MATERIAL DEVELOPMENT AND CHARACTERIZATION FOR HIGH SAILINITY WATER DESALINATION BY MEMBRANE DISTILLATION AT HIGH TEMPERATURE AND PRESSURE

BY

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THESIS
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ABSTRACT

Ever increasing demand of water for different applications is creating more pressure on limited freshwater resources. In addition to domestic, public, and agricultural usage, industrial use of water is contributing to the water shortage. The use of non-traditional water resources for the energy sector may help meet the expected increase in water demand. Many produced water sources in the US have total dissolved solids (TDS) values more than 50,000 ppm, much higher that the TDS value of the seawater (~35,000 ppm). Desalination of high salinity water, which is currently being disposed by underground injection, can provide an alternative water source for industrial applications. As Reverse osmosis and thermal-based techniques cannot be applied either technically or in a cost-effective manner for treating high TDS water, membrane distillation (MD) might be a potential economically viable option for this purpose. But, current membrane distillation technology that is operated at low temperatures (e.g. ~50°C) produces low water flux. By increasing the driving potential by means of increasing the feed water temperature, flux can be increased. The work lost due to vapor flow through the membrane at low temperature and pressure can be minimized by running the process at the critical condition of water, where the compressibility is almost infinite, and thus eliminating the need for a large pressure differential across the membrane.

The focus of this MS research, presented in this thesis, is on the development and characterization of suitable materials for high temperature and pressure MD applications. My future work will aim at developing more advanced materials and systems for MD desalination. Several commercially-available or laboratory-fabricated carbon materials including graphite, porous graphite, diamond-coated stainless steel, and carbon-coated ceramics; and various other ceramics (e.g. TTZ, ZTA etc.) are tested at supercritical conditions of water under oxic and anoxic conditions. Experiments are conducted to establish carbon-based materials as suitable membrane materials for use at supercritical temperature and pressure of water under anoxic conditions. Contact angle measurements of samples before and after exposure to supercritical water are used to show that hydrophobicity of carbon materials does not change due to hydrolysis at supercritical condition of water under anoxic conditions.

Samples are extensively characterized using XPS (X-ray Photoelectron Spectroscopy), FTIR (Fourier Transform Infrared Spectroscopy), XRD (X-ray Diffraction), AES (Auger
Electron Spectroscopy), SEM (Scanning Electron Microscopy), and surface profilometry. Results indicate that the majority of carbon materials tested maintain their original physical and chemical properties after exposure to supercritical water in the absence of dissolved oxygen. However, under oxic conditions, a significant change in the surface chemistry of materials is observed due to oxidation and hydrolysis reactions in supercritical water.
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Chapter 1: Introduction

1.1 Objective

The objective of this project is to find or develop suitable materials that remain hydrophobic i.e. allow transport of water vapor and repel liquid water and hydrophilic salts after exposure to supercritical water, and therefore can be used as a membrane in a membrane distillation system, which can operate at high temperature and pressure conditions.

1.2 Fresh water resources and demand

A limited volume of freshwater resources is available for human use. In the world, 97.5% of the total water reserve is salt water, and among 2.5% fresh water, 1.63% is almost unavailable because it is found in icecaps, glaciers and ice-snow in two poles. The fresh water that can be utilized by humans without any treatment only accounts for 0.77% of the total water reserve [1]. Water pollution has further aggravated the freshwater shortage. Thermoelectric power plants and agricultural irrigation are the two main sectors which account for about 80% of the total water withdrawal in the US (Fig. 1).

Water, as having four times the specific heat capacity compared to air, is suitable for transporting heat in power plants and other heat transfer applications. Coal-fired power plants are the second largest users of freshwater in the United States. In Illinois, the thermoelectric power sector accounts for approximately 84 percent of the estimated 14 billion gallons per day of freshwater withdrawals and one-third of the State’s 1 billion gallons per day of freshwater consumption [2, 3]. Water consumption by thermoelectric power generation is predicted to significantly increase in the future due to higher electricity demands and possible implementation of CO$_2$ capture and sequestration.
Figure 1: Water withdrawal by category in the USA in a percentage scale ([4])

About one third of the energy consumed in the USA is attributed to the transportation sector [5]. Large volumes of water are needed for the extraction and production of conventional fossil-based liquid fuels used by the transportation sector. Alternative emerging fuels and energy carriers such as biofuel and hydrogen also consume water and further increase fresh water demands of the energy sector.

The use of non-traditional water resources for the energy sector may help meet the expected increase in water demand. Reuse of produced water from CO₂ enhanced oil recovery, coal-bed methane, and mine pool water from coal-fired power plants may provide a solution to the problem. Reuse of saline water from CO₂ sequestration in deep saline aquifers may be another solution.

The amount of produced water collected in the US in 2007 from oil and gas fields combined is 57.4 million gallons/day [6]. More than 98% of that produced water from onshore wells is injected underground for disposal [6]. The majority of produced water resources is contaminated with hydrocarbons and other contaminants, and has high salt contents. Many produced water sources in the US have total dissolved solids (TDS) values more than 50,000 ppm, much higher that the TDS value of seawater (~35,000 ppm) (Fig. 2).

Desalination of high salinity water by conventional distillation-based technologies is costly and requires a large energy input. Lowering the energy requirements for desalination of high TDS water is a major challenge, but it can be accomplished by developing innovative water
desalination systems. Cost-effective and efficient water desalination technologies for treating high salinity water are needed to make the utilization of produced water resources feasible.

Figure 2: TDS level of produced water in the USA (Source: Mercier Tracey [7])

1.3 Water desalination and membrane distillations

Distillation or thermal evaporation and membrane processes are currently being used for seawater and brackish water desalination. Advantages of membrane processes over thermal processes are: low energy consumption, accessible operation conditions and simple maintenance, as well as high construction compactness. Current Membrane technologies include microfiltration, ultrafiltration, nanofiltration and reverse osmosis (RO). RO is generally not suitable for high TDS water desalination due to an increase in osmotic pressure and concentration polarization with an increase in the TDS value. At high salinities and high recoveries (55,000 mg/L TDS and above 35% recovery), the pressure required for membrane desalination can exceed the maximum allowable pressure of the membrane module [8]. Seawater reverse osmosis membranes are usually operated between 10,000-60,000 ppm [8]. With increasing salt concentration, the salt rejection rate of RO starts to decline [1]. In the case of RO,
the major energy required for desalination is for pressurizing the feed water, typically up to 60 bars for seawater which is supplied by electrical energy. The disadvantage of RO is the sensitivity of RO membranes to fouling by e.g. suspended solids, damage by oxidizing compounds such as chlorine or chlorine oxides, and relatively low removal of lower molecular weight contaminants. Scaling by compounds such as CaCO₃, CaSO₄, and BaSO₄ is another possible problem. Increasing the recovery has a negative impact on membrane scaling as well. Two emerging techniques for desalination are forward osmosis and membrane distillation (MD). MD is less affected by concentration polarization phenomena as it is the case in pressure driven processes and contrary to RO, a high salt concentration retentate can be achieved in MD. For comparison, membrane distillation flux can be as high as 35 L/m²hr (for direct contact membrane distillation) similar to RO flux operated at the same condition [9].

Table 1: Energy requirement of different desalination processes for seawater desalination
(Source: V.G. Gude, N. Nirmalakhandan, and S. Deng [10])

<table>
<thead>
<tr>
<th>Process</th>
<th>Multi-effect distillation (MME)</th>
<th>Multi-stage distillation (MSF)</th>
<th>Multi-effect distillation (MED)</th>
<th>MVC</th>
<th>MED-TVC</th>
<th>Reverse osmosis</th>
<th>ED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal energy (kJ/kg)</td>
<td>1500</td>
<td>250-300</td>
<td>150-220</td>
<td>-</td>
<td>220-240</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Electrical energy (kWh/m³)</td>
<td>0</td>
<td>3.5-5</td>
<td>1.5-2</td>
<td>11-12</td>
<td>5-9</td>
<td>2-5.5</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen from Table 1, RO requires more electrical energy and no thermal energy as compared to conventional thermal distillation systems. As electrical energy is expensive compared to thermal energy, desalinated water cost for RO is higher than conventional thermal system at smaller scale as shown in Table 2. But at large scale, RO performs better than MED (Multi Effect Distillation) and MSF (Multi Stage Flash). Small scale membrane distillation shows inferior performance than RO and conventional distillation techniques due to its small capacity, heat transfer challenges, low flux, and other issues. Therefore, membrane distillation currently is not economically viable for sea water desalination. But for high TDS water, where RO cannot operate due to a high osmotic pressure barrier, membrane distillation provides a membrane based alternative. Membrane distillation can also be used in conjunction with other distillation techniques to desalinate high TDS retentate solution. Membrane distillation, which combines the advantage of thermal energy and compactness of membrane systems, may give better energy efficiency when operated at high temperature and pressure.
Table 2: Energy cost of different desalination techniques for sea water desalination (Source: V.G. Gude, N. Nirmalakhandan, and S. Deng [10])

<table>
<thead>
<tr>
<th>Desalination process</th>
<th>Capacity (m³/day)</th>
<th>Energy source</th>
<th>Energy cost ($/kWh)</th>
<th>Desalinated water cost ($/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD</td>
<td>0.1</td>
<td>Solar</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>0.5</td>
<td>Solar</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>1</td>
<td>Geothermal</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>MSF</td>
<td>1</td>
<td>Solar</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>Solar still</td>
<td>5</td>
<td>Solar</td>
<td>0.52–2.99</td>
<td></td>
</tr>
<tr>
<td>ED</td>
<td>5</td>
<td>Electric</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>RO</td>
<td>10</td>
<td>Electric</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>MED</td>
<td>&lt;100</td>
<td>Conventional</td>
<td>2.5–10</td>
<td></td>
</tr>
<tr>
<td>MVC</td>
<td>375</td>
<td>Conventional</td>
<td>2.9–3.8</td>
<td></td>
</tr>
<tr>
<td>Large-scale applications</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dual-purpose MSF</td>
<td>20,000</td>
<td>Natural gas/steam</td>
<td>0.0001</td>
<td>0.08</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>2000</td>
<td>Diesel generator</td>
<td>0.06</td>
<td>2.23</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>5000</td>
<td>Diesel generators</td>
<td>0.06</td>
<td>1.54</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>10,000</td>
<td>Diesel generators</td>
<td>0.05</td>
<td>1.18</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>20,000</td>
<td>Diesel generators</td>
<td>0.05</td>
<td>1.04</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>50,000</td>
<td>Diesel generators</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>95,000</td>
<td>Conventional</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>100,000</td>
<td>Conventional</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>100–320 × 10³</td>
<td>Conventional</td>
<td>0.45–0.66</td>
<td></td>
</tr>
<tr>
<td>MED</td>
<td>91–320 × 10³</td>
<td>Conventional</td>
<td>0.52–1.01</td>
<td></td>
</tr>
<tr>
<td>MSF</td>
<td>23–528 × 10³</td>
<td>Conventional</td>
<td>0.52–1.75</td>
<td></td>
</tr>
</tbody>
</table>

Also, effectiveness of the salt separation during MD is relatively constant and the purity of distillate is practically independent of the contaminant feed concentration. Other advantages of MD include the possibility of using of low grade thermal energy and less dependency on pretreatment. Four types of MD are direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD) and vacuum membrane distillation (VMD). For VMD, enhanced mass transfer can be achieved due to the application of low pressure on the permeate side. No concentration polarization effect was observed for vacuum membrane distillation up to the salt concentration of 300g/L [11]. Also, For VMD with deionized water used as feed solution, water flux increases with the increase in temperature and circulation velocity as shown in Figure 3 [12]. The same phenomenon is observed and predicted for other MD processes as well [9, 13].
Figure 3: Membrane distillation flux for pure water at different temperature and different circulation velocity (deionized water was used as feed water) (Source: J.I. Mengual, M. Khayet, and M.P. Godino [12])

In MD, heat energy and a net mechanical work can be used to lower the saturation temperature for condensation. Also, work required for maintaining the transmembrane vapor pressure difference is lost. One way to recover this loss is to heat feed water to its critical temperature. Water at its critical point has almost infinite compressibility. Therefore, a minimal pressure difference across the membrane is sufficient to pass through supercritical water. The working principal of supercritical membrane distillation is schematically shown in Figure 4. Subcritical saline feed solution is pressurized and heated to the supercritical conditions at the membrane module. The supercritical (or subcritical) permeate is later utilized in a supercritical power cycle to generate electricity. The low heat value steam is then condensed to produce purified water.

In conventional MD systems, hydrophobic membranes are used to repel liquid water and allow transport of water vapor. Hydrophobic membranes are also needed when MD is operated at supercritical conditions. Supercritical water is very hydrolyzing and corrosive. Lowering the concentration of dissolved oxygen before heating the water may reduce the formation of hydroxyl and other oxygen-containing and polar groups on the material surface during supercritical water exposure and maintain surface hydrophobicity. A material that can withstand supercritical water and remain hydrophobic at that condition should be used to fabricate the membrane.
Figure 4: Schematic of supercritical water membrane distillation concept

1.4 Supercritical water

High temperature and pressurized water above its critical point i.e. supercritical water can be used for heat transport applications as well as other applications. Supercritical water (SCW) has attracted increasing attention in supercritical water oxidation (SCWO) [14,15], supercritical water gasification (SCWG) [16], hydrothermal synthesis, waste water oxidation, radioactive waste reduction, biomass conversion, plastic degradation, synthesis of nano-particles, fossil fuel thermoelectric plants, as well as being considered for future Generation IV (Gen IV) nuclear reactors. SCW has attracted interest as a coolant for next generation nuclear reactor concept systems because of its higher thermal efficiency which enables a nuclear system with a smaller volume and a simpler design. Supercritical water reactors which operate on supercritical steam cycles are more efficient as compared to current light water reactors (about 40% versus about 36% efficiency [17-19]). This is due to the use of a single phase coolant with high enthalpy, leading to the elimination of components such as steam generators, steam separators, dryers, and a low coolant mass inventory; and resulting in a more compact and efficient system. SCW has been successfully used in steam cycles in supercritical advanced fossil fuel power plants for many years to achieve high thermal efficiency and reduce plant emission. A major problem of using supercritical water is that it is highly corrosive, and for power plant applications it can corrode the reactor wall. Special reactor designs limiting contact of the corrosive species with the
reactor wall is an ongoing research topic. Supercritical water is highly oxidizing in SCWO environments found in waste treatment; while it is highly reducing in SCWG environments in industrial wastewater treatment and biomass gasification for hydrogen production in partial or total absence of dissolved oxygen. Specific heat of water is maximized at its critical conditions. This is a very attractive property for heat transport applications. Supercritical water has both liquid-like and gas-like properties, high diffusivity as vapor and good heat-transporting properties as liquid water. By changing the temperature and pressure in the supercritical region, supercritical water becomes completely miscible with nonpolar compounds, while polar and ionic compounds remain soluble as well. At low density nonpolar organic substances and gases can be dissolved. Therefore, SCW behaves like a non-aqueous solvent. In the presence of oxygen, acids, halogen and sulfur compounds supercritical water has a corrosive action on the reactor material and fittings. Water molecules at supercritical conditions participate in breaking and combining chemical bonds by lowering the activation energy [15, 16]. Specific heat of supercritical water is also very high (29.2 kJ Kg$^{-1}$K$^{-1}$) at 400°C and 29 MPa and changes with variations in temperature and pressure [15]. The viscosity of supercritical water is lower than water at ambient conditions (Fig. 5). The low viscosity reflects high molecular mobilities. Cluster formation occurs intensely in supercritical fluid and there is a local increase in density around the cluster. The molecules involved are in dynamic equilibrium with the solvent molecule. A local decrease in density around the cluster is also possible [15]. Dielectric constant decreases with increasing temperature and increases with increasing density (Fig. 6). This is due to the fact that at supercritical condition, the number of hydrogen bonds is small compared to the ambient conditions. At that temperature and pressure the extended network structure responsible for the unique properties of liquid water is lost. At dense supercritical water, hydrogen bonding is retained to an appreciable extent. The ion product (K_w) of water increases with temperature and density. Therefore, the auto dissociation of water is lower in supercritical water as compared to ambient water (Fig. 7).
With high solubility of oxygen in supercritical water, the oxidizing power of the solution increases. In SCWO, typical oxygen concentration is 5 mol/kg [14]. Usually, oxide formation is
more likely than hydroxide formation at the material surface near supercritical temperature of water [14]. The number of surface defects in the oxide layer on the material surface increases with the increase in temperature. Therefore, the protective nature of the oxide decreases with an increase in temperature. In cases where there is no more oxidizing agent (e.g. dissolved oxygen) that could further oxidize the pure metal surface after initial oxide removal, corrosion rate should decline. Therefore, corrosion rate can be controlled by reducing the concentration of dissolved oxygen in supercritical water. High or low values of pH of the solution can lead to a chemical dissolution, which is described as dissolution of the protecting oxide at constant electrochemical potential. This form of dissolution is caused by the amphoteric character of most oxides; they can be dissolved either in acidic or in alkaline solutions. At 25 MPa and 300°C (Kw = 10^{-11}) the concentration of H^+ and OH^- are more than an order of magnitude higher than that at ambient conditions (Kw = 10^{-14}) [14]. Under these conditions, water can be considered both acidic and alkaline.

The dissociation of salts, acids, and bases are related to the density or the ionic product of water. Both protective oxides on metal and alloys and the primary corrosion products are polar species. Increasing their solubility automatically means enhancing corrosion. Low density Supercritical water (pressure around 22.1 MPa) can only slowly and slightly remove salts in their ionic form. Under these conditions, the energy necessary to break the salt crystal lattice cannot be provided by hydration energy. Consequently, salts, which are highly soluble at ambient condition, are nearly insoluble in low density high temperature water (Fig. 8). But, the formed primary corrosion products can plug the surface and pose a new problem for systems operating with low density SCW.
The complete miscibility of oxygen with low density supercritical water and thus high partial pressure of oxygen should accelerate the cathodic corrosion reaction. On the other hand, the low solubility of ions hinders corrosion processes on metal surfaces. The cathodic reaction at the metal solution interface follows reaction (1) [14],

\[ O_2 + 2H_2O + 4e^- = 4OH^- \ldots \ldots \text{(reaction 1)} \]

However, this reaction leads to an enrichment of negatively charged hydroxyl ions at the metal surface, which cannot be dissolved by the non-polar solvent. Thus, a further cathodic reaction cannot occur. Therefore, corrosion is negligible at low densities (densities below 200-300 kg/m\(^3\)). The low density supercritical water region is the region of interest for our experiments. Corrosion does not affect the material performance in this region, but surface interaction with water or wettability will change if hydroxyl ions enrich the material surface. Our intention is to measure the contact angle after exposure to supercritical water of low density to find out any permanent change in the surface wettability characteristics of materials tested.

Computer simulation of supercritical electrolyte solutions flowing through a membrane has shown that stable ionic clusters present in that condition prevent the solute from penetrating the membrane [13]. Low shear cross flow microfilters were tested with water under supercritical conditions [20]. The filter elements were made of sintered stainless steel 316L tubes with a nominal pore size of 0.5 microns. Separation performance for alpha alumina particles of size 1.6 microns from supercritical water was checked. Particle separation efficiency was found to be
more than 99.9%. Increased shear rate (typical of supercritical water) resulted in increased amount of flux (50% increase in shear rate resulted in 10% increase in filtrate flux). Also, filtrate flux decline (10% in 90 minutes as compared to 80% within 25 minutes for low shear) was less significant at a higher shear rate in the cross flow microfiltration experiments. The reason given is that higher shear delayed the establishment of steady state conditions [20]. A 40% decrease in viscosity (typical of supercritical water) resulted in an increase in filtrate flux by a factor of five. Conclusion was the same filter element could handle higher filtrate fluxes at SCWO (supercritical water oxidation) conditions as compared to the ATP (atmospheric temperature and pressure) conditions, even with a smaller driving force (ΔP), but as the density of SCWO conditions is one third of the density at ATP, the SCWO filtrate mass flow rates were about one half of the ATP mass flow rates. Filtrate flow deterioration over time and the required transfilter pressure drop were about 40% less at supercritical water conditions as compared to the performance obtained at ambient conditions. Filter cake build up and membrane fouling were higher at ambient conditions as compared to supercritical conditions. At supercritical conditions back flushing was deemed unnecessary for the narrow range of particle concentration [20]. Operating at near-supercritical conditions might be beneficial as viscosity and mass diffusion coefficients are similar but the density is 3 to 4 times higher than supercritical water and thus the filtrate mass flow rate will be higher than that at supercritical conditions by a factor of 3 to 4 for a given filter [20]. But, operating at subcritical conditions will increase the probability of corrosion when inorganic salts are present in the filter feed [20].

1.5 Contact angle

On most surfaces, contact angle determines the behavior of the water – surface interaction rather than the surface tension of the solid. Contact angle between a liquid film and solid substrate is of primary concern for a number of processes e.g. adhesion, lubrication, floatation, transport in soil, development of biocompatible surfaces, control of bio fouling, boiling heat transfer, condensation, membranes and more. By investigating the surface property of materials after exposure to supercritical water by means of contact angle measurement, permanent change in material wettability due to supercritical water hydrolysis can be determined. Since there is no known technique to measure contact angle at supercritical conditions, no change in measurement of the change in material hydrophobicity after supercritical water exposure is one way to
determine if a material is suitable for supercritical membrane distillation.

As real surfaces are rough, the actual contact angle is the angle between the tangent to the liquid-fluid interface and the tangent to the local surface of the solid. But macroscopic measurement techniques give the apparent contact angle which is the angle between the tangent to liquid fluid interface and the line that represents the projected solid surface. Inclination of the solid surface may vary due to roughness. Thus, each point of a solid surface may have a different contact angle and only one which is at a global energy minimum will be equivalent to Young’s contact angle. In addition, other complexities like static and dynamic conditions, surface adsorption, penetration of the liquid into the solid, swelling of the solid by the liquid, and chemical reaction make the apparent contact angle deviate from Young’s contact angle (to be discussed later in this chapter). A goniometer is used to measure static contact angles. Some limitations of the goniometer technique involve the inability to reflect complexities of the solid-liquid interactions such as slip/stick mechanisms and physicochemical reactions. In cases where the liquid vapor surface tension of the sessile drop decreases due to the dissolution of the surface, a goniometer cannot indicate any change. Otherwise, goniometers give reliable contact angle values on flat solid surfaces.

A water droplet on a surface can be either in Wenzel or Cassie state. Homogeneous wetting governed by the Wenzel equation (Eqn. 1) [21].

\[ \cos \theta^* = R \cos \theta \] .................................................. (1)

Here \( \theta^* \) = apparent contact angle, \( \theta \) = Young’s contact angle, \( R \) = ratio of true solid surface area to apparent area.

This equation is based on the assumption that the liquid completely penetrates into the roughness grooves of the material surface. When the roughness of the surface is high, air bubbles may get trapped inside the roughness grooves, underneath the liquid. Contact angle for the later situation follows Cassie’s equation (Eqn. 2) [21] and this situation is referred to as heterogeneous wetting or Cassie’s state.

\[ \cos \theta^* = R_f \cos \theta + f - 1 \] .................................................. (2)
Here, $\theta^*$ = apparent contact angle, $\theta$ = Young’s contact angle, $R_f$ = roughness ratio of the wet solid area, $f$ = fraction of projected area of the solid that is wet by the liquid.

The apparent contact angle of the water droplet on a rough surface is determined by the average of the contact angles in air and on the solid surface with respect to their respective area fraction. Two states are distinct but droplets in the Cassie state can be transformed to Wenzel state by applying pressure, voltage, or by applying vibration. Both Wenzel and Cassie equations become better when the drop size is two or three orders of magnitude larger than the roughness of the surface. Therefore, Cassie and Wenzel equations can be used for surfaces with small roughness value. These equations are valid for axisymmetric drops as according to theory and simulations. For a drop to be axisymmetric, it has to be sufficiently large compared to the scale of roughness or heterogeneity. A goniometer measurement that uses the side view of the water droplet does not ensure the axisymmetry of the droplet. In practice, most surfaces have a roughness on the order of microns, while typical drops are on the order of millimeters. Therefore, the goniometer readings are reliable indicators of surface wettability for practical applications.

If only air were present between the solid and the liquid (as for a water drop on a very hot plate), the contact angle would be 180°. This is due to the Leidenfrost effect. The Leidenfrost effect is a phenomenon in which a liquid, in near contact with a mass significantly hotter than the liquid's boiling point, produces an insulating vapor layer which keeps that liquid from boiling rapidly.

Liaw and Dhir studied the contact angle of water on a copper surface [22]. They reported the values of 38° for an oxidized surface and 107° for a nonoxidized surface. Hong, Imadojemu and Webb commented that oxidation has a roughening effect on the material surface [23]. Also, the roughening effect seems to diminish as the original surface is made smoother. They also commented that contamination of the fluid and surface oxidation decreases the contact angle. They found when two surfaces are similarly oxidized, the surface that was smoother before oxidation, showed a smaller contact angle.
1.6 Wetting transition

Under saturated vapor conditions, equilibrium contact angle \( \theta \) of water on a solid surface can be measured by Young’s equation (Eqn. 3),

\[
\sigma_{gs} = \sigma_{ls} + \sigma_{lg} \cos \theta \quad \ldots \ldots (3)
\]

Here, \( \sigma_{gs} \)=Surface tension between gas and solid
\( \sigma_{ls} \)= Surface tension between solid and liquid
\( \sigma_{lg} \)= Surface tension between gas and liquid
\( \theta \)= Young’s contact angle

This equation can be simplified by using the Sharp Kink approximation. By using this approximation, gas-liquid interface gap can be considered as negligible, and the liquid density is thought to change abruptly from its bulk value to zero at a certain distance above the substrate [24]. The equation becomes (Eqn. 4),

\[
\sigma_{ls} = \sigma_{gs} + \sigma_{lg} + \Delta \rho \int_{z_{\min}}^{\infty} V(z) \, dz \quad \ldots \ldots \ldots (4)
\]

Where \( \Delta \rho \) is the change liquid density, \( z \) is the distance from surface, \( V \) is the potential energy, and \( z_{\min} \) is the position of the minimum of the potential energy near the surface, \( V(z) = V_s - V_l \) describes the net preference of the adsorbate molecule for wetting the substrate instead of forming a droplet. \( V_s \) is the potential energy of the adsorbate molecule due to the substrate, and \( V_l \) is the potential energy of the adsorbate molecule due to a hypothetical puddle of bulk liquid at the same location as the substrate.

Then using equation (3) and (4) we get (Eqn. 5),

\[
\cos \theta = -1 + \frac{\Delta \rho}{\sigma_{lg}} \int_{z_{\min}}^{\infty} V(z) \, dz \quad \ldots \ldots \ldots (5)
\]

In the complete wetting case, \( \cos \theta = 1 \). We get (Eqn. 6),

\[
\frac{\sigma_{lg}}{\Delta \rho} \geq -\frac{1}{2} \int_{z_{\min}}^{\infty} V(z) \, dz \quad \ldots \ldots \ldots \ldots (6)
\]
Let, \( T_w \) be the wetting temperature, indicating a transition from nonwetting behavior to wetting behavior of a solid surface. Wetting transitions are observed when the adsorption energy is smaller than, or comparable to, the cohesive energy within the film [25]. From equation (6), \( T_w \) can be measured given the temperature dependence of \( \sigma_{fg}, \Delta \rho, \) and \( V \). For graphite, wetting transition temperature (with water) has not been found experimentally, but predicted to be somewhere between 220\(^\circ\)C to 240\(^\circ\)C [25]. For a two phase mixture of fluid at the critical point, the contact angle against any third phase becomes zero [26].

1.7 Graphite water interaction

In membrane distillation, the membrane material needs to be in contact with water all the time. Since, graphite is a prospective material in this work; the water graphite interaction is an important topic to discuss. In graphite, each carbon atom uses only 3 of its 4 outer energy level electrons in covalently bonding to three other carbon atoms in a plane. Each carbon atom contributes one electron to a delocalized system of electrons that is also a part of the chemical bonding. It is slightly more reactive than diamond as the reactants are able to penetrate between the hexagonal layers of carbon atoms in graphite. The graphite water interaction has been studied extensively over the years. In case of solid liquid interaction, the surface roughness, chemical heterogeneity, and surface heterogeneous charge distribution affect the structural and dynamic properties of the interfacial water molecules, as well as their rate of exchange with bulk water [27]. Water-surface and water-water interactions, in particular hydrogen bonds, may be largely responsible for macroscopic interfacial properties such as adsorption and contact angle [27].

Molecular dynamics simulation showed the density of water molecules is higher near the surface of graphite as compared to bulk [28]. The water molecules in contact with the graphite surface tend to project some hydrogen atoms toward the solid. Although no hydrogen bonds are formed with the surface, this configuration is thought to maximize the number of water-water hydrogen bonds. Argyris et al. suggested not only the solid surface, but also preferential interaction between interfacial water molecules may result in macroscopic phenomena typically used to discriminate between hydrophobic and hydrophilic surfaces [28]. Another molecular dynamics simulation shows that for warm water between graphite plates 9, 12, 15 Å apart, the average number of hydrogen bonds decrease with an increase in temperature [29].
Molecular dynamics results were presented for water at ambient and superheated states inside a graphene channel. A typical depletion layer of excluded volume (width 2.5 Å) is observed at the two interfaces [30]. This is a region characteristic of water near hydrophobic surfaces. At high and supercritical temperatures, molecular disorder increases and preferential orientations tend to be less marked than at ambient and low temperatures. Water inside the graphene slab shows a tendency to diffuse faster than at unconstrained conditions, and diffusion of water at interfaces is slower than that of water in the central bulk-like regions. In SCW states, confinement tends to further increase water diffusion, regardless of the location of the water molecules in the system (either interfaces or bulk region). Furthermore, water at low densities diffuses much faster than in closely packed systems.

Reaction of carbon with water at supercritical water has been studied at different temperatures and pressures for carbon particles by a number of researchers [31-34]. Important findings from their work are as follows:

- Schlieren images of activated carbon and synthetic graphite in supercritical water indicate that activated carbon reduced in size considerably after 900 seconds in supercritical water with 3.6% O₂. Activated carbon and synthetic graphite in supercritical water without oxygen did not show any considerable change in shape and size.

- As shown in figure 9(a), radius of round activated carbon sample reduces with time in 773K, 30 MPa supercritical water having 10 wt.% O₂ concentrations. Radius of synthetic graphite sample, after an induction time of approximately 1400 seconds starts to become smaller at a rate slower than activated carbon. HOPG (highly Oriented Pyrolytic Graphite) does not show any change in shape and weight after long exposure time (greater than 2500 seconds). For the synthetic graphite and HOPG, the temperature of supercritical water was 873K. Samples were approximately 4 mm in diameter. With an increase in oxygen content of water, the rate of radius reduction increases for both activated carbon and synthetic graphite (Fig. 9(b)). The rate of size reduction for constant dissolved oxygen level differed because of two factors: (1) difference in the specific surface area, and (2) the degree of the surface crystallinity. The mass transfer of O₂ to the particle surface limited the reaction rate of the particles of activated carbon, whereas the reaction of the synthetic graphite particles was limited by the surface reaction. For the
reaction of the synthetic graphite, an induction time of considerable length ($10^3$-$10^4$ s) was observed before the size of the particle started to decrease.

![Figure 4](image1.png)  
**Figure 4.** Time evolution of the particle radius for three types of carbon: the activated carbon (●), the synthetic graphite (□) and the highly oriented pyrolytic graphite (HOPG) (▲). The fixed-sample cell was used at 30 MPa, 0.50 cm$^3$ min$^{-1}$ flow rate, and 10 wt % in O$_2$/Ar (at 100 K). The graph shows the time evolution of the radius of the particles for different induction times.

![Figure 5](image2.png)  
**Figure 5.** Effect of O$_2$ fraction on the decreasing rate of the particle radius ($dR/dt$) for the activated carbon (●) and the synthetic graphite (□). The fixed-sample cell was used at 30 MPa, 0.50 cm$^3$ min$^{-1}$ flow rate, at either 773 K (activated carbon) or 873 K (graphite). Regression lines show the reaction order of 1.17 for the activated carbon and 0.98 for the synthetic graphite.

Temperature programmed desorption (TPD) and XPS studies of O$_2$, CO$_2$, and H$_2$O adsorption on clean polycrystalline graphite had been done by Marchon et al. to find out the structure and stability of the various species formed. Oxidation with O$_2$ led to dissociation of the molecule and formation of strongly bound Oxo, or Semi Quinone groups, which decompose above 900K to yield CO (Table 3). Subsequent O$_2$ absorption on these semi Quinone groups results in lactone groups that thermally desorb as CO$_2$ at lower temperatures [35].

Table 3: desorption temperature and activation energies of CO and CO$_2$ after adsorption of CO$_2$, H$_2$O, and O$_2$. (Source: B. Marchon, J. Carrazza, H. Heinemann, and G.A. Somorjai [35])

<table>
<thead>
<tr>
<th>Adsorption gas</th>
<th>Adsorption temp (K)</th>
<th>Desorption product</th>
<th>Desorption temp (K)</th>
<th>$E_a$ (kcal/mol)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>room temp</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>500–900</td>
<td>CO</td>
<td>973–1253</td>
<td>64–83</td>
<td>Semi Quinone groups</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>room temp</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>room temp</td>
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<td>423</td>
<td>27</td>
<td></td>
</tr>
<tr>
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<td>CO$_2$</td>
<td>463–923</td>
<td>28–60</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>room temp</td>
<td>400–900*</td>
<td>21–51</td>
<td></td>
<td>Lactones</td>
</tr>
</tbody>
</table>
Chapter 2: Material properties and preparation, and supercritical water exposure experiments

2.1 Material properties

The majority of available membranes cannot be used at high temperatures. Polymeric membranes cannot tolerate high temperatures due to their low glass transition temperatures. Nickel-based alloys are thermally stable, but not suitable for high temperature membrane applications because an ultrathin oxide layer (about 1 nm) forms when exposed to water at high temperature, changing wettability characteristics [36]. Ceramic and carbon membranes, offer the advantages of thermal stability, chemical compatibility, and good mechanical strength over membranes made of organic polymers. However, ceramic membranes are hydrophilic by nature. Grafting alumina membranes with FAS (fluoroalkylsilane) makes them hydrophobic, but at high temperature the membrane undergoes weight loss [37]. Carbon membranes have been used for wastewater processing and gas separation due to their thermal stability, chemical compatibility, and good mechanical strength. Although Carbon nanotube (CNT) membranes are reported to allow water flows that are 1000 times faster compared to conventional membranes, fabrication of these membranes is complex.

Ceramics without any surface modification, graphite, HOPG (Highly Oriented Pyrolytic Graphite), porous graphite, diamond-coated stainless steel, Diamonite, and some natural corundums are tested to find the suitable materials for high temperature membrane distillation application. Several carbon-coated materials are also prepared, according to the procedure described in the next section. Ceramic samples (ZTA, TTZ, FG-995, and Mullite) were obtained from the Coors ceramic company (currently Coorstek Inc.) of approximate dimensions of 1 x 1 x ¼ inches. Samples had smooth and unpolished surfaces. A Ruby half ball lens, sapphire half ball lens, window sapphire, and Borofloat window samples were acquired from Edmund optics. A diamond-coated stainless steel sample was acquired from Morgan Crucible Company plc. The surface of the diamond coated SS sample was smooth and polished. A sialon sample was obtained from International Syalons limited. The surface of the sample was smooth and unpolished. Diamonite, a proprietary sample, was acquired from Secoa technology.
Graphite samples (10 mm x 10 mm x 3mm) were cut using EDM (electrical discharge machining) from a high density, ground finish, isomolded graphite plate bought from the graphite store (grade-GM-10). Composition of the graphite plate includes Synthetic Carbon and Graphite C.A.S. # 7782-42-5. The Density of the graphite plate is 1.82 g/cm$^3$, its particle size is 0.00102 cm, CTE (coefficient of thermal expansion) is 5.9 microns/m°C, porosity 12%, thermal conductivity is 83 W/K.m, and the sample is stable up to 399°C in the presence of air. The HOPG sample used is SP-1 grade or “calibration grade” HOPG, exhibits a 0.4° +/- 0.1° mosaic angle, and has a density of 2.27 g/cm$^3$.

2.2 Carbon-coated membrane fabrication

Carbon-coated membranes can be manufactured by in-situ pyrolysis of polymers, and chemical vapor deposition of hydrocarbons on a porous substrate. Activation of natural carbon materials or hollow carbon fibers can be done by a burn-off method. Controlling the temperature is important for controlling the pore size and other properties of the formed graphite layer. In situ formation is done by deposition of a polymeric resin on top of a support followed by thermal treatment to pyrolyze the polymer [38]. Carbon-coated ceramic membranes can be made by a chemical vapor deposition (CVD) method, which requires passing hydrocarbon vapor through the ceramic membrane while controlling the exposure temperature and pressure [39]. An in-situ formation method leads to formation of a separate layer whereas a CVD method uniformly coats the material grains. The difference between two coating methods is schematically shown in Figure 10 below.

![Carbon coating methods](image)

Figure 10: carbon coating methods. (Source: Y. Li, A. Sakoda, and M. Suzuki [40])

In the temperature range of 800-1000°C, CVD of pyrolytic carbon is achieved by methane pyrolysis [38]. In an open reactor, the dynamic pyrolysis of a gaseous hydrocarbon is always incomplete and the heavier hydrocarbons and tar that are produced are condensed in the cooler
part of the reactor, outside the furnace. Using methane pyrolysis, the main product is pyrolytic carbon with heavy hydrocarbons. Lighter hydrocarbons and hydrogen are also produced in small amounts. Light hydrocarbons that are produced are found to be acetylene, ethylene, and benzene. Heavier hydrocarbons that are produced contained mostly polyaromatic hydrocarbons with six nonsubstituted molecules: naphthalene, anthracene, phenanthrene, acenaphtylene, pyrene, and fluoranthene. The fraction of pyrolytic carbon from pyrolysis increases with an increase in temperature and pressure, while, at constant temperature and pressure, the fraction decreases with flow rate. The pyrolysis process is described below [38]:

- Methane yields free radicals which react to form acetylene
- Acetylene condenses into benzene
- Benzene transforms into naphthalene
- Naphthalene transforms into three ring aromatics and then to four ring and larger molecules (PAH-Poly Aromatic Hydrocarbon)
- PAH transforms into carbon (mostly pyrolytic carbon, and some carbon black)

Methane pyrolysis, when diluted with helium (20% methane) results in formation of pyrolytic carbon which has a “smooth laminar” microstructure with a density of more than 2 g/cm$^3$ and is graphitizable at high temperature [38]. Dilution also increases carbon production. Therefore dilution has the same effect as intensifying the pyrolysis conditions, but strong dilution tends to produce less dense and less graphitizable pyrolytic carbon.

The following CVD procedure, shown in Figure 11, is used to coat several ceramics, porous graphite, and quartz fiber filter samples with carbon:

1. Sample was placed at the middle of the quartz reaction tube.

2. The quartz tube was heated to 1000°C, using a tubular furnace, at approximately 10°C/min heating rate while maintaining a nitrogen flow rate of approximately 400ml/min throughout the reaction tube.

3. After one and a half hours methane gas was introduced inside the quartz tube at a flow rate of 105 ml/min with the help of one way and three way valves. Atmospheric pressure
was maintained throughout the system during the pyrolysis. Duration of pyrolysis was 3 hours.

![Diagram](image)

**Figure 11:** Chemical vapor deposition setup for carbon coating

Several inorganic membranes including tissue quartz filter, tubular alumina filter (from SJE-Rhombus Environmental group), porous graphite discs (fabrication procedure mentioned in subsection 2.3), and Anodisc alumina filter with support (from Whatman) were used for the fabrication of carbon-coated membranes by CVD method. Tissue quartz filters from SKC inc are 432 micron thick and 25 mm in diameter. They are autoclavable, binder-free, heat-treated to remove trace organic impurities, and can withstand temperature up to 1000°C. This tissue quartz filter was carbon coated by the CVD method described above. As a result of the carbon coating, the resultant material becomes extremely hydrophobic and water droplet rolls off from the surface of the material (Fig. 12). But the carbon coated tissue quartz filter was comparatively more brittle than original tissue quartz filter.

![Image](image)

**Figure 12:** Water droplet on carbon-coated tissue quartz filter
2.3 Porous graphite membrane fabrication

A porous graphite bar was obtained as a free sample from Toyo Tanso Company. The sample has the density of 1.76 g/cm$^3$, and an average grain size of 2 microns. Porous graphite membranes are obtained by cutting a porous graphite bar in an EDM machine. A 500 micron piece was cut from the bar by a thin brass wire at low cutting speed of approximately 2mm/hr. The slow cutting speed was due to breakage at higher speeds. After obtaining the large thin rectangular piece of graphite from the bar, squares and discs were cut by using another EDM machine with a thinner brass wire. During the cutting process, DI water was used to provide a conductive medium and to remove heat. The porous graphite membrane is relatively hydrophobic as shown by the shape of water droplet on the membrane in Figure 13, and contact angle measurements in Chapter 3.

![Figure 13: Water droplet on the graphite membrane](image)

2.4 Hydrogen treatment of graphite

The sample was placed into a ceramic tube furnace and the tube was nitrogen purged. Then the sample was heated to 900°C under nitrogen. Hydrogen gas was allowed to flow inside the tube furnace after switching off nitrogen flow. After two hours, the sample was allowed to cool to room temperature under nitrogen.

2.5 HOPG surface preparation

A common practice to expose fresh HOPG surface for testing is to peel off the top most layers of HOPG by a transparent tape. Another way to clean the surface is to expose the surface to argon plasma. One HOPG sample was prepared by the peeling off method and two samples by argon plasma treatment to investigate the wettability characteristics of fresh HOPG sample surface. For argon plasma treatment, exposure time was 1 minute at 100 watts for one sample and 6 seconds at 90 watts for another.
2.6 Supercritical water exposure

Ceramics (TTZ, ZTA, FG-995, Sialon), different forms of graphite, diamond-coated stainless steel, corundums (ruby and sapphire), and other coated materials were tested with deionized water at supercritical temperature and pressure (374°C and 220.1 bar) of water inside a pressure reactor. The pressure reactor used was a Parr instrument pressure reactor model 4651-with capacity of 250 mL, a maximum pressure rating of 6000 psi @ 350°C, a maximum temperature rating of 600°C, a maximum pressure rating at maximum temperature of 4200 psi, and a vessel body made out of HASTELLOY C-276. J type thermocouples and a stainless steel bourdon tube pressure gauge were used for measuring the temperature and pressure respectively. The cleaning procedure for graphite samples with solvents includes the following steps:

1. Samples were cleaned with laboratory wipes to remove dust.

2. Samples were submersed in beakers filled with acetone, isopropyl alcohol (IPA), DI water, and again IPA sequentially for 1 minute each. In the end, a nitrogen gun was used to dry the surface as much as possible. This procedure was used to degrease the small samples.

3. Samples were kept in a container filled with DI water and sonicated for 20 minutes. This procedure was used to remove any debris on the surface of the samples.

4. Samples were placed in a clean Pyrex container and the container was placed on a hot plate at 250°C for 14 minutes. This procedure was used to remove all the water from the sample surface.

Initially all the experiments were done without altering the dissolved oxygen level of feed water. The procedure for those experiments is as follows:

The pressure vessel was cleaned with DI water, and wiped dry. An air gun was used to clean the vessel and head to remove any undesirable particles left during changing of the graphoil gasket. The samples (other than graphite) were cleaned by IPA, acetone, ultrasound, and then vacuum annealed. Using a goniometer CAM 200 instrument (KSV Instruments); the contact angle for each sample was measured after cleaning. The cleaned sample was weighed, and then placed in the Parr pressure vessel with the help of tweezers with plastic tips. The top consisting
of the cylinder head and split ring halves were securely fastened, and screws on the split ring were tightened to the required amount of torque to ensure a leak proof seal between the cylinder head and body. Vacuum was established with the help of a vacuum pump, and a known amount of water (60ml) was introduced into the vessel. After that, the vessel was placed inside the heater, and the controller was programmed using a ramp and soak profile. The controller took approximately 1 hr. and 5 minutes to reach 374°C and 218 bars, and the program allowed the controller to keep the pressure vessel at 385°C and at least 220 bars for approximately 30 minutes. After the run, the pressure vessel was allowed to cool down to 40°C to ensure that the pressure difference between the vessel and the surrounding air was as small as possible. The cool down cycle took approximately nine and a half hours. Each sample was run separately, and afterwards, the sample was removed and mass and contact angles were measured. Deionized (DI) water was used throughout the experiment to make sure no contaminants were introduced into the vessel. A procedure was prepared for safe operation of the pressure vessel (Appendix-A).

Schematic diagram and actual picture of the experimental setup used are shown in Figure 14 and 15 respectively. Experimental procedure for supercritical water testing with dissolved oxygen reduction is as follows:

A sample was placed inside the pressure vessel and the vessel was sealed. Then, 60 ml of DI water was introduced into a 125 ml gas washing bottle with the help of a graduated flask. This gas washing bottle was used as a bubbler to purge nitrogen through the DI water. Ultra high purity nitrogen from S.J. Smith CO. was used for this experiment. An FL- 3405ST-HRV rotameter from Omega was used to regulate the flow of nitrogen to 1,417 mL/min into the bubbler. Nitrogen flow through the DI water was maintained for 30 minutes. The dissolved oxygen (DO) level of DI feed water goes down to 0.55 ppm after 30 minutes of nitrogen flow. The tube attached to the exit port of the bubbler was connected to a three way valve with barbed ends. One port of that three way valve was attached to a tube with a check valve which prevented incoming air and also ensured that dissolved oxygen replaced by nitrogen can escape to the atmosphere. The third port of the valve was connected to another three way valve with threaded ports. This second three way valve was connected to the pressure vessel and a vacuum pump. The vessel was nitrogen & water vapor purged, and a vacuum pump was used to remove the
purge gas four times to ensure proper vacuum. After that, the bubbler was tilted, and the nitrogen purged water went from the bubbler into the pressure vessel by nitrogen back pressure and also due to the vacuum. The valve connected to the vessel was closed, and the pressure vessel was placed inside the heater. The temperature and pressure of the water was increased to 385°C and 220 bars respectively using a PID controller. With the help of that controller, the sample was exposed to the supercritical water for 30 minutes. After 9-10 hours, the vessel cools down to room temperature. Then, the sample was removed from the pressure vessel and vacuum annealed for 10 minutes at 60°C.

Figure 14: Schematic diagram of the experimental setup used for exposure of samples to supercritical water

Figure 15: actual setup for supercritical water experiment
Chapter 3: Material characterization

3.1 Methodology

As-received and prepared materials were characterized by various characterization methods including contact angle measurements, XPS (X-ray Photoelectron Spectroscopy), AES (Auger Electron Spectroscopy), XRD (X-ray Diffraction), FTIR (Fourier Transform Infrared Spectroscopy), SEM (Scanning Electron Microscopy), and surface profilometry. Contact angle measurements use microliter droplets placed on the sample to measure the wettability of the sample with the help of a camera and computer software and the Young-Laplace formulation to find a static contact angle with water. XPS is used to determine the composition, and the type of chemical bond present on the surface of the sample for elements having an atomic number higher than hydrogen. Auger electron spectroscopy can also be used for characterization of the surface composition and chemical functionalities, but instead of photoelectrons, auger electrons are used for analysis. Auger or photoelectrons can only escape from the top atomic layers of the sample that does not exceed 10 nm. Therefore, both techniques are surface sensitive. Either XPS or AES can be used to determine carbon and oxygen composition at different depths from the sample surface. Auger electron spectroscopy was used due to better oxygen composition reading on the surface and faster sputtering rate. Both XPS and AES operate under ultra-high vacuum. XRD can be used to determine crystal structure and composition identification. The reason for using XRD was to determine the effect of crystal structure on wettability of polycrystalline graphite samples. Diffracted X-rays can come from below the surface, and therefore XRD is not a surface sensitive technique. FTIR is a vibration based spectroscopy where photons at a certain frequency hits the sample and changes the nuclear vibration of the molecules. Vibrational spectroscopy uses long wavelength electromagnetic waves (in the order of $10^{-7}$ m), unlike X-rays which have short wavelengths (on the order of $10^{-10}$ m). FTIR uses infrared light, which in reflectance mode, gets reflected to produce interference patterns. Fourier transform is used to process the data to produce an infrared spectrum in a range of wavenumbers simultaneously. Reflectance spectrum can contain information from the top 1-10 μm from the surface of the sample. In reflectance mode, a solid bulk sample can be used. SEM uses focused electron beams to hit the atoms, which emit secondary electrons to be detected by an Everhart-Thornley detector.
3.2 Contact angle measurements for different materials

KSV CAM200 goniometer was used to measure the water contact angle of all the samples. Static contact angle measurements of materials are subcategorized according to their common features for clarity. Static contact angle measurements of different samples are presented below.

Zirconia-, silica- and alumina-based ceramics

All the ceramics samples were tested with feed water low in dissolved oxygen levels at supercritical temperature and pressure of water. As can be seen in Figure 16, all of the tested samples showed lower contact angles after exposure to supercritical water indicating increased hydrophilicity probably due to formation of hydrophilic hydroxide compounds at the surface. No changes in weight of the samples were observed. These results are similar to the results of Boukis et al [41] where they showed several alumina-, silica-, and zirconia-based ceramics exposed to water at similar conditions that had negligible weight losses. The samples were cleaned with acetone, IPA and water before testing and the chances of impurities causing intergranular attacks or general corrosion are reduced. As the tests were performed in low density water, chances of corrosion are negligibly low. Also, the availability of oxidizing agent was reduced by lowering the amount of dissolved oxygen, which is completely miscible with low density supercritical water. Reactions leading to the formation of various hydroxides on the surface of tested ceramics are summarized below. Alumina most likely reacts with subcritical water and forms Boehmite in the following way [42]:

$$Al_2O_3 + 6H_2O \rightarrow 3Al(OH)_4^- + Al^{3+} \ldots \ldots \ldots \ldots (reaction \ 2)$$

$$Al^{3+} \rightarrow AlOOH \ldots \ldots \ldots \ldots \ldots \ldots \ldots (reaction \ 3)$$

Similarly Zirconia can form zirconia hydroxide with high temperature water (Reaction 4).

$$ZrO_2 + 2H_2O \rightarrow Zr(OH)_4 \ldots \ldots \ldots \ldots \ldots \ldots \ldots (reaction \ 4)$$

Similarly for Mullite, which contains both silica and alumina, hydroxide formation can occur by reaction of silica with high temperature water to form silicon hydroxide.
Figure 16: Contact angle vs. time for different ceramic samples at different conditions

**Sialon, boron nitride, and corundums**

All the samples shown in Figure 17 are tested with feed water containing low dissolved oxygen level and at supercritical temperature and pressure of water. Ruby and sapphire were stable and undergo negligible weight loss in supercritical water whereas the boron nitride surface was eroded, which is similar to results of Boukis et al and Anderson et al [41][43]. Corundum like ruby was found to be transformed to Al(OH)$_3$.nH$_2$O in supercritical water. Therefore, the hydroxide formed on the surface should make the surface more hydrophilic [44]. Sialon (ceramic material composed of silicon, nitrogen, aluminium, and oxygen) showed contact angles of almost zero after supercritical water exposure. Sialon may react with supercritical water in the following way [45]:

\[
Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3 \quad \ldots \ldots \ldots \quad (reaction \ 5)
\]

\[
SiO_2 + OH^- \rightarrow HSiO_3^- \quad \ldots \ldots \ldots \quad (reaction \ 6)
\]

Sapphire and boron nitride samples showed higher contact angles after exposure. The increase in contact angle for boron nitride may be due to the fact that the surface of the sample became completely eroded after exposure to supercritical water leading to a rougher surface.
rough surface may cause a higher water contact angle. For sapphire, no significant change of the surface was noticed and therefore the cause of the increase in contact angle is unknown at this point.

Diamonite and diamond coated stainless steel

All the samples shown in Figure 18 were tested with feed water low in dissolved oxygen (DO) at supercritical temperature and pressure. After exposure to supercritical water, diamond-coated stainless steel showed contact angles which were similar to the contact angles before exposure. Due to a lower number of starting points of corrosion, polished surfaces are known to be more resistant to corrosion than unpolished ones [14]. Therefore, the diamond coating most probably remained unaltered during supercritical water exposure. For Diamonite samples, after exposure to supercritical water, the coating partially came off, and the sample showed lower contact angles.
Figure 18: Contact angle vs. time for different coated samples at different conditions

Graphite and carbon coated materials

As can be seen from Figure 19, as-received graphite samples (polycrystalline) are initially hydrophobic, but the contact angle goes down with time. Wettability of a solid is dependent on surface characteristics i.e. surface heterogeneity, composition, and roughness. Monolayer surfaces containing high concentrations of OH groups on mobile organic chains are not stable [46]. Hydrophilic moieties (such as OH and other polar oxygen functionalities) on the surface can orient themselves towards the air interface or towards the bulk of the solid, and depending on this phenomena, contact angle will vary [47]. Surface functional groups present on the as-received graphite surface and their reorganization with time may be one reason for the contact angle variation with time. The driving force in the direction of increasing wettability arises from an imbalance of different forces namely hydrodynamic friction force and forces due to surface tension at the front and rear end of the droplet acting on the contact line around the droplet.
periphery. Another possibility is that some portion of the sample is more oxidized and thus forms hydrophilic points, which allow the water drop to advance in one direction. Other reasons for changes in wettability can be due to contamination, deposition, and irregular roughness. The contact angle of the cleaned graphite sample shows higher values as compared to the as-received sample. Also, contact angle values for the cleaned samples do not change appreciably with time. The as-received graphite samples were then exposed to water at different conditions. Graphite samples tested with feed water with low dissolved oxygen elevated to supercritical condition showed enhanced hydrophobicity. The graphite sample tested with feed water with high dissolved oxygen level became hydrophilic. The graphite sample that was exposed to 300°C water with high dissolved oxygen level showed contact angles close to 90° (strictly hydrophobic). Hydrogen treated graphite samples showed contact angles just above 30°. When the sample was tested with feed water high in dissolved oxygen, contact angle values were less than 90°. It is interesting to note that, the contact angles for samples exposed to supercritical water condition were higher than samples exposed to near-supercritical water (temperature was 385°C, but at pressures just below 220 bars). Lastly, for samples tested with feed water low in dissolved oxygen, contact angle values were found to be higher than 105°. No changes in mass of the graphite samples were observed.

In Figure 20, both carbon-coated porous graphite and porous graphite showed higher contact angles after exposure to supercritical water while testing with low dissolved oxygen (DO) containing distilled feed water. But when feed water containing high dissolved oxygen (around 5 ppm) was used for the test, the contact angle for porous graphite became lower. Carbon-coated alumina samples remained hydrophobic (contact angle greater than 115°), after testing at supercritical temperature and pressure of water using feed water containing low DO.

As-received HOPG samples (10 mm x 10 mm x 2mm) were hydrophobic (contact angle just above 90°) (Fig. 21). However, after testing the sample with feed water containing low DO at supercritical temperature and pressure of water, the contact angles were less than 90°. A Fresh HOPG surface exposed by a transparent tape peeling also showed contact angles less than 70°. Sputtered HOPG samples showed contact angles around 10° (less than 10° for sputtering time of 1 minute, slightly greater than 10° for sputtering time of 6 seconds (not shown in Fig. 21)). All the HOPG samples showed approximately the same weight before and after the test.
Figure 19: Contact angle of graphite samples vs. time before and after exposure to hot and pressurized water

Figure 20: Contact angle vs., time of porous graphite and carbon-coated samples before and after exposure to SCW
Figure 21: contact angle vs. time for HOPG samples at different conditions

3.3 XPS

XPS experiments were done using Kratos Axix ULTRA instrument with a monochromatic Al Kα X-ray source. A 0.7 mm by 0.3 mm slit was used with an electron energy analyzer for collection of emitted photoelectrons. The reason for wettability changes of graphite can be determined by examining the surface elemental composition, and chemical bonds that are present. XPS can detect carbon and oxygen composition and chemical bonds between carbon and oxygen. Graphite and carbon-coated alumina samples were analyzed with XPS. The signals were calibrated according to the carbon peak at 284.5 eV binding energy (except for HOPG, which showed peaks at 284.5 eV before calibration). A survey scan over the full binding energy range according to the source (0 to 1486 eV) and high resolution spectra were collected for carbon 1s and oxygen 1s spectra for each sample. The carbon 1s high resolution spectrum was analyzed with casaXPS software. The software allows curve fitting of the high resolution spectra according to peak position provided as an input. Peak position for different carbon oxygen bonds were determined from the literature and matched with NIST database. Bonds under consideration were C-C, C-O, C=O, carboxylic, and π-π* interaction. The software also allows residue determination i.e. the amount of signal from the original curve not covered by the synthetic curve. With the help of this residue function, proper matching of the synthetic curves with the original curve was ascertained. Carbon and oxygen composition were calculated from their high resolution spectra by determining area under the curve and by using RSF (relative sensitivity factor).
factor) for carbon and oxygen (0.278 for carbon and 0.711 for oxygen). Table 4 shows the atomic concentration of carbon and oxygen on different sample surfaces.

Table 4: Carbon and oxygen surface atomic concentration (excluding hydrogen) of different samples obtained from XPS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Angle</th>
<th>C 1s CPSeV</th>
<th>O 1s CPSeV</th>
<th>C 1s %</th>
<th>O 1s %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly crystalline graphite</td>
<td>1.00</td>
<td>114664</td>
<td>10316</td>
<td>91.7459</td>
<td>8.254</td>
</tr>
<tr>
<td>Graphite tested with high DO at supercritical point of water</td>
<td>1.00</td>
<td>144667</td>
<td>9804.91</td>
<td>93.6526</td>
<td>6.34739</td>
</tr>
<tr>
<td>Graphite tested with high DO at 300°C</td>
<td>1.00</td>
<td>156792</td>
<td>5012.48</td>
<td>96.9021</td>
<td>3.09786</td>
</tr>
<tr>
<td>Graphite tested with low DO at supercritical point of water</td>
<td>1.00</td>
<td>278773</td>
<td>4776.95</td>
<td>98.3153</td>
<td>1.6847</td>
</tr>
<tr>
<td>Carbon coated alumina</td>
<td>1.00</td>
<td>164751</td>
<td>3060.49</td>
<td>98.1762</td>
<td>1.82376</td>
</tr>
<tr>
<td>HOPG</td>
<td>1.00</td>
<td>196633</td>
<td>993.558</td>
<td>99.4973</td>
<td>0.503</td>
</tr>
<tr>
<td>Porous graphite</td>
<td>1.00</td>
<td>84507.3</td>
<td>21701.5</td>
<td>79.57</td>
<td>20.43</td>
</tr>
<tr>
<td>Porous graphite tested with low DO at supercritical point of water</td>
<td>1.00</td>
<td>86664.1</td>
<td>12934.4</td>
<td>87.0135</td>
<td>12.9865</td>
</tr>
<tr>
<td>Coated porous graphite tested with low DO at supercritical point of water</td>
<td>1.00</td>
<td>115424</td>
<td>7766.03</td>
<td>93.6959</td>
<td>6.3041</td>
</tr>
</tbody>
</table>

During the sample analysis, sample points that seem to be contaminated (presence of foreign elements such as nickel, Zinc etc. was detected along with carbon and oxygen) are avoided. Data showed the oxygen content on the surface of the polycrystalline sample (as-received), and a sample tested with supercritical water containing high dissolved oxygen (DO) was higher than other polycrystalline graphite samples. For polycrystalline graphite samples tested with 300°C water containing high dissolved oxygen, the atomic oxygen concentration was found to be lower than the as-received sample, suggesting desorption of some carbon oxygen complexes from the surface at high temperature. Samples tested with supercritical water containing high DO had higher oxygen concentrations than samples tested at 300°C water and the original sample. This observation suggests that at supercritical conditions, the polycrystalline graphite samples are oxidized due to the presence of dissolved oxygen in supercritical water. The sample tested with feed water containing low DO showed higher contact angles and lower atomic oxygen concentrations than the as-received sample after exposure to supercritical water. It is possible that the enhanced hydrophobicity after supercritical water exposure may be due to
decomposition of some surface functionalities containing oxygen at high temperatures, leaving exposed hydrophobic functional groups on the surface (Fig. 19). At anoxic supercritical water conditions, the surface does not oxidize back due to a lack of oxidizing agents in the supercritical water. Surface complexes may leave the surface as carbon monoxide or carbon dioxide as shown in Table 3 in the introduction section. M.E. Schrader commented that carbon is hydrophilic in its purest form, and the hydro carbonaceous contaminations are thought to be responsible for the hydrophobicity of the graphite surface [48]. Similar phenomena were observed for porous graphite, and carbon-coated porous graphite samples, which is in agreement with their contact angle results (Fig. 20). Also, carbon coated alumina, which is hydrophobic, had very low oxygen concentration on the surface (Fig. 20). Fresh HOPG surface (by transparent tape peeling) was analyzed by XPS, and the results show very low atomic concentration of oxygen on the surface. Therefore, for HOPG, other factors (other than carbon oxygen complexes on the surface) may be responsible for low contact angles (Fig. 21).

Although the curve fitting routine (included in Appendix-B) seems to indicate that the (C-O-) bond is dominant on all sample surfaces as compared to other bonds, identifying the actual structure is difficult for functional groups like C-OH or C-O-R (e.g. C-O-CH₃) as XPS cannot detect hydrogen. FTIR experiments were done to detect the presence of functional groups on sample surfaces. The presence of methyl groups (-CH₃) or hydrogen (-C-H) on the surface will make the surface hydrophobic whereas hydroxyl (-OH) groups or other carbon oxygen complexes may make the surface hydrophilic.

3.4 FTIR

Diffuse reflectance Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the presence of different functional groups on the surface of the graphite and carbon-coated samples. Specular reflection needs large samples and is less effective for rough samples, and therefore was not suitable for our samples. The instrument used for FTIR was a Thermo Nicolet Nexus 670. Figure 22 shows the infra-red active groups on carbon surface.
Figure 22: IR active groups on carbon surface. (Source: P.E. Fanning, M.A. Vannice [49])

Figure 23 shows FTIR plots for polycrystalline graphite samples and fresh HOPG surface (by transparent tape peeling) over the entire range of wavenumbers in the infrared region. No peak fitting routine is used in this case. HOPG showed higher reflectivity than polycrystalline graphite, and peaks near 2800-3100 cm$^{-1}$, 1500-1700 cm$^{-1}$, and 1000-1200 cm$^{-1}$ were observed, which may be due to carboxylic groups [49]. For materials like polycrystalline graphite, it is very difficult to find peaks from the FTIR reflectance spectra itself. FTIR signals come from both the surface and bulk of polycrystalline graphite samples and show average values of all signals.

Reflectance FTIR peaks for symmetric –CH$_2$, symmetric –CH$_3$, asymmetric –CH$_2$, asymmetric –CH$_3$ are around 2850 cm$^{-1}$, 2870 cm$^{-1}$, 2930 cm$^{-1}$, 2960 cm$^{-1}$ respectively [50]. The spectra obtained for polycrystalline graphite contains thickness interference fringes and finding the peaks is difficult from the collected data in between wavenumbers of 2800 and 3000 cm$^{-1}$. Therefore, a MATLAB peak fitting program was used to collect the peak points of the interference fringes. All the polycrystalline graphite samples tested with anoxic feed water at the supercritical condition of water showed small peaks in the –CH$_2$, and –CH$_3$ stretching regions as observed in the Figures 24 and 25. The, hydrophilic sample is polycrystalline graphite samples exposed to supercritical water with high dissolved oxygen, and the hydrophobic sample is polycrystalline graphite samples exposed to supercritical water with low dissolved oxygen. From the excel plots, the reflectance of hydrophilic and as received graphite samples showed higher reflectance, which may be due to higher oxygen content. For both asymmetric and symmetric –
CH$_3$ stretching, the hydrophilic samples showed no discernible peaks in the middle region. The as-received graphite samples showed some peaks and for asymmetric stretching showed comparatively intense peaks. Both hydrogen-treated polycrystalline graphite and hydrophobic samples showed comparatively intense peaks. From the XPS and FTIR results, low amounts of hydrogen in the form of –CH$_3$ (methyl end group is water repellent) (Fig. 24, 25) are possibly coming from hydro carbonaceous contamination and very low oxygen content (Table 4) (due to desorption of oxygen-containing functional groups at high temperatures and anoxic conditions) compared to hydrophilic samples may be the reason for this enhanced hydrophobicity (Fig. 19). For accurate determination of hydrophobic functional groups containing hydrogen, other surface characterization techniques such as SIMS (Secondary Ion Mass Spectroscopy), or RBS (Rutherford Back Scattering) should be used.

Figure 23: FTIR spectra of polycrystalline graphite and HOPG. (a) Over the entire range, (b) from 2800 to 3100 cm$^{-1}$, (c) from 1350 to 1650 cm$^{-1}$. HOPG is plotted according to vertical axis scale shown on the left and polycrystalline graphite is plotted according to the vertical axis shown on the right.
Figure 24: FTIR results for different polycrystalline graphite samples in –CH$_3$ asymmetric stretching region. Hydrophilic and as received graphite sample data is plotted according to the y axis shown at the right side (0.03 to 0.07) and hydrophobic and H$_2$ treated graphite are plotted according to the y axis shown on the left (from 0 to 0.035)
Figure 25: FTIR results for different polycrystalline graphite samples in –CH\(_3\) symmetric stretching region. Hydrophilic and as received graphite sample data is plotted according to the y axis shown at the right side (0.03 to 0.065) and hydrophobic and H\(_2\) treated graphite are plotted according to the y axis shown on the left (from 0.009 to 0.029)

### 3.5 Roughness

KLA Alphastep IQ profilometer was used to determine the roughness of the graphite samples. Scan speed was 10 microns/sec, rate -100 Hz, range-2mm/119 pm, and length-1900 microns. Roughness measurements by profilometer were done for as-received polycrystalline graphite, chromium sputtered graphite (to make the surface scratch proof), graphite tested with low DO level, and fresh HOPG surface (by transparent tape peeling). Three data points were recorded for each sample. An Average of three data points for both average roughness values and R.M.S. (Root Mean Square) values of roughness are shown in table 5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average roughness(micron)</th>
<th>R.M.S. roughness(micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received graphite</td>
<td>0.392</td>
<td>0.504</td>
</tr>
<tr>
<td>Chromium sputtered graphite</td>
<td>0.408</td>
<td>0.00984</td>
</tr>
<tr>
<td>HOPG</td>
<td>0.0077</td>
<td>0.455</td>
</tr>
<tr>
<td>Graphite tested with low dissolved oxygen feed water at supercritical point of water</td>
<td>0.374</td>
<td>0.477</td>
</tr>
</tbody>
</table>
According to the above mentioned data, roughness does not seem to be the reason for changes in wettability for polycrystalline graphite and HOPG samples.

### 3.6 XRD

The instrument used for this purpose is Phillips X’pert. As shown by Semmelhack et al (Fig. 26), HOPG was found to be highly oriented and showed only two crystal planes.

![XRD Graph](image)

**Figure 26:** Diffraction data for HOPG. (Source: H.C. Semmelhack, R. Höhne, P. Esquinazi, G. Wagner, A. Rahm, K.H. Hallmeier [51])

Experimental XRD data for three different samples of polycrystalline graphite of different wettability characteristics is shown in figure 27.

![Graphite XRD Curves](image)

**Figure 27:** 2 theta curves for three polycrystalline graphite samples
No differences were observed among the polycrystalline graphite samples even though they showed different contact angles. Similar curves were obtained for all three polycrystalline graphite samples by performing rocking curve and glancing angle analysis as can be seen in appendix-C. However, there are significant differences between polycrystalline graphite and HOPG diffraction data. Isotropic and anisotropic graphite have different crystallite sizes, and isotropic graphite has some non-graphitized carbon on the surface which results in a higher hydrogen content [52]. HOPG is highly anisotropic, has low non-graphitized carbon content, and should contain less hydrogen as compared to polycrystalline graphite.

3.7 AES with ion beam milling

The instrument used for AES was Physical Electronics PHI 660. LaB6 filament type electron gun was used as a source and single pass mirror analyzer & single pass electron multiplier was used in the detection system. For sputtering, a differentially pumped 1-5 KeVAr ion gun was used. The amount of oxygen at a certain depth from the surface of the polycrystalline graphite was determined using AES with ion beam milling. Results from the experiment are shown in figure 28.

![Graph showing AES with ion beam milling results for as-received polycrystalline graphite](image)

**Figure 28:** AES with ion beam milling results for as-received polycrystalline graphite

High oxygen concentration at the top layer was probably due to contamination. Figure 28 shows that polycrystalline graphite sample only has oxygen on some top layers (sputter depth
cannot be determined exactly). A rough sputter rate estimate is 4.4 nm/min [53]. Hydrophobicity and hydrophilicity is controlled by the thin surface layer. Surface hydrogen and oxygen functionalities contribute to hydrophobic and hydrophilic properties, respectively. Therefore, wettability characteristics of polycrystalline graphite seem to be controlled by surface functional groups rather than the bulk carbon.

3.8 SEM

Scanning electron microscopy images were taken using JEOL 6060LV General Purpose SEM. SEM images of porous graphite (as-received), porous graphite exposed to supercritical water with low dissolved oxygen, and carbon-coated porous graphite samples exposed to supercritical water with low dissolved oxygen showed similar pore structures (figure 29). Even though the average pore size of porous graphite was mentioned as 0.26 microns, pores as large as 2 microns and as small as 100 nm were observed (Figure 30, Figure 31). Secondary electron (SE) images of porous graphite show topographic contrast with bright areas at the edges of the pores. Back scattered electrons (BSE) come from surface layers deeper than secondary electrons and show compositional contrast. The contrast seen in the BSE may arise due to pore tortuosity and the presence of closed pores (figure 32). Otherwise the sample seems to be homogeneous. For carbon coated tissue quartz membrane, SEM image shows fibrous structures (figure 33).

![Figure 29: SEM images of a) porous graphite b) carbon coated porous graphite exposed to supercritical water with low DO c) porous graphite exposed to supercritical water with low DO](image-url)
Figure 30: SEM image of porous graphite (5000X)

Figure 31: SEM image of coated porous graphite after exposure to supercritical water with low dissolved oxygen (25000X)

Figure 32: (a) Secondary electron image of porous graphite (b) backscattered electron image of porous graphite

Figure 33: carbon coated tissue quartz filter
Chapter 4: Conclusion and future work

Polycrystalline graphite, and pyrolytic carbon (both having sp² hybridization) were found to be suitable materials for anoxic supercritical water membrane distillation. Membranes made of porous polycrystalline graphite were fabricated from porous graphite blocks. Carbon-coated porous graphite and tissue quartz membranes have been prepared by a chemical vapor deposition method using dilute methane gas at 800°C. Hydrophobicity of the polycrystalline graphite and pyrolytic carbon-coated membranes increase or remain the same after exposure to supercritical water with low dissolved oxygen. By material characterization techniques, the reduction of carbon oxygen complexes on the surface functional groups along with probable presence of hydrophobic –CHₙ functional groups were found to be the reasons for the hydrophobicity of polycrystalline graphite, porous graphite, and pyrolytic carbon samples after exposure to anoxic supercritical water. Diamond-coated stainless steel was hydrophilic before exposure to supercritical water and remained hydrophilic after exposure to anoxic supercritical water. But the variation of contact angles of diamond coating before and after anoxic supercritical water exposure was less. Hydrophilic behavior of diamond compared to graphite might be due to the carbon bonds (sp³ in diamond vs. sp² in graphite) and existence of –CHₙ hydrophobic groups on the graphitic or pyrolytic carbons. Ceramic samples and Diamonite became hydrophilic after exposure to anoxic supercritical water. The reason behind their hydrophilicity is most likely due to surface hydroxide formation. When tested with oxic supercritical water, all the tested materials became hydrophilic. This result is expected due to complete miscibility of oxygen in supercritical water, making supercritical oxic water an extremely oxidizing medium.

To know more about surface functional groups present on different carbon samples tested, XPS with chemical labeling, Raman analysis to obtain basal to edge site ratio, and SIMS can be used. Also, work needs to be done on membrane structure (pore size, tortuosity, void fraction etc.) to ensure proper flow passage of water vapor. Ascertaining suitable characteristics e.g. good permeability, mechanical strength, proper thickness etc. of thin disc shape membranes is a critical issue. Initial experiments have been done with porous graphite membranes with custom made membrane distillation systems. More improvement needs to be done on both the system and the materials to achieve satisfactory performance. The primary focus of high pressure and high temperature membrane distillation experiments is to have a reliable system that can operate
at high temperatures and pressures. For this purpose a stainless steel membrane distillation system has been built. Modification is currently being done on the system for proper functioning. The actual picture of the current setup is shown in Figure 34. Future work will focus on developing advanced carbon membranes and innovative high temperature/pressure membrane distillation systems.

Figure 34: Stainless steel membrane distillation setup
List of References


Appendix-A

Name of the Procedure-Exposure of material samples to supercritical water inside a Parr pressure reactor

Location-MEB 109

Hazards-

- High pressure(maximum-250 bar)
- High temperature(maximum 400°C)
- Compressed gas(nitrogen)
- Electrical hazard(energized device.115 V,12 A,50/60 Hz)

Engineering controls-

1. Puppet valve
2. Rupture disk (material: HASTC, Performance specification: 5000 psig +/- 5% @72°F, Anticipated performance at maximum operating temperature: 4200 psig +/- 5% @393°C, replacement frequency: after 5000 cycle @ 90% of design pressure, operating ratio: 0.86). Rupture tube submerged in a water bucket (covered with lid and clamped to the nearby table) full of water to absorb the shock.

Administrative controls-

1. Only trained personal should operate this equipment. A trained personal is one who has reviewed the standard operating procedure, Parr instrument manuals for reactor 4651 and controller 4838, and conducted supervised runs of the pressure vessel once.
2. Needs to notify other lab occupants before starting the experiment
3. Working alone with this device is acceptable provided there is a regular check-in with Research Coordinator at the start and in the end of the heating cycle.
4. Follow manufacturer’s instructions and follow operating instructions as they appear in this document.
5. Head screws should not be dry at any time and if necessary, need to be lubricated with lubricant (N-5000) supplied by Parr instruments for this specific pressure reactor.
6. Sealing graphite gasket need to be inspected before every experiment and changed if found damaged. All the remaining parts of the pressure reactor need to be inspected before every run and if any defect is found, Parr instruments should be notified to get further directions.

**Protective equipment**-

1. Safety glasses
2. Disposable gloves

**Waste disposal**-

Only DI water is used as feed. Used graphite gasket can be disposed in regular bin placed in MEB 109.

**Prior Approval**-

Prior Approval from research coordinator is required.

**Operating procedure**-

1. Clean the pressure vessel cylinder and cylinder head with clean DI water and dry using clean wipes
2. Place the sample in the pressure vessel
3. Check the sealing surface of the head and the cylinder. They should be clean and undamaged (this is to make sure the vessel seals properly). If the graphite gasket is damaged, remove the gasket completely and replace with a new one.
4. Set the head on the cylinder
5. Put the two split ring halves
6. Raise the outer band and tighten the cone pointed screws
7. Check the threads of the compression bolts. They should be clean and lubricated.(they should never be dry)
8. Tighten the compression bolts finger tight
9. Tighten the compression bolts with 10 ft lbs using a torque wrench in a star pattern
10. Tighten the compression bolts with 20 ft lbs using a torque wrench in a star pattern
11. Tighten the compression bolts with 30 ft lbs using a torque wrench in a star pattern
12. Tighten the compression bolts with 40 ft lbs using a torque wrench in a star pattern
13. Connect the three way valve-1 to the gas release valve mounted to the cylinder head. One end of the three way valve connects to the vacuum pump and the other end connects to three way valve-2 (three way valve-1 and three way valve-2 are shown in the figures below). The three way valve-2 connects to the gas washing bottle and check valve.
14. Introduce 60 ml of DI water into a 125 ml gas washing bottle with the help of a graduated flask. This gas washing bottle is used as a bubbler to purge nitrogen through the DI water. Water can be introduced by opening the head of the gas washing bottle keeping the connections at the inlet leading to rotameter and outlet leading to three way valve-2 intact.
15. Introduce ultra-high purity nitrogen at 1417 mL/min into the gas washing bottle using FL-3405ST-HRV rotameter. (nitrogen compressed gas cylinder should be carefully handled)
16. Switch the three way valve-2 attached to the outlet of the gas washing bottle to connect the gas washing bottle to the check valve. (check valve acts as an escape route for oxygen and nitrogen)
17. Purge nitrogen through the DI water for 30 minutes (DO level decreases to 0.55 ppm)
18. Switch the three way valve-1 connected to the pressure vessel head to connect the pressure vessel with the vacuum pump. Open the gas release valve.
19. Switch on the vacuum pump
20. Wait until vacuum has been established. Monitor the gage of the pump (the maximum pressure the pump reaches is -0.85 KPa)
21. Close the gas release valve and switch the three way valve -1 to connect to three way valve-2.
22. Switch three way valve-2 to connect gas washing bottle outlet to pressure vessel.
23. Open the gas release valve to let water vapor and nitrogen to flow inside the pressure vessel.
25. Switch three way valve-2 to connect to the check valve.
26. Repeat steps from 18-25 four times to pump and purge the vessel and establish high vacuum.

27. Repeat steps 18-21(to remove remaining water vapor and nitrogen)

28. Tilt the gas washing bottle upside down.

29. Switch three way valve-2 to connect gas washing bottle outlet to pressure vessel.

30. Open the gas release valve to let water and nitrogen to flow inside the pressure vessel due to established vacuum.

31. Repeat steps 24-25.(to prevent pressure buildup inside the gas washing bottle)

32. Repeat steps 18-21.(to remove remaining nitrogen and water vapor)

33. Disconnect the hose from the pump(the pump cannot be switched off right away because that would damage the pump)

34. Disconnect three way valve-1 from the gas release valve

35. Stop the flow of nitrogen by closing the valve on the gas cylinder

36. Put the pressure vessel into the heater

37. Plug the thermocouple into the “Temperature input” slots and put the thermocouple into the head of the vessel (thermocouple should be put as far as possible to ensure it is in touch with the surface of the slot).

38. Attach the steel hose (rupture tube) to the rupture disc assembly.

39. Switch on the controller using the power switch in the bottom left corner of the controller

40. Switch the heater switch to II (setting I is only for temperatures up to 175°C)

41. Make sure the high temperature alarm set point is set to 400°C.
   a. Press the circular arrow key three times. The upper display will read AL1H and the lower display will read the High Temperature Alarm set point
   b. If it is not set to 400 ºC use the up or down arrow to adjust this to 400°C.
   c. Press the “set” button. The lower display will stop blinking.
   d. Press the “set” Button again to return to the main menu.

42. Set the High Temperature Cut-Off Module(HTM)
   a. Press the up or down arrow until the lower display shows 400 ºC. The lower display will blink, showing the value has not been set yet.
   b. Press the set button. The lower display will stop blinking, showing the new value has been set.
43. Program the Temperature Profile

a. Enable Ramp and Soak: Hold the “set” button for three seconds. The upper display will change to “input”, and the lower display will show the thermocouple type.

b. Press the circular arrow key until the upper display shows “ctrl” and the lower display shows the control method (“PID” on default). Use the arrow keys to change this value to “Prog”. The display will blink; pressing the “set” button will solidify the change.

c. Press the circular arrow key once. The upper display will show “Ptn” and the lower display will show pattern number. Change this to 0, or whatever program number intended to be used. Select the desired program number with the desired arrow keys and set.

d. Press the circular arrow key once. The upper display will show “SP00”, where the “00” represents the pattern number and the step number, respectively. The lower display will show the set point for this step. Adjust this set point using arrow keys and set.

e. Press the circular arrow key once. The upper display will show “tI00”, where the “00” represents the pattern number and the step number, respectively. The lower display will show the time to hold the current set point in “HH:MM” format. Adjust this time using arrow keys and set.

f. Repeat steps d & e for “SP01” through “SP07” and “tI01” through “tI07”. Once all the set point desired are entered, leave the remaining “SP” and “tI” variables to zero and press the circular arrow key to advance.

g. Press the circular arrow key to display the “PSy1” on the upper display. This represents the number of steps that will be executed.

h. Press the circular arrow key to display “CyC0” where “0” represents the pattern number. If repetition of the pattern is desired, the variable should be set to the number of repeats desired.

i. Press the circular arrow key to display “Lin0”, where “0” represents the pattern number. If all the set points desired have been entered, set this value to “off”. If more than seven set points are required in the process, set this variable to a different pattern number, which tells the controller to execute a different pattern after the first is complete. Then program an additional pattern.
j. Press set to return to the main screen.
k. Press the arrow once to display “r-s”. Change this to “stop”. Press the circular arrow key again to display “Ptrn”. Change this to the pattern number that has been set at step C
l. Press “set” to return to main screen. Note that the lower display has changed to show the program step. By using the arrows the display mode between “P-St”(pattern and step), “SP”(current temperature set point), and “r-tc”(time left in minutes) can be changed.
m. Press the circular arrow once to display “r-s”. Change this to “run” to engage the program. Press “set” to return to the main screen. To disengage the program, press the circular arrow to display “r-s” and set it to stop.

The advantage of making a program is that the heater will switch off automatically after the hour has elapsed.

44. After 5 minutes, switch off the pump
45. Wait until the program is done.(In case of leakage and white water vapor coming out in large amounts stop the controller immediately)(Electrical, High pressure and High temperature hazard may occur during this step)
46. Switch off the controller
47. Wait until the vessel has cooled down to 40°C(this is important so the pressure difference between the vessel and the surrounding air is as small as possible)
48. Remove the thermocouples from the cylinder head.
49. Take off the steel hose which is connected to the rupture disk assembly.
50. Open the gas release valve. Air will flow into the vessel as the pressure decreases in the vessel.
51. Loosen compression bolts on top of the split ring in a star pattern.
52. Loosen the cone pointed screws in the outer band.
53. Lower the outer band to the ground
54. Remove split rings
55. Remove head
56. Take out the sample
Figure 35: C1s high resolution spectra curve fitting of graphite sample tested with high DO feed water up to supercritical temperature and pressure
Figure 36: C1s high resolution spectra curve fitting of graphite sample tested with high DO feed water up to 300°C
Figure 37: C1s high resolution spectra curve fitting of carbon coated alumina sample tested with high DO feed water up to supercritical temperature and pressure.
Figure 38: C1s high resolution spectra curve fitting of HOPG sample tested with high DO feed water up to supercritical temperature and pressure
Figure 39: C1s high resolution spectra curve fitting of graphite sample tested with low DO feed water up to supercritical temperature and pressure
Figure 40: C1s high resolution spectra curve fitting of graphite sample

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
<th>L. Sh.</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>284.403</td>
<td>0.849043</td>
<td>DS(0.1,490)SGL(30)</td>
<td>25798.9</td>
<td>82.76</td>
</tr>
<tr>
<td>C-O</td>
<td>285.303</td>
<td>1.23651</td>
<td>GL(30)</td>
<td>3232.6</td>
<td>10.37</td>
</tr>
<tr>
<td>Pi-Pi*</td>
<td>290.816</td>
<td>2.12803</td>
<td>GL(30)</td>
<td>507.1</td>
<td>1.62</td>
</tr>
<tr>
<td>C=O</td>
<td>286.603</td>
<td>1.23651</td>
<td>GL(30)</td>
<td>951.7</td>
<td>3.05</td>
</tr>
<tr>
<td>carboxylic</td>
<td>288.803</td>
<td>1.23651</td>
<td>GL(30)</td>
<td>687.8</td>
<td>2.20</td>
</tr>
</tbody>
</table>

The data shows the C1s high resolution spectra curve fitting of a graphite sample. The table lists the various components with their binding energies, full widths at half maximum (FWHM), line shapes (L. Sh.), areas, and percentage areas. The figure illustrates the spectra with fitted curves for different components such as C-C, C-O, Pi-Pi*, C=O, and carboxylic.
Figure 41: C1s high resolution spectra curve fitting of porous graphite sample
Figure 42: C1s high resolution spectra curve fitting of coated porous graphite sample exposed to supercritical water with low DO

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
<th>L. Sh.</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>284.483</td>
<td>0.871988</td>
<td>DS(0.1,490)/SGL(30)</td>
<td>26427.6</td>
<td>85.10</td>
</tr>
<tr>
<td>C-O</td>
<td>285.383</td>
<td>2</td>
<td>GL(30)</td>
<td>2084.1</td>
<td>6.71</td>
</tr>
<tr>
<td>Pi-Pi*</td>
<td>290.896</td>
<td>3.91038</td>
<td>GL(30)</td>
<td>1585.1</td>
<td>5.09</td>
</tr>
<tr>
<td>C=O</td>
<td>286.683</td>
<td>2</td>
<td>GL(30)</td>
<td>502.7</td>
<td>1.62</td>
</tr>
<tr>
<td>carboxylic</td>
<td>288.883</td>
<td>2</td>
<td>GL(30)</td>
<td>460.6</td>
<td>1.48</td>
</tr>
</tbody>
</table>
Figure 43: C1s high resolution spectra curve fitting of coated quartz sample exposed to high DO supercritical water

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
<th>L. Sh.</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>284.422</td>
<td>0.936663</td>
<td>DS(0.1,490&lt;$GL(30)$)</td>
<td>21442.0</td>
<td>81.33</td>
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<tr>
<td>C=O</td>
<td>285.322</td>
<td>2</td>
<td>GL(30)</td>
<td>1500.4</td>
<td>5.69</td>
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<tr>
<td>Pt-P*</td>
<td>290.835</td>
<td>4.57411</td>
<td>GL(30)</td>
<td>2007.3</td>
<td>7.59</td>
</tr>
<tr>
<td>C=O</td>
<td>286.622</td>
<td>2</td>
<td>GL(30)</td>
<td>1096.4</td>
<td>4.16</td>
</tr>
<tr>
<td>carboxylic</td>
<td>288.822</td>
<td>2</td>
<td>GL(30)</td>
<td>325.0</td>
<td>1.23</td>
</tr>
</tbody>
</table>
Figure 44: C1s high resolution spectra curve fitting of porous graphite sample exposed to low DO supercritical water
Appendix-C

Figure 45: Rocking curve of three polycrystalline graphite samples

Figure 46: Glancing angle 2 theta curve for three polycrystalline graphite samples