THE SEQUESTRATION OF GOLD BY NANOPOROUS, S-DOPED, ACTIVATED CARBON SPHERES

By

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Authors Declaration

I, Natasha Farr, hereby declare that the following work was composed solely by myself and is entirely my own, unless otherwise specified. All sources are fully acknowledged and referenced. This research was carried out under the supervision of Artur Deditius and Piotr Kowalczyk during the year 2018. This thesis is submitted as part of the requirements for the Bachelor (Hons) of Chemical and Metallurgical Engineering at Murdoch University, Western Australia. It has not been submitted for any other degree or professional qualification.

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Abstract

Homogenous spherical nanoporous carbon beads (NCB) were made from pure polymeric precursors and successfully synthesised under varying conditions to improve the adsorption kinetics of gold onto the surface. The aim of this project was to optimize the surface structure and chemistry of NCB for the sequestration of gold. The nanopore structure and surface chemistry of the NCB were tailored through the presence of sulphur-doped heteroatoms, impregnation with toluene solution containing a ferrocene/melamine mixture and the variation of activation time.

The carbon samples were examined using low temperature nitrogen adsorption, scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS). The experimental results from this work have shown that the synthesised NCB exhibit a homogenous, sponge-like surface and improved adsorption kinetics through increased adsorbance speed in comparison to the benchmark industrial carbon. The NCB samples have narrow pores with a diameter of <~2 nm which are distributed between a size fraction of micro and mesopores. Sample MU-4 developed the greatest surface area (1971 m²/g), pore volume (1.113 cm³/g) and kinetic rate constant 0.077 min⁻¹.
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Thank you so much to my friends and family, for your love and support over the past 5 years. I know you have always truly believed in me and brought much inspiration and joy to my life. You have not only supported me in being a diligent student but provided many unforgettable memories that I will always cherish.

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1.0 Introduction

1.1 Overview

The global demand for gold continues to rise, with economic development leading to an increase in the exploration and extraction of this valuable metal. There are many challenges faced by the gold mining industry today, including declining ore grades, increased energy demands and rising environmental challenges [1]. Accessible and high-grade deposits are being depleted globally, and the challenge the mining industry currently faces is to process increasingly complex and lower-grade ores in a more sustainable and economical way [2]. The general trend of resource grades in Australia can be seen below which demonstrates the need for technical advancements that can successfully process the increasingly challenging ores (Figure 1).

![Figure 1: Declining trend of ore grades from 1840 to 2005 [2]](image)

The main industries that drive the global demand for gold include the jewellery industry (52.44%), bars and coins (25.29%) and electronics (9.12%) [3]. The process involved to extract the gold from the orebody varies with mineralogy, but
the most common is the hydrometallurgical route of leaching and carbon adsorption.

The research conducted in this thesis focuses on the development of a more effective carbon product that can help mitigate some of the previously mentioned challenges the industry is facing. A larger gold adsorbance capacity and increased rate of gold loading may increase the recovery of gold and the ability to concentrate previously uneconomical deposits.
1.2 Background and Motivation

Australia is a world leader in gold production and as economically viable gold deposits diminish, there is an increased need for technological process development (Figure 2). The most commonly used extraction processes are Carbon-in-Leach and Carbon-in-Pulp, where the gold is leached from the ore with cyanide and adsorbed onto carbon either simultaneously (CIL) or separately (CIP) [4].

The mineralogy of the ore has a large effect on the efficiency of extraction, with carbonaceous ores and competing metal species decreasing the recovery of gold [6]. The development of activated carbon that has a higher rate of gold loading and selectivity against specific metal ions will be a huge step in the development of better mining practice.
1.3 Project Scope and Objectives

The aim of this project is to produce nanoporous carbon beads and optimize the surface structure and chemistry for the sequestration of gold. The super-activated carbon spheres produced from the synthetic precursor have a hierarchical pore structure and a potential specific surface area of 3000 m$^2$/g, with up to 8 wt. % of sulphur doped heteroatoms [7].

The benefit of this project is the development of an activated carbon product that has a higher surface area and gold adsorbance capacity than is currently available. The nanoporous carbon beads are produced by carbonizing and activating a resin with both high purity nitrogen (N$_2$) steam and carbon dioxide (CO$_2$), respectively. The acidic, gel-type cation exchange resin is based on a styrene-divinylbenzene copolymer [7]. The aim is for the pore structure to increase in width with longer CO$_2$ activation time, with no change in the chemical composition of the carbon surface. This is to be examined using scanning electron microscopy (SEM) and low-temperature nitrogen adsorption. The pore volume of the carbon beads will be calculated using the Nguyen and Do methodology (ND) and the surface area with the Brunauer–Emmett–Teller (BET) method. The NCB will contain a residual amount of sulphur after the carbonisation and these sulphur heteroatoms (up to 8 wt. %) may promote gold adsorption due to sulphurs hydrophobicity and its ability to form complexes with the aurocyanide ion [8]. A secondary carbon, supplied by a standard industry provider, will be studied to set a benchmark for current industry activated carbon performance and provide a comparison to the newly generated carbon.
Improved adsorption kinetics can lead to a decrease in the volume of tanks in the CIL process and an increase in the loading capacity of the carbon in the available time, meaning less carbon is required and the amount of carbon transferred to elution and regeneration is decreased. This leads to reduced capital and operating expenditures [9].
2.0 Literature Review

2.1 Introduction

A comprehensive literature review was completed to fully comprehend the research objectives discussed in the previous chapter. The focus is the use of carbon in the gold industry, and the chemical and physical properties that drive the relationship between gold and carbon.

The comparison between the various carbon samples is driven by the difference in kinetics and surface properties, which is the focus of the following research. The chapter begins with a review of the history and general method of gold extraction in mining before delving into the activated carbon itself, its properties and the gold adsorption mechanism and kinetics. The chapter is concluded with the process of final gold recovery and the production of gold doré.
2.2 Gold Extraction

2.2.1 History

Gold (Au) is a valuable metal found as both coarse, visible nuggets and invisible gold, often disseminated in sulphide and oxide deposits [10]. It is used in a multitude of industries and is Australia’s third largest exported commodity, with most of its mining and refining completed in Western Australia [11]. Due to a stable global demand, the recovery of gold is a thoroughly explored concept, and with low profit margins, the industry is dependent upon optimising methods and reducing costs [12]. Gold processing is based on traditional techniques that have been providing high recoveries for a century [13]. The characteristics of gold allow for selective extraction from ores through hydrometallurgical processes; as it only dissolves in oxidising solutions containing complexing agents [13].

The process flowsheet for gold extraction relies on the ore type, grade, gold distribution and grain size. Generally, it follows the standard path of crushing, grinding, leaching, elution and recovery before pouring gold bars, which are then sent for refining [14]. This typical gold processing path is demonstrated by Gold Fields Tarkwa Gold Mine, where a CIL plant processes 12.3 Mtpa. It uses two trains of eight tanks in series, fed by a common leach tank. The loaded carbon passes into a 15-tonne acid wash column and the gold is recovered in two 15-tonne elution circuits. The gold is then plated using electrowinning and smelted using an induction furnace [15].
2.2.2 Leaching

The most common hydrometallurgical process in the gold mining industry is leaching; the oxidation of gold in the presence of a ligating agent [16]. The process of gold dissolution takes place in an aqueous solution with oxygen (O$_2$) as an oxidant and cyanide as the complexant. Cyanide is the standard ligating agent used in the industry due to its high effectiveness and low cost. [4].

The cyanide is supplied to the leaching process by cyanide salts, which dissolve and ionize in water; this produces a metal cation and free cyanide ions (1). The three commercially viable salts used in the industry are sodium, potassium and calcium cyanides [13].

$$NaCN \leftrightarrow Na^+ + CN^-$$ (1)
The cyanide ions then hydrolyse to form hydrogen cyanide (HCN) and hydroxyl ions (OH\(^-\)) (2). Hydrogen cyanide is a weak acid, which does not completely dissociate (3).

\[
H_2O + CN^- \leftrightarrow HCN + OH^-
\]

(2)

\[
HCN \leftrightarrow H^+ + CN^-
\]

(3)

The degree of dissociation is heavily dependent on pH and can be found using the acid dissociation constant (\(K_A\)) (Figure 4) [17]. The solution is kept at a pH 9.5 – 11 to minimise loss of cyanide as hydrogen cyanide and make for a safer working environment [18].

![Figure 4: The Change in HCN/CN- with pH [16]](image)

The overall dissolution of gold is based on the reduction of gold stability by a complexing ligand. Depending on the species used to form the gold complexes, both Au(I) and Au(III) complexes are produced. This is based on the usage of soft or hard electron donor ligands; cyanide is a soft donor and therefore complexes with Au(I) [13]. This research also found that a hard donor will complex with Au(III) and result in a planar structure.

The resulting aurocyanide complex, \(\text{Au(CN)}_2^-\), is present in the aqueous solution, available for adsorption.
The dissolution reaction (4) of gold in an aerated, sodium cyanide solution \[19\] relies on the cyanide and oxygen concentrations, pH, surface area, agitation and temperature. Competing species may also be present, and this will reduce the efficiency of the gold complexation \[13\].

2.2.2.1 Carbon-in-Leach Process

The carbon-in-leach (CIL) circuit is a process that utilizes the selective complexation of gold with cyanide. It is a prevalent process in the mining industry and is an integral part of gold recovery. The CIL flowsheet is a series of continuously stirred tank reactors (CSTR) where gold is continuously leached from the ore with counter-current adsorption onto activated carbon. The residence time in the agitated leach reactors can range from 20-40 hours, with the final tank having a minimum cyanide concentration of 120 ppm \[18\].

Activated carbon is used for gold recovery as a step to concentrate the gold in solution, from around 3 g/t in ore up to 6000 g/t on the carbon \[20\]. Ore containing the gold enters the first tank, where the leaching process begins. Fresh carbon is placed into the final tank and is moved counter current to the leached solution (Figure 5). The carbon is collected in the first tank and is sent to elution for gold recovery \[20\]. The use of activated carbon in gold recovery has only been practical for the last 30 years, due to the development of an appropriate method for stripping the carbon of gold. The elution method is placing the carbon in an environment that has the reverse conditions under which adsorption is favoured \[21\].
A similar process is carbon-in-pulp (CIP) which used the same principles as CIL, except that leaching is completed before the adsorption stage. CIL is commonly used in low grade or preg-robbing ores where the carbon competes with carbonaceous material for the adsorption of gold. A CIP circuit requires a smaller carbon inventory due to a higher gold load level, and is commonly used in high grade, slow leach ores [21]. One of CILs main advantages is the decreased capital expenditure [9].
2.3 Activated Carbon

Activated carbon is a versatile material used extensively across many industries, from the purification of water and air to chemical processing and battery electrodes [22]. The raw material is prepared, carbonized and activated [23], to produce a highly porous adsorbent. Activated carbon can be produced through physical (thermal) and chemical processes, and these can also be combined to prepare a specific activated carbon with desired properties [24].

2.3.1 Source

The materials used for activated carbon production are chosen based on their availability, sustainability, and physical properties including density and hardness. These materials have a high carbon and low inorganic content and must be non-graphitizable [23]. This consists of conventional materials such as coal and cellulosic raw materials as well as synthetic polymeric precursors [25]. Conventional sources include: coal, wood, fruit stones, nutshells, and coconut shells [24] and recent technical advancements have seen an increase in polymer based activated carbons. Among various synthetic polymeric precursors, homogenous spheres of the styrene-divinylbenzene copolymer are commonly used to produce activated carbons with tuned pore size. These carbon spheres have up to 4 times the mechanical strength of traditional activated carbon [22] which minimizes the fragmentation into dust due to their high resistance to abrasion. The availability of the source material is pertinent as it takes approximately 1 t of material to produce 0.4 t of activated carbon [24].
2.3.2 Physical Activation

The physical (thermal) activation of carbon requires a two-step process, the carbonisation and subsequent activation of the resulting char [26]. If both steps are carried out concurrently, the process is called direct activation [23].

2.3.2.1 Carbonisation

Carbonisation is the heat treatment of the source material to increases the carbon content while decreasing the number of heteroatoms and removing volatile impurities [27]. This is completed in a solid, liquid or gas phase at high temperatures in an inert atmosphere [24].

A solid phase carbonisation forms a decomposed profile of the parent material, with a similar shape but lower bulk density [24]. The source material has an influence on the pore volume and particle size distribution of the final product. The material is heated to temperatures of up to 500-700 °C (depending on the precursor) in a steam of an inert gas (N₂, He, or Ar), which removes impurities as gases or leaves them as a residue on the carbon surface [13]. This produces non-graphitizable, isotropic activated carbons with micro porosity [24]. The surface area and micro porosity are further developed and tuned during the activation processes.

In the liquid-phase carbonisation, liquid-crystal structures (mesophase systems) are grown during the carbonisation of aromatic pitch substances [28]. This pitch is a liquid product from the manufacturing of metallurgical coke or by-product from the petroleum industry [24]. The mesophase is formed by the polycyclic aromatic molecules which assemble into parallel sheets, running normal to the surface to form a sphere. When heated at low temperatures, the spheres amalgamate into
a semi-coke [26]. These are then heated to graphitizing temperatures, and the spheres become small graphite crystals [29].

The gas-phase carbonisation process is called cracking or pyrolysis. The main gases used in pyrolysis are methane, propane or benzene that are often diluted with helium to ensure a low relative pressure [24]. The carbonisation is completed in the absence of oxygen, with a stable gas that causes the degradation of the source without oxidation [30]. The gases and the substrate interact, and a hexagonal lamellar structure of graphite is formed through carbon atom movement. The use of catalysts such as nickel ensures the production of tubes and fibres [24].

2.3.2.2 Activation

The carbonized material is then activated by gasification using steam or carbon dioxide (CO₂) as the activating reactant [31] at temperatures between 700 – 1100 °C [32]. The steam and CO₂ can be used individually or together to extract carbon atoms from the surface to increase pore volume. The removal of carbon atoms (5, 6) is an endothermic reaction [24], with the appropriate temperature choice high enough that the activation takes place on the inner surface of the carbon [27].

\[
\begin{align*}
C + CO_2 & \rightarrow 2CO \quad (5) \\
C + H_2O & \rightarrow CO + H_2 \quad (6)
\end{align*}
\]

Prauchner [32] found that the physical activation process allows for specific tailoring of pore size for the required application, with less pore size distribution. However, that study also found that the activated carbon had low packing densities due to the amount of empty space developed from the precursor. The
activation duration should eliminate all moisture but not enlarge pores to the point of sacrificing surface area [31]. The main advantage of physical activation is that it is a more environmentally friendly and effective method to produce activated carbon [25]. Moreover, activated carbons obtained using physical activation are free of any additional chemicals used in chemical activation (such as K, Na, and P, amongst others) that may potentially leach during the operational processes.

2.3.3 Chemical Activation

Chemical activation produces activated carbon in a single step method. It is a widely used process in carbon activation as it achieves a higher percent yield and larger surface areas at lower temperatures than physical activation [31]. The use of lower temperatures also improves pore development in the carbon structure [33].

The precursor is saturated with dehydrating agents that infiltrate the material. The chemicals affect the thermal decomposition and inhibit the formation of tar [26]. The infused precursor is then carbonized by gasification in an inert atmosphere and washed to remove the chemical agent [32].

Common chemical agents used are alkali substances including KOH, NaOH, H₃PO₄ and ZnCl₂. The choice of chemical agent is especially important in the activation of biomass, where the interaction of the lignocellulosic chains and the chemical changed the formation of porous structures [32]. That study found that the amount of chemical agent needed to achieve high porosity up to four times the mass of the precursor. Molina-Sabio and Rodrigues-Reinoso [34] identified that the use of KOH leads to powdered carbons, so is avoided in the production of granular activated carbon [35]. Their work showed that highly developed
porosity can be prepared using $\text{H}_3\text{PO}_4$ and $\text{ZnCl}_2$. The carbon produced from each of these had specific properties, so the use of the activated carbon must be kept in mind when deciding on the chemical agent. The chemical activation is an inexpensive process; however, it can be very dangerous as highly reactive metallic K is produced during the activation of the carbonised precursor with KOH, which can lead to an explosion [36]. The removal of all residual elements requires a large amount of water for washing; this can lead to water shortages and environmental concerns. Gases produced during activation can also be transported through a scrubber to capture all contaminants.

2.3.4 Regeneration

The commercial viability of activated carbon as an adsorbent is dependent on its reusability which is decreased by carbon fouling, a build-up of organic and inorganic substances on the surface. Carbon fouling has a negative impact on the kinetics and equilibrium loading of gold adsorption onto the surface [13].

To counteract the effect of species adsorbed onto the surface and inorganic salts blocking the active sites, a process of regeneration (reactivation) is used. This process removes impurities from the carbon surface and pores through acid washing and heat treatment [37]. The regeneration method is selected based on the contaminant. In gold mining, barren carbon is acid washed to remove organic adsorbates and then thermally treated in a rotary kiln at 650 °C to remove organic adsorbates and refresh the active sites [38].

Activated carbon can be reused up to 400 times, depending on the robustness of the particles and the effectiveness of the regeneration process [18].
2.3.5 *Surface Structure*

Active carbons have a disordered microcrystalline structure with low density and graphitization. The carbon has an internal surface with a capillary structure made up of pores of different sizes and shapes [39]. The porosity of the activated carbon is the cause of the high surface area of up to 1000 m$^2$/g [40]. The surface area of smaller particles is significant due to an increased ratio of surface area to overall volume and reactions that are occurring at the surface of these particles are more pronounced [41].

2.3.5.1 *Structure*

The porous surface structure of activated carbon is first formed during the carbonisation stage. It is then enhanced during activation, when the volume and diameter of the pores are increased [39]. The activated carbon has a turbostratic structure [42] with an interlayer spacing of 0.34-0.35 nm. The turbostratic structure consists of disordered microcrystalline layers due to the presence of heteroatoms and vacant lattice sites. The strong cross-linking between the layers causes a porous structure [39].

The pores can be classified into three categories; micropore, mesopore and macropore, which have a pore width of <2, 2-50 and >50 nm, respectively (Figure 6) [43].
Recent research has suggested that microporous carbon may also have a fullerene-like structure with a pentagonal arrangement of carbon rings [44]. Each type of pore has a specific role in the adsorption process and the method of activation determines the dominant pore types of the carbon [40]. Molecules enter macropores and travel through mesopores into the micropores that offer a large surface area and volume [39]. The activated carbon structure leads to a high mechanical strength, adsorption capacity and adsorption rate. The carbon structure must be strong enough to withstand agitation and transport within the CIL process [45].

2.3.5.2 Surface Chemistry

The activated carbon structure contains more than just carbon atoms. It includes elements such as hydrogen, oxygen, nitrogen and sulphur, which are known as heteroatoms [23]. Hydrogen only bonds to the edges of the carbon particle, while the others can also be present within the graphene layers [24]. The presence of heteroatoms, which make up surface groups, give the activated carbon various chemical properties and determine the charge of the surface, its hydrophobicity.
and the electronic density of the graphene layers (Figure 7) [46]. This has an impact on the interaction between the carbon and the adsorbent. Leon and Radovic [47] found that the surface chemistry can be tailored by oxidation with different agents, or heat treatment to selectively remove certain heteroatoms.

![Figure 7: Schematic diagram of main surface functional groups [48]](image)

The two main effects the surface group may have on the carbon surface is the hydrophobicity and the acidity or basicity of the surface. Activated carbon is naturally hydrophobic and amphoteric, but this may be adjusted with the effect of functional groups and doping of heteroatoms [23].

The carbon also has positive active sites, formed by the hydrolysis of carbon-oxygen surface groups (7).

$$C_xO + H_2O \rightarrow C_x^{2+} + 2OH^-$$  \hspace{1cm} (7)

An increase in pH shifts equilibrium to the left, increasing the amount of positive active sites and aurocyanide complex adsorbed [39].
2.4 Gold Adsorption

The extraction of gold from the leached liquor relies on the selective adsorption of the aurocyanide complex, in the form of \( \text{Au(I)} \) dicyanide \( (\text{Au(CN)}_2^-) \). Adsorption occurs via physical and chemical adsorption, which binds the adsorbent and adsorbate through Van der Waals forces and chemical bonding respectively [39].

2.4.1 Mechanism

The aurocyanide ion is adsorbed from the liquid phase, through the liquid film separating the carbon and solution phases and into the pores of the carbon particles [9]. Yin [49] found that carbon adsorption sites have a convex, concave or planar structure, with gold adsorbing onto the concave sheet defects or edges first rather than the basal plane. This research also found that the adsorption energy of \( \text{Au(CN)}_2^- \) is five times higher than \( \text{OH}^- \) in an alkaline solution, compared to two times higher in an acidic solution; this demonstrates favourable adsorption process in alkaline conditions.

Schmidbaur [50] has shown that \( \text{Au(CN)}_2^- \) tightly aggregates on the activated carbon surface as a rodlike, five-atom anion and tends to have a parallel orientation to the carbon sheet. Gold is not reduced to its metallic state by the addition of activated carbon as the reduction potential of activated carbon is not sufficient to separate the strong gold cyanide complex [51]. The exact mechanism of gold adsorption is not known, but Lagerge [52] has suggested that positive carbonium active sites adsorb unpaired anion \( \text{Au(CN)}_2^- \) through electrostatic interactions and less active sites adsorbed ion-paired neutral \( \text{KAu(CN)}_2 \) through Van der Waals forces. The mechanism of adsorption as an ion pair \( \text{M}^{n+} [\text{Au(CN)}_2] \) is also supported by Davidson [53] as it was observed that the presence of
spectator ions such as Ca\(^{2+}\), Mg\(^{2+}\) and K\(^{+}\) increased the gold adsorption. These spectator ions are used to create the adsorbed ion pair (8) [13].

\[
M^{n+} + nAu(CN)_2^- \leftrightarrow M^{n+}[Au(CN)_2]_n \tag{8}
\]

### 2.4.2 Kinetics

The kinetics of sorption of gold onto activated carbon is based on three stages [19]:

- The deposition of gold onto the exterior surface of the carbon through the liquid film, which is rate limiting
- The diffusion of adsorbed gold into the carbon micropores, where intra-particle diffusion is rate limiting
- Equilibrium loading as the gold moves over the internal pore surface, with surface diffusion being rate limiting

In the initial stage the aurocyanide crosses the liquid film between the carbon and solution. This is based on the Nicol-Fleming model, which assumes that the rate of adsorption can be defined by a single transfer coefficient. For the initial 12 hours of adsorption, the rate of loading is first order with respect to the concentration of gold in solution. After this time, the rate of loading decreases and the intra-particle diffusion is rate limiting as the gold is transported down into the micropores. Surface diffusion is rarely, if ever, a rate limiting step as equilibrium is very slow and could take months to reach and is purposefully not achieved to maintain the capacity to handle fluctuations in gold concentration [9].

The equation developed by Nicol to describe the rate of gold loading with a constant concentration of gold in solution is shown below (9), where \(k\) is the kinetic constant and \(K\) is the equilibrium constant [54].
\[
\frac{d[Au]_c}{dt} = k(K[Au]_s - [Au]_c)
\] (9)

If the concentration of gold in solution is changing, such as in CIL, the equation evolves (10).

\[
\ln \left( \frac{[Au]_{s,0} - B}{[Au]_s - B} \right) = k \left( \frac{KM_C}{M_S} + 1 \right) t
\]

(10)

where

\[
B = \frac{M_S[Au]_{s,0} + M_C[Au]_{c,0}}{KM_C + M_S}
\]

(11)

There are many factors affecting the kinetics of gold adsorption as shown in Table 1 [55, 13].

Table 1: Factors influencing adsorption kinetics [55, 13].

<table>
<thead>
<tr>
<th>Factor</th>
<th>Influence on Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp Agitation</td>
<td>Increases with agitation to a certain extent</td>
</tr>
<tr>
<td>Pulp Viscosity and Density</td>
<td>Decreases as these increase</td>
</tr>
<tr>
<td>Temperature</td>
<td>Increases with temperature</td>
</tr>
<tr>
<td>Carbon Size</td>
<td>Inversely proportional to particle size</td>
</tr>
<tr>
<td>Carbon Fouling</td>
<td>Decreases with an increased presence of organic and inorganic compounds blocking the pores</td>
</tr>
<tr>
<td>Gold Concentration</td>
<td>Increases with increased concentration</td>
</tr>
<tr>
<td>Free Cyanide Concentration</td>
<td>Decreases with increased concentration</td>
</tr>
<tr>
<td>pH</td>
<td>Increases with a decrease in pH</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>Increase with concentration</td>
</tr>
</tbody>
</table>
Temperature has a positive effect on the rate of adsorption, but overall has a negative effect on the adsorption efficiency. The adsorption of gold onto activated carbon is an exothermic reaction, and an increase in temperature lowers the loading capacity [13]. The concentration of cyanide also has different effects on the adsorption of gold; increased free cyanide competes with gold for adsorption sites, which decreases the adsorption rate, but also increases the selectivity of activated carbon for gold [54].

A decrease in pH increases both the rate and capacity but is maintained at pH ~10 to avoid the loss of cyanide and maintain a safe work environment [13].
2.5 Gold Recovery

Recovery is the process of removing gold from the activated carbon and into a concentrated solid. The loaded carbon is eluted to desorb the gold cyanide into a concentrated gold bearing solution. The gold is then recovered from the solution through reduction using electrical power or chemical reagents in electrowinning and zinc precipitation respectively. This solid is then processed to produce a gold doré bar, a semi-pure product that is sent for refining.

2.5.1 Elution

The loaded carbon is treated in an elution step to desorb the gold back into solution, and the mechanism is the reverse of the adsorption process (8). This stripping process produces a concentrated high-grade solution that is treated further for gold recovery [13]. The most common elution stage is the Zadra process, which uses a hot caustic cyanide solution recycled through a loaded carbon bed to desorb the gold aurocyanide. This can take up to 72 hours to complete at 100°C but is regularly modified to use high temperature and pressure vessels to increase desorption rate [56]. An increase in temperature requires an increase in pressure to maintain a liquid phase.

A similar process, the Anglo elution, pre-soaks the carbon in a 5% and 1% w/v NaCN and NaOH solution respectively (Figure 8). This carbon is then washed with deionised water at 120°C to remove the gold in 8-12 hours [57].
The pregnant liquor is then transferred for final gold recovery, and the barren carbon is regenerated and recycled back into the adsorption circuit.

2.5.2 Electrowinning

Electrowinning cells are used to treat the high-grade eluate by passing an electrical current through the solution. A voltage, which exceeds the reversible electrode potential of the reaction, is applied across a pair of electrodes immersed in the solution [59]. The cathodes and anodes are aligned inside a tank, and the current supplied by a rectifier. The pregnant solution is pumped through a series of tanks.

Gold is deposited onto the cathode through a reduction reaction (12), which forms hydrogen gas (13) [60].

\[ \text{Au(CN)}_2^- + e \rightarrow 2\text{Au}^0 + 2\text{CN}^- \]  \hspace{1cm} (12)

\[ 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \]  \hspace{1cm} (13)

Oxidation occurs at the anode, which generates the electrons consumed at the cathode. This also forms oxygen gas (14).
The standard electrochemical potentials for the cathodic reactions of gold deposition and hydrogen production are -0.6V and -0.8V respectively. Therefore, these reactions happen in parallel at a reduced current efficiency [60]. After the reaction has reached equilibrium, the cathodes are removed and washed to remove the gold from the cathode surface. The gold is then smelted and poured into bars.

2.5.3 Zinc Precipitation

Zinc precipitation, also called the Merrill-Crowe process, has been in use since the 1890’s, initially in the direct recovery of gold from clarified leach solutions until now being used in the treatment of concentrated gold eluate solutions [13]. It has been widely replaced by CIP/CIL processes but can still be found in gold mines with high grade gold ore or high silver to gold ratios [21].

Zinc precipitation is a cementation process involving redox reactions (15, 16, 17) using a zinc dust. The solution is first clarified and degassed to remove solids and oxygen, which inhibit effective cementation [61]. Zinc is a more reactive reagent, which reduces the gold due to its higher affinity towards the cyanide ion.

\[
2Zn + 8CN^- + O_2 + 2H_2O \rightarrow 2Zn(CN)_4^{2-} + 4OH^- \quad (15)
\]

\[
2Au(CN)_2^- + Zn \rightarrow 2Au + Zn(CN)_4^{2-} \quad (16)
\]

\[
Zn + H_2O + 2Au(CN)_2^- \rightarrow 2Au + HZnO_2 + 3H^+ + 4CN^- \quad (17)
\]

The gold precipitate is filtered out of the solution and smelted into the gold doré bars.
2.6 Conclusion of Literature Review

The literature review concluded that the use of activated carbon in gold concentration is a complicated process with many challenges, including pregrubbing ores, cyanide concentration and pH. Similar studies are investigating carbon to attempt to understand the mechanisms behind gold adsorption, and the effect on selectivity with doping and impregnation. It was found that carbon pores are classified into three categories: micropore, mesopore and macropore. The method of activation determines the dominant pore types, and the effect of the distribution of these pore types on the surface area, volume and gold loading capacity of carbon has been thoroughly researched.

It is clear there is room in the market for the development of a more effective, environmentally sustainable product to remove gold from a pregnant solution. With the long-term decline in ore gold grade [1] alternative sources of carbon that can help mitigate the increased energy consumption and decrease loss of gold in the mining industry is an important area of research. The potential of nanoporous carbon beads to fulfill these requirements will be investigated in the following chapters.
3.0 Experimental

The various materials and methods used to examine the adsorption kinetics of the carbon samples are outlined in the following chapter. The methods of preparation and experimental setup applied are also detailed, along with the tools of measurement that provided the results analysed in later chapters.
3.1 Materials

The nanoporous carbon beads were generated from Lewatit® MonoPlus S108 H resin produced by LANXESS, Germany. This is a strongly acidic, monodisperse gelular cation exchange resin that is strongly resistant to chemical and mechanical stress. It was carbonised and activated using high grade $\text{N}_2$ and $\text{CO}_2$ gas in a laboratory. The NCB were compared to a commercially available carbon, Acticarb GC25PAU, supplied by Activated Carbon Technologies Pty Limited (ACT).

The potassium dicyanoaurate(I), used as the main reagent in the gold stock solution, and potassium cyanide (KCN) were both supplied by Sigma-Aldrich in a solid powder form. The sodium hydroxide (NaOH) used to increase the pH of the solution was supplied by Merck Pty Ltd Australia in a pelletized form. Deionised water was used exclusively to ensure there was no added impurities that may influence the gold adsorption.

All materials were kept at the on-site laboratory facility, in a clean and dry storage area. Due to the nature of the materials, the laboratory was kept locked and the hazardous chemicals stored in the appropriate chemical cupboard.
3.2 Methods

The methodology required to successfully prepare the nanoporous carbon beads, gold aurocyanide solution and complete the subsequent kinetic testing are found below.

3.2.1 Preparation of Carbon

There were seven carbon samples prepared for analysis. This included the production of five varieties of nanoporous carbon beads and two industrial carbon samples. The carbon samples prepared are found below (Table 2).

<table>
<thead>
<tr>
<th>Name</th>
<th>Carbon Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>MU-1</td>
<td>NCB 18 hr Activation</td>
</tr>
<tr>
<td>MU-2</td>
<td>NCB Impregnated Post-Synthesis</td>
</tr>
<tr>
<td>MU-3</td>
<td>NCB Deposition Post-Synthesis</td>
</tr>
<tr>
<td>MU-4</td>
<td>NCB 15 hr Activation</td>
</tr>
<tr>
<td>MU-5</td>
<td>NCB 8 hr Activation</td>
</tr>
<tr>
<td>MU-6</td>
<td>Industrial Carbon -400μm</td>
</tr>
<tr>
<td>MU-7</td>
<td>Industrial Carbon Granules</td>
</tr>
</tbody>
</table>

3.2.1.1 Nanoporous Carbon Beads

The nanoporous carbon beads were prepared at Murdoch University by the activation and carbonisation of a Lewatit resin from LANXESS, Germany. This product is based on a styrene-divinylbenzene copolymer which forms an acidic, gel-type cation exchange resin, commonly used in the softening of water. The sulphur doping is an inclusion of the selected precursor.

The carbonisation and activation of the resin was completed in a horizontal, split tube furnace. This was pre-heated to 30°C before the sample was placed inside.
Either 4.5 g (MU-1 and MU-5) or 2.0 g (MU-4) of the resin was placed into a ceramic crucible which was sat in the centre of the tube. It was carbonized at 650°C in a high-purity N₂ steam (2.0 dm³/min) for 90 minutes. The carbonized beads were subsequently activated for 8, 15 and 18 hours in a high-purity CO₂ steam (2.0 dm³/min) at 900°C. To prevent an uncontrolled reaction, N₂ gas was used until the desired temperature was reached and the gases switched over. This procedure was repeated until a sufficient mass of carbon was produced for testing (around 2 grams). This was an extensive process as there was approximately a 60% mass loss in the production of the beads, depending on activation time.

Two more samples of nanoporous carbon beads were prepared from the post-synthesis modification of MU-1. The aim of this modification was to decrease the pore size of the MU-1 NCB. These samples, MU-2 and MU-3, were prepared using the 18-hour activated sample and the pyrolysis of ferrocene/melamine mixtures. The ferrocene is iron with carbon rings, and melamine is a carbon with nitrogen. MU-2 was prepared by the impregnation of MU-1 with toluene solution containing 0.8 g of melamine and 0.3 g of ferrocene, which was then evaporated for 24 hours in the fume cupboard. The impregnated carbon beads were then carbonized at 1000°C for 30 minutes. During pyrolysis, the ferrocene and melamine decomposed into carbon and was deposited on the internal and external structure of the micropores. MU-3 was prepared by placing a ceramic crucible containing MU-1 NCB into the furnace. A ferrocene/melamine powder was also placed inside the furnace, at a point closer to the gas steam entry. During the carbonisation at 1000°C, the powder decomposed, and carbon was deposited on the internal and external structure of micropores. The product was
then washed for 6 hours with 6M HCl to remove any residual Fe and rinsed with distilled water until it reached a neutral pH.

The activation step generated hydrogen sulphide (H$_2$S), sulphur dioxide (SO$_2$) and sulphur trioxide (SO$_3$). The H$_2$S and SO$_2$ were removed as gases while SO$_3$ remained locked in the carbon at 6-8 wt. %.

3.2.1.2 Industry Carbon

The industrial carbon Acticarb GC25PAU, supplied by Activated Carbon Technologies Pty Limited (ACT), is a highly activated granular coconut carbon commonly applied in gold mining for the adsorbance of gold in CIP, CIL and heap leaching. The Granular Activated Carbon (GAC) products are milled to achieve a particle size of 0.2 to 5 mm and recommended for the adsorption of the gold cyanide complex [62]. This size fraction is supplied due to the size of the tank screen aperture.

The carbon sample MU-7 is the original granular Acticarb supplied by ACT. The pieces had a larger diameter than the NCB, and therefore a smaller surface area. To increase this surface area, and increase the accuracy of the comparison of carbon, it was crushed to between 300 to 400 µm and treated separately as MU-6. This size fraction was chosen so the granules would be of a similar size to the beads. The carbon was ground with a mortar and pestle and then wet sieved to achieve the required size fraction and remove carbon dust.

3.2.2 Preparation of Au(CN)$_2^-$

The kinetic testing of the various carbon samples required a gold stock solution. This was used in the gold adsorption testing and production of standards for atomic adsorption spectrophotometer (AAS) measurements.
The 1000 ppm Au solution was prepared by combining the appropriate quantity of potassium dicyanoaurate(I) (K[Au(CN)₂]), potassium cyanide (KCN) and sodium hydroxide (NaOH) in a 100 ml volumetric flask. The potassium dicyanoaurate(I) provided the gold for adsorption, and the potassium cyanide and sodium hydroxide created an industry standard environment that gold adsorption may occur in.

This gold stock solution was used to create the 10ppm feed solution for kinetic testing by dilution with deionized water. Subsequent dilutions of the Au stock solution also formed the standards of 5, 7.5 and 10 ppm used in AAS measurements. The concentration of 10 ppm was chosen for two main reasons;

- It meant that no further dilutions or changing of wavelengths was required to meet the limits of the AAS. Further dilutions or breaking the reading of samples may have introduced error.
- The selected concentration of 10 ppm is equivalent to 10 g/tonne of gold in the slurry. This falls between the average gold concentration of 1-20 g/tonne that can be found in industry [13].

The diluted solutions maintained a pH of 10 and a potassium cyanide concentration of 150 ppm.

3.2.3 Gold Adsorption Kinetics

The gold adsorption kinetic testing of the Acticarb and synthesised nanoporous carbon beads was conducted using a modified industrial batch procedure. Each carbon sample was tested in duplicate to ensure accuracy.

A 500 mL reaction vessel for each carbon sample was cleaned, dried and labelled before adding 500 mL of the 10 ppm Au feed solution to each one. A 5 mL sample
was extracted from each one to measure the exact initial concentration (MU-x-0hr). Approximately 0.5 grams of each carbon sample was carefully weighed and added to each vessel. The pH was recorded with a calibrated meter to ensure it was above 9.5.

The reaction vessels were placed in a shaking water bath (80 strokes/min) that was set at a temperature of 30°C. A 5 mL sample was drawn every 5 minutes for the first half an hour, and then at 30, 40, 50 and 60 minutes. After the first hour, the sampling continued at intervals of 1.5, 2, 4, 8 and 24 hours (MU-x-xhr). After the 24-hour sample was collected, the solution was filtered, and the loaded carbon collected for examination.

The collected solution samples were then analysed with an Atomic Adsorption Spectrophotometer (AAS) using the prepared standards. This gave the concentration of gold in solution at each time interval. This data can be used to determine the activity of the carbon sample for gold loading. The rate constant (k) can be calculated using the following equation (17), which is based on the Nicol-Fleming Model [6].

\[
-\frac{d[Au]_s}{dt} = k[Au]_s
\]  

(17)

Where \( k \) is the rate constant and \( [Au]_s \) is the concentration of gold in solution. The integration of this equation (18) gives the rate constant (k) in relation to the initial concentration of gold \( [Au]_0 \), time (t) and the concentration of gold in solution at that time.

\[
\ln[Au]_s = \ln[Au]_0 - kt
\]  

(18)

The AAS results gathered from each sample are the used to plot \( \ln[Au]_s \) versus
time, which produces a straight line with a slope of $-k$. This is due to nature
of a first order reaction.

This data was also used to calculate the gold on carbon per gram. This was
calculated by converting the results of the AAS from the change in ppm
concentration over time, to the total mg of gold adsorbed from the solution. This
was the divided by the total mass of carbon added to the solution.
3.3 Measurements

The physical properties examined that indicate the carbons suitability as an adsorbent include the total surface area, extent of micro porosity and pore size distribution. The surface composition and gold adsorption kinetics were also analysed to determine the impact of changes in surface area and doping on the surface chemistry. Both the collected solution and carbon were of interest in examining any changes to the carbon surface and how the carbon and gold interacted.

3.3.1 Structural Morphology

The loaded carbon produced during the kinetic testing was gathered for investigation and taken to the CMCA at the University of Western Australia. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray analysis (EDX) were used to produce images of the carbon surface and determine the composition of the activated carbon.

3.3.2 Gold Concentration

The concentration of gold in the solution extracted during the gold adsorption kinetic testing was subsequently measured using Atomic Adsorption Spectroscopy (AAS, Agilent Technologies 55 AA) at Murdoch University.

3.3.3 Nitrogen Adsorption

The adsorption-desorption nitrogen isotherms were determined at a temperature of 77.5 K and the relative pressure range of $2.5 \times 10^{-5} - 0.2$. Nitrogen was chosen as the adsorbent as it is standard for both micropore and mesopore analysis. To gather these values, the carbon sample is carefully weighed and then prepared for analysis. This method requires a pure, dry sample which is achieved through
drying the sample thoroughly to remove moisture and the degassing with heat and a vacuum. The adsorption of nitrogen is then measured using a surface area analyser which provides the volume of gas introduced per gram of sample and the relative pressure during analysis. This data is then analysed for total surface area and pore volume, as well as pore size distribution.

3.3.4 Surface Area

The Brunauer-Emmett-Teller (BET) is a multi-molecular adsorption process that evaluates the surface area of porous materials and is commonly used to quantify the effective area available for adsorption by the specified adsorbant [63]. It assumes a homogenous surface, limited molecular interactions, local equilibriums and a kinetically limited process [41]. The BET method is a two-stage process, where the physisorption isotherm is first transformed into the BET plot and the monolayer capacity, \( n_m \), is derived (19). The BET area is then calculated from \( n_m \) by using the appropriate cross-sectional area. The BET value is then plotted against the relative pressure, which yields a straight line. The straight line is found between the relative pressure range of 0.05 – 0.25, and the slope and intercept of the resulting linear equation are used to calculate surface area. The BET specific area \( (a_s(BET)) \) of the mass \( (m) \) is found using the molecular cross-sectional area \( (\sigma_m) \) occupied by the adsorbate in the monolayer, as see in equation 20.

\[
\frac{p/p^o}{n\left(1 - \frac{p}{p^o}\right)} = \frac{1}{n_mC} + \frac{C - 1}{n_mC} \left(\frac{p}{p^o}\right) \\
\]

\[
a_s(BET) = \frac{n_m \cdot L \cdot \sigma_m}{m} \\
\]

Where \( n \) is the amount adsorbed at the relative pressure \( p/p^o \) [63].
3.3.5 Pore Volume

The Nguyen and Do (ND) method for the characterization of pore size will be used in conjunction with the adsorption stochastic algorithm (ASA) to determine the pore-size distribution curve. The method uses the nitrogen adsorption isotherms determined at 77.5 K in the [64]:

- n-BET/BET equation, which is enhanced due to stronger dispersive forces in smaller pores and is used to describe the layering in pores
- Kelvin equation which is used to calculate the pore filling behaviour.

The method is generally used to distinguish 5 separate groups; strictly microporous, microporous, micro-mesoporous, micro-mesoporous fibres and micro-mesoporous carbosils. The method will only be used to differentiate between micropore and mesopore in this investigation.
4.0 Results

This chapter presents the carbon properties and gold adsorption kinetics of the synthesised nanoporous carbon beads and industry carbon. Kinetic testing was completed on each carbon sample to determine the rate of gold loading while BET, ND and SEM-EDX analysis was conducted on each carbon type to establish the surface area, pore volume and surface characteristics. The results of the previously discussed procedures are outlined below.
4.1 Surface Morphology

The surface of the nanoporous carbon beads and industrial carbon was observed using scanning electron microscopy (SEM). The SEM images of all remaining NCB samples are displayed in the appendices. These images of homogenous groups of NCB infer that the yield of activated beads is 100%. The general physical features of the carbon particles examined can be seen in Figure 9.

![SEM images of NCB samples](image)

**Figure 9:** a) SEM image of the MU-1 sample activated at 900°C for 18 hours. b) SEM image of the MU-2 sample impregnated with ferrocene/melamine and activated for 30 minutes at 1000°C. c) SEM image of the Acticarb granules (MU-7). d) SEM image of the -400 µm crushed Acticarb (MU-6).

The 18-hour NCB sample (MU-1) is presented above which shows that the nanoporous carbon beads are porous spheres with a ~400 µm diameter that is maintained through the gold loading process (Figure 9a). MU-2, the ferrocene impregnated sample is smoother with an increased amount of charge on the surface, notable due to the difficulty in retaining clean images (Figure 9b). The images indicate that no large flaws or cracks were formed on the carbon. The
Acticarb granules had a semi-rectangular shape that was reduced to random particles of a size <400 µm during the crushing process (Figure 9c, d).

The SEM images of the MU-4 sample shows that pore entrances cover the entire NCB surface (Figure 10a). Microscopic observations show an increase in the surface area covered by pore entrances with activation time (Figure 10b).

The high magnification SEM image of MU-1 shows a sponge-like carbon with pore sizes of <2 nm (Figure 11a). The crushed Acticarb sample MU-6 shows a highly porous amorphous surface with pore sizes >50 nm, which is classified as a macroporous surface (Figure 11b).
The nanoporous carbon bead samples MU-1, 4, 5 and Acticarb MU-6, 7 show no visual occurrence of gold on the carbon surface.

The SEM scanning images of the ferrocene doped samples MU-2 and MU-3 show a decreased quantity of pores on the carbon surface (Figure 12a). At high magnification a substance can be seen deposited on the carbon surface (Figure 12b).

Figure 12: a) SEM image of the MU-2 sample made from sample MU-1 and activated for a further 30 minutes after being impregnated with ferrocene/melamine. b) High magnification SEM image of MU-2 showing deposition of impurity on carbon surface
4.2 Composition

Points of interest were selected during SEM scanning and examined using EDX analysis which found the average weigh percent of each element over a thickness of 5-6 µm from the surface. The EDX images associated with the spectra shown below can be found in the appendices. EDX analysis of sample MU-1 resulted in the spectra shown below, with a major and minor peak showing the presence of sulphur and silicon, respectively (Figure 13). Due to the significant carbon peak at approximately 0.5 keV, further minor peaks cannot be identified. This analysis shows no presence of gold in the shallow region examined by EDX.

![EDX pattern of sample MU-1](image)

Figure 13: EDX pattern of sample MU-1

The SEM imaging located a broken nanoporous carbon bead in the MU-1 sample which enabled the examination of the NCB core. The EDX pattern revealed major peaks of sulphur and gold and a minor peak of silicon (Figure ). The presence of gold in the beads core is an important discovery due to the lack of gold close to the carbon surface. Sulphur will be found in all NCB due to the nature of the precursor.
Two major points of interest were identified on sample MU-2; the porous surface and the deposited material. The spectrum associated with the deposited material can be seen in below, which shows two major peaks that were identified to be sulphur and gold, and two minor peaks of chlorine and silicon (Figure 15). The spectrum confirmed that substance deposited on the surface is not an impurity such as Fe but could be silicon as this is the only additional substance not seen in Figure 16.
The general carbon surface of MU-2 has a similar concentration of sulphur, gold and chlorine as seen in the previous spectra, but shows an absence of silicon (Figure 16). Comparatively, the concentration of gold in both spectrum 9 and 11 is very similar (36.1 and 34.8%, respectively) which indicates that the deposited substance is not crystallised gold. Elemental analysis of the EDX spectra for sample MU-3 reveals that it also contains gold (19.2%), however in smaller concentrations than MU-2 (34.8%) (Figure 17). MU-3 contains half the concentration of chlorine found in MU-2 but has an increased presence of impurities with the addition of potassium and iron (4.3 and 3.5%).

The occurrence of gold in the shell of MU-2 and MU-3 establishes that the post synthesis modification of these samples with ferrocene and melamine to the NCB and the development of smaller pores has an impact on the kinetics or surface chemistry of the carbon. Further crushing of these samples also revealed gold further into the bead, but at much smaller concentrations (3 Wt. %, spectra found in appendices).
The EDX pattern for sample MU-4 is similar to the surface of MU-1, in that it only contains sulphur and silicon, with no occurrence of Au (Figure 18). The impact of activation time between 15 hours (MU-5) and 18 hours (MU-1) is negligible.

The subsequent crushing of sample MU-4 supported the previous findings of MU-1 when the crushed sample revealed the presence of gold closer to the carbon core (Figure 19). The concentration of gold is at 1.6 Wt. %, which is lower than sample MU-1, but this could be due to the position of the scanning image.
The effect of activation time is visible in sample MU-5, as the elemental identification shows 10.5% of gold close to the carbon surface (Figure 20). This demonstrates that the activation time between 8 hours (MU-5) and 15 hours (MU-4) does have an impact on the transportation of gold through the carbon pores.

EDX analysis of the industrial carbon Acticarb shows a high concentration of potassium (62.9%) and gold (31.7%) close to the surface (Figure 21). MU-6 has no other impurities other than potassium, which was also identified on MU-3.
Figure 21: EDX pattern of sample MU-6
4.3 Surface Area

The BET method established the effective surface area available for gold adsorption. Straight lines were generated between the relative pressures of 0.05 – 0.25, and this data was used to calculate the surface area in m$^2$/g.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>MU-1</td>
<td>1525</td>
</tr>
<tr>
<td>MU-2</td>
<td>967</td>
</tr>
<tr>
<td>MU-3</td>
<td>829</td>
</tr>
<tr>
<td>MU-4</td>
<td>1971</td>
</tr>
<tr>
<td>MU-5</td>
<td>675</td>
</tr>
<tr>
<td>MU-6</td>
<td>890</td>
</tr>
</tbody>
</table>

The activation time has a significant impact on the surface area, as can be seen by the increase from 675 m$^2$/g in sample MU-5 (8 hours) to 1971 m$^2$/g in MU-4 (15 hours), which is an increase of 292% in 7 hours. A decrease in the surface area can be seen after 15-hours, with MU-1 (18 hours) having an area of 1525 m$^2$/g, a difference of 22.6%. The optimum surface area was developed at 15 hours. Samples MU-2 and MU-3, which were developed by the addition of ferrocene to sample MU-1 and further activation, have a smaller surface area than the original sample. The post synthesis modification of these samples with ferrocene and melamine had a substantial impact on the surface area. The impregnation (MU-2) and deposition (MU-3) of ferrocene and melamine caused a decrease in surface area of the parent carbon of 37% and 46% respectively.

The Acticarb sample MU-6 had a similar surface area to the ferrocene doped carbon and a similar surface area than the 8-hour activated carbon (MU-5). Sample MU-7 was not examined due to the assumption that the surface area would the same as MU-6.
4.4 Pore Volume

The total pore volume of the carbon samples was calculated, and then divided into the percentage of micro and mesopores (Table 4). There is a direct correlation between surface area and total pore volume.

Table 4: The pore volume and percentage of micro and mesopores.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Volume (cm$^3$/g)</th>
<th>Micropore (%)</th>
<th>Mesopore (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MU-1</td>
<td>0.812</td>
<td>82.34</td>
<td>17.66</td>
</tr>
<tr>
<td>MU-2</td>
<td>0.487</td>
<td>91.59</td>
<td>8.41</td>
</tr>
<tr>
<td>MU-3</td>
<td>0.420</td>
<td>91.23</td>
<td>8.77</td>
</tr>
<tr>
<td>MU-4</td>
<td>1.113</td>
<td>73.19</td>
<td>26.81</td>
</tr>
<tr>
<td>MU-5</td>
<td>0.343</td>
<td>94.24</td>
<td>5.76</td>
</tr>
<tr>
<td>MU-6</td>
<td>0.450</td>
<td>94.45</td>
<td>5.55</td>
</tr>
</tbody>
</table>

The higher the percentage of mesopores located in the carbon, the larger the total volume. The activation time has the same effect on volume as surface area, with an increase between 8 (MU-5) and 15 (MU-4) hours before declining after further activation (MU-1). Samples MU-2, 3 have a smaller total volume than MU-1 and the catalysis of carbon growth due to ferrocene/melamine correlates to an increased percentage of microporosity.

![Figure 22: The distribution of volume with pore width](image.png)
The obtained microporous carbon exhibits two main sub categories of porosity. The distribution of volume with pore width identifies a major portion of the volume is found in ultramicropores (<0.7 nm) and most of the remaining volume is found in supermicropores (0.7-2 nm) [65]. A dip is identified in the pore width distribution between 1-1.2 nm and a decline after 2 nm that illustrates the small amount of mesopores (Figure 22).
4.5 Kinetics

Kinetic data was collected to observe the overall performance in gold recovery of each carbon sample. The kinetics of adsorption was examined over a 24-hour period, but the rate constant results presented are limited to 8 hours. This is due to the rate of loading being first order over the initial 12-hour period before intraparticle diffusion becoming rate limiting [9]. Throughout the shaking experiment, samples MU-1 and MU4-7 amalgamated into larger branches that moved through the solution. This was not seen in MU-2 and MU-3, which were finely dispersed throughout the entire 24 hours.

The following graphs demonstrate the first order principle, where the slope of the curve is the rate of gold loading in min$^{-1}$.

![Graph showing the effect of activation time on the kinetic rate constant](image)

*Figure 23: The effect of activation time on the kinetic rate constant*

The variation of the kinetics rate constant of gold loading follows the same trend as the surface area and volume (Figure 23). Sample MU-4 has the quickest rate of gold loading, at 0.077 min$^{-1}$, and increased in speed with time. Samples MU-1 and MU-5 had a k value of 0.0405 and 0.0369 min$^{-1}$ respectively (Table 5) and exhibited slower adsorption kinetics.
The post synthesis modification with ferrocene and melamine to the carbon in MU-2 and MU-3 improved the kinetics and increased the kinetic rate constant of MU-1 to 0.0566 and 0.0738 min\(^{-1}\) respectively. This is an enhancement of 139% and 182% on the original 18-hour sample.

The industrial carbon Acticarb had the slowest rate of gold loading at 0.0113 min\(^{-1}\). This rate doubled to 0.0239 min\(^{-1}\) when the carbon was crushed to <400 µm.
A summary of the k values calculated for each sample can be found below (Table 5). These values have an estimated uncertainty of ± 0.017.

Table 5: Rate constant of gold loading for each sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate constant (k) min⁻¹</th>
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<tr>
<td>MU-1</td>
<td>0.0405</td>
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<td>MU-2</td>
<td>0.0566</td>
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<td>0.0738</td>
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<td>0.0369</td>
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<td>MU-6</td>
<td>0.0239</td>
</tr>
<tr>
<td>MU-7</td>
<td>0.0113</td>
</tr>
</tbody>
</table>

Sample MU-4 had the highest concentration of gold loading until it was overtaken at 18 hours by MU-1 and again at 21.5 hours by MU-5 (Figure 26). MU-1 had a total of 8.9 mg/g of gold adsorbed into the pores which coincides with the final concentration of gold in solution which was the lowest at 0.9 ppm (Table 7). At 24 hours, the only samples that are approaching gold loading capacity are MU-2, 3, 4 as the curves demonstrate a decline in the loading ability of the carbon.

Figure 26: Amount of gold on carbon per gram over 24 hours
The original Acticarb granules had the lowest concentration of gold adsorbed, with only 3.43 mg/g of gold. This was doubled by crushing the carbon, as MU-6 had 6.15 mg/g of gold on carbon.

![Graph](image)

*Figure 27: Amount of gold on carbon per cm³*

The amount of gold per cm³ of carbon gives an insight into the effectiveness of the available volume (Figure 27). While MU-4 has the largest surface area and volume, it does not use this efficiently as it has the smallest amount of gold per cm³, at 7.05 mg/cm³. Sample MU-5, which had the smallest total volume was also the most efficient, with 24.1 mg/cm³ of gold.
5.0 Discussion

This chapter aims to summarise the results obtained and analyse individual carbon types detailed in the previous chapter. The aim of this investigation was to optimize the NCB for overall performance in gold loading ability, and the key differences that differentiate each carbon samples ability to adsorb gold will be identified.
5.1 Surface Morphology and Composition

The surface morphology of the carbon species is an insight into the diffusion path of gold to the micropores. The diameter of the pores of the NCB is ~2 nm which means that the micropore entrances are directly connected to the surface. Conversely, the commercial carbon is predominantly macropores and we can conclude that the micropores are not directly connected to the surface but follows the branched tree model (Figure 6). The SEM images also indicate that the NCB samples produced are robust and homogenous in appearance, with a distinctive sponge-like surface.

Activation time has a distinct effect on the carbon surface with microscopic observations showing an increase in the surface area covered by pore entrances between 8 and 15 hours. This is due to the formation process of pores on the carbon surface where ultramicropores (<0.7 nm) are initially formed before merging into supermicropores (0.7-2 nm) and subsequent merging into mesopores (>2 nm). An understanding of pore development leads to engineered pore sizes. Sample MU-5 has irregularly shaped pores which is due to the shorter activation time which produces shallower pores; longer activation time straightens the pores and removes constrictions that impair diffusion. The shallower pores did correspond to the detection of gold in the shell of the carbon bead, which relates to a restriction that limits the transport of gold to the core. Samples MU-1 and MU-4, which had an activation time of 15 and 18 hours, did not have any gold present within the detection range of the EDX on the NCB surface. The discovery of a broken NCB of MU-1 enabled the analyzation of the beads core which revealed the presence of gold at 17 Wt. %. This infers a well-developed pore network that enables the loading of gold from the core to the
surface. This is further evidenced by the crushing of sample MU-4, which also presented no gold in the shell. Gold was also found in the core of this sample, which supports the hypothesis that an increased activation time will increase the depth of the available pores.

The post synthesis modification of MU-1 with ferrocene and melamine had a significant impact on the appearance of the sample. MU-2 and MU-3 have very a smooth surface with a significantly decreased occurrence of pores. This supports the hypothesis that the growth of carbon fragments catalysed by ferrocene leads to the development of smaller pores; it also appears that some of the pores may have been blocked during this process. MU-2 and MU-3 had high concentration of gold on the surface, which is significant as none was identified on sample MU-1. This provides further evidence that the pores were narrower due to the catalytic decomposition of ferrocene and the growth of carbon. The EDX analysis provided further insight into the effect of ferrocene addition technique because there were two compositional difference between MU-2 and MU-3, which was the presence of iron and potassium. Sample MU-2, which was impregnated with a solution containing ferrocene/melamine and then washed contained no impurities of iron, however MU-3, which had a ferrocene/melamine powder deposited on it during activation did show 3.5 Wt. % of Fe and 4.3 Wt. % of K. Due to potassium’s association with cyanide and gold, it was considered to have been attached to either or both of these species. The iron could be due to the powder depositing further into the carbon pores of MU-3, indicating that the residual iron from ferrocene was not fully removed with HCl. Further washing is required in future post synthesis modifications. Whether there is a relationship between the presence of potassium and iron needs further investigation. Both samples
contained chlorine, which was introduced during the purification of the carbon beads by the removal of residual iron with 6M HCl. A further washing step to remove lingering chlorine is required.

The Acticarb samples were identified as macroporous due to the presence of large (>50 nm) pores. The sample is amorphous in both particle and pore shape, and the crushing of the sample had an insignificant impact on its appearance. The industrial carbon had no impurities, only a high concentration of K (62.9 Wt. %) and gold (37.1 Wt. %). The presence of potassium may support the theory that the complex anion aurocyanide Au(CN)²⁻ pairs with the positive K⁺ and is adsorbed neutrally. This is inconclusive due to potassium not being present on all samples.

Some impurities are seen on the surface of the NCB, which were analysed with EDX and identified as Co. Cobalt was not used in the process, and contamination may have come from outside sources, such as measuring equipment. An unidentified issue when planning this investigation was the need to crush the samples to enquire into gold adsorption. This entailed a further crushing step and imaging that had not been planned for.
5.2 Surface Area and Pore Volume

The largest surface area was sample MU-4, at 1971 m$^2$/g, followed by MU-1 at 1525 m$^2$/g. This data did not support the hypothesis that further activation increased surface area and pore volume, but that it begins to decline after 15 hours. Other research does not support this, as an 18-hour sample that reached a total surface area of 3200 m$^2$/g has been previously created by Piotr Kowalczyka [7]. His sample was produced with less precursor placed in the furnace and had a 5% weight production from the small amount placed in the crucible. This was not efficient for the timeframe of this test work, as 5 grams of NCB was necessary for testing. The larger amount placed in the furnace may have caused less diffusion through the crucible and formed pockets of CO$_2$ which meant that fresh gas could not reach the beads and formed gas could not escape. This could be fixed by putting less Lewatit® MonoPlus S108 H resin into the crucible or using a rotating furnace. The difference in surface area between MU-5 and MU-4 does support the hypothesis, as the surface area and pore volume triple between 8 and 15 hours.

Sample MU-4, which had the greatest surface area, has narrow hydrophobic micropores with well-developed pore walls. It was the highest total volume with the biggest concentration of mesopores at 26.8%. These mesopores are necessary to facilitate the transport of gold from the surface to the core. The volume of the pore present is crucial to the transportation of gold to the carbons core. As can be seen by comparing the composition analysis and total pore volume, the smaller the total available volume, the closer the gold is to the surface.
The post synthesis modification with the ferrocene/melamine mixture decreased the surface area of MU-2 and MU-3 by 558 m$^2$/g and 696 m$^2$/g respectively. This further supports the shrinking of the pores by carbon deposition on pore walls. This is confirmed by the pore volume analysis, where there is a ~10% increase in micropores in these samples when compared to MU-1.

A restriction of nitrogen adsorption is the size of the nitrogen atom. There could be smaller pores present that cannot be identified due to the minimum nitrogen penetration size being 0.4 nm. This is also true for the opposite – macropores cannot be seen by nitrogen adsorption and the examination of pores of that size would require mercury porosimetry. Therefore, the volume of MU-6 is still divided between micro and mesopores, even when macropores can be seen visually.
5.3 Kinetics

Sample MU-4 has the closest behaviour to the Langmuir adsorption model, as most of the pores are filled within 250 minutes. This is the best sample for practical applications. MU-1 and MU-5 have the highest saturation capacity, as they not only have the highest concentration of gold on carbon (in mg/g) but are still straight lines at the end of 24 hours, which means they have further adsorption capacity.

Samples MU-2 and MU-3 had an increased rate constant when compared to MU-1 of up to 45%. This is due to the blocking and narrowing of the pores by the post synthesis modification with ferrocene/melamine, which corresponded to the rate being less transport reliant as the gold was just being adsorbed into the shell. Notably, this also meant that samples MU-2 and MU-3 had a decreased gold loading capacity due to a lack of mesopores facilitating transport. Samples MU-3 and MU-4 have similar rate constant, even though they vary in surface area and volume. This is potentially due to the narrow micropores close to the surface of MU-3, which could account for its comparably smaller surface area.

The effect of particle size in relation to kinetics is demonstrated in the rate constant found for MU-6 and MU-7. Crushing the Acticarb granules to <400 µm doubles the k value which is due to increased reaction kinetics. The industrial carbon only adsorbed 20-50% of gold compared to the NCB. Even though MU-5 has less surface area than MU-6, it has a faster adsorption rate (0.369 vs 0.0239 min⁻¹). This is possible due to the narrow micropores of MU-5 being closer to the surface, thus having a shorter diffusion path.
The direct competition between hydrophobicity and electrostaticity means that the carbon will be more hydrophobic when electrostatic interactions are small. Equally, with increased charge density, the carbon may become more hydrophilic [66]. Due to the activated carbons ability to adsorb the gold particles, the nanoporous carbon beads are hydrophobic, which also indicates that the number of oxygen containing functional groups should be minimal.

No sample reached saturation at 24 hours, and while their final capacity would be of interest it is not required due to the industries purposeful avoidance of ever nearing equilibrium.
5.4 General Discussion

The post synthesis modification of MU-1 with ferrocene and melamine lead to the decomposition of the ferrocene into Fe and carbon, with melamine as an additional carbon source. The iron then catalysed the growth of carbon fragments inside pores. The aim of this procedure was to narrow the carbon pores, which was considered successful. This is evidenced by the visual appearance of the sample, the reduction in surface area and decrease in pore volume but higher percentage of micropores than MU-1 (Figure 9b).

The two samples with the largest amount of mesopores (MU-1 and MU-4) also correlated to the distribution of gold into the core rather than remaining in the shell. This supports the need for mesopores, as well as a large proportion of micropores, to facilitate the transport of gold to the core.

The differences in MU-1, 4, 5 showcases that the activation time does have an impact on the shape, structure and connectivity of the pores, and that it can be used to optimize the nanoporous carbon beads. The generated nanoporous carbon beads outperformed the industrial carbon in almost every investigation, and when MU-5 did have a smaller surface area and volume than the Acticarb, it still used these more efficiently. The high percentage of sulphur in the NCB due to the S-heteroatoms leads to favourable gold adsorption due to its ability to form complexes with the gold-cyanide ion. This is supported by previous work completed by Ramirez-Muniz et al. who also found that they achieved greater levels of adsorption after impregnating their activated carbon with sulphur [8].
6.0 Conclusion and Recommendations

Nanoporous carbon beads were successfully synthesised from a polymeric precursor through carbonisation at 650°C before subsequent activation for 8, 15 or 18 hours at 900°C. The beads exhibited a homogenous spherical shape with a sponge-like surface, narrow pore sizes of <~2 nm and no identifiable flaws. An investigation into properties of the NCB through experimental analysis of the surface and kinetics led to the conclusion that they were suitable for use in hydrometallurgical applications, specifically for adsorption of the gold-cyanide complex.

The aim of this project was to optimize the surface for the sequestration of gold by tailoring the carbonisation and activation process. This was achieved, and the experimental results suggest an enhanced adsorption capacity and gold loading kinetics of the synthesised NCB when compared to the industrial benchmark carbon Acticarb. The post-synthesis modification of sample MU-1 with ferrocene and melamine resulted in a decreased surface area and volume but improved gold loading efficiency when compared to the initial 18-hour sample.

Sample MU-4 proved to be the most effective sample with a 15-hour activation time. It had the largest surface area, pore volume and rate constant and the highest percentage of mesopores. Further investigation is required due to the mass of carbon placed in the crucible effecting the efficiency of activation; this may lead to improved results for an 18-hour activation.

The results from this investigation lead to multiple recommendations for future works.
For the repetition of this work, the production of the NCB requires a set starting mass that accounts for the 60% mass loss, as well as the production of enough carbon for this test work to completed in triplicate to allow for the estimation of uncertainty. SEM images of the carbon should also be taken before gold adsorption to compare. The post-synthesis modification of sample MU-1 can be extended into the modification of sample MU-4 to investigate if the results of MU-1 can be replicated and improved. The effect of the modification process on the surface chemistry and functional groups of the NCB could also be examined. The kinetic figures had poor linear fittings, which should be examined in the future. The data was treated as a first order reaction over the first 12 hours, as was found standard in the industry and other works throughout the literature review; however, a change in slope over the 12 hours is visible.

Transforming this research into an applicable industrial source requires further exploration into the elution of gold from the NCB and the price of production. To be a practical carbon source for current industrial gold extraction, larger nanoporous carbon beads are required. This is due to the use of interstage screens between tanks in CIL and CIP processing which commonly have apertures of 0.6 to 0.8 mm [67]. This may be achieved through the use of a larger precursor of the same composition.
7.0 References


8.0 Appendices

8.1 Surface Morphology

Figure 28: SEM image of (a) MU-1 (b) MU-3 (c) MU-7 (100 µm) (d) MU-7 (30 µm)

Figure 29: High Magnification SEM image of (a) MU-1 (b) MU-2 (c) MU-4 (d) MU-7
8.2 Composition

Figure 30: EDX images of (a) MU-1 (b) MU-1 broken (c) MU-2 Spectrum 9 and 11 (d) MU-3

Figure 31: EDX images of (a) MU-4 (b) MU-5 (c) MU-6 (d) MU-4 broken
Figure 32: EDX Spectra for sample MU-2 post crushing

Figure 33: EDX Spectra for sample MU-3 post crushing
### 8.3 Pore Volume

*Table 6: Pore Volume Original Data*

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<th>Sample</th>
<th>Total Volume (cm$^3$/g)</th>
<th>Micropore Volume (cm$^3$/g)</th>
<th>Mesopore Volume (cm$^3$/g)</th>
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### 8.4 Kinetic Data

**Table 7: Gold Concentration Raw Data**

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Table 8: Amount of gold on carbon (mg/g)

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Table 9: Gold on Carbon by Surface Area (mg/m²)

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