (SSA and SPV) of raw petroleum coke and SIAC.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Size (μm)</th>
<th>SSA (m²/g)</th>
<th>SPV (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Petroleum Coke</td>
<td>212-300</td>
<td>7.5 [24]</td>
<td>Negligible</td>
</tr>
<tr>
<td>SIAC</td>
<td>53-106</td>
<td>440</td>
<td>0.303</td>
</tr>
</tbody>
</table>
Chapter 3  Results and Discussions

3.1  Effect of oxygen on Hg$^0$ uptake capacity

To investigate the effect of oxygen on Hg$^0$ uptake by the untreated SIAC, the fixed-bed adsorption/desorption experiments were first conducted under nitrogen and then under air. The amounts of total uptake, physisorption, and chemisorption for both cases are listed in Table 3.1.

Table 3.1. Comparisons of overall Hg uptake, physisorption, and chemisorption amounts for virgin SIAC in nitrogen and air.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Overall Hg Uptake (μg/g)</th>
<th>Physisorption (μg/g)</th>
<th>Chemisorption (μg/g)</th>
<th>Physisorption in Percentage (%)</th>
<th>Chemisorption in Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIAC-N$_2$</td>
<td>220</td>
<td>40</td>
<td>180</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>SIAC-air</td>
<td>5200</td>
<td>2700</td>
<td>2500</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

For virgin SIAC, it is apparent from the table that replacing nitrogen with air resulted in a substantial increase in Hg removal from 220 μg/g to 5200 μg/g, indicating that oxygen greatly enhances Hg uptake. The enhanced Hg adsorption by oxygen in air is expected, as oxygen oxidizes Hg$^0$ and the oxidized Hg is more susceptible to chemisorption by combining with heteroatoms on carbon surface. The formation of HgO/Hg$_2$O on carbon surfaces in the presence of oxygen has been reported in the literature [7, 25]. Under nitrogen, Hg adsorption on SIAC is largely chemical in nature (81%). This is expected because SIAC is a carbon product activated with SO$_2$ at high temperature, thus sulfur groups can form on the carbon surfaces and enhance
mercury uptake by chemically combining with oxidized Hg. Sulfur groups in SIAC have been found to be thiophene and other carbon-sulfur complexes, as reported by Morris et al. [26]. Moreover, it is interesting that the presence of oxygen has enhanced physisorption to a significantly greater extent. Under air, chemisorption and physisorption contributes almost equally (2500 μg/g and 2700 μg/g) to Hg uptake. The much enhanced physisorption suggests that carbon surface sites in air might be different from those in nitrogen; the products of chemisorption alter the surface chemistry of carbon and have made the surface more ready for Hg physisorption. Given the fact that both HgO and HgS are stable below 500°C [25, 27], it seems logical to suggest that, at 120°C or 180°C, the products of chemisorption (e.g. HgO etc.) on the carbon surface can provide physisorption sites that are more active than carbon and sulfur in the SIAC. Pitoniak et al. conducted a study on Hg vapor removal by silica-titania nanocomposites and reported that Hg⁰ is more attracted to HgO than to a silica surface [27]. Being a heavy atom, Hg on carbon surface would induce a greater London dispersion force. The orders of magnitude increase in Hg physisorption is thus attributed to the change in surface chemistry resulting from the formation of mercuric compounds via chemisorption – the compounds have a greater physical affinity towards Hg⁰. Consequently, the enhancement of physisorption would be determined by the quantity of chemically adsorbed mercury. The fact that there were approximately equal amounts of physisorption and chemisorption for SIAC in air seems to suggest a one-to-one ratio between the chemically-bonded Hg and the physically-bonded Hg. The proposed mechanism of the entire process is illustrated in Figure 3.1.

In the absence of oxygen, i.e. under the condition of flowing nitrogen, Hg⁰ is either physically adsorbed onto the carbon surface by Route 1 or chemically adsorbed by the sulfur functional groups by Route 2. It has been reported that the carbon-oxygen groups on carbon has no effect
on Hg uptake by SIAC [7, 21]. In this case, Route 2 dominates the adsorption, as shown in Table 1. However, considering the large amount of sulfur in the SIAC and the small amount of chemically adsorbed Hg without oxygen, the ability of sulfur as an electron accepter to chemically capture Hg$^0$ seems rather limited.

![Figure 3.1. Illustrative diagram of proposed mechanism of Hg adsorption on SIAC surfaces in with and without the presence of oxygen.](image)

In the presence of oxygen, i.e. under the condition of flowing air, oxygen molecules, atoms, or radicals, shown as O* in Figure 2, can readily get adsorbed onto carbon surfaces by Route 3, and some of the Hg$^0$ atoms on or close to AC surfaces are oxidized by the adsorbed oxygen by Route 4. Route 4 is preferable as the reaction is catalyzed by the carbon surfaces. Once it is oxidized, mercuric ions are more readily bound to sulfur via Hg-S bond, while some will bind to oxygen forming HgO. Afterwards, additional Hg$^0$ atoms are adsorbed onto the HgS or HgO molecule by Route 5, driven by the London dispersion force, which is much stronger than that between Hg and carbon or oxygen or sulfur. The remaining Hg$^0$ atoms, which are believed to be the minority compared to the Hg$^0$ adsorbed via the previous path, are physically and chemically adsorbed on the surfaces by 1 and 2 directly. This is similar to what occurs without oxygen. During the
desorption process, Hg\textsuperscript{0} is desorbed either by Route 6, the desorption of free Hg\textsuperscript{0} adsorbed on the carbon surfaces, or Route 7, the desorption of Hg\textsuperscript{0} physically attached on HgS and/or HgO. From Table 1, it can be indicated that most of the Hg\textsuperscript{0} desorbed by purging flowing nitrogen comes from the latter. It is therefore concluded that O\textsubscript{2} is the main electron accepter and the oxidation of Hg\textsuperscript{0} is critical to chemisorption, and physisorption of Hg\textsuperscript{0} is enhanced by chemisorption due to the greater affinity of Hg\textsuperscript{0} to HgO and/or HgS.

3.2 Effect of H\textsubscript{2}SO\textsubscript{4} on Hg\textsuperscript{0} uptake capacity

3.2.1 Effect of concentrated H\textsubscript{2}SO\textsubscript{4}

Fixed-bed adsorption/desorption experiments under air and nitrogen were also carried out for SIAC-CSA series samples. As shown in Figure 3.2, impregnating concentrated H\textsubscript{2}SO\textsubscript{4} into the SIAC significantly decreased the Hg uptake capacity by orders of magnitude under air, and Hg uptake was negligible in samples impregnated with more than 14 wt% of H\textsubscript{2}SO\textsubscript{4}. A similar trend was observed under N\textsubscript{2} when comparing the Hg adsorption amount of SIAC-CSA-14% with the virgin SIAC. The hindering effect of the concentrated H\textsubscript{2}SO\textsubscript{4} is attributed to pore blockage which reduces the total available pore volume and surface area of the SIAC samples. Pore blockage by H\textsubscript{2}SO\textsubscript{4} has been confirmed by porosity measurements, and is consistent with a recent study by Yao et al., who pretreated activated carbon fibers (ACF) with concentrated H\textsubscript{2}SO\textsubscript{4} first and sodium tetrasulfide (Na\textsubscript{2}S\textsubscript{4}) afterwards. Compared to the Na\textsubscript{2}S\textsubscript{4} treated ACF samples, the specific surface area and pore volume of H\textsubscript{2}SO\textsubscript{4}-Na\textsubscript{2}S\textsubscript{4} treated ACF samples decreased by 57% and 53%, respectively [28]. As a result of pore blockage, the intraparticle diffusion of Hg\textsuperscript{0} vapor into the inner pores is hindered, so is the adsorption capacity.
Figure 3.2. Effect of concentrated H$_2$SO$_4$ on Hg uptake for SIAC under N$_2$ (black) and air (gray).

As shown in Figure 3.3 in the presence of oxygen, about a half of the adsorbed Hg on SIAC was due to physisorption and reversible. After impregnation with H$_2$SO$_4$, however, the adsorption became less reversible, suggesting that physisorption may be more sensitive to the pore blockage.

Figure 3.3. Amount of physisorption (black), chemisorption/chemical absorption (dark gray), and total uptake (light gray) for the virgin SIAC and the concentrated acid treated SIAC under air.
3.2.2 Effect of H$_2$SO$_4$ dilution

Given the strong affinity of concentrated H$_2$SO$_4$ to water, moisture in flue gases would be absorbed by the acid and lower its concentration. The SIAC-DSA series samples were prepared to study the effect of dilution that may occur due to the presence of moisture. As shown in Figure 3.4, similar to the cases with concentrated acid, the Hg uptake capacity of SIAC-DSA in air declined as more diluted H$_2$SO$_4$ was added into the SIAC. The Hg removal performance in N$_2$ remains very poor and the uptake amount becomes negligible when 10 wt% or more acid is impregnated into the samples. In addition, it can be seen from the figure that the advantage of air over N$_2$ in Hg capture disappears when 15 wt% or more H$_2$SO$_4$ is impregnated, suggesting a complete pore blockage and the inability of dilute H$_2$SO$_4$ in absorbing Hg.

![Figure 3.4](image)

**Figure 3.4.** Effect of diluted H$_2$SO$_4$ on Hg uptake for SIAC under conditions of N$_2$ (black) and air (gray).

From the analysis above, it is clear that pore blockage caused by H$_2$SO$_4$ treatment also hinders the performance of SIAC-DSA. Moreover, if compared with concentrated acid, the same amount
acid in dilute form hindered the performance of SIAC more and resulted in even less Hg removed. This result is expected since dilution increases the volume of acid and hence the extent of pore blockage. To further verify this dilution effect, a subsequent experiment was conducted by placing one of the SIAC-DSA samples, SIAC-DSA-5\%, into a desiccator for 180 days, and then repeated the Hg adsorption experiment with the same approach. Hg uptake capacity was almost doubled (to 2600 μg/g from 1300 μg/g) after sufficient amount of moisture was removed from the carbon and the acid became concentrated.

### 3.2.3 Limitations of Hg-H₂SO₄ interactions on the SIAC surface

The observed hindering effect of concentrated and diluted H₂SO₄ on Hg uptake is completely different from the enhancing effect reported by Morris et al. [21], who suggested that H₂SO₄ impregnated in AC substantially increased Hg uptake capacity by absorption particularly in the presence of oxygen. An uptake capacity of 500 mg-Hg/g-AC was reported, which was attributed to the dissolution of Hg in H₂SO₄. The following section addresses this apparent discrepancy.

With the presence of oxygen and an ample supply of H₂SO₄, the following reaction is thermodynamically feasible.

\[
\text{Hg} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{HgSO}_4 + \text{H}_2\text{O} \quad G^0(120 \degree \text{C}) = -177.4 \text{ kJ} \tag{3.1}
\]

Its reaction equilibrium constant, \( K_{eq} \), can be expressed as,

\[
K_{eq} = \frac{a_{\text{HgSO}_4} \times p_{\text{H}_2\text{O}}}{p_{\text{Hg}}^{\frac{1}{2}} \times p_{\text{O}_2} \times a_{\text{H}_2\text{SO}_4}} \tag{3.2}
\]
where \( a_{\text{HgSO}_4} \) is the activity of \( \text{HgSO}_4 \) in \( \text{H}_2\text{SO}_4 \), \( P_{\text{H}_2\text{O}} \) is the partial pressure of water vapor, \( p_{\text{Hg}^0} \) is the partial pressure of \( \text{Hg}^0 \) vapor, \( P_{\text{O}_2} \) is the partial pressure of oxygen, and \( a_{\text{H}_2\text{SO}_4} \) is the activity of \( \text{H}_2\text{SO}_4 \).

Rearranging Equation 3.2 results in Equation 3.3, which can be simplified by assuming the partial pressure of oxygen and the activity of \( \text{H}_2\text{SO}_4 \) within the pores remain unchanged during the reaction,

\[
a_{\text{HgSO}_4} = K_{eq} \frac{p_{\text{Hg}^0}^{1/2}p_{\text{H}_2\text{O}}a_{\text{H}_2\text{SO}_4}}{p_{\text{H}_2\text{O}}} = K_{eq} \frac{p_{\text{Hg}^0}}{p_{\text{H}_2\text{O}}}
\]

(3.3)

It can be seen from Equation 3.3 that \( a_{\text{HgSO}_4} \) is proportional to \( p_{\text{Hg}^0} \) when the reaction is in equilibrium. If Hg uptake is dominated by absorption (or dissolution) rather than adsorption, the Hg uptake capacity is proportional to the partial pressure of \( \text{Hg}^0 \) in the system.

The static experiments were carried out by Morris et al. at 100 to 200 °C with a large pool of liquid Hg; in their closed system, the equilibrium Hg vapor concentration was 1.3 to 102 g-Hg/m³-air. This work however was conducted under a dynamic condition with a constant inflow of gas carrying only 25 μg-Hg/m³-air. The \( p_{\text{Hg}^0} \) in the semi-continuous flow system was therefore 5×10⁴ to 4×10⁶ times lower than that in the closed system used by Morris et al. This difference in \( p_{\text{Hg}^0} \) thus significantly limits the chemical absorption in this study. In other words, Hg absorption in \( \text{H}_2\text{SO}_4 \) may be negligible when Hg vapor concentration in the gas phase is at the level of power plant flue gases. Compared to the 500 mg Hg/g-AC reported by Morris et al., the chemically absorbed Hg would be less than 0.01 mg/g-AC using the concentration ratio 5×10⁴.
excluding chemical absorption as the dominant reaction mechanism for the H₂SO₄ treated samples. The only possible chemisorption mechanism still remains as the Hg-O* and Hg-S* reactions on the surface.

**Figure 3.5.** Amount of physisorption (black), chemisorption (dark gray), and total uptake (light gray) for SIAC-CSA-14% under the conditions of N₂ at 120°C, air at 120°C, and air at 180°C.

To further verify this possibility, SIAC-CSA-14% was tested under the dynamic condition of air at 180°C, and the results were compared with those at 120°C, as shown in Figure 3.5. It’s apparent that at a higher temperature (180°C), the chemisorption of SIAC-CSA-14% is greatly inhibited (decreasing by ~1000 μg/g, or 88%) compared to the result at 120°C, suggesting that the chemisorption reactions are exothermic. Therefore, this experiment supported the feasibility of Hg-O* and Hg-S* interactions as the dominant reaction mechanism even in the presence of H₂SO₄. On the other hand, an increase in physisorption suggests that more physisorption sites might be available at higher temperatures because of reduced pore blockage – less moisture
would be present at 180°C and the blocking volume would be decreased, for example. Without further study, this remains as a hypothesis.

### 3.3 Hg adsorption isotherms and reversibility

It is assumed that under the conditions in this study (up to 180 °C) physisorption is reversible while chemisorption is irreversible. Reversibility of Hg uptake is then determined by the relative contribution of physisorption and chemisorption. In coal-fired power plants, the Hg\(^0\) concentration in the flue gases can vary from time to time. Reversibility of Hg\(^0\) uptake would change with Hg\(^0\) concentrations. Indeed, one of the most important aspects of AC performance is the contributions of physisorption and chemisorption and their dependence on Hg\(^0\) inlet concentration, \(C_{in}\). They can also be investigated by varying \(C_{in}\) while keeping the sample, mass, carrier gas, and flow rate unchanged. In this study, SIAC-DSA-5% was selected and successively tested under the conditions of \(C_{in} = 23, 67,\) and 115 μg/m\(^3\). The total uptake was calculated after the completion of each breakthrough and a follow-up desorption experiment was conducted to obtain the amount of physisorption and chemisorption.

The change in the total Hg\(^0\) adsorption, physisorption, and chemisorption with \(C_{in}\) is plotted in Figure 3.6. According to the literature, physisorption obeys Henry’s law when \(C_{in}\) is below 500 μg/m\(^3\) [23]. In this case, the mercury uptake on the solid phase is proportional to the Hg\(^0\) concentration in the vapor phase. As a result, the physisorption isotherm follows a straight line through the origin, which is consistent with the physisorption behavior shown in the figure. On the other hand, due to the constant number of chemical active sites, the chemisorption isotherm would be a horizontal line if sufficient time were allowed for adsorption saturation. The
deviation of chemisorption at 23 μg/m³ from the trend line seems to suggest unsaturated chemisorption sites at low Hg⁰ concentrations. Figure 3.6 suggests that physisorption can dominate Hg uptake at high \( C_{in} \), while chemisorption becomes the main mechanism when \( C_{in} \) is low. The results supported our assumption in terms of the reversibility of physisorption and chemisorption, both of which follow certain yet different adsorption and desorption laws.

**Figure 3.6.** Relative contributions of physisorption and chemisorption and their dependence on Hg inlet concentrations for SIAC-DSA-5%. Physisorption, chemisorption, and total uptake are plotted in ■, ◇, and △, respectively.

### 3.4 Hg adsorption models

For a fixed-bed adsorption system, a complete breakthrough curve is required to determine Hg adsorption capacity for a given inlet concentration of Hg. Theoretically, for a given temperature and a given dimension of the bed, the breakthrough curve is fundamentally determined by the kinetics and uptake capacity which are the functions of the adsorbent and the adsorbate. It is
theoretically possible to simulate the breakthrough process based on fundamental mass transport and equilibrium adsorption equations. In practice, however, many assumptions had to be made; simplified models were developed and employed to predict the breakthrough curve due to the complexity associated with real systems.

The Thomas model is one of the most widely used methods in fixed bed performance prediction. It applies the Langmuir kinetics of adsorption and desorption and assumes that the rate-limiting step is a second order reversible process. The Thomas model is therefore suitable for the situation where the controlling step of adsorption is a chemical reaction. The prediction can deviate from the experiments when the adsorption process is limited by other factors such as external or internal mass transfer. The model can be described by the following form:

\[
\frac{C}{C_{in}} = \frac{1}{1 + \exp(k_{th} \left( \frac{q_{th} m}{F} \right) C_{in} t)}
\]

(3.4)

where \( k_{th} \) is the Thomas rate constant (L/μg/min), \( q_{th} \) is the predicted maximum uptake (μg/g), \( m \) is the adsorbent sample mass (g), and \( F \) is the carrier gas flow rate (m³/min) [29, 30].

The Thomas Model often fails in predicting the early part of a breakthrough curve and overestimates the concentration at time zero and the breakthrough time. Yan et al. proposed an empirical model to overcome this drawback and reported a better description of heavy metal removal from a biosorption column by using this model. The equation is expressed as follows,

\[
\frac{C}{C_{in}} = 1 - \frac{1}{1 + \left( \frac{F^2 t}{k_q q_f m} \right)^{k_{th} C_{in} / F}}
\]

(3.5)
where $k_Y$ is the Yan rate constant (L/μg/min), $q_Y$ is the predicted maximum uptake (μg/g), $m$ is the adsorbent sample mass (g), and $F$ is the carrier gas flow rate (m$^3$/min) [31].

In this study, the Thomas and the Yan models were used to fit the experimental breakthrough curves obtained for all the SIAC samples in the presence of oxygen. The model fitting was carried out using ORIGIN via nonlinear regression – keeping the parameters $C_{in}$, $m$, and $F$ fixed at their experiment values and solving for rate and capacity parameters, $k$ and $q$. The results are shown below in Table 3.2 and Table 3.3 for the Thomas and the Yan models, respectively.

**Table 3.2.** Predicted parameters and standard deviations of the Thomas model for Hg adsorption by untreated and H$_2$SO$_4$-treated SIAC samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$k_{Th}$ (L/μg/min)</th>
<th>$q_{Th}$ (μg/g)</th>
<th>$q_{exp}$ (μg/g)</th>
<th>$q_{Th}/q_{exp}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIAC-air</td>
<td>4.43</td>
<td>5218</td>
<td>5200</td>
<td>0.996</td>
<td>0.972</td>
</tr>
<tr>
<td>SIAC-DSA-5%-air</td>
<td>21.70</td>
<td>1106</td>
<td>1200</td>
<td>0.910</td>
<td>0.975</td>
</tr>
<tr>
<td>SIAC-DSA-10%-air</td>
<td>154.78</td>
<td>32</td>
<td>60</td>
<td>0.582</td>
<td>0.986</td>
</tr>
<tr>
<td>SIAC-DSA-15%-air</td>
<td>337.61</td>
<td>-4</td>
<td>20</td>
<td>-</td>
<td>0.946</td>
</tr>
<tr>
<td>SIAC-DSA-20%-air</td>
<td>390.09</td>
<td>-9</td>
<td>10</td>
<td>-</td>
<td>0.808</td>
</tr>
<tr>
<td>SIAC-CSA-14%-air</td>
<td>9.56</td>
<td>987</td>
<td>1300</td>
<td>0.738</td>
<td>0.879</td>
</tr>
<tr>
<td>SIAC-CSA-20%-air</td>
<td>126.38</td>
<td>15</td>
<td>70</td>
<td>0.208</td>
<td>0.936</td>
</tr>
<tr>
<td>SIAC-CSA-30%-air</td>
<td>253.60</td>
<td>8</td>
<td>60</td>
<td>0.125</td>
<td>0.772</td>
</tr>
</tbody>
</table>
Table 3.3. Predicted parameters and standard errors of the Yan model for Hg adsorption by untreated and H$_2$SO$_4$-treated SIAC samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$k_Y$ (L/μg/min)</th>
<th>$q_Y$ (μg/g)</th>
<th>$q_{exp}$ (μg/g)</th>
<th>$q_{Th}/q_{exp}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIAC-air</td>
<td>20.85</td>
<td>2590</td>
<td>5200</td>
<td>0.494</td>
<td>0.961</td>
</tr>
<tr>
<td>SIAC-DSA-5%-air</td>
<td>23.03</td>
<td>541</td>
<td>1200</td>
<td>0.445</td>
<td>0.971</td>
</tr>
<tr>
<td>SIAC-DSA-10%-air</td>
<td>5.82</td>
<td>31</td>
<td>60</td>
<td>0.564</td>
<td>0.787</td>
</tr>
<tr>
<td>SIAC-DSA-15%-air</td>
<td>5.78</td>
<td>4</td>
<td>20</td>
<td>0.211</td>
<td>0.910</td>
</tr>
<tr>
<td>SIAC-DSA-20%-air</td>
<td>5.25</td>
<td>2</td>
<td>10</td>
<td>0.143</td>
<td>0.932</td>
</tr>
<tr>
<td>SIAC-CSA-14%-air</td>
<td>5.64</td>
<td>676</td>
<td>1300</td>
<td>0.505</td>
<td>0.936</td>
</tr>
<tr>
<td>SIAC-CSA-20%-air</td>
<td>4.85</td>
<td>16</td>
<td>70</td>
<td>0.222</td>
<td>0.827</td>
</tr>
<tr>
<td>SIAC-CSA-30%-air</td>
<td>6.27</td>
<td>6</td>
<td>60</td>
<td>0.094</td>
<td>0.876</td>
</tr>
</tbody>
</table>

From Table 3.2 it is apparent that the Thomas model successfully predicted the adsorption capacity for samples that have a greater capacity such as SIAC, SIAC-DSA-5% and SIAC-CSA-14%, but tends to fail when the capacity of the samples decreases, as we can see from the underestimated and even negative values for some samples. The failure of capacity prediction occurs when more acid is impregnated into the samples and the capacity decreases greatly due to pore blockage. The Thomas model assumes that the adsorption process is limited by chemical reaction kinetics, thus it may become less applicable when intra-particle diffusion becomes the rate-limiting due to the pore blockage by acid. It is also observed from Table 3.2 that the rate coefficient $k_{Th}$ increases greatly as more diluted or concentrated H$_2$SO$_4$ is added to the samples.
As a result of pore blockage, most of the deeper sites may not be available any more; and, the remaining available sites are easily accessible to Hg. Hence, the rate coefficient $k_{Th}$ increased with pore blockage.

Judging by the value of $R^2$ (0.77-0.99), the untreated SIAC data fit the Thomas model better, which is reasonable since chemisorption dominates Hg adsorption on the raw SIAC. As noted by other researchers, the model prediction for the earlier stage of the curve was worse for all the samples.

Different from the Thomas model, the Yan model, however, tends to predict more poorly for the later stage of the breakthrough curves. The Yan model significantly underestimates the adsorption capacity for all the samples and the predicted values are only half or even less than half of the experimental values (see Table 3.3). However, the uncertainties of the predicted values are generally smaller than that of the Thomas model and no negative values are falsely obtained. As more acid is added into the samples, no significant correlation is found between the rate coefficient $k_Y$ and the experimental capacity or the acid impregnation amount, as determined by the empirical characteristic of the model [31] and confirmed in the literature [32, 33]. Judging by the value of $R^2$ (0.79-0.97), the Yan’s model’s overall performance seems similar to that of the Thomas model. Clearly, none of the simplified models are ideal for simulating Hg adsorption by SIAC with and without acid impregnation and more sophisticated models are needed. However, the Thomas model seems a more suitable choice.
Chapter 4  Conclusions and recommendations

4.1  Conclusions of Part I

1. The presence of oxygen significantly enhanced Hg adsorption onto SIAC. The enhancement was probably due to the oxidation of Hg\(^0\) that facilitates chemisorption and the subsequent physisorption of Hg\(^0\) onto the chemically adsorbed Hg;

2. Impregnated H\(_2\)SO\(_4\) blocked pores and masked adsorption sites in SIAC and hindered both chemisorption and physisorption. The dilution of H\(_2\)SO\(_4\) further reduced the Hg uptake capacity of SIAC due to the increase in volume of H\(_2\)SO\(_4\) and associated pore blockage.

3. The absorption of Hg in H\(_2\)SO\(_4\), with and without oxygen, was not a substantial contributor to Hg uptake by SIAC if Hg\(^0\) vapor concentrations were at the level of typical power plant flue gases (~ 25 μg/m\(^3\)).

4. In the presence of oxygen, physisorption and chemisorption contributed almost equally to Hg uptake by SIAC. The presence of H\(_2\)SO\(_4\) made Hg uptake a chemisorption-dominated and less reversible process. While physisorption was reversible and follows Henry’s Law, chemisorption was limited by chemically active sites and showed a constant capacity, independent of Hg\(^0\) vapor concentrations.

4.2  Recommendations for future studies

1. Effects of other acidic species in flue gases, such as NO\(_X\) and HCl, on the performance of SIAC should be investigated;
2. The enhancing effect of O$_2$ should be further investigated with a lower concentration, given the actual O$_2$ concentration in flue gases (~10 vol%); 

3. The changes in sulfur species after Hg uptake in the presence of O$_2$ deserve further attention, since this knowledge may be useful in better understanding the potential interactions between sulfur and oxygen and their effects on Hg uptake; 

4. H$_2$SO$_4$ impregnation, though concluded not favorable, can be further investigated if better experimental methods can be proposed to impregnate the acid in a more controllable way such that the mesopores are still accessible and the kinetics won’t be significantly affected; 

5. In the study of reversibility, more tests at higher Hg$^0$ inlet concentrations will help verify the theory proposed; 

6. A more sophisticated Hg uptake model is needed to better simulate the breakthrough process in a fixed-bed reactor and extract the rate and capacity parameter from experimental breakthrough curves.
PART II

Wettability of Graphitic Carbon and Its Dependence on Crystal Structure and Surface Chemistry
Chapter 5  Introduction

Graphitic carbons are elemental carbon in the sp² bonding state, including natural graphite, highly oriented pyrolytic graphite (HOPG), graphene etc. Natural graphite is stable in metamorphic rocks in nature with a variety of types; HOPG is a pyrolytic graphite with an angular spread of the c-axes of the crystallites of less than 1°, which is typically produced by stress annealing at approximately 3100°C [34]; graphene is a single layer of graphite structure first isolated in 2004 by scientists [35], and it is known as the first 2-D material and for its remarkable mechanical strength, heat and electric conductivities [36, 37].

Graphite has long been widely used for a variety of purposes including lubrication [38, 39], battery electrodes [39-42], catalysis and catalyst support [43, 44], steelmaking [45], refractories [46], composites [39, 47], adsorbents [48] and more [49]. Given its versatile applications in aqueous phases [39-44, 48] and frequent interactions with water drop/vapor in many systems [50, 51], the wettability of graphite plays a significant role for process design and optimization. As a homogeneous and pure carbon material, graphite is generally used as a model or alternative to study the wettability of carbonaceous materials [52].

The wettability of graphite and graphene has been extensively studied since the experiment by Fowkes et al. in 1940, who concluded a water contact angle (WCA) of 86° using natural graphite on a tilting plate [53]. However, values of WCA reported in literature since have been highly variable. Before the sessile drop method utilizing HOPG is generally used after 1980s, some other methods were employed to directly or indirectly measure the contact angle of graphite. Tadros et al. reported the advancing WCA of 63-65° by the captive bubble method on pure isotropic carbon [54], and Morcos indirectly obtained the contact angle of 83.9° on pyrolytic
graphite from the experimentally determined meniscus rise [55]. More recently, more and more studies reported relatively large contact angles (80-95°) of graphite and multi-layer graphene [56-61]. In a recent study by Li Y. et al., the WCA on a graphite sheet used as electrode was found to be 126.5° [62]. In another study by Gribanova et al., contact angles of acidic solutions on graphite plates were found to be 90-105° [63]. These large contact angles reported seem to support the hydrophobicity of graphitic materials, and some researchers based their theoretical or experimental studies on this property including computational simulations on water-carbon interactions [64, 65], study of microscopic structure of nanodroplets [50], and the structure and dynamic of interfacial water on the graphite surface [66] etc.

Dating back to 1975, Schrader measured the WCA of HOPG in ultra-high vacuum (10^{-10} Torr) by the vapor phase transfer method and reported a WCA of 35±4°. He concluded that the higher contact angles (50-80°) previously reported were due to hydrophobic organic contamination in air [67]. In 1980, Schrader suggested the hydrophilicity of freshly cleaved high-quality HOPG via a rapid measure of contact angles in open air by the sessile water drop method, and the WCA was found to be 46±3° [68]. However, similar experiments conducted later using the freshly cleaved HOPG in open air yielded larger contact angles ranging from 75° [52] to 79±2° [58] and to 91° [60]. This variation can be partially explained by the ambiguity of the term “freshly cleaved” - how fresh is fresh, or in other words, the sensitivity of fresh HOPG surfaces to subsequent external contamination such as airborne hydrocarbon etc. Recently, Li Z. et al. brought up the issue of airborne contaminants again by experimenting with single-layer graphene on different substrates as well as freshly exfoliated HOPG, confirming that the graphitic surfaces are very sensitive to airborne contamination and that the WCA can increase significantly within a short period of time when exposed to open air [69]. The low WCA of HOPG found (64.4°) was
further studied by their colleagues Kozbial et al. and the contact angle was determined to be 64.4°±2.9° when measured within 10 s after exfoliation in air [70]. Table 5.1 below is a complete list of WCA measures in the literature in a chronological order. In spite of these studies since 1940, “is the surface of graphite hydrophobic or hydrophilic” remains an unanswered question.

Table 5.1. List of WCAs reported in the literature from 1940 to 2014.

<table>
<thead>
<tr>
<th>WCA on graphite materials</th>
<th>Year</th>
<th>Method</th>
<th>Type of graphite</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>86°</td>
<td>1940</td>
<td>Tilting plate</td>
<td>Natural graphite</td>
<td>Fowkes et al. [53]</td>
</tr>
<tr>
<td>83.9°</td>
<td>1972</td>
<td>Indirectly obtained from experimentally determined meniscus rise</td>
<td>Pyrolytic graphite</td>
<td>Morcos [55]</td>
</tr>
<tr>
<td>63-65°</td>
<td>1974</td>
<td>Captive bubble (advancing)</td>
<td>Pure isotropic carbon</td>
<td>Tadros et al. [54]</td>
</tr>
<tr>
<td>35°</td>
<td>1975</td>
<td>Vapor phase transfer in vacuum (9E-10 Torr)</td>
<td>HOPG</td>
<td>Schrader [67]</td>
</tr>
<tr>
<td>46±3°</td>
<td>1980</td>
<td>Sessile water drop in open air (Rapid measurement)</td>
<td>High quality (ZYA) HOPG</td>
<td>Schrader [68]</td>
</tr>
<tr>
<td>86°</td>
<td>1990</td>
<td>Advancing angle</td>
<td>N/A</td>
<td>Adamson et al. [56]</td>
</tr>
<tr>
<td>90-105° (pH 1-4)</td>
<td>1999</td>
<td>Sessile water drop on water vapor saturated graphite plate</td>
<td>Graphite plate (fine granular)</td>
<td>Gribanova et al. [63]</td>
</tr>
<tr>
<td>79±2°</td>
<td>2002</td>
<td>Sessile water drop on freshly cleaved HOPG in open air</td>
<td>HOPG</td>
<td>Kogen et al. [58]</td>
</tr>
<tr>
<td>60-90°</td>
<td>2004</td>
<td>Simulations of H contamination</td>
<td>Graphite</td>
<td>Walther et al. [71]</td>
</tr>
<tr>
<td>75°</td>
<td>2007</td>
<td>Sessile water drop on freshly cleaved HOPG in open air</td>
<td>HOPG</td>
<td>Westreich et al. [52]</td>
</tr>
<tr>
<td>Degree</td>
<td>Year</td>
<td>Description</td>
<td>Material</td>
<td>Reference</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
<td>---------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>98.3°</td>
<td>2009</td>
<td>Sessile water drop in open air</td>
<td>Graphite film</td>
<td>Wang et al. [61]</td>
</tr>
<tr>
<td>91°</td>
<td>2010</td>
<td>Sessile water drop on freshly cleaved HOPG in open air</td>
<td>HOPG</td>
<td>Shin etc. [60]</td>
</tr>
<tr>
<td>90-95°</td>
<td>2012</td>
<td>Sessile water drop on multi-layer graphene in open air when “not transparent”</td>
<td>Multi-layer graphene on different substrates</td>
<td>Raflee et al. [59]</td>
</tr>
<tr>
<td>92°</td>
<td>2013</td>
<td>Sessile water drop</td>
<td>HOPG</td>
<td>Friedman et al. [57]</td>
</tr>
<tr>
<td>37-56°</td>
<td>2013</td>
<td>Sessile water drop in open air</td>
<td>Graphene on different substrates &amp; HOPG</td>
<td>Li Z. et al. [69]</td>
</tr>
<tr>
<td>126.5°</td>
<td>2013</td>
<td>Sessile water drop in open air</td>
<td>Graphite sheet (max. 50 μm of grain size)</td>
<td>Li Y. et al. [62]</td>
</tr>
<tr>
<td>64.4 ± 2.9°</td>
<td>2014</td>
<td>Sessile water drop in open air (Rapid measurements)</td>
<td>HOPG</td>
<td>Kozbial et al. [70]</td>
</tr>
</tbody>
</table>

The measured wettability of graphitic carbons can be affected by different factors, which may explain the discrepancy of the reported wettability in the literature. First, the crystal orientation of graphite grains can vary. For example, crystal grains in HOPG have the same orientation while natural graphite and regular multi-grain graphite (MGG) are a mixture of crystal grains of different orientations. The side surface of HOPG also has a different crystal orientation compared to the basal plane. Given the difference in energy between edge carbon and basal carbon, WCA of the basal surface is expected to be different from that of the side surface. However, the effect of crystal orientation on the wettability of graphitic carbon materials has not been explored; Second, surface roughness can also greatly affect the apparent wettability of graphitic materials and mask the intrinsic wettability. Understanding the effect of roughness and
deducing the intrinsic wetting properties are thus important yet challenging; Last, the heteroatoms chemically and/or physically bound to carbon change surface energy and hence wettability. Changes in surface chemistry may induce hydrophilicity or hydrophobility. For example, a layer of hydrocarbon less than 1 nm can increase the WCA of HOPG to about 90° from 64.4° [70], and ion bombardment of the evacuated HOPG surface can result in a WCA of 0° in ultra-high vacuum [67, 68]. Improper surface cleaning can also change the surface chemistry and cause surface damage or introduce contaminants, thus alters the surface wettability.

Therefore, the objective of this study is three-fold:

1. Determine the intrinsic/corrected wettability of graphitic carbon materials with different crystal orientations, including HOPG and MGG. For HOPG, both the basal and side surfaces were examined;

2. Understand the effect of roughness on the wettability of HOPG and MGG surfaces; and

3. Investigate the effect of surface chemistry changes on the wettability. These changes included surface oxidation, acetone sonication, surface sulfurization by SO₂ and H₂SO₄ and adsorption of airborne contaminants.
Chapter 6  Materials and Methods

6.1  Materials and sample preparation

6.1.1  HOPG

HOPG samples were purchased from MikroMasch (Grade: ZYH, 10 mm×10 mm×1.7 mm). The fresh HOPG surfaces are homogeneous, smooth, dust-free, and shiny. Freshly exfoliated HOPG surfaces were obtained by carefully peeling off the top layers of graphene using the Scotch tape method [35] right before the WCA measurements. To measure the WCAs on the HOPG sides (the surfaces perpendicular to the basal plane), the sides were polished by sandpaper (220 grit) first and then further polished on a piece of clean and fine paper. Side surfaces of different angles

<table>
<thead>
<tr>
<th>Cutting angle (°)</th>
<th>Side view</th>
<th>% of edge carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>~90°</td>
<td>0.34 nm</td>
<td>100%</td>
</tr>
<tr>
<td>HOPG-Side-90°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~60°</td>
<td>0.39 nm</td>
<td>87%</td>
</tr>
<tr>
<td>HOPG-Side-60°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~30°</td>
<td>0.68 nm</td>
<td>50%</td>
</tr>
<tr>
<td>HOPG-Side-30°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOPG-basal</td>
<td></td>
<td>0%</td>
</tr>
</tbody>
</table>

Figure 6.1. Diagram illustrating the polished HOPG sides with different cutting angles.
to the basal surface (~30°, ~60°, and ~90°) were prepared, as shown in Figure 6.1. The 90° side surface should consist of only edge atoms, while 30° and 60° side surfaces will be a mixture of edge and basal atoms. The side surfaces are approximately 2-4 mm wide, which is wide enough for water drops (d < 1 mm) placed onto them. To make the side surfaces horizontal when measuring the WCA, plastic sample holders were made to hold the samples with different cutting angles.

6.1.2 Multi-grain graphite (MGG) disks

Multi-grain graphite (MGG) disks are 3-4 mm thick cylindrical graphite samples cut from a multi-grain graphite rod (diameter: 8 mm, length: ca. 300 mm) that is made of small graphite grains (20 μm). To polish the coarse and uneven surface after cutting, a piece of sandpaper (220 grit) was applied on both sides of the disk. All MGG samples were treated in this same manner unless otherwise specified. The carbon content of this graphite material obtained from the elemental analysis is over 99.9% and the ash content is less than 0.1%.

6.1.3 Heat treatment

All heat treatments, including annealing and SO₂ treatment, were completed in a high-temperature tubular furnace [21]. Readers are referred to Appendix A for details of the set-up and the procedure. For annealing, HOPG or MGG samples were first placed onto the quartz disk inside a vertical glass work tube and then heated up at 600-700°C with a flow of high purity He or N₂ (99.999%) for 30 or 60 minutes. After the heating was completed, the samples were cooled by the same gas to the room temperature. The WCAs were measured right after the samples were discharged from the furnace.
6.1.4 Sulfurization of graphite samples

SO$_2$ gas or concentrated H$_2$SO$_4$ were used to add sulfur to the surface of graphite samples. Using the same set up for annealing, a mixed flow of 50% SO$_2$ and 50% N$_2$ was introduced into the work tube with a piece of MGG disk in at 700°C. The SO$_2$ treatment lasted either 10 or 30 minutes. For H$_2$SO$_4$ treatment, MGG disks were placed in a beaker, and approximately 50 mL concentrated H$_2$SO$_4$ (95-98 wt.%) was then mixed with the samples using a magnetic bar and heated up at 120°C on a hot plate for 17 hours. Afterwards, the samples were washed with deionized water to pH=7 and dried in open air at room temperature.

6.1.5 Acetone and deionized water sonication

Acetone and deionized water sonication was done for intentional surface contamination of the graphitic samples. HOPG or MGG samples were first placed into a small beaker that was filled with a generous amount of acetone. The beaker was then partially submerged into the water tank of the ultrasonic cleaner and the samples were sonicated for 3 minutes. Afterwards, the beaker was refilled with deionized water and the samples were sonicated for another 3 minutes. After the sonication was completed, the samples were rinsed with deionized water thoroughly and dried in open air at room temperature.

6.1.6 Surface roughness

To study the effect of surface roughness, different grades of sandpapers (150, 220 and 320 grit) were used to polish the MGG samples to difference roughness. The higher the grade is, the finer the sandpaper and thus the smoother sample surface. The roughness was quantified using an atomic force microscopy (AFM).
6.2 Characterization of graphitic carbons

6.2.1 Surface chemistry with XPS

The surface elements and functional groups were characterized with X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific Theta Probe instrument with a monochromatic Al-Kα source. High-resolution spectra of C1s, O 1s, and S 2p were obtained and analyzed with peak fitting to reveal possible functional groups on the surfaces of graphitic materials.

6.2.2 Surface roughness with AFM

The surface roughness of HOPG basal surface, side surfaces in different angles, and the MGG surfaces polished with different sandpapers were characterized using an atomic force microscopy (AFM). For consistency, a scanning area of 50 μm by 50 μm was selected for imaging, and the average roughness parameters were calculated and used for estimating intrinsic WCA of graphitic carbons.

The surfaces were imaged with an Asylum MFP-3D scanning probe microscope (Asylum Research, Oxford Instruments) under ambient conditions. The instrument was operated in tapping mode using a Nanoworld FMR20 cantilever. The tapping mode is a non-destructive imaging mode in which the height of the cantilever above the surface is adjusted and the oscillation amplitude of the cantilever is maintained. The force between the tip and the sample surface is then recorded for imaging [72].
6.2.3 Crystal structure with XRD

The crystal structure of MGG disks was examined with X-ray diffraction (XRD). A piece of the MGG sample was mounted directly on the sample holder, and an XRD pattern was collected on a Bruker AXS D2 Phaser diffractometer. High-resolution CuK$\alpha$ source operating at 30 KV and 10 mA was used. The system is equipped with the Ni-filter for elimination of CuK$\beta$ peaks and a solid state Lynxeye XE detector. A step scan mode was used for data collection with the step size of 0.02 degrees and time 0-0.4 s per step.

The XRD analysis confirmed the sample’s dominant characteristic as graphite, as shown in Figure 6.2. The pronounced 004 peak at 26.5° is the signature peak for graphite and the sample is free of the rhombohedral polytype. The broadening of 102 peak indicates some structural irregularities along [H0L] direction in the lattice, which is common. Due to the presence of impurities, it also contains traces of other non-identified phase, which is not related to carbon. Overall, there are no specific structural and/or compositional differences from graphite revealed on this XRD pattern.

![XRD pattern of the MGG disk](image)

*Figure 6.2. XRD pattern of the MGG disk.*
6.2.4 Elemental analysis of bulk phase

The elemental compositions of MGG samples were determined by the AI CE-440 Elemental Analyzer (Exeter Analytical Inc., UK). The Instrument uses a thermal conductivity detection method for measuring carbon, hydrogen, and nitrogen content after combustion and reduction. The operating temperature for combustion and reduction is about 975°C and 800°C, respectively. A schematic diagram of the AI CE-440 Elemental Analyzer is shown below in Figure 6.3 [73]. For each sample, the measurement was repeated at least three times and then averaged.

![Schematic diagram of the AI CE-440 Elemental Analyzer](image)

**Figure 6.3.** Schematic diagram of the AI CE-440 Elemental Analyzer [73].

6.3 Wettability measurement

6.3.1 Set-up

The water contact angles of HOPG and MGG samples were measured using a NRL Contact Angle Goniometer (100-00-115) under the open-air condition with a relative humidity of 40-50%. The wettability measurement system consists of two parts: the contact angle goniometer and the
computer used for image processing and WCA calculation. The schematic diagram is shown below in Figure 6.4.

![Figure 6.4. Schematic diagram of water contact angle measurement. Legend: 1. Light source; 2. Subdued light board; 3. Syringe; 4. Sessile water drop; 5. Graphitic carbon sample on a glass slide; 6. Adjustable lifting platform; 7. NRL Contact Angle Goniometer (main body); 8. CCD camera; 9. Computer.]

### 6.3.2 Procedure

The sample was first placed on a clean glass slide sitting on the top of the adjustable lifting platform and a water drop of about 1 μL was carefully touched to the sample surface. The image was immediately captured by a CCD camera and saved in the computer for contact angle measurement. Each static measurement was repeated for three or more times for every surface and the results were averaged. Time was recorded at the moment the water drop touched the surface when needed. The contact angles were measured by the LB-ADSA method using the image processing software ImageJ with a plugin specially created for contact angle measurement [74]. Readers are referred to Appendix C for detailed procedures.
6.3.3 Uncertainty (data quality)

Like any other measurements, WCA measurements are associated with uncertainties which may be caused by the change in the quality of water drops (symmetry, completeness, shape, size etc.), timing of a measurement and the natural variation in characteristics among samples. To minimize the uncertainty in WCA values, multiple measurements were conducted for any given conditions (at least 3 times, most of cases 5 to 6 times). The final results were presented as the average value $\pm$ one standard deviation. On the other hand, the image processing software is very accurate in calculating the water contact angles shown in the snapshot, because it not only has an automatic contact angle fitting and optimization feature based on the Young-Laplace Equation [74] but also allows manual fine adjustments if the optimization fails. As a result, the uncertainty comes primarily from the WCA measurements. In addition, the statistical t-test was used when comparing two WCAs with great standard deviations. This method allows us to distinguish whether the two values are statistically different at certain $\alpha$ (0.05 for example). Readers are referred to Appendix D for details of this methodology and examples.
Chapter 7  Results and Discussions

7.1  Intrinsic WCA of HOPG

7.1.1  Basal surface

For freshly exfoliated HOPG, we found that the fresh WCA was lower than most of the measurements in the above-mentioned literature and changed very slightly within the first few minutes in the ambient air (Figure 7.1a). The average WCA within the first 5 min was found to be $61.8 \pm 3.3^\circ$, suggesting that the fresh HOPG basal surface is intrinsically hydrophilic. However, as the exposure time increased, the WCA was found increasing at a steady rate (shown by the linear fitting in Figure 7.1a), and the WCA after 2 hours of exposure was $76.3 \pm 2.4^\circ$, a significant increase compared to the fresh contact angle. The fitting line intersects the y-axis, giving the WCA at time zero – $61.6^\circ$, which is the intrinsic WCA of HOPG basal surface. It is smaller than one reported recently Kozbial et al. ($64.4 \pm 2.9^\circ$) [69, 70], which confirms the intrinsic hydrophilicity of HOPG basal plane. However, the rate of change of the WCA in this study is much slower than that in the literature. The increase in WCA with time is likely due to the adsorption of air contaminants on the surface of carbon. This difference may be explained by the difference in laboratory environment including air quality, humidity etc.

To find out the stable contact angle of HOPG when exposed to air for a long time, the WCA of an aged HOPG surface, prepared by exfoliating the top layers and exposing it to air for 1day, was measured within 2 hours (Figure 7.1b). The average WCA of the aged HOPG was found to be $81.9 \pm 2.9^\circ$, which was statistically unchanged within the 2-hour period, suggesting that the
adsorption has reached equilibrium after one day’s exposure to air. Consistent with the evidence reported in the literature [69, 70], the HOPG basal surface becomes less hydrophilic when exposed to ambient air as a result of airborne contamination. In this study, the difference in WCA between the fresh and the contaminated surface could be as great as 20°, thus caution must be applied when reporting or citing the wettability of graphite or graphene products as it can be affected by the ambient environment to a great extent.

Figure 7.1. Effect of airborne contaminants on WCA of the HOPG basal surface.  

**a.** Static WCA of freshly exfoliated HOPG in air. The dotted line is the linear fitting of the measured data.  

**b.** Static WCA of aged (1 d in air) exfoliated HOPG in air. The dotted line represents the average WCA (81.9°) of the measured data. For a and b, each data point is the averaged WCA (± standard deviation) of three or more measurements completed within 2 min.

### 7.1.2 Side surfaces

To understand the effect of crystal orientation on the wettability of HOPG, WCAs of the polished HOPG sides (HOPG-Side-30°, HOPG-Side-60°, and HOPG-Side-90°) within the first 90 min exposed to air are shown in Figure 7.2. This was the first time that WCAs of the HOPG side surfaces were measured. As shown in the figure, the measured WCAs fluctuate across the
time axis for all of the three samples. The results of t-test indicated there was no statistically significant difference in the average WCA among the three samples. The average WCA of HOPG-Side-30° is $62.0 \pm 8.7^\circ$, that of HOPG-Side-60° is $60.9 \pm 9.2^\circ$ and that of HOPG-Side-90° is $56.2 \pm 8.4^\circ$. The overall average WCA of all three samples is $60.8 \pm 9.0^\circ$, which is almost same as the intrinsic WCA of the basal surface ($61.6^\circ$). Unlike the basal surface, however, the trend line of side surface WCAs doesn’t show any time dependency.

Figure 7.2. Static WCA of HOPG sides (HOPG-Side-30°, HOPG-Side-60°, and HOPG-Side-90°) within the first 80 min exposed to air. Each data point is the averaged WCA (± standard deviation) of at least three measurements completed within 2 min. The dotted line presents the average WCA ($60.8^\circ$) of the measured data.

This similarity in WCA between the basal and side surfaces doesn’t suggest that the two surfaces share the same characteristics. On the contrary, this observation supported the hypothesis that the side surface consists of more high energy carbon atoms and should have a smaller intrinsic WCA than the basal surface. As a truly fresh side surface couldn’t be created, the side surface of all
samples was contaminated. Therefore, the measured WCAs of side surfaces were that of contaminated surface. Assuming the contamination adds 20° to the intrinsic WCA, the intrinsic WCA of the side surface would have been about 40°. Given the higher energy of edge atoms, the adsorption of contaminants on the side surface would be more intensive; the enhanced adsorption might further increase the apparent WCA. The 40° is likely the upper limit of the intrinsic WCA of HOPG side surface. The lack of time dependency in measured WCA for the side surface supported our theory of contaminated side surface.

![Figure 7.3](image)

**Figure 7.3.** Difference in WCA across the surface of HOPG-Side-60° within the first 80 min exposed to air. 1, 2, 3, and 4 represent the four different locations on the surface from left to right. Each bar is the average value of six or more tests ± standard deviation.

As shown in Figure 7.2, the uncertainty associated with the WCA values of side surface seems greater than that of the basal surface. There are many reasons behind the large uncertainty, including the small area of side surfaces which limits the number of droplets and the difficulty in creating a smooth side surface. Figure 7.3 shows that the side surface of the same sample can be highly variable. The following section examines the effect of roughness on WCA.
7.1.3 Effect of surface roughness

7.1.3.1 Theory

As previously mentioned, roughness of the surface plays an important role in determining the apparent WCA. In the literature, different models have been proposed to calculate the apparent WCA on a rough surface. One of the most cited models was proposed by Wenzel in 1936, which suggests that the roughness of a homogeneous solid surface affects the apparent WCA in the following manner:

$$\cos \theta_{\text{app}} = R_w \cos \theta_Y$$

(7.1)

where $\theta_{\text{app}}$ is the apparent WCA in equilibrium, $\theta_Y$ is the Young WCA that corresponds to the ideal condition of perfect smoothness, and $R_w$ is the surface area ratio of the rough surface’s real area to the projection area of the solid. The parameter $R_w$ can be determined by atomic force microscopy (AFM) or stylus profilometers. This law is valid when the characteristic length of roughness is much smaller than the size of the water drop. In our case, the roughness of the sample surfaces is in nanometer scale while the water drop size is in millimeter scale, satisfying the conditions Equation 7.1 requires. From this equation the law predicts that the apparent WCA decreases when $\theta_Y < 90^\circ$ and increases when $\theta_Y > 90^\circ$. That is to say, a hydrophilic smooth surface would become even more hydrophilic and a hydrophobic smooth surface would become even more hydrophobic when it is rough.
7.1.3.2 Roughness parameters by AFM

In Section 7.1.2, the intrinsic WCA of $< 40^\circ$ was suggested for the side surface of HOPG. The $40^\circ$ was deducted from the measured WCAs while factoring in the effect of adsorbed contaminants and without considering the effect of surface roughness. Figure 7.4a is a typical surface image for the freshly exfoliated HOPG basal surface, while Figure 7.4b illustrates the surface conditions of the polished HOPG sides.

![AFM images](image)

Figure 7.4. AFM images of a typical freshly exfoliated HOPG basal surface (a) and a polished HOPG side surface (b). The scanning area is 50 μm × 50 μm with the same color map scale for both of the images. The scale on the right of each image represents the vertical depth of bumps and hollows in the scanning area.

It is apparent from Figure 7.4a that the HOPG basal surface is very smooth and homogeneous except two bright areas that represent hanging pieces likely from the Scotch tape used for exfoliating the sample surface. Hence, the wettability measurements completed on the basal surface should not be subject to the effect of roughness. On the other hand, the HOPG side surface looks rougher than the HOPG basal surface, as shown in Figure 7.4b. Bumps and hollows are visible on the surface after polishing with sandpapers. To quantitatively compare the
surface roughness of these two samples, the roughness parameters $R_q$ (root mean square roughness) and $R_w$ (Surface area ratio for the Wenzel model, see Section 7.1.3.1) are calculated for the HOPG basal surface and polished side surfaces, as shown in Table 7.1. For the side surfaces, three locations on the rectangular side surface were chosen and scanned by AFM, namely the upper, middle, and lower positions.

**Table 7.1.** List of roughness parameters $R_q$ and $R_w$ for the HOPG basal and side surfaces.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_q$ (nm)</th>
<th>Average $R_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Upper</td>
<td>Middle</td>
</tr>
<tr>
<td>HOPG-Basal</td>
<td>-</td>
<td>18.54</td>
</tr>
<tr>
<td>HOPG-Side-30° (after annealing)</td>
<td>95.25</td>
<td>69.08</td>
</tr>
<tr>
<td>HOPG-Side-60° (after annealing)</td>
<td>192.79</td>
<td>83.10</td>
</tr>
<tr>
<td>HOPG-Side-90° (original)</td>
<td>75.62</td>
<td>158.67</td>
</tr>
</tbody>
</table>

* $R_w$ calculated from the scanned area in the middle of the HOPG basal surface.
From the table it is seen that the $R_q$ data supported the significant roughness difference of the basal and side surfaces. As a result, the surface area of the side surfaces is greater and thus the area ratio $R_w$ is also greater than that of the basal surface. Nonetheless, the $R_w$ (1.005-1.010) are only slightly greater than 1 and can hardly yield a significant change ($< 1^\circ$) to the apparent WCA $\theta_{app}$ following Equation 7.1, suggesting that our estimation of the intrinsic wettability (WCA < 40°) of the side surfaces is reasonable. The practical reason behind this negligible difference is that the side surface after polishing is not that rough as it appears in the graph – the color map exaggerates the roughness by using a sub-micron scale, which is 1~2 orders of magnitude smaller compared to the lateral dimension of the scanned area.

However, from the table we can definitely see the inconsistency of the side surfaces in terms of the $R_q$ at different positions. For all the side surfaces, no matter annealed or not, $R_q$ varies a lot across the surface. That is to say, one position can be two to three times rougher than another. This inconsistency can contribute to the increase of uncertainties when measuring the WCAs, affecting the quality of the water drops (symmetry, shape, rate of success etc.) placed on the surface. In addition, the high roughness at some specific positions, together with the airborne hydrocarbon contaminants, may decrease or increase the apparent WCA to some extent. The specific mechanistic reason that causes this great uncertainty remains to be further studied.
From the roughness analysis, it can be summarized that although the roughness caused by the polishing process is too weak to affect the average wettability, it can result in some uncertainties or deviations of WCA when taking the measurements.

**7.2 Corrected WCA of MGG**

**7.2.1 Apparent WCA of MGG and comparison with HOPG**

As a graphitic carbon material, the MGG consists of countless crystal orientations due to the extruding process using graphite grains, which can be considered as small graphite crystals with different orientations. WCAs were measured on the polished MGG samples to investigate the intrinsic wettability of this graphitic carbon, and were also compared with that of HOPG basal and side surfaces to study their consistency in wettability.

The raw MGG sample, which is neither annealed nor cleaned with acetone after polishing, was found unexpectedly to be hydrophobic by the WCA measurements. The apparent contact angle 120.8±3.6° was found similar with that reported by Li Y. et al (126.5°) recently [62]. This WCA is also qualitatively different from that of the HOPG basal and side surfaces reported in the previous sections. However, this apparent WCA does not necessarily represent the intrinsic wettability of the MGG because of contamination and roughness, which can greatly alter the surface wettability. The surface can be dirty outside and inside - external contamination such as airborne hydrocarbon can get adsorbed and accumulate on the surface, and internal contamination such as the binders used (coal tar pitch, petroleum pitch or synthetic resins) [75] to bind graphite grains may internally affect the wettability. Roughness, on the other hand, can directly change the apparent surface WCA as described by the Wenzel model. Therefore more
studies in contamination and roughness is a necessity to estimate or determine its intrinsic wettability.

### 7.2.2 Effect of surface roughness

As previously mentioned, the MGG samples were polished on sandpapers of different grades: 150 grit, 220 grit, and 320 grit, which are in the order of rough, less rough and least rough. All samples were annealed in He (99.999%) for 1hr to remove surface contaminants. The oxidation effect by the annealing would be discussed later in Section 7.3.1 and considered when estimating the intrinsic contact angle. No sonication by acetone or water was applied afterwards to ensure no external contaminants were introduced. Samples polished by the sandpapers and thermally treated were named as MGG-He-1hr-150, MGG-He-1hr-220, and MGG-He-1hr-320 in the order of sand paper grades.

![Figure 7.5](AMW-002-044_06061631)

**Figure 7.5.** A typical image (50 μm × 50 μm) of the polished MGG surface.

Figure 7.5 shows the typical topography of the MGG surfaces by AFM. From the figure it is seen that the surface is rough with bumps and hollows. The unusual topography in the lower part of the image was caused by the over-deflection of the AFM tip due to the high roughness of the surface. Given this excessive roughness of the MGG samples, the average roughness parameter
calculated from the entire image would not be correct due to the involvement of the over-
deflected area. Therefore each of the samples, MGG-He-1hr-150, MGG-He-1hr-220, and MGG-
He-1hr-320, were scanned at three random positions on the surfaces and a rectangular area that
show clear surface topographic information were selected from each of them for regional
roughness analysis. The roughness parameter $R_a$ (the arithmetic average roughness) and the area
ratio $R_w$ were calculated and shown below in Table 7.2. Despite that the data was not
representative of the entire surface and $R_a$ varies a lot from position to position, it reveals the
relative roughness of the three samples – the data is consistent with the sandpaper grades used.
This result quantitatively tells us that the MGG surfaces indeed become rougher when using a
rougher piece of sandpaper.

Table 7.2. List of regional roughness parameters $R_a$ for the MGG surfaces polished with
different sandpapers. Three clear positions were selected from three random scans on each
surface.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_a$ (nm), regional</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position 1</td>
<td>Position 2</td>
</tr>
<tr>
<td>MGG-He-1hr-150</td>
<td>583.32</td>
<td>1060</td>
</tr>
<tr>
<td>MGG-He-1hr-220</td>
<td>608.76</td>
<td>698.95</td>
</tr>
<tr>
<td>MGG-He-1hr-320</td>
<td>332.49</td>
<td>572.55</td>
</tr>
</tbody>
</table>
The effect of roughness was further studied with the WCA measurements. Contact angles were measured right away after the three samples were annealed, and measured after 120 min and 7200 min to investigate if the wettability would remain or change after long exposure to air, as shown in Figure 7.6. It is observed from Figure 7.6a that all the three surfaces are very hydrophilic, which is a result of the intrinsic hydrophilicity of the graphitic carbon surface, or the oxidation effect by the annealing treatment, or both. Moreover, it is seen that as the surface becomes less rough, the WCA measured increases. This makes sense for a rough hydrophilic surface according to the Wenzel model. After 120 min, it is found that the WCAs of all three surfaces increase markedly by 60% on average. Given this consistent increase of all three samples, it is reasonable to attribute it to the external contamination in air. Despite this effect of contamination, it is found that the relative wettability of the samples were not changed, with the roughest sample being the most hydrophilic and the least rough sample being the least hydrophilic. This trend remained after 7200 min or 5 d later in air, with the WCAs barely changed. This interesting finding suggests that airborne contaminants got saturated on the surfaces after 120 min and no longer affected the apparent wettability, and that the hydrophilicity could maintain or not much affected even with the presence of airborne contamination. It is therefore concluded that the effect of surface roughness agrees with the Wenzel model and would greatly affect the apparent WCAs, which will remain effective even after the external contamination by airborne hydrocarbons.
Figure 7.6. The WCAs measured within 10 min (a), 120 min (b), and 7200 min (c) in air after the annealing treatment for MGG samples of different surface roughness. MGG-He-1hr-150 is the sample polished with the 150 grit sandpaper (white bars), MGG-He-1hr-220 polished with the 220 grit sandpaper (gray bars), and MGG-He-1hr-320 polished with the 320 grit sandpaper (black bars).

7.2.3 Corrected WCA of MGG

To correct the WCA on the MGG surface, it is necessary to understand the effects of different factors on it. A summary of the effects are shown below in Table 7.3 based on the experiments, analyses, and literature review in this study.

Table 7.3. Factors affecting the surface wettability of graphitic materials.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Effects on wettability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing*</td>
<td>1. Removes the surface contaminants and partially recover the wettability;</td>
</tr>
<tr>
<td></td>
<td>2. Introduces heteroatoms and oxidizes the surface, and lower the WCA.</td>
</tr>
<tr>
<td>Airborne contamination</td>
<td>Main effect: hydrocarbons from the air accumulate on the</td>
</tr>
<tr>
<td>Internal contamination</td>
<td>Comes from the manufacturing process, such as the binders used (coal tar pitch, petroleum pitch or synthetic resins) [75], exposure to organics from air or reagents etc., and increases the WCA.</td>
</tr>
<tr>
<td>------------------------</td>
<td>----------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Roughness</td>
<td>Decreases the WCA when the surface is hydrophilic and increases it when the surface is hydrophobic. The decrease/increase is greater when surfaces are rougher.</td>
</tr>
</tbody>
</table>

*Details will be discussed in Section 7.3.

Considering the above-mentioned factors that can affect the surface wettability, neither of the high WCA measured (120.8±3.6°) on MGG-raw and the low WCAs measured on the annealed samples in Figure 7.6 represent the real wettability of this graphitic carbon. The different wettability on these surfaces is a result of combinations of different factors shown above. For MGG-raw, it is proposed that the shown hydrophobicity is a result of internal contamination during the manufacturing process, which is further magnified by roughness. This explains why the WCA measured was almost the same (121.0±2.8°) for the MGG-raw that was intentionally contaminated with acetone. Acetone was found to significantly increase the WCAs of all the hydrophilic graphitic carbons in this study (see Section 7.3.2.). This experiment indirectly suggests and agrees with the literature that the raw MGG surface was originally contaminated with some compounds that make the surface hydrophobic such that additional contamination was overridden. On the other hand, for the annealed MGG surfaces, the hydrophilicity shown in Figure 7.6a can be a combination of the annealing and roughness. The annealing not only removed the surface hydrocarbons, but also oxidized the surface and introduced oxygen. The latter has been proved by XPS and was found to lower the WCA by about 10~20° for the HOPG
basal and side surfaces (see Section 7.3.1). Due to the presence of high roughness, the hydrophilic surface then becomes even more hydrophilic. Similar results were reported by Li Y. et al, who found that the original hydrophobic graphite anode (126.5°) becomes superhydrophilic (0°) after electrolytic exfoliation [62]. The process was found to oxidize and roughen the graphite anode surface, which works indeed similarly as described above.

To help us estimate the WCA of MGG, the effects of the above-mentioned factors are quantitatively estimated. For the effect of roughness, the average $R_w$ was found to be 1.8-3.1 based on the data of the AFM analysis (see Table 7.4), which helps us to estimate the Young WCA $\theta_y$ using the Wenzel model; for the effect of annealing, since the surface is much rougher, the decreasing effect of WCAs after the annealing can be more serious as greater surface area can contribute to more efficient surface reactions. Based on the data from the HOPG samples, this effect was estimated to lower the WCA by 20° or more; hydrocarbon contamination can increase the WCA of a smooth graphite surface by 20-30° (see Sections 7.1.1. and 7.3.2.). The results of the estimations are shown below in Table 7.4.

**Table 7.4.** Estimations of the intrinsic WCA of MGG.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Apparent WCA (°) (measured)</th>
<th>Average $R_w$</th>
<th>WCA eliminating roughness (°) (estimated)</th>
<th>WCA eliminating oxidation (°) (estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGG-He-1hr-150</td>
<td>10.9</td>
<td>3.1</td>
<td>71.5</td>
<td></td>
</tr>
<tr>
<td>MGG-He-1hr-220</td>
<td>13.7</td>
<td>2.8</td>
<td>69.7</td>
<td>80-90°</td>
</tr>
</tbody>
</table>

64
Starting with the average fresh WCAs of the annealed MGG samples shown in Figure 7.6a, the WCA after eliminating the effect of roughness is calculated to be 58.0°-71.5° using the area ratio $R_w$, as shown in Table 7.4. The theoretical $\theta_y$ is then estimated to be 80°-90° if the effect of surface oxidation is eliminated. This estimation can be double checked with the apparent WCA (121°) of the raw MGG, which becomes 100.6° after applying the Wenzel model. This weaker hydrophobicity can be readily achieved by the internal/external hydrocarbon contamination for a graphitic hydrophilic surface. Therefore the estimated WCA of MGG was concluded to be 80-90° from the analysis above.

7.3 Effect of surface chemistry

7.3.1 Surface oxidation by annealing

7.3.1.1 HOPG basal surface

Li et al. proposed in their recent work that the adsorbed hydrocarbon from ambient air could be partially removed by an annealing process – heating samples at 550°C in flowing Ar (99.999%) for 1 hour followed by a fast cooling to room temperature in the protection of Ar [69]. This treatment was confirmed effective in their work and also seemed to be working in our experiments. As shown in Figure 7.7, the previously contaminated HOPG surfaces became much
more hydrophilic right after the annealing treatment, and bounced back quickly to the contaminated status within one hour. However, it is worth noticing that the WCA right after the annealing was as low as $51.4 \pm 2.0^\circ$, an approximately $10^\circ$ drop compared to that of the freshly exfoliated HOPG surfaces. In addition, compared to the steady WCA increase of the fresh HOPG after exposure to air (Figure 7.1), the fast rate of WCA increase after the heat treatment seems to suggest that the surface after the annealing may not be same with the fresh one. These differences imply that the annealing process not only removes contaminants from the surface, but also modifies the surface such that it is more hydrophilic and less “dustproof” in the ambient air.

Considering that the apparatus was well sealed during the thermal treatment and no deformation of surfaces was observed at high temperature the only factor that can attribute to this modification is the impurities in the inert gas in spite of its high purity. The impurities, including oxygen and moisture in ppm level, can interact with the surface to some extent at such high temperatures. The oxidized or heteroatom-impregnated surface can then become more hydrophilic due to the local polarization by oxygen or hydrogen atoms, which increase the surface energy and adsorb polarized molecules from air or water in a stronger and faster manner. This explains the differences in the WCA at the beginning and the rate of adsorbing airborne contaminants. It is thus summarized that caution also must be applied when using annealing as a cleaning method, especially when the inert gas is not pure enough. The details of evidence from the XPS analysis for other samples would be discussed later in other sections.
Figure 7.7. Static WCA of aged HOPG in air after annealing in He at 600°C for 1 hour. The square and triangle dots represent the WCA data from two different HOPG surfaces that were exposed to air at the same time. Data points are presented in average value of three or more tests ± standard deviation.
7.3.1.2 HOPG side surfaces

The effect of oxidation was also studied for the HOPG sides by the annealing method. The samples, HOPG-Side-30° and HOPG-Side-60°, were treated with He (99.999%) for 1 hour at 600°C. Figure 7.8 plots the WCAs of the samples within the first 120 min exposed to air after the annealing. The average WCA was found to be $42.9 \pm 6.7^\circ$, and similar to the untreated side surfaces, the WCAs of the two samples cannot be statistically distinguished from each other by the t-test – the average WCAs of HOPG-Side-30° and HOPG-Side-60° within the 120 min were found to be $43.3 \pm 6.7^\circ$ and $42.6 \pm 6.7^\circ$, respectively. Meanwhile, no increasing trends were found for both of the samples across the time axis. The possibility that the roughness on the side surfaces may change and then alter the apparent WCA after the annealing is excluded as no statistical changes in roughness were found as shown in Table 7.1, leaving surface oxidation the

![Figure 7.8. WCAs of HOPG-Side-30° and HOPG-Side-60° within the first 120 min exposed to air after the 1 hour annealing treatment in He at 600°C. Each data point represents the WCA from single tests, and the dotted line represents the average WCA (42.9°) of the two surfaces.](image-url)
only possibility. Given the fast recovery of WCA in air for the HOPG basal surface after annealing, it is reasonable to hypothesize that the annealed side surfaces experienced an even faster increase in WCA – the high-energy edge carbon atoms are more susceptible to oxidation and thus the airborne contaminants would adsorb on the side surfaces in a faster manner. The much lower average contact angle of the side surfaces compared to that before annealing seems to suggest this thermal treatment permanently may have changed the surface chemistry, making the surface more hydrophilic. Further studies such as XPS or elemental analysis on the annealed side surfaces are needed to verify these hypotheses.

7.3.1.3 MGG surface

7.3.1.3.1 Effect of annealing

The annealing treatment was also applied to the MGG samples for the purpose of removing surface contaminants. However, like HOPG, this graphite material can also be subject to surface modification by the impurities in the inert gas. Considering the roughness on the surface and porosity inside, the annealing process may cause even more serious surface and bulk oxidation. To test this effect, MGG-raw samples were heated up at 600°C in flowing He (99.999%) for 1 hour (MGG-He-600-1hr), and the WCA of the treated sample was measured right away after it cooled down. Compared with the MGG-raw (120.8 ± 3.6°), the MGG-He-600-1hr became extremely hydrophilic, and the WCA of the two sides were 14 ± 2° and 28 ± 3°, respectively (see Table 7.5).

In another set of tests, to check if this effect can be masked or removed by cleaning, MGG-raw samples were treated with both He (99.999%) and N₂ (99.999%) at 700°C for 0.5 hours (MGG-
He-700-0.5hr and MGG-N$_2$-700-0.5hr, respectively) and sonicated with acetone/deionized water for 3 min. Two blank samples, MGG-He-25-0.5hr and MGG-N$_2$-25-0.5hr, which were treated at room temperature (25°C) and also washed with acetone and deionized water, were also prepared and the apparent WCAs were measured (see Table 7.5). In either case of He or N$_2$ annealing, the apparent WCAs were always lower than that of the room temperature treated or the raw graphite samples even after acetone/deionized water sonication. The results indicated that high temperature treatment lowers the apparent surface WCA of MGG samples and this effect would not be masked or removed by organic and/or water cleaning.

Table 7.5. WCAs (both sides) of raw and treated MGG samples. All samples were polished with the sandpaper of the same grade (220 grit).

<table>
<thead>
<tr>
<th></th>
<th>MGG-raw</th>
<th>MGG-raw – acetone</th>
<th>MGG-He-600-1hr acetone</th>
<th>MGG-25-He-0.5hr acetone</th>
<th>MGG-700-He-0.5hr acetone</th>
<th>MGG-N$_2$-25-0.5hr acetone</th>
<th>MGG-N$_2$-700-0.5hr acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Side 1</td>
<td>120.8±3.6°</td>
<td>121.0±2.8°</td>
<td>13.7±2.4°</td>
<td>125.0±6.2°</td>
<td>96.9±6.9°</td>
<td>128.2±4.1°</td>
<td>83.7±3.7°</td>
</tr>
<tr>
<td>Side 2</td>
<td>27.7±3.1°</td>
<td>126.8±3.9°</td>
<td>27.7±3.1°</td>
<td>126.8±3.9°</td>
<td>117.9±3.7°</td>
<td>138.1±3.1°</td>
<td>97.0±5.4°</td>
</tr>
</tbody>
</table>

As previously mentioned, it is argued that impurities such as oxygen and moisture in ppm level can interact with graphite surfaces at high temperatures and impregnate the surfaces with heteroatoms. In order to verify this hypothesis, O1s XPS analyses of MGG-raw and MGG-N$_2$-700-0.5hr after acetone and deionized water washing were carried out by peak fitting, as shown
in Figure 7.9 (a, b, and c). The detailed data of peak binding energies and intensities are listed in Table 7.6.

![Figure 7.9](image)

**Figure 7.9.** The O 1s XPS spectra for MGG-raw (a), MGG-N₂-700-0.5hr side 1 (b), and MGG-N₂-700-0.5hr side 2 (c) to illustrate the effect of surface oxidation by thermal treatment. All sides of samples were sonicated with acetone and deionized water.

**Table 7.6.** O 1s XPS peak binding energies and intensities for MGG-raw and MGG-N₂-700-0.5hr (both sides).

<table>
<thead>
<tr>
<th>O 1s</th>
<th>B.E. of Peak 1 (eV)</th>
<th>B.E. of Peak 2 (eV)</th>
<th>Peak 1 intensity (cps·eV)</th>
<th>Peak 2 intensity (cps·eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGG-raw-acetone</td>
<td>531.3</td>
<td>532.1</td>
<td>348.5</td>
<td>2214.1</td>
</tr>
<tr>
<td>MGG-N₂-700-0.5hr-acetone (side 1)</td>
<td>531.4</td>
<td>532.8</td>
<td>1511.2</td>
<td>2648.7</td>
</tr>
<tr>
<td>MGG-N₂-700-0.5hr-acetone (side 2)</td>
<td>531.6</td>
<td>532.9</td>
<td>1189.1</td>
<td>1906.4</td>
</tr>
</tbody>
</table>

It is seen from Figure 7.9 that oxygen is present in both of the raw and annealed samples, and this is not surprising at all since both of them were intentionally “cleaned” with acetone and deionized water. The oxygen component introduced by acetone can be shown by the left peak
with a higher binding energy, or Peak 2 (532.1-532.9 eV) in Table 7.6, which represents the carbonyl group (C=O) available in acetone. The Peaks 2 for both of the samples are consistent in binding energy and intensity, confirming the presence of acetone on the surface. More important, it is observed from both the figure and the table that the intensities of Peaks 1 for MGG-N$_2$-700-0.5hr (1511.2 and 1189.1 cps·eV) are much greater than that of MGG-raw (348.5 cps·eV), suggesting some new species of oxygen group was present in the thermally treated sample on both sides. Regarding the binding energy of Peak 1 (531.3-531.6 eV), the oxygen group could be carbonates as a result of oxidation at elevated temperatures. We therefore believe that although high temperature treatment can help to remove surface contaminants, oxidation by the annealing process is an issue present in our experiments due to the impurities in the feeding inert gases despite of the high purity as labeled. Thus caution must be taken when using high-temperature thermal treatment as a cleaning method. In terms of wettability, just like the case of HOPG, the decrease of apparent WCA can be attributed to the introduction of heteroatoms. However, due to the complexity of MGG surfaces, other factors such as roughness can also affect the surface wettability, which has been discussed in previous sections.

7.3.1.3.2 Side-to-side difference in WCA after annealing

It is also interesting to notice that there exists a side-to-side difference in WCA after the thermal treatment, no matter whether the MGG samples were sonicated with acetone or not, as shown in Table 7.5. This suggests that the difference in WCA is determined by the properties of the surface itself after the treatment, as opposed to external factors caused by acetone sonication or airborne contamination etc. Moreover, this effect indicates that the extent to which the MGG samples were exposed to the flowing gases was different from side to side as opposed to the
difference in thermal contact considering that the temperature gradient from side to side is negligible for such a small piece. This effect makes sense as the backside of the sample, facing down and contacting with the quartz disk, would have no direct contact with the gas flow coming down from the top, therefore less impact of the gas-solid interactions would be expected compared to the top side.

![Graph showing linear correlation between accumulated weight loss and polishing times.](image)

**Figure 7.10.** Test illustrating the linear correlation of the accumulated weight loss (mg) and polishing times. Each data point is the averaged value of three tests ± standard deviation.

In order to investigate how different the two sides were in terms of gas contact and how deep the oxidation could occur inside the MGG samples, the samples were polished with the sandpaper (grit 220) to remove the surface carbon, which is in a similar fashion with the process used to polish MGG-raw samples. All polishing followed the same procedure to ensure the consistency of surface roughness. The amount of carbon that was removed every time was approximately the same as verified by a test shown in Figure 7.10. From this linear correlation of the accumulated weight loss and the polishing times, we can derive the depth of removal per polishing time according to the cylindrical geometry and the sample’s density, which turned out to be about 114
μm in depth. Readers are referred to Appendix E for details of the calculations. After each polishing, WCA was measured a few times and averaged.

**Figure 7.11.** Comparison of apparent WCA of the MGG-raw (black) and MGG-N\textsubscript{2}-700-0.5hr (light gray) and its samples after being polished once (gray) and twice (dark gray). All samples are sonicated with acetone and deionized water after polishing.

MGG-N\textsubscript{2}-700-0.5hr was used to test this side-to-side difference effect. The WCAs for both sides of the original treated sample and its polished samples are shown in Figure 7.11. All samples were sonicated with acetone and deionized water for consistency. As seen in Figure 7.11, the MGG-N\textsubscript{2}-700-0.5hr before polishing had a much lower WCA on both sides compared to MGG-raw (black bars), and after the first polishing, one of the sides (Side 2), had a WCA equivalent to MGG-raw and the other side (Side 1) remained the same (gray bars). After the second polishing, it is found that the WCA of Side 2 remained high and that of Side 1 increased from around 84° to 102° (dark gray bars). The lower WCAs of the original thermally treated sample suggest that both sides, more or less, were subject to oxidation on the surfaces. After the first polishing, the results indicated that the oxidized top graphite was thoroughly removed for the side facing down,
while heteroatoms were still present even after over 100 μm of carbon was removed in depth from the other. After the second polishing, it was not surprising that Side 2 remained the same in WCA, confirming the depletion of all heteroatoms on this side, however, it was interesting to find the WCA increased by over 20% on Side 1, indicating that the oxygen groups were decreasing in quantity, leaving the wettability of Side 1 less affected by oxidation. From this test we can summarize that the side-to-side difference in oxidation can be very significant – over 200 μm in depth for the directly exposed side and less than 100 μm for the backside. This test concluded that at such high temperature, impurities in the gas feed is a great issue because the ppm level oxygen can penetrate through the surface and oxidation can occur very deep inside the bulk for a multi-grain carbon material with some degree of porosity.

7.3.2 Acetone and deionized water cleaning

One action that may also make the surface less hydrophilic is improper cleaning. Acetone and other organic solvents are frequently found used for cleaning of graphite [76, 77]. However, when using organic solvents to clean graphite or graphene samples, especially using sonication for a thorough cleaning, chances of contaminating the surface are great - the organic residuals can result in a much more hydrophobic surface due to the decrease of surface energy and they will still be present even after cleaning with water sonication for a couple of times, as shown by the results below.

For the HOPG basal surface, three samples were sonicated with acetone and deionized water in sequence for 3 min, and then collected once they became dry. Figure 7.12 illustrates the WCA changes with respect to time after the HOPG surfaces were collected. It is shown from the figure
that the average WCA is $87.4 \pm 4.9^\circ$ for the three intentionally contaminated surfaces and no increasing trends were found for the contact angles. These numbers are slightly higher ($\sim 5.5^\circ$) than the aged HOPG sample after a day’s exposure to air, suggesting that this intentional contamination by acetone sonication is a bit more serious than the airborne contamination such that it overrides the presence of latter in terms of surface wettability. It is therefore recommended that direct cleaning of graphite or graphene by organic solvents be avoided or used in caution when studying wettability.

Similar to the HOPG basal surface, the side surfaces can also get affected by acetone sonication. The WCA of HOPG-Side-90° can reach as high as $103.2 \pm 4.8^\circ$ when intentionally contaminated with acetone, which is much higher than the intrinsic WCA estimated. Similar to the effect of surface oxidation, the contamination effect on the sides by acetone sonication seems to be worse than that on the basal surfaces. This can be explained by the relative higher roughness and higher energy of side surfaces, which can help to trap more acetone molecules on the surfaces.
Figure 7.12. Static WCA of three acetone-and-deionized-water-sonicated HOPG surfaces exposed to air at the same time. Each data point represents the WCA from single tests, and the dotted line represents the average WCA (87.4°) of all three surfaces.

For MGG samples, following the discussions of surface oxidation in Figure 7.9 and Table 7.5, we also found that acetone sonication can have a great impact on wettability. In Figure 7.9, the presence of acetone has been verified by the O 1s peak consistently appeared; compared to MGG-He-600-1hr in Table 7.5, as well as MGG-He-700-0.5hr and MGG-N2-700-0.5hr before acetone and deionized water sonication (data not presented), the latter two samples after the sonication (see Table 7.5) became much less hydrophilic or even hydrophobic. Considering the roughness and porosity, the MGG samples can be more susceptible to acetone contamination compared to HOPG, which partially accounts for a much greater difference in WCA before and after the acetone sonication.

It can thus be summarized that acetone sonication will affect the surface wettability of all the graphitic samples used in this study due to the acetone residue detected on the surfaces. Therefore cautions should be taken when using acetone sonication as a cleaning method when investigating surface wettability.
7.3.3 Sulfurization

As previously mentioned, the porous carbon material – multi-grain graphite – is a good alternative to study the wettability of chemically treated activated carbon. It is porous in the bulk yet relatively flat and smooth on the surface, providing the appropriate conditions for taking water contact angle measurements. SO$_2$ treated samples MGG-SO$_2$-10min and MGG-SO$_2$-30min, which were treated in SO$_2$ flow for 10 and 30 min at the same temperature, respectively, were tested for their WCAs on both of the sides immediately after the treatment. WCA of the H$_2$SO$_4$ treated sample MGG-H$_2$SO$_4$-17hr was also measured for comparison as an aqueous method of sulfur impregnation. Figure 7.13 shows the WCAs of MGG-SO$_2$-10min, MGG-SO$_2$-30min, MGG-H$_2$SO$_4$-17hr, and that of MGG-He-1hr-220 for comparison. All samples were polished by the same piece of sandpaper and acetone-free.

It is seen from the figure that the side-to-side difference in WCAs was also present for SO$_2$ treated samples, which is expected in a similar fashion with the annealed samples. However, the effect seemed to be weakened when longer time of SO$_2$ treatment was applied, which enhances the contact of SO$_2$ with the graphite surfaces. More important, it is worth noticing that MGG-SO$_2$-30min has smaller contact angles on both of the sides compared to MGG-SO$_2$-10min, suggesting that a longer contact time of SO$_2$ with the MGG surfaces at high temperatures resulted in more hydrophilic surfaces due to the introduction of more heteroatoms such as sulfur and oxygen. The result of becoming hydrophilic also occurred for MGG-H$_2$SO$_4$-17hr, which has a similar WCA with MGG-SO$_2$-30min. 17 hr of contact between H$_2$SO$_4$ and carbon was long enough for the reaction to reach equilibrium and introducing sufficient amount of sulfur groups such as sulfate and sulfonic acid groups etc. However, comparing all the sulfur treated samples with MGG-He-1hr-220, it is found that the latter sample is more hydrophilic, even for the side
that was less exposed to Helium flow during the treatment. Given the similar roughness conditions of all samples in the figure, and considering that all the WCA measurements were completed within the first minutes of air exposure, the difference in WCAs comes from the difference in the surface treatments: the differences in the treatment time and the reagent used.

One may argue that the reason why the surfaces of MGG-He-1hr-220 were more hydrophilic is caused by the longer reaction time compared to the SO$_2$ treated samples. This sounds reasonable if time is the only difference; however, in this comparison, given the orders of magnitude lower oxygen concentration (in ppm) in the He stream compared to the SO$_2$/N$_2$ mixed stream, we believe that oxygen functional groups that were impregnated onto the graphite surfaces were more effective than the sulfur functional groups in terms of enhancing the wettability of the MGG samples.

![Figure 7.13. Comparison of WCAs of MGG-He-1hr-220 (white bars), MGG-SO$_2$-10min and MGG-SO$_2$-30min (grey bars), and MGG-H$_2$SO$_4$-17hr (black bar). None of the samples were sonicated with acetone and deionized water.](image)
For detailed information of the functional groups on the surfaces of sulfur treated samples, S 2p XPS analyses were carried out using the peak fitting method. The detailed data of peak binding energies and intensities are listed in Table 7.7.

The S 2p signals, no matter strong or weak, were split into two ranges – Peak 1 (168.1-168.9 eV) and Peak 2 (163.8-164.3 eV). For MGG-raw, it is seen from Table 7.7 that there seems to exist some trace amount of sulfur on the surface. However, given the fact that the raw MGG is relatively pure (99.9%) in carbon, the signals of Peak 1 and Peak 2 detected in S 2p could only be regarded as background noise; for MGG-SO2-30min-S1 and MGG-SO2-30min-S2, we can hardly justify the validation of Peak 1 intensities, as the values are just slightly higher than that of the raw graphite, the background level. The Peak 2 intensities, on the other hand, stand out the background value, suggesting some form(s) of sulfur is present on the surfaces. The difference in

### Table 7.7. S 2p XPS peak binding energies and intensities for MGG-raw, MGG-SO2-30min (Side 1 and 2), and MGG-H2SO4-17hr.

<table>
<thead>
<tr>
<th>S 2p</th>
<th>B.E. of Peak 1 (eV)</th>
<th>B.E. of Peak 2 (eV)</th>
<th>Peak 1 intensity (cps.eV)</th>
<th>Peak 2 intensity (cps.eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGG-raw</td>
<td>168.3</td>
<td>164.3</td>
<td>106.3</td>
<td>54.3</td>
</tr>
<tr>
<td>MGG-SO2-30min-S1</td>
<td>168.1</td>
<td>164.0</td>
<td>121.7</td>
<td>131.0</td>
</tr>
<tr>
<td>MGG-SO2-30min-S2</td>
<td>168.4</td>
<td>164.2</td>
<td>137.0</td>
<td>234.0</td>
</tr>
<tr>
<td>MGG-H2SO4-17hr</td>
<td>168.9</td>
<td>163.8</td>
<td>577.7</td>
<td>17.0</td>
</tr>
</tbody>
</table>
Peak 2 intensity of MGG-SO₂-30min-S1 and MGG-SO₂-30min-S2 (131.0 cps.eV vs. 234.0 cps.eV) further confirms the side-to-side difference and indicates that the sulfur is impregnated via the SO₂ treatment. The corresponding binding energy of Peak 2 falls in the range of 164.0-164.2 eV, suggesting the presence of sulfide, disulfide, and/or elemental sulfur on the surfaces; for MGG-H₂SO₄-17hr, the result turned out to be the opposite from the two sides of MGG-SO₂-30min, as a Peak 1 of great intensity appeared whereas almost no signal was detected for Peak 2. The corresponding binding energy of Peak 1 in this case is 168.9 eV, which could represent the presence of sulfate, sulfonic groups, or both. Both of the results for MGG-SO₂-30min and MGG-H₂SO₄-17hr make sense because the corresponding functional groups are originated from the reagents used for different sulfur treatments. It is also suggested that although these sulfur functional groups are hydrophilic on the whole, the oxygen functional group(s) introduced by the annealing could be even more hydrophilic, as reflected by the lower WCAs shown in Figure 7.13.
Chapter 8  Conclusions and recommendations

8.1  Conclusions of Part II

The following conclusions could be drawn from the work in Part II:

1. For HOPG, the basal surface was found intrinsically hydrophilic (61.6°), which is consistent with, or even lower than the latest finding in the literature; the side surfaces were also found hydrophilic (most likely < 40°), which was the first time WCA was reported for HOPG sides. Moreover, the observed roughness of the side surfaces was found to have negligible effect on the surface wettability due to its relative small scale; however, it can result in some uncertainties when measuring the WCAs;

2. For MGG, the apparent surface WCA was measured and the raw surface was found hydrophobic (120.8±3.6°). Nonetheless, the WCA didn’t represent the intrinsic WCA due to contamination and roughness. It is suggested that the surface roughness can be easily altered by different grades of sandpapers, which significantly affects the surface WCAs. In addition, corrections of the wettability of MGG were made based on the affecting factors. It was estimated that MGG is also hydrophilic (80-90°) if the surface is smooth and contamination-free.

3. Among the factors that can alter the surface chemistry, airborne hydrocarbon contamination decreases the surface energy and thus increases the WCA significantly for the HOPG basal surface; the annealing, a process that was designed for removing surface contaminants, was found to oxidize the surfaces all the graphitic carbons. The introduced
oxygen groups were detected by XPS and make the surface more wettable by increasing the surface energy, which decreases the WCAs by 10-20° for HOPG and even worse for MGG; residual of acetone via sonication cleaning can remain on the surfaces of the graphitic carbons and make the surfaces less hydrophilic or even hydrophobic; graphite sulfurization via high temperature SO₂ treatment and hot H₂SO₄ bath was found effective and can keep the surface hydrophilic (about 40°), though it may be less effective than the oxygen functional groups introduced by the annealing (about 15-30°).

4. Based on the studies above and considering the great roughness of pore wall and the presence of high-energy edge carbon and sulfur atoms, the internal surface of SIAC is expected to be highly hydrophilic.

8.2 Recommendations for future studies

1. For the study of the wettability on the HOPG side surfaces, machine cutting and polishing techniques are recommended for flatter and smoother surfaces, which helps to reduce systematic errors and deviations from the true WCA;

2. Techniques or methods that can remove surface contaminants without introducing new contamination are favorable and remain to be further investigated, which helps to reveal the intrinsic wettability of surfaces;

3. Quantitative estimation and determination of surface oxidation and contamination for smooth and rough surfaces based on atomic or molecular scale interactions is to be further studied;

4. Comprehensive modeling and predictions of wettability on rough and contaminated surfaces would be a necessity for surface wettability studies.
References


Appendices

A. Petroleum coke SO$_2$ activation procedures

1. Load samples into the furnace work tube. For activated carbon, no more than 20g are allowed per batch for safety concerns. It is recommended to place some glass wool (not too much) on the quartz disk before loading samples. A way of determining the maximum capacity per batch: load the sample and flush the work tube with N$_2$ at 100 mL/min. The final reading of the pressure gauge should never go over 2/3 of the range.

2. Apparatus setup. See Figure A - 1. Special care is needed to handle with glassware. All connections should be applied with high-temperature grease (DuPont Krytox) and fastened with appropriate ball & socket stainless steel clamps.

3. Add a generous amount of NaOH to the scrubbing solution and dissolve it. For 5 hr of SO\textsubscript{2} activation, at least 50 g is needed.

4. Flush the system with N\textsubscript{2} at room temperature for leakage check using the bubble test. Make sure no bubbling is detected around the connections. The flow rate meter at the rear is used to help identify if there is a leakage.

5. Turn on the furnace and go on flushing the system with N\textsubscript{2} (SO\textsubscript{2} off) for 15 min at 100-120 °C to drive out moisture.

6. Turn on the H\textsubscript{2}S detector.

7. The temperature of the furnace will increase from 100°C to 700°C at a rate of 15°C/min (already set). Before the temperature reaches 400°C, divert the gas flow to bypass by turning the 3-way stopcock near the pressure gauge.

8. Turn on the SO\textsubscript{2} cylinder and let it stabilize at about 100 mL/min. The flow rate of SO\textsubscript{2} at first will fluctuate, and approximately 10 min would allow it to stabilize.

9. When 700°C is reached, introduce SO\textsubscript{2}+N\textsubscript{2} to the reactor by turning back the 3-way stopcock.

10. Count time for a 5 hr-long reaction period.

11. When 5 hr is reached, shut off SO\textsubscript{2} immediately. Leave N\textsubscript{2} flowing to cool down the system.

12. When the furnace is cooled to 60°C or blow, stop the N\textsubscript{2} feed. Clean the socket of the work tube and collect the samples.
13. Weigh the treated samples. Calculate the difference before and after the treatment.

14. Clean the work tube, connectors and the sulfur collection tube.
B. Procedures for mercury analyzer calibration and mercury concentration analysis

The mercury analyzer was calibrated every time before use to ensure the concentration reading of Hg\(^0\) vapor is accurate. The calibration instrument used was a Tekarn 2505 Mercury Vapor Calibration Unit, which supplies an accurate concentration of Hg vapor at a given temperature. The calibration follows the procedure below:

1. Run the vendor software “TekMDS 2.5” and fill in the working information, including the syringe temperature, descriptions, operator etc.;

2. In the spreadsheet, set the first two lines in “Clean” mode by selecting the cells under the Sample column of the first two rows and right click to choose “Clean”;

3. Overwrite the Sample cells of three separate lines with “vol0”, “vol4”, “vol6”, and “vol7” for Hg injections. The “vol” is short for “volume” and the number behind it represents the volume in μL of Hg vapor to be injected. Allow 1-2 blank lines between the overwritten lines to avoid signal overlapping and noise buildup;

4. Run the program by clicking the “Run Worksheet” button in the menu bar;

5. Use a 10 μL syringe (Hamilton Co.) and take the amount of Hg vapor as set when the small black figure walks in the corresponding overwritten line. Inject the vapor into the mercury analyzer when it beeps. For “vol0”, do not inject any amount of Hg vapor and leave the instrument run by itself;

6. After the completion of all injections, a calibration line will be formed automatically and can be viewed by clicking in the menu bar. The equation will also be displayed at the top of the spreadsheet. An example of the calibration curve is shown below in Figure A-2.
Figure A - 2. Example of a calibration curve generated for Hg vapor analysis by the vendor software TekMDS 2.5.

To measure the Hg vapor concentration from the fixed-bed reactor, a 2 mL syringe was used to sample the inlet and out Hg\(^0\) vapor and then inject into the analyzer. Readings of the concentrations will be available within 3 min and automatically saved in an Excel worksheet. To obtain the breakthrough curve, time will be recorded for each injection.
C. Procedures for calculating water contact angles in ImageJ (with drop analysis plugin)

1. Download ImageJ and the drop analysis plugin from the link below:
   http://bigwww.epfl.ch/demo/dropanalysis/.
   Extract drop_analysis.zip in the "plugins" folder of ImageJ;

2. In ImageJ, click “Open” in the “File” menu to open a WCA image. Then click “Image” in
   the menu bar and click “Type” to select “8-bit” to convert the image into gray scale;

3. In the “Plugin” menu, go under “drop_analysis” to select one of the two methods
   provided: “DropSnake” or “LB-ADSA”. The latter method was chosen for demonstration;

4. In the pop-up window, several drop parameters can be used to roughly adjust the water
   drop profile using the sliders. Make sure the drop is surrounded by the rough green
   profile;

5. Click the “Region Energy” button at the bottom left corner to optimize the profile and
   obtain the contact angle. If the optimization fails, that is to say the optimized green
   profile doesn’t match the drop shape and the WCA deviates much from the approximate
   value, fine adjustments can be made by zooming in the image and slightly sliding the
   parameter bars using the arrow buttons on keyboard.

   An example of the software interface and the parameter window is shown below in Figure A
   - 3.
Figure A - 3. Interface and parameter window for WCA calculation by the LB-ADSA method in ImageJ (with drop analysis plugin).
D. **T-test method**

To compare the mean values of two groups of WCA measurements, t-tests were used to determine if they are significantly different. A significance level of $\alpha=0.05$ was used.

The following formula was applied:

$$t = \frac{\bar{x}_1 - \bar{x}_1 - \Delta}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

where $\bar{x}_1$ and $\bar{x}_2$ are the means of the two measurements, $\Delta$ is the hypothesized difference between the two means, $s_1$ and $s_2$ are the standard deviation of the two groups, and $n_1$ and $n_2$ are the sizes of the two groups. The degrees of freedom equals the smaller number of $n_1 - 1$ and $n_2 - 1$.

The calculated t value, together with the degrees of freedom, will be used to look up the critical parameter in the t-table available in most of the statistical handbooks. If the computed t doesn’t exceed the corresponding value in the table, it will indicate that the two groups are not statistically different. If it does, then the two groups will be different from the statistical scope.

Here is an example, to determine if the WCAs of $27.8 \pm 3.4^\circ$ and $28.8 \pm 2.1^\circ$ are significantly different, the t was found to be 0.546 and the critical parameter was found to be 3.182. As 3.182 is greater than 0.546, it is concluded that the two means are not significantly different.
E. Calculations of carbon removal by MGG polishing

To calculate the average carbon removal amount (mg) per polishing by the sandpaper (220 grit), three MGG disks were prepared and polished following the same procedure:

1. Weigh the sample every time before polishing;
2. For each polishing of every sample, rub the sample on the sandpaper in circles with a constant, gentle force applied on the sample;
3. Keep rubbing for 20 circles;
4. Clean the sample with deionized water sonication for 3 min and let it dry;
5. Weigh the sample again when it becomes dry;
6. Clean the sandpaper for other trials.

Table A - 1 lists the data used to calculate the carbon removal amount. The diameter and the density of the MGG samples were measured beforehand.

Table A - 1. Data measured for calculation of carbon removal amount by polishing for MGG.

<table>
<thead>
<tr>
<th></th>
<th>Disk 1</th>
<th>Disk 2</th>
<th>Disk 3</th>
<th>AVG</th>
<th>SDev.</th>
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</thead>
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<tr>
<td>D (mm)</td>
<td></td>
<td></td>
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<td>7.90</td>
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<tr>
<td>m0 (mg)</td>
<td>288.64</td>
<td>292.02</td>
<td>305.76</td>
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<td>ρ (g/cm3)</td>
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<tr>
<td>m_after 1st polishing (mg)</td>
<td>281.18</td>
<td>281.60</td>
<td>296.18</td>
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<td>m_after 2nd polishing (mg)</td>
<td>271.27</td>
<td>269.60</td>
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<td>m_after 3rd polishing (mg)</td>
<td>263.68</td>
<td>260.11</td>
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<td>Δm1 (mg)</td>
<td>7.46</td>
<td>10.42</td>
<td>9.58</td>
<td>9.15</td>
<td>1.25</td>
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<tr>
<td>Δm1+Δm2 (mg)</td>
<td>17.37</td>
<td>22.42</td>
<td>20.17</td>
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<td>31.91</td>
<td>29.94</td>
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<td>Δm1 (mg)</td>
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<td>AVG depth of loss (μm)</td>
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