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Study on the surface features of Preg-Robbing carbonaceous matter during oxidation treatment

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A thesis submitted in partial fulfillment of the requirements for the Master of Science degree in Geology

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Abstract

Carbonaceous gold ores have the ability to adsorb gold (I) cyanide from leach solutions during processing. This phenomenon, known as preg-robbing, is responsible for poor recoveries as the carbonaceous materials of the ore compete with activated carbon used during the leaching and adsorption phase of processing. Chemical oxidation of carbonaceous materials by different reagents has been utilized to investigate and compare the mechanism of $\text{Au}(\text{CN})_2$ adsorption onto carbonaceous materials prior to and following the treatment.

The procedure for characterization of the carbonaceous materials (plain and modified) in the sample combines the use of several analytical techniques and test assays such as Scanning Electron Microscope (SEM), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Raman spectroscopy, Ultraviolet visible (UV-Vis) and Atomic Absorption (AA) in order to provide complete information on all the variables affecting preg-robbing capacity, namely its composition, degree of C disorder, surface area and surface chemistry. This thesis investigated the surface chemistry and surface structure of various carbonaceous materials in the context of factors governing adsorption characteristics towards providing a better estimation of the preg-robbing capacity and strategies for its reduction.

Keywords: Gold, Carbonaceous matter, Preg-robbing, Surface Chemistry, TOF-SIMS, XPS, Raman, SEM

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Table of Contents

Abstract	i
Acknowledgments	ii
Table of Contents	iii
List of Tables	vi
List of Figures	viii
Chapter 1	1
1 Introduction	1
1.1 Statement of the problem	2
1.2 Background	2
3	
1.2.1 Preg-Robbing gold treatments	4
1.3 Objectives	5
1.4 Research Approach and Methodology	5
1.5 Impact	6
1.6 Thesis overview	7
Chapter 2	8
2 Background and Literature Review	8
2.1 Gold deposits in different rock types, a brief overview	9
2.1.1 Gold in igneous rocks	10
2.1.2 Gold in sedimentary rocks	10
2.1.3 Gold in metamorphic rocks	11
2.2 Gold deposits containing carbonaceous material	11
2.3 Metallurgical perspective of gold classification	12
2.3.1 Preg-robbing gold ores	14

2.4 Objective.....	25
2.5 References:.....	26
Chapter 3.....	31
3 Methodology and research approach	31
3.1 Cyanidation and gold dissolution.....	31
3.2 Analytical techniques.....	33
3.2.1 UV-VIS.....	33
3.2.2 Raman	35
3.2.3 SEM-EDX.....	36
3.2.4 XRD	37
3.2.5 TOF-SIMS	37
3.2.6 XPS	39
3.3 Ore preg-robbing characterization	40
3.3.1 Experimental Design and selection of testing criteria	40
3.3.2 Oxidation treatment	40
3.4 Final experiments on Activated Carbon	53
3.4.1 Oxidation treatment	53
3.4.2 Adsorption tests	54
3.5 Tests with a composite preg-robbing carbonaceous gold ore.....	55
3.5.1 Experiments for the composite sample of preg-robbing carbonaceous gold ore	55
3.6 References.....	60
Chapter 4.....	63
4 Analytical results and evaluation	63
4.1 Measurement of Au adsorption by UV-VIS spectroscopy	63
4.1.1 Results.....	63

4.2 Raman	65
4.2.1 Results.....	65
4.3 Surface structure and chemical analysis by SEM/EDX.....	67
4.3.1 Composition analysis	67
4.3.2 Surface Morphology	69
4.4 BET surface area analyses	72
4.5 Surface chemical analysis of activated carbon subjected to oxidation by TOF-SIMS	73
4.5.1 Primarily TOF-SIMS study.....	73
4.5.2 Detailed TOF-SIMS surface evaluation of oxidized carbon.....	77
4.6 Surface chemical analysis of activated carbon subjected to oxidation by XPS....	81
4.6.1 Results from the XPS analysis	81
4.7 Results from oxidation investigations on a carbonaceous gold ore	85
4.7.1 Sample characterization	85
4.7.2 Mineralogical analysis	85
4.7.3 Au deportment	88
4.7.4 Carbonaceous material characterization	88
4.7.5 BR-20 Au adsorption results and discussion	90
4.8 References.....	97
Chapter 5.....	99
5 Conclusion and future work.....	99
5.1 Conclusion	99
5.2 Future work.....	102

List of Tables

Table 2-1 Common gold minerals [1,3].....	8
Table 2-2 Concentrations of gold in common minerals [3].....	9
Table 3-1 Oxidation experimental conditions.....	41
Table 3-2 Adsorption experimental conditions.....	42
Table 3-3 Selected Factors and levels of adsorption test.....	43
Table 3-4 Adsorption tests experiments	44
Table 3-5 Analysis of variance of the model	48
Table 3-6 Evaluation of model accuracy	50
Table 3-7 Final experimental conditions for oxidation.....	53
Table 3-8 Final experimental conditions for adsorption.....	54
Table 3-9 Experimental conditions for micro flotation	56
Table 3-10 Flotation results	56
Table 3-11 Carbon content in the sample	57
Table 3-12 Experimental conditions for the oxidation of the preg-robbing gold ore.....	58
Table 4-1 BET analysis on AC and OAC.....	73
Table 4-2 Primary samples studied by TOF-SIMS.....	73
Table 4-3 Surface carbon and oxygen content of plain and oxidized activated carbon as determined by XPS analysis	81

Table 4-4 Relative proportion of the assigned peaks as measured by XPS on the surface of (PAC) and (OAC).....	82
Table 4-5 Major oxide concentration for sample BR-20 before oxidation.....	85
Table 4-6 Trace element results for sample BR-20 before oxidation. All data in ppm....	85

List of Figures

Figure 1-1 Common flowchart for gold processing.....	3
Figure 2-1 Simplified schematic illustration of the most common types of gold deposits [8].....	10
Figure 2-2 metallurgical categorization of gold deposit [9]	13
Figure 2-3 Common gold extraction flowsheet [13].....	15
Figure 2-4 Common surface functional group [36]	21
Figure 2-5 FT-IR spectra of AC and oxidized products [33].....	23
Figure 2-6 schematic picture of different types of porosity in activated carbon structure [44].....	25
Figure 3-1 Au-H ₂ O Pourbaix diagram (the left), Au-CN-H ₂ O Pourbaix diagram (the right) at 25° c [3].....	32
Figure 3-2 Adsorption spectra of K[Au(CN) ₂] solutions versus concentration by UV-VIS	34
Figure 3-3 UV-Vis wavelength calibration at 210 nm and 230 nm.....	35
Figure 3-4 Adsorption test solution	42
Figure 3-5 (a) Comparison between plain AC, oxidized AC with H ₂ O ₂ and HNO ₃ in gold adsorption.....	46
Figure 3-6 Graphical representation of the steps performed in the activated carbon Au adsorption testing program	47
Figure 3-7 Probable significant factors in adsorption test	48
Figure 3-8 Significant factors in process efficiency and their relations	52

Figure 3-9 Graphical representation of the steps performed in the ore sample Au adsorption testing program	59
Figure 4-1 Au (CN) ₂ ⁻ adsorption over a 3-hour period	64
Figure 4-2 Au(CN) ₂ ⁻ adsorption for the plain AC and oxidized AC	64
Figure 4-3 Raman spectra showing the characteristic G (1585) and D (1315) bands for the samples; fresh activated carbon (A), fresh activated carbon + gold (B), oxidized activated carbon + gold (C), overlay of Raman spectra of from [(A),(B),(C)] D	66
Figure 4-4 Raman ratio for activated carbon (ACT C), oxidized activated carbon (OAC) and graphite.....	67
Figure 4-5 EDX surface analyses data. Box plots illustrating the concentration of oxygen (%), carbon(%) and C/O on the surface of plain AC and oxidized AC.....	69
Figure 4-6 SEM images with pore size measurements of plain activated carbon (A), oxidized activated carbon (B)	71
Figure 4-7 Pore size distribution of plain activated carbon and oxidized activated carbon	72
Figure 4-8 : TOF-SIMS surface analyses image. Distribution of elements H, C, O and Au(CN) ₂ in a grain of activated carbon (A) , activated carbon +gold (B), oxidized activated carbon + gold (C) (Field area: 500*500 μm ²)	74
Figure 4-9 TOF-SIMS surface analyses data. Box plots illustrating the normalized intensity of carbon , oxygen, carbon oxygen ratio (C/O) and Au(CN) ₂ on the surface of plain activated carbon (AC), plain AC + gold and oxidized activated carbon + gold.....	77
Figure 4-10 TOF-SIMS surface analyses data. Box plots illustrating the normalized intensity of carbon (C) and oxygen (O) on the surface of fresh activated carbon (FAC) and oxidized activated carbon (OAC).....	78

Figure 4-11 TOF-SIMS spectra in the mass regions of carboxylic acid. The left of the double line shows the peak position for the parent molecule, to the right, first mass fragment (parent –OH).....	79
Figure 4-12 normalized intensity of mass positions representative of the carboxylic parent molecule and the first mass fragment (parent – OH) on the surface of (FAC) and (OAC)	80
Figure 4-13 General formula of carboxylic acid illustrating the polar nature of the compound. R represents the C-H chain	80
Figure 4-14 High resolution C 1s XPS spectra showing peak fits and their assignment as measured on the surface of plain activated carbon (upper), oxidised activated carbon (lower).....	83
Figure 4-15 Stacked XRD patterns for BR-20. A: the fresh un-oxidized sample, B the HNO ₃ oxidized sample.....	86
Figure 4-16 Relative proportion (%) of all minerals identified by the QEMSCAM (quantitative evaluation of mineralogy by scanning electron microscopy) technique. Data was provided by Barrick.	87
Figure 4-17 SEM images of carbonaceous materials accompanied with numerous fine silicate particles and agglomerates in sample BR-20	89
Figure 4-18 Au (CN) ₂ adsorption on plain ore and different types of treated ore (a) and with 50 ppm gold added (b)	91
Figure 4-19. EDX analysis for C, O along with the C:O ratio for grains from sample BR-20. The Boxes show outliers, 95th and 5th percentiles along with the mean (solid line) and the median (dashed line). Data shown is for all grains with >80% carbon in the analysis.....	93

Figure 4-20 Raman ratio for carbonaceous materials in the BR-20 samples before and after oxidation along with carbonaceous materials from a number of other carbonaceous gold ores within Nevada.	93
Figure 4-21 Process schematic of the HNO ₃ oxidation results and process of potentially increasing the preg-robbing capacity of the oxidized carbonaceous material in sample BR-20.....	95
Figure 4-22 TOF-SIMS spectra in the mass regions of Si, Al and Mg on the surface of no oxidized and oxidized carbon grains from sample BR-20. The data show an increase in proportion of Si, Al and Mg on the surface of the oxidized carbon.	96

Chapter 1

1 Introduction

The gold industry is facing a challenge. Easily processed ore bodies are becoming limited and the ores which are now of economic significance are complex and require significantly more input in the extraction process. Hence, the industry requires innovative approaches in order to treat the complex mineralogical features of gold deposits. Deposits which contain carbonaceous material (CM) are one example of complex ores. From a metallurgical point of view, they can be categorized into several different groups based on the difficulty of separation of the gold from the ore. Carbonaceous gold ores are considered problematic as the native CM within the ore acts as a sink for the gold cyanide complex competing with the added activated carbon during leach and recovery operations. These ores are commonly called preg-robbing (PR) as the Au cyanide complex is “robbed” or adsorbed by the inherent CM from the pregnant leach solution. They are commonly considered complex as the ultra-fine carbonaceous particles are not easily separated from the gold (Vaughan 2004; Adams 2006). From the advent of the cyanide leaching process in 1880, the CM present in gold deposits has been considered a significant cause of gold loss (Dunne et al. 2013).

Understanding the mineralogical characteristics of the ore along with the gold deportment are significant in order to determine the processing stages and the methods for extraction. Numerous studies have been performed to evaluate and reduce the PR effect of CM, some of which have been applied in the industry. However, links to variability in CM PR capacity are poorly understood, Much of this arises from the limited understanding of the surface attachment mechanisms of $\text{Au}(\text{CN})_2^-$ to the CM. This research will focus on evaluating the effect of surface oxidation on the PR capacity of CM. The overall goal of the research is to better understand the attachment mechanism of $\text{Au}(\text{CN})_2^-$ to CM with the goal of identifying new strategies for reducing the PR capacity and the subsequent gold loss in carbonaceous gold ores.

1.1 Statement of the problem

The most common carbonaceous refractory gold ores are made up of various sedimentary rocks containing both inorganic and organic carbon. They are called “preg-robbing ores” as the dissolved Au (CN)⁻ complex generated during the leaching process is robbed by adsorption of inherent CM which competes with the added activated carbon in the leach process. This phenomenon is responsible for gold loss during processing on the order of less than 20% and up to 90% (Helm et al. 2009). Much of this variability is due to the nature and presence of the CM, however, in other instances, it may be related to the operation (pulp chemistry, competing species etc.) and the variability in surface chemical characteristics of the CM. The goal of this study is to evaluate surface chemical effects linked to PR. The research focuses on the oxidation of CM and the surface chemical changes which may be linked to variability in the degree of PR. The ultimate goal of this study is to provide the industry with information on a potential mechanism by which the PR capacity of CM can be reduced and may help define alternative strategies for improved gold recovery.

1.2 Background

The occurrence of the gold in an ore defines the recovery process. Some of the techniques to upgrade an ore prior to cyanide leaching include; selective sorting, gravity separation and froth flotation; often all of these are used together. Generally, the gravity portion recovers the free “coarse” gold. The lees from the gravity portion are commonly subjected to froth flotation where gold grains are recovered along with sulphide hosted solid solution or sub-microscopic gold. The later can be subjected to roasting but more commonly to pressure oxidation in order to make the gold available for leaching. The product is then fed into a cyanide leaching circuit (Wills 2010). In this process, a dilute cyanide solution (normally NaCN or KCN) dissolves the gold which can then be recovered by a number of different processes involving adsorption onto activated carbon (McDougall et al 1980). Cyanidation is the most common method for gold extraction and is used in more than 75% of the gold production operations.

Extraction of the solubilized gold from solution can be performed by a number of different techniques: electro winning, the Merrill-Crowe process, ion-exchange/solvent extraction and carbon adsorption. Due to its high porosity and effective surface area, activated carbon has an extremely high adsorption capacity which makes it an effective and economic recovery method of gold cyanide. Subsequent to leaching and adsorption, the loaded carbon is directed to the stripping tank for desorption (Davidson et al. 1979; McDougall et al. 1980). A common gold extraction process is illustrated in Figure 1-1.

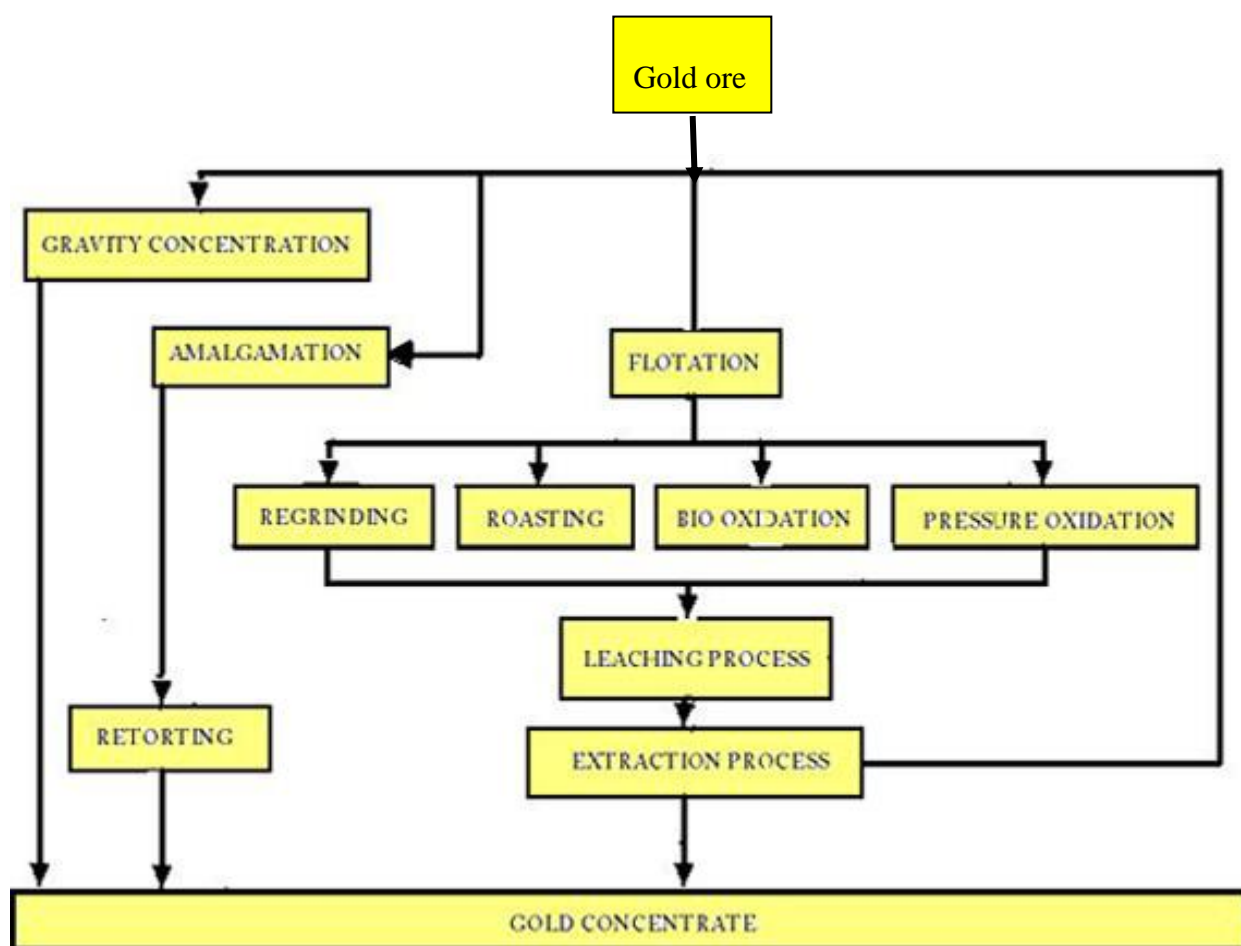


Figure 1-1 Common flowchart for gold processing

1.2.1 Preg-Robbing gold treatments

Various techniques have been employed for the prevention of PR by CM. Most are limited in their effect and commonly fall short in PR reduction due to the existing challenges associated with each method as discussed below.

- **High temperature roasting** (primarily for the conversion of sulphides to oxides to make the Au available): As a secondary consequence it also decomposes the CM. As a downfall, this method has a high energy consumption as well as some significant environmental consequences (Dunne 2013). This method is not favored and is currently being phased out.
- **Bio-oxidation**: In this method, fungi or microbes oxidize and/or partially passivate or decompose the CM (Yang et al. 2013). The bio-oxidation reaction requires a significant amount of time, making it only suitable in specific installations.
- **Pressure oxidation**: This technique is used for refractory gold ores (sulphides with solid solution gold) as an alternative to the roasting process. In some instances the process results in passivating the CM within the ore. The fact that gold and or hosting minerals need to be less than 45 μm in size and that the autoclaves are operated at 225°C or greater makes this a relatively costly method of recovery (Dunne 2013).
- **Blinding**: This method involves addition of diesel oil, kerosene or similar natural or manufactured reagents to passivate or coat the surface of the CM. A drawback with this method is that it can also result in fouling of activated carbon in pulp and consequently a decrease in gold recovery (Adam et al. 2006; Cay et al. 2014).
- **Flotation**: Oil flotation can be performed on gold deposits in order to pre float the CM from the ore. (Wills 2010; Guo et al. 2016). Separating gold particles from the CM by flotation can be problematic due to froth stability issues when floating with oil. Furthermore, for some ores, the gold is adsorbed on in-situ carbon and therefore rejection of the inherent CMs will result in gold loss (Dunne 2016).

1.3 Objectives

Given the strong relation between CM surface chemistry and various processes to minimize the effect of PR, this research aims at evaluating the effect of surface oxidation as the contributing factor to $\text{Au}(\text{CN})^-$ adsorption in order to identify opportunities or strategies for PR capacity reduction. In doing so, several short-term objectives must be met which include the following:

- 1- Evaluating the adsorption capacity of CM through chemical oxidation with different reagents in order to assess how oxidation will affect the mechanism of gold attachment to CM.
- 2- Investigating how surface features such as porosity, surface area and pore volume, C maturity and surface functional groups are affected by chemical oxidation and how changing these features influences the PR adsorption.
- 3- Determining what type of reagent and under which condition is most effective in reducing PR capacity.

1.4 Research Approach and Methodology

This study was motivated by numerous investigations which have indicated that, while the CM in highly preg-robbing ores is very similar structurally to activated carbon, the Au adsorption capacity can show significant differences. The question then focuses on potential differences in the surface chemical make up of the different CMs.

Studies on preg-robbing ores and coal have shown that oxidation of CM results in significant changes in surface chemistry affecting both flotation recovery and PR capacity. Oxidation methods involve oxidizing gases (O_2 , O_3 , carbon dioxide, etc.) or oxidizing liquids (HNO_3 , H_2O_2 , Ammonium peroxydisulfate, etc.) and can potentially be applied before either flotation or cyanidation. Following the oxidation of activated carbon, changes in the porous structure, surface area and volume, functional groups and overall degradation of the carbonaceous material in gold ores can result in a less adsorbent surface (Jaramillo et al. 2010; Castilla et al. 1996).

Given these observations the current methodology involves a comparative investigation on the adsorption capacity of fresh versus modified CM using various oxidation techniques.

In order to achieve the objectives of this study, namely an understanding of the variability in adsorption of $(\text{Au}(\text{CN})_2)^-$ on CM and its relation to modification of the CM in response to various degrees of oxidation, several tests will be performed:

- Oxidation of activated carbon (comparison to non-oxidized samples):
- Raman spectroscopy: evaluation of structural changes due to oxidation (Beyssac et al. 2002).
- SEM: morphological evaluation of the CM after oxidation
- BET: changes in the surface area and volume of micro pores, meso pores and macro pores (Kacan 2016).
- AAS and UV-Vis: Au and $\text{Au}(\text{CN})_2$ solution analysis of leach test filtrates and evaluation the changes in PR capacity.
- Surface modification: Raman spectroscopy, time of flight secondary ion mass spectrometry (TOF-SIMS) and x-ray photoelectron spectroscopy (XPS) were used to understand how the oxidation process changes the CM surface and contributes to changes in adsorption. These spectroscopy methods can reveal details about the molecular structure of the CM surface and can identify organic and/or inorganic compounds which may have been altered due to the oxidation process (Serrano et al. 1993; Jaramillo et al. 2010; Castilla et al. 1996). The TOF-SIMS technique is an effective and accurate tool for detecting $\text{Au}(\text{CN})_2^-$ ions with high sensitivity (ppm-ppb) on the surface of CMs (Hart et al, 2011).

The thesis attempts to evaluate the effectiveness of oxidation for reducing CM PR capacity using two different liquid oxidants, HNO_3 and H_2O_2 . The effectiveness and mechanisms for a change in PR will be evaluated using the tests and analytical tools outlined above.

1.5 Impact

The study of surface chemical parameters that are potentially associated with the CM in PR ores provides a more complete view of the factors contributing to this phenomena.

The results from the research will be directed towards providing a better understanding of the surface chemical factors linked to the PR mechanism. To the industry this potentially will:

- Aide in interpreting the results from PR tests.
- Define a better testing strategy to evaluate the PR capacity of individual ores.
- Potentially aide in the definition of the best fit mechanism for diminishing the PR capacity of an ore.

Gold losses due to inherent CM are significant, difficult to evaluate and be reduced. Within this context, the ultimate goal of the project is, to provide a better understanding of the preg robbing phenomena towards aiding the metallurgical community in its search for process improvement opportunities.

1.6 Thesis overview

Chapter 1 states the problems caused by carbonaceous gold ores affected low gold recovery, briefly introduces its occurrence, possible treatment methods and the objectives of this research.

Chapter 2 describe different types of gold deposits which result in PR issues and the different treatment methods that have been applied to address them.

Chapter 3 explains the research approach and methodology which is applied in this study.

Chapter 4 discusses the effects of oxidation on PR capacity and contributing factors identified from the experiments.

Chapter 5 summarizes the main findings and conclusions of this research and suggests future work that needs to be conducted.

Chapter 2

2 Background and Literature Review

From ancient times to the present-day, mankind has valued gold due to its occurrence in nature in limited reserves. Gold has an atomic number of 79, atomic weight of 196.967 and density of 19.3 gcm^{-3} . Its average concentration in the Earth's crust or lithosphere is approximately 5 ppb, and in certain sedimentary rocks it may achieve concentrations of up to 2100 ppb or 2.1 parts per million (ppm). Most gold occurs as native metal or alloyed with different amounts of Ag, Cu, Sb, Bi, As, Zn, Pb, Te and Se and more rarely, Pt and Pd, [1,2] which form various gold minerals, several of which are listed in Table 2-1.

Table 2-1 Common gold minerals [1,3]

Mineral	Formula	Au content (%)
Gold	Au	100
Electrum	Au-Ag	55-80
Maldonite	Au_2Bi	65
Krennerite	$\text{Au}(\text{Te}_2)$	39.5
Calaverite	$(\text{Au-Ag})\text{Te}_2$	39.5
Sylvanite	$(\text{Au-Ag})\text{Te}_4$	24.5
Petzite	Ag_3AuTe_2	18-25
Fischesserite	Ag_3AuSe_2	18-25

Several minerals are typically associated with gold; the most important are pyrite, arsenopyrite, pyrrhotite, chalcopyrite, galena and stibnite [4]. A number of sulfide minerals can carry Au in solid solution and a selection is listed in Table 2-2.

Table 2-2 Concentrations of gold in common minerals [3]

Mineral	Gold concentration
Arsenopyrite (FeAsS)	<0.3 ppm-1.7 wt.%
Loellingite (FeAs ₂)	1.5–1,087 ppm
Pyrite (FeS ₂)	<0.25–800 ppm
Tetrahedrite (Cu ₁₂ As ₄ S ₁₃)	<0.25–59 ppm
Pyrrhotite (Fe _{1-x} S)	0.006-1.8 ppm
Marcasite (FeS ₂)	0.05-4.1 ppm
Chalcopyrite (CuFeS ₂)	0.01–20 ppm

2.1 Gold deposits in different rock types, a brief overview

The mineralization form, environment and hydrothermal alteration make each Au deposit unique. A very simplified representation of the geological characteristics from three main groups of Au deposits (igneous, sedimentary and metamorphic rocks) is showed in Figure 2-1.

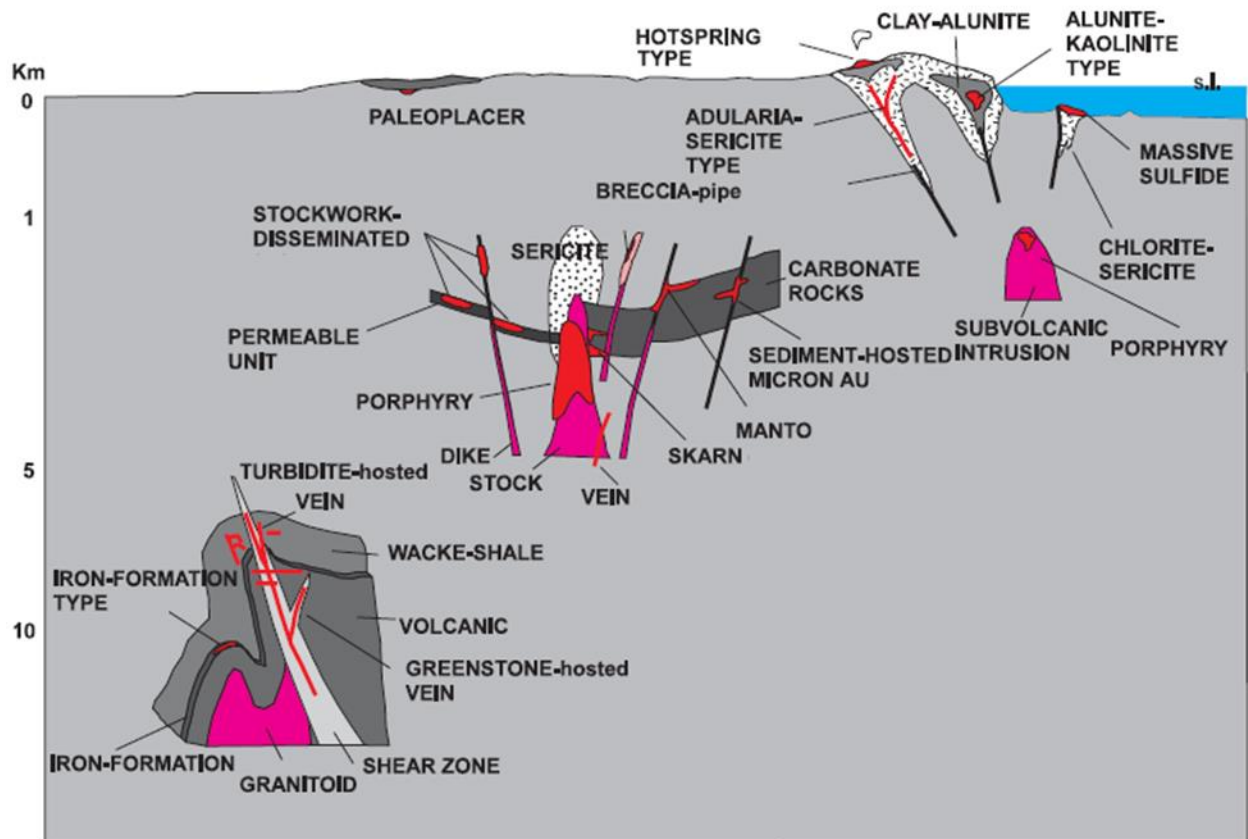


Figure 2-1 Simplified schematic illustration of the most common types of gold deposits [8]

2.1.1 Gold in igneous rocks

The gold average content varies from 0.5 to 5 ppb. There is a slight increasing trend of gold grade from felsic to mafic rocks; in other words, lower gold in late crystallizing felsic magmas (containing quartz and feldspar) compared to higher gold in early crystallization of mafic magmas (containing Fe-Mg-Ti silicate minerals)[1, 5].

2.1.2 Gold in sedimentary rocks

Precambrian clastic sedimentary rocks have formed a large proportion of the world's gold deposits. The best example would be from the Witwatersrand Basin, South Africa, which has an average gold content of 8 ppm. The highest gold contents are found in the coarse to medium grained sedimentary rocks. Shales have a relatively high amount of gold while the carbonates contain the lowest proportion of gold in the group. Gold content in Precambrian

iron formations and ferrous rocks vary significantly. Some sulfide type deposits can exceed 100 ppb while oxide-rich deposits have much lower gold [1,5].

2.1.3 Gold in metamorphic rocks

Redistribution and differences of gold content in lower grade, younger rocks of metamorphic complexes compared to older rocks with higher grade implied that gold is mobilized in response to regional metamorphism. There is a correlation of higher gold with intermediate type rocks and lower gold with acid type granulites as in the case with igneous rocks. Therefore, regional metamorphism resulted in gold loss if granulites are formed [1,5].

2.2 Gold deposits containing carbonaceous material

There is a strong link between the metallurgical treatments of a gold ore and the geology of the deposit. The nature of this study, factors associated with the PR capacity of CM, necessitates the inclusion of inherent CM within the gold ore. Given the greatest proportion of gold ores with inherent CM are sediment hosted, the following is a very brief outline of the geologic factors defining this type of Au deposit. It is included primarily to provide metallurgists with some information regarding the deposit type and the links to origin which, in most instances, will have a significant impact on treatment strategies.

Carlin-type deposits

In 1962, the Carlin gold deposit in Nevada was explored by the Newmont Mining Corporation. Following that, deposits with similar host rocks, mineralogy and trace elements to Carlin have become known as 'Carlin-type deposits'. North America (Nevada) and south eastern China are best-known for having this type of deposit [5, 6].

The deposits are hosted by clastic sedimentary, carbonate rocks and greenstones which usually occur adjacent to skarn or calc-silicate rocks and hornfels. They can be associated with porphyry copper, molybdenum, silver-lead-zinc vein deposits[8]. Mineralization consists of sub-micron grain size gold distributed as a thin coating or film on pyrite, on the surface of amorphous carbon and encapsulated in silica. Carlin type deposits in Nevada are hosted by carbonaceous silty carbonates and carbonate-bearing siltstones and shale. In

the Carlin mine area, it is a fine grained (average 0.05mm) dolomitic limestone with 5-40% of the rock containing 5-40% quartz and lesser amounts of K-feldspar, illite, chlorite, kaolinite, collophane, epidote, hornblende, plagioclase and tourmaline. Typical sulfides include pyrite, arsenian-pyrite, arsenopyrite, along with minor Cu-sulphides, cinnabar, orpiment, realgar, and stibnite. Barite is commonly present throughout the ore. The total organic carbon content varies from 0.4 to 1.6% in dolomitic siltstones, limestone and cherts. A number of studies have been completed to characterize the nature of CM. One study concluded that ores at Carlin contain bituminous matter which is a petroleum residue embedded in the host rocks prior to gold mineralization. Another study implied that the CM was heated and mobilized by hydrothermal solutions during hydrothermal activity and are believed to have had a significant effect on gold precipitation. Research by Well and Mullens (1973) showed that gold in Carlin and Cortez mines is mostly distributed within or is associated with pyrite with little contained in the CM [5,7].

2.3 Metallurgical perspective of gold classification

From a metallurgical point of view, gold ores can be categorized as "free milling", "complex" or "refractory" (Figure -22). Free milling ores are defined as those with >90% Au recovery (particle size > 80% passing 75 micron; $d_{80}=75$ um) with a typical 20-30 hour cyanidation leach. Ores that require significantly higher cyanide or oxygen to facilitate >90% Au recovery are referred to as "complex", while the term "refractory" is used when conventional cyanidation along with enhanced reagent addition still gives poor gold recovery [9] .

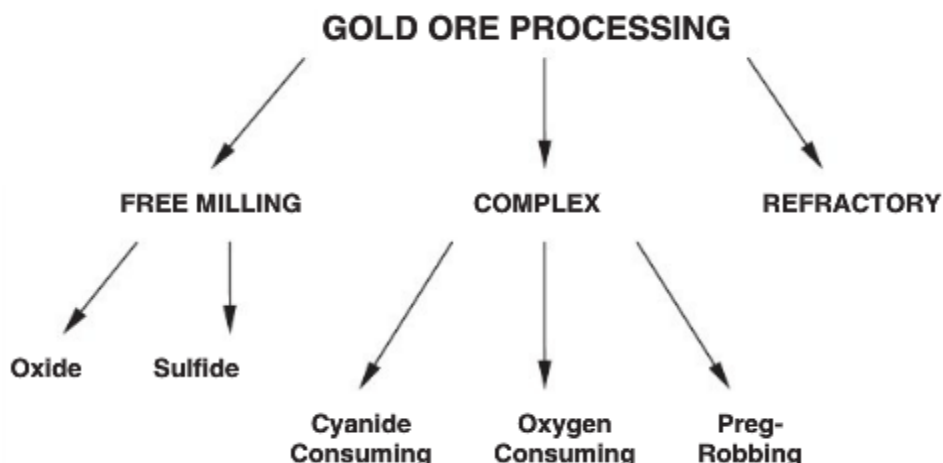


Figure 2-2 metallurgical categorization of gold deposit [9]

Conventional cyanidation may not be efficient for gold recovery for three essential reasons. First, in refractory ores, the gold can be locked up in the mineral matrix (solid solution) so that leach reagents are unable to dissolve it. Second, in complex ores, some reactive minerals can consume the leach reagents in side reactions which result in insufficient cyanide and/or oxygen in the pulp to leach the gold. Third, some components of the ore may adsorb or precipitate the dissolved gold cyanide complex which limits the proportion of recoverable gold in the final stages of the process. Some deposits may have one or more of these characteristics or all of which determining the processing methodology [9].

Therefore, the occurrence of the gold in the ore defines the recovery process. Some of the techniques to upgrade an ore prior to cyanide leaching include; selective sorting, gravity separation and froth flotation; often all of these are used together. Generally, the gravity portion recovers the free “coarse” gold. The residue from the gravity portion is commonly subjected to froth flotation where gold grains are recovered along with sulphide hosted solid solution or sub-microscopic gold. The later can be subjected to roasting but more commonly to pressure oxidation in order to make the gold available for leaching. The product is then fed into a cyanide leach circuit [10]. In this process, a dilute cyanide solution (normally NaCN or KCN) dissolves the gold which can then be recovered by a number of different processes. Cyanidation is the most common method for gold extraction and is used in more than 75% of the gold production operations [11].

Extraction of the solubilized gold from solution can be performed by a number of different techniques: electro winning, Merrill-Crowe process, ion-exchange/solvent extraction and carbon adsorption. Due to its high porosity and effective surface area, activated carbon has an extremely high adsorption capacity which makes it an effective and economic recovery method of gold cyanide. Then the loaded carbon is directed to the stripping tank for desorption [11, 12]. A common gold extraction process is illustrated in Figure 2-3.

2.3.1 Preg-robbing gold ores

Naturally occurring CMs are found in many metasedimentary rock hosted gold deposits such as the Carlin trend (northeastern Nevada, USA), the Zacatecas region north central Mexico and Guizhou province of southeast China. The CMs are components of the rock and occur as stringers and disseminated fragments between mineral grains within the matrix of the host rock. The occurrence, morphology and structure of the CM in the host results from the solid-state metamorphic transformation of the original organic material present in the host sedimentary rock. This transformation is called graphitization and depending on temperature, pressure and type of organic carbon precursor, the structure can vary from fine grained amorphous carbon to crystalline graphite with a maturity similar to coal [14, 15].

Studies have suggested that combination of graphitic and amorphous form the structure of the inherent carbon. There is a range in maturity between this combination which is defined by a growth in the size of the graphite crystallites in the CM. As it matures, the functional group content in the organic material is decreased and the crystalline organization becomes more ordered toward Graphite [16].

The existence of CM in gold ores leads to two main detrimental effects: (1) imprisonment of gold with difficult release from the CM matrix and (2) loss of dissolved gold due to the capability of CM to adsorb it from the pregnant cyanide leach solution during processing stages. This phenomenon, known as preg robbing, is responsible for poor recoveries as the carbonaceous component of the ore competes with activated carbon used during the leaching and adsorption phase of processing [11,17]

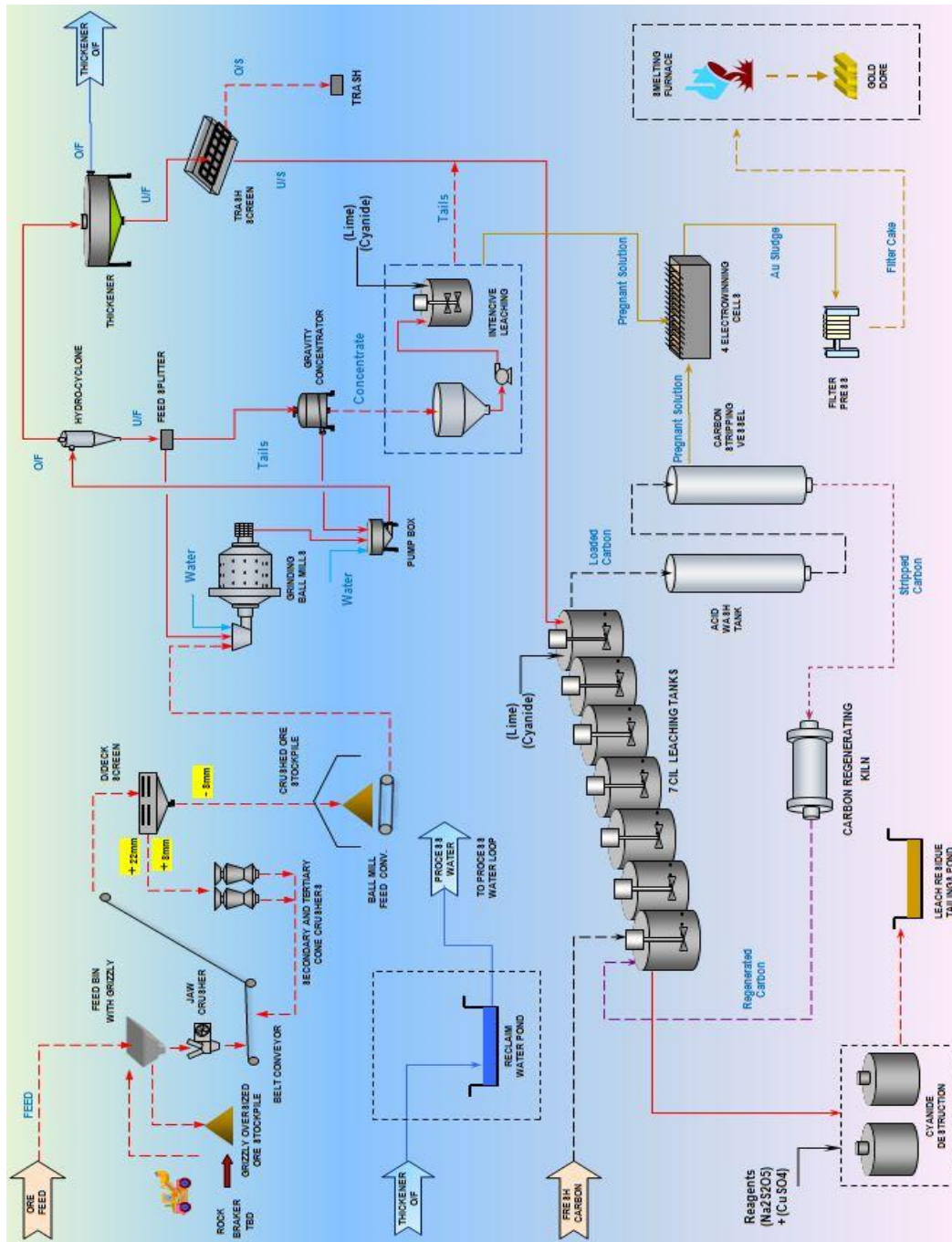


Figure 2-3 Common gold extraction flowsheet [13]

2.3.1.1 Preg-Robbing gold treatments

PR capacity varies widely between carbonaceous ores. Mild PR ores may have the capacity to adsorb <1 g Au/t ore, while extreme PR ores may have the capacity to adsorb >500 g Au/t ore [18].

In order to reduce the loss of Au during processing the CM can be eliminated or passivated before cyanidation or, strongly competitive adsorption strategies are employed during the leach process. Some of the available techniques include;

2.3.1.1.1 Activated carbon-in-leach (CIL) and resin-in-leach (RIL)

The adsorption method employs a competitive effect by the addition of adsorbents with stronger adsorption capacity such as ion exchange resin and activated carbon in the cyanidation process to reduce the PR capacity of CM. Regarding the reduction of the effect of CM, resins are more effective for reducing the effects of PR than activated carbon. In the CIL process, the adsorbent is added to the leach tank and so that competes with the inherent CM in the ore for gold adsorption. The CIL or RIL process have limited effects on the ores with high PR capacities while for mild PR ores, can be an effective method [18,19].

The efficiency of the activated carbon is defined by its gold-adsorption capacity, which can be two times stronger than that CM. In mild PR ores, the CIL process recovers about 70% of the gold compared to 15% gold recovery without using the activated carbon process. The later CIP process is typically a 2 stage operation where the leaching and adsorption process are separated and activated carbon is only added to the adsorption stage [16].

One important issue with the CIL process is the carbon losses due to duration of the process (18 h). The carbon (3.35-1.7mm) used in CIL, is under stress because of contact with silicate particles of ore which causes attrition and yields gold-loaded fine-carbon particles that will carry the attached gold to the tailings, similarly to PR material.

In the Resin-in-leach (RIL) method, ion-exchange resins are added to the cyanidation pulp to recover gold. High selectivity, high loading capacity, higher rate of adsorption relative to activated carbon and the possibility of combination with blinding agents make resins more effective. However, the higher cost of the resins compared with activated carbon is a disadvantage [19, 20].

2.3.1.1.2 Blinding or blanking

The surface of CM can be passivated by the addition of blanking agents such as kerosene, diesel and other hydrocarbon products which act selectively and coat the surface of CM.

The development of an electrostatic repulsion layer on the CM surface results in the reduction of the number of available sites for Au adsorption reducing the PR activity of the CM [19].

According to a study by Newmont Metallurgical Services, these following reagents can act to passivate the carbon to some extent: ammonium persulfate, hydrogen peroxide, boric acid, guanidine nitrate, triethanolamine hydrochloride, potassium permanganate, potassium dichromate, sodium hypochlorite, chromic acid, humic acid, oleic acid. Gold recovery with cyanide reached 50% or higher with the last five. Other studies showed that xanthates, pine oil, fuel oil, diesel, light oil, kerosene, soap, lauric acid salt and Paraffin wax also have a blinding effect [16, 21].

Research by Dimov et al [22] indicated that the adsorption of surfactants on CM/activated carbon can be attributed to various mechanisms. They also identified that the adsorption on CM can be greatly affected by ore mineralogy, temperature and the pH of the solution. Furthermore, adsorption is affected by the inherent characteristics of the CM. Parameters such as surface area, porosity, pore volume, surface charge and surface functional groups all affect the CMs capacity for surfactant adsorption.

Anionic and nonionic surfactants have been reported to be effective blanking agents.

Also, the passivation by cationic surfactants would suggest that the more severe the PR capacity of the ore is, the higher the gold recovery increase is. Treating the Goldstrike CM with cationic surfactants revealed good potential to de-activate CMs [23].

However, some studies on cationic surfactants of alkyl amine and alkyl ammonium salts indicated a negative effect on gold recovery. The disadvantage of using the surfactant is the generation of foam which will potentially influence plant operations [6, 21]. Since the surfactant has the potential to also adsorb onto the activated carbon, it can also negatively impact carbon activity to uptake the gold. Experimental testing indicated that depending on surfactant type and dosage, up to an 80% decrease in activated carbon activity was observed [21].

2.3.1.1.3 Roasting

The roasting technique typically used to oxidize sulphides carrying solid solution Au, has been commonly applied to decompose CM. Roasting temperatures are usually less than

600 °C (the range depends on ore mineralogy), and oxidize both the CM and sulfide minerals in the ore [16].

However, this method has the following drawbacks: 1) high energy consumption and non-environmental friendly products; 2) gold grain encapsulation and closure of pores in sulphides by excessive roasting which can potentially generate a secondary refractory gold product; 3) improvement of the surface reactivity of the CM due to lack of proper control of the roasting conditions; 4) gold will form arsenic-gold alloy and volatilize if temperature exceeds 700 °C [19].

2.3.1.1.4 Chlorination

Gaseous chlorine (Cl_2) and sodium or calcium hypochlorite (NaOCl , $\text{Ca}(\text{OCl})_2$) have been used to passivate CM. The oxygen and hypochlorite that is produced reacts with the CM, forming a thin chloride-carbon complex on the surface of CM by oxidation and by substituting sulfur of the organic carbon leads to de-activation of the CM [16,19].

The research by Sibrell (1991) showed that a pH of 5 and a Cl_2 addition of 450 kg/t led to the formation of carbonyl structures. Deactivation with strong oxidation conditions was similar to autoclave with high oxygen pressure. Other studies reported that gaseous chlorine is more effective compared to using sodium hypochlorite. Formation of a chloro hydrocarbon layer or carbonyl structures which modified the CM surface, contains carboxyl groups ($-\text{COOH}$). These surface functional groups de-active the carbon by blocking adsorption sites. Ionization in alkaline solution leaves a negative charge on the CM surface and as a result, repels the gold-cyanide ions with negative charge which decreases gold adsorption [24,25].

In general, depending on the mineralogy of the ore, the chlorine consumption varied from 30 to 50 kg/t ore. Carbonaceous ores with sulfide content exceeding 0.5–1%, increase the chlorine consumption which is not desirable. Increasing sulfide content and a decrease in carbonaceous oxide ore, which both cause high chlorine consumption, along with a significant increase in chlorine price resulted in Newmont's chlorination plant shutting down in the early 1990s [16].

2.3.1.1.5 Pressure oxidation

This method, suitable for the treatment of highly refractory gold bearing sulfide ores, uses autoclave leaching with air/oxygen, high pressure and temperature to release gold for further cyanidation. These ores usually contain chalcopyrite, pyrite, pyrrhotite and arsenopyrite [16].

Goldstrike utilized an oxidation step involving either autoclaving or roasting the ore prior to CIL circuit. Autoclaving is mostly used to process low PR sulphidic ores (single refractory) as it has little effect on oxidizing the CM [21]. Some researchers [24, 25] revealed that some autoclaved natural carbon develops carbonyl functional groups which led to significant decrease in PR capacity.

Pressure oxidation to reduce the PR capacity of CM in normal plant operating conditions is not effective. To passivate the CM, the feed needs to be smaller than 25 microns and the autoclave operated at temperature of 225 °C or more, conditions not typical to these types of operations. Other problems associated with the autoclave process include the presence of chloride bearing mineral. Mineral decomposition and chlorine concentrations of 15- 20 mg cl/L in the autoclave feed can result in gold solubilization and adsorption of the AuCl onto the CM in the autoclave product which is not recovered in the downstream leach circuit [6].

2.3.1.1.6 Microbial deactivation

Bio-oxidation is a new treatment of carbonaceous refractory gold ores. In this method, fungi or microbes oxidize both the sulphide minerals and CM resulting in passivation of the CM and reduction of its gold adsorption capacity by microbial metabolism. Process simplicity, low energy consumption and being environmentally friendly are considered the advantages of this method. However, the microbial reactions require a significant amount of time compared to other techniques [19, 26]. Use of thermophilic bacteria, like *Sulfolobus* and facultative-thermophilic bacteria has been reported as an effective way to passivate CM in gold ores [16].

2.3.1.1.7 Thiosulfate leaching

In recent years, thiosulfate has been considered as a substitute for cyanide in leaching. Low toxicity and its limited affinity for CM in carbonaceous gold ores are the main advantages of this method over the conventional cyanidation [27].

Numerous laboratory scale studies and heap-leaching pilot-plant tests were completed on a variety of complex ores using ammoniacal thiosulfate leaching. Depending on the ore characteristics, relatively high recoveries were reached. The reason for the high efficiency of the process in the treatment of carbonaceous ores is that activated carbon doesn't attract the gold thiosulfate complex [6, 28, 29, 30].

There has been a successful thiosulfate process in pilot scale in Nevada (Goldstrike complex) subsequent to the autoclaving of high PR ore usually treated in a roaster [31].

In a study by Miller et al., 2005, two samples of the Gold Quarry ore after bio-oxidation pre-treatment, were treated by different leach methods. One sample was treated by chlorination followed by CIL, while the other sample was fed directly to an ammonium thiosulfate leach. Since the chlorination did not completely deactivate the CM, the results indicated the gold in the CIL residue which led to preg-robbed gold after cyanidation whereas, preg-robbed gold was not remarkable in the thiosulfate residue [16].

A study by Schmitz et al., 2001, showed that use of copper-catalysed ammonium thiosulfate leaching on autoclaved carbonaceous ores gold led to an increase in recoveries from 90% to 100%, due to encapsulation of 60% of the gold in sulfides. Hence, thiosulfate released all the preg-robbed gold by the CM during cyanidation [30].

2.3.1.1.8 Flotation

Oil flotation was the first commercial treatment to address the PR ores issue. This method is mostly used to pre float the CM from the sulfide deposit gold ores [10, 32]. Froth stability issues with oil as well as the recovery of gold in the flotation concentrate are the drawbacks of this technique. Gold deportment in the ore has an influence on the selection of flotation. Some gold ores have gold attached to the inherent carbon and thus floating the carbon will cause some gold loss [6]. Flotation of carbonaceous ores had been suggested for treating the Goldstrike ores, however, this method would demand major capital expenditure [21].

2.3.1.1.9 Chemical Oxidation

Chemical oxidation is capable of oxidizing and passivating organic carbon within carbonaceous refractory gold ores. This oxidation method, done in either a dry or wet phase, involves oxidizing gases (O_2 , O_3 , carbon dioxide, etc.) or oxidizing liquids (HNO_3 , H_2O_2 , $(NH_4)_2S_2O_8$, etc.). This method is generally applied prior to cyanidation. Following the oxidation of activated carbon, changes in the pore structure, surface area and volume, functional groups and degradation of carbonaceous gold ores can result in a less adsorbent surface [33, 34].

Oxidation treatment either in the gas phase or in solution produces oxygen surface complexes (Figure 2-4) on activated carbon which can be categorized in three main functional groups: basic, acidic and neutral. The development of acidic functional groups is favoured as it reduces the PR capacity of the CM. Formation of the acidic groups increases the negative surface charge density, makes surface of activated carbon less hydrophobic and decreases the point of zero charge. However, the method can affect the surface area and pore texture of the activated carbon. The surface chemistry of the activated carbon plays an important role in comparison to its surface area and pore texture in the adsorption of inorganic materials from solutions [34, 35]. Thus, to introduce mainly acidic surface groups, oxidation treatment on activated carbons with different oxidizing solutions can be performed as discussed below.

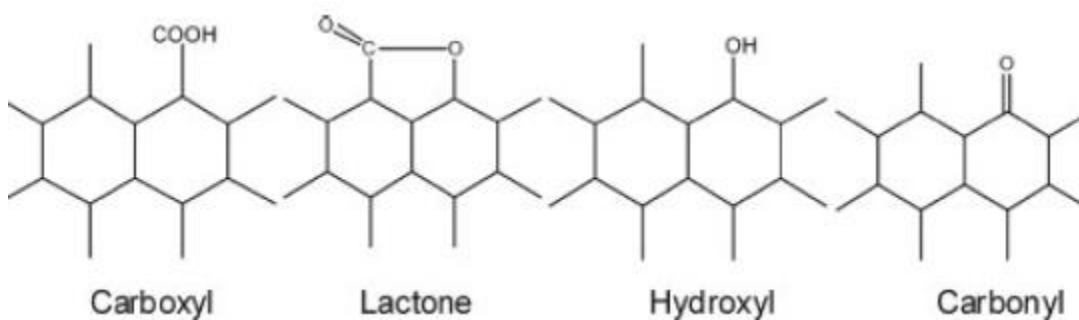


Figure 2-4 Common surface functional group [36]

Ozone (O_3) treatment: Ozone has been used in the gas phase as an oxidant in the treatment of activated carbon and CMs such as amorphous carbon, chars, and glassy

carbon. The activated carbon oxidation with O_3 produces carboxylic groups, lactone groups, and anhydride groups. A study showed that O_3 treatment of the ACs generated greater amount of carboxylic groups than lactone groups, hydroxyl groups and carbonyl groups [33].

Nitric acid (HNO_3) treatment: The Nitro process has been established for sulfide refractory gold ores and may be applied to carbonaceous ores since oxidation with nitric acid can result in deactivation of CM, consequently reducing gold adsorption [37]. Although, the reaction kinetics are fast, the nature of the processes is chemically complex. Moreno-Castilla et al. (1995) studying different degrees of activated carbon oxidation indicated that the nitric acid oxidation decreases the surface area and the microporosity. Carbon with higher degrees of activation have been more changed. The presence of carboxylic groups and carboxylic-carbonate structures, nitro and nitrate groups were formed. An investigation on HNO_3 treated activated carbon by using XPS and FTIR analyses identified oxygen surface groups with C–O bond (lactone, quinone or ketone), as well as the carboxyl and carboxyl-carbonate groups [33,34,35,36,38,39,40,41,42]. Since CM in preg-robbing gold ores acts the same as activated carbon in terms of functionality, it is expected that the decrease in gold adsorption indicated for HNO_3 treated activated carbon will also be applied to inherent CM with the same treatment.

Hydrogen peroxide (H_2O_2) treatment: The surface chemistry of activated carbon is greatly modified by oxidation of the material using H_2O_2 solutions of varying concentration or pH. The modification impact is by the generation of oxygen functional groups such as hydroxyl groups and ether type structures [33,34, 35].

However, H_2O_2 in aqueous solutions decomposes to H_2O and O_2 . The decomposition lessens the power of the H_2O_2 solution as an oxidant. The decomposition of H_2O_2 causes a reduction in its proportion and correspondingly its effectiveness for oxidation of CM [43]. A study of activated carbon oxidation by different oxidants showed that each generated some specific functional groups which modify the CM surface, resulting in a decrease in its capacity for adsorbance. Figure 2-5 shows FT-IR spectra for activated carbon and its oxidation products. The broad peak in the region of 3500 cm^{-1} indicates the presence of hydroxyl groups. The absorption of energy in the range $1650\text{--}1720\text{ cm}^{-1}$ was likely caused by C-O vibrations in oxygen surface groups such as lactones, carboxylic acid, and quinone.

The concentration of the oxygen surface groups absorbing infrared radiation around 1700 cm^{-1} is higher for AC- O_3 and AC- HNO_3 , whereas the variety of oxygen functional groups is greater for AC- O_2 and AC- H_2O_2 [33].

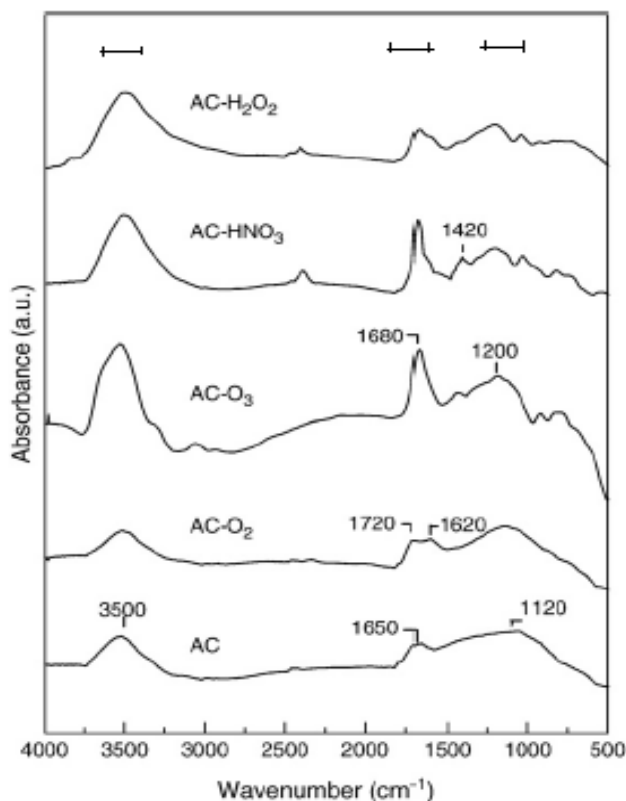


Figure 2-5 FT-IR spectra of AC and oxidized products [33]

Considering the number and variety of oxygen surface groups that were generated in this study the results obtained suggest that H_2O_2 is less effective than HNO_3 as an oxidant. In studies using H_2O_2 , HNO_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the oxidation of activated carbons [34], HNO_3 treatment produced higher total surface oxygen content and surface acidity. H_2O_2 treatment at room temperature, didn't considerably impact the surface chemistry of activated carbon. Higher concentration of H_2O_2 and increasing the temperature, improved the effectiveness of the treatment. 10 M H_2O_2 solution resulted in the formation of higher amounts of oxygenated groups, mainly carboxylic acid. FT-IR analyses indicated that

activated carbon oxidation with H_2O_2 at $100\text{ }^\circ\text{C}$ generated higher concentrations of lactone groups than the HNO_3 -treated product at the same temperature.

Physical characteristic changes from oxidation treatments: In terms of physical characteristics such as surface area and porosity, important factors in adsorption, the total surface area was significantly decreased by HNO_3 and O_2 , total volume had a slight decrease by HNO_3 and O_2 , microporosity decreased for all oxidizing agents but more so by HNO_3 and O_2 and mesoporosity increased for all except O_2 . Different types of pores in activated carbon are illustrated in Figure 2-6. Investigations with HNO_3 oxidation identified a decrease in surface area and in microporosity of the activated carbons, and these effects are more extreme with higher degrees of activation of the activated carbon. In some samples the treatments with H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ also result in the oxygen surface complexes blocking the micropores. FT-IR analysis identified carboxyl groups as well as nitro and nitrate groups after the HNO_3 treatment, whereas after the H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ treatments carboxyl, ketone, ether groups were found. The amount of oxygen generated after these treatments followed this order $\text{HNO}_3 > (\text{NH}_4)_2\text{S}_2\text{O}_8 > \text{H}_2\text{O}_2$. The most significant difference is that the treatment with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ generated stronger acid groups than the HNO_3 treatment. Despite this, the treatment with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ didn't modify the surface area and pore texture of the original activated carbon to a great extent compared to HNO_3 [33,34,38,39,40].

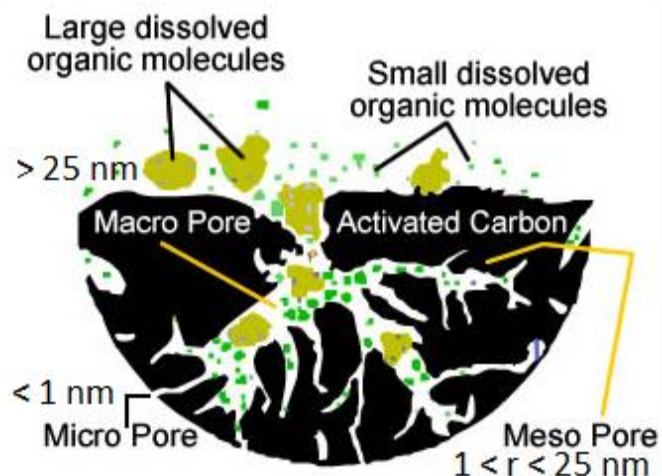


Figure 2-6 schematic picture of different types of porosity in activated carbon structure [44]

2.4 Objective

Thus far, several options have been investigated for the treatment of PR ores, however, only a few have been applied in commercial operations. The option designated will depend on economic considerations as well as the PR capacity of the ore.

According to the studies that have been completed, the oxidation methods seem to be most promising to potentially reduce the PR capacity of CM in gold ores. Chemical oxidation might be considered as an effective pretreatment tool to minimize the PR capacity. As mentioned earlier, HNO_3 and H_2O_2 appear to be strong oxidants of activated carbon. Given the similar nature of the CM to that of activated carbon in many gold ores, chemical oxidation by HNO_3 and H_2O_2 can potentially decrease the PR capacity largely in response to the changes in surface chemistry similar to those identified by studies performed on activated carbon. This research attempts to further the understanding of AC and CM chemical oxidation using HNO_3 and H_2O_2 by linking changes in surface chemistry to a reduction in the $\text{Au}(\text{CN})_2^-$ adsorption capacity of CMs.

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Chapter 3

3 Methodology and research approach

Hydrometallurgical processes are used to extract, purify and recover minerals and metals in aqueous systems. These processes are complex due to the different species present in ore. Gold can be chemically extracted from an ore, the degree of recovery being dependent upon a number of factors including the gold mineralogy and deportment and the mineralogy and composition of the host ore. Gold, oxidized and dissolved in mild oxidizing solutions, reacts with various added lixiviates such as cyanide, thiosulphates, acids and halides to form stable soluble complexes. The oxidation of gold is accompanied by the reduction of dissolved oxygen. The gold complexes are then extracted from solution by adsorption on various adsorbents followed by desorption, cementation and/or electro winning and finally purification by smelting and refining [1].

3.1 Cyanidation and gold dissolution

The principal oxidation states of gold are either aurous (Au^{+1}) or auric (Au^{3+}) which are found in the following complexes: $[\text{Au}(\text{CN})_2]^-$, $[\text{AuCl}_2]^-$, $[\text{AuCl}_4]^-$, $[\text{AuS}_2\text{O}_3]^-$, $[\text{Au}(\text{OH})_4]^-$ and $[\text{AuCl}_3\text{OH}]^-$; the first listed being the most stable [2]. The potential-pH pourbaix diagrams for the Au-H₂O and Au-CN-H₂O are shown in Figure 3-1. Note, the majority of Au extraction operations are performed in the pH range of 9-12 coinciding with the wide stability range of $[\text{Au}(\text{CN})_2]^-$.

Currently, the majority of gold is extracted by alkaline cyanide leaching. According to the E-pH diagram, at pH >11, gold dissolves into cyanide solution to form an Au cyano complex $[\text{Au}(\text{CN})_2]^-$ [1]. Cyanide consumption is dependent on the mineral composition of the ore. For instance, gold deposits associated with quartz and aluminosilicate minerals consume less cyanide as compared to the ones associated with copper or iron minerals. Also, other factors such as pulp density, time, oxygen supply rate, temperature, particle size and cyanide concentration affect the kinetics of Au dissolution.

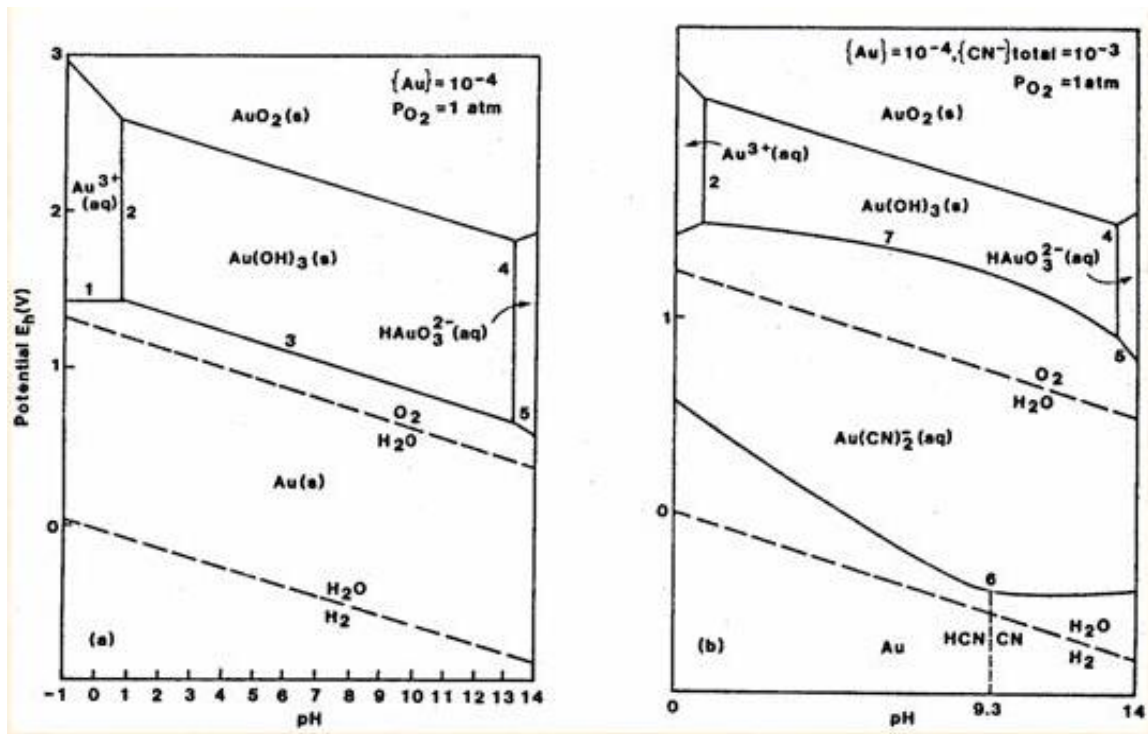
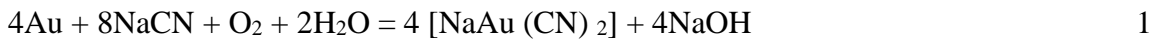


Figure 3-1 Au-H₂O Pourbaix diagram (the left), Au-CN-H₂O Pourbaix diagram (the right) at 25° c [3]

Important reactions for gold dissolution are described below. The overall reaction as proposed by Elsner [1] is given as:

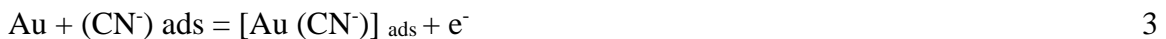


The dissolution of Au is an electro chemical process involving anodic reduction of Au and cathodic reduction of oxygen

(a) adsorption of cyanide on the gold surface :



(b) electrochemical extraction of an electron:



combination of the adsorbed intermediate with another cyanide ion:



The anodic reaction is accompanied by the cathodic reduction of oxygen to H_2O_2



The linkage of these steps results in Elsner's equation (Eq 1) [1]

As previously stated, a major problem in the recovery of the $[\text{Au}(\text{CN})_2]^{-}$ is the presence of inherent CM in the ore being processed. The inherent CM competes with the various adsorbents (typically activated carbon) in the leaching process reducing the Au content of the pregnant solution—a process commonly referred to as preg-robbing. With the aim of preg-robbing (PR) capacity evaluation and reduction, various experiments were performed in order to investigate the influence of the chemical oxidation of carbonaceous matter on surface chemistry as well as surface structure as potential contributing factors to PR capacity reduction.

3.2 Analytical techniques

In order to achieve the objectives of this study, namely the variability in adsorption of $\text{Au}(\text{CN})_2^{-}$ on CM and its relation to modification of the CM in response to various degrees of oxidation, several experiments were performed.

3.2.1 UV-VIS

Ultraviolet-visible spectrophotometry (UV-VIS) is an absorption spectroscopy technique. Ultraviolet and visible radiation interacting with matter cause electronic transitions, i.e., the promotion of electrons from the ground state to a high energy state. In absorption spectroscopy these transitions are measured by absorption [4]. The adsorption falls in the range between 190-380 nm for ultraviolet radiation and between 380-750 nm for the visible radiation.

UV-Vis spectroscopy is routinely used for the quantitative analysis of different analytes, for example transition metal ions and organic compounds. The spectroscopic analysis in this study was carried out on various solutions containing $\text{Au}(\text{CN})_2^{-}$ of known and unknown concentrations.

3.2.1.1 Calibration

In this study, the instrument (Shimadzu model 1201) was calibrated using the adsorption spectra of different concentrations of $K[Au(CN)_2]$ solutions in the ultraviolet range (Figure 3-2). A study by Rawashdeh et al, (2000) showed that the $Au(CN)_2^-$ complex is detectable in a range of 205- 245 nm. Their research also indicated that increasing the concentration of the $Au(CN)_2^-$ complex in solution leads to the enhancing the intensity of the higher absorption bands whereas for the measurement low concentrations, shorter wavelength (higher frequency) are more sensitive [5]. Given this, the wavelengths in the region of 210 and 230 were selected as the wavelengths for the detection of the $Au(CN)_2^-$ complex (Figure 3-3). For the analyses, the wavelength of 230 nm was chosen as the correlation of absorbance with concentration showed the best linear response (Figure 3-3).

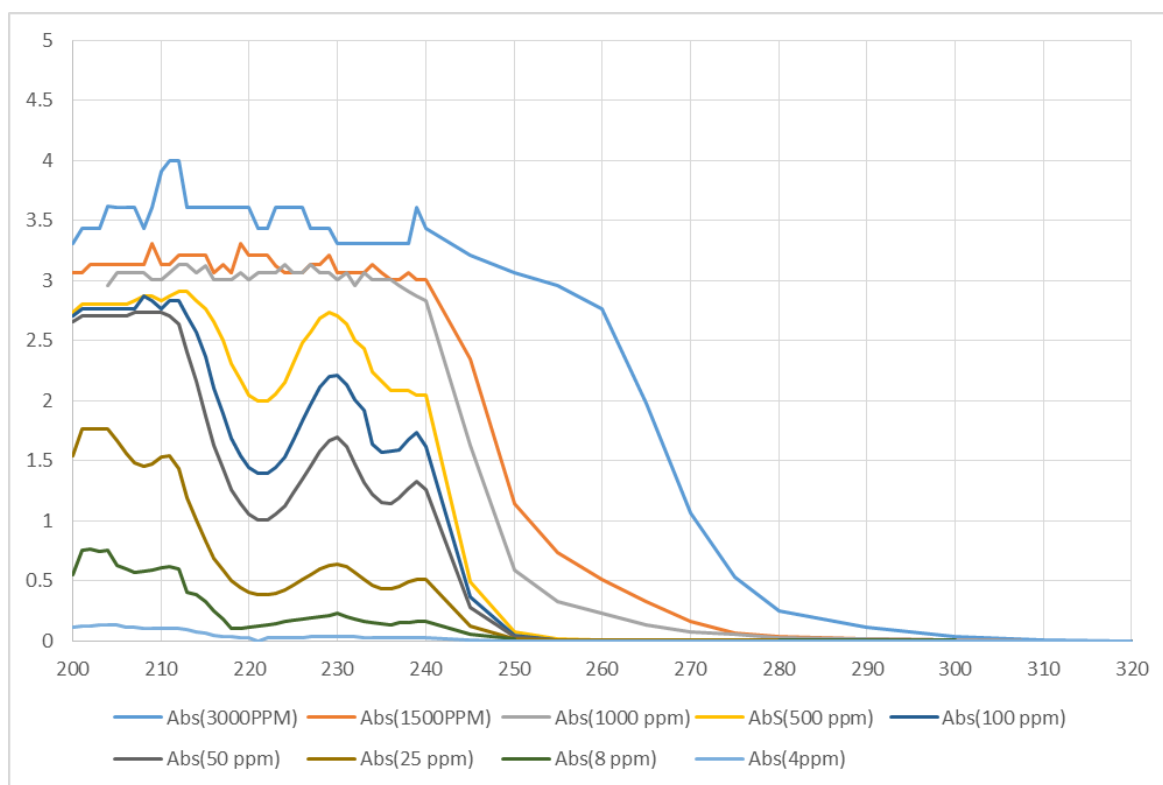


Figure 3-2 Adsorption spectra of $K[Au(CN)_2]$ solutions versus concentration by UV-VIS

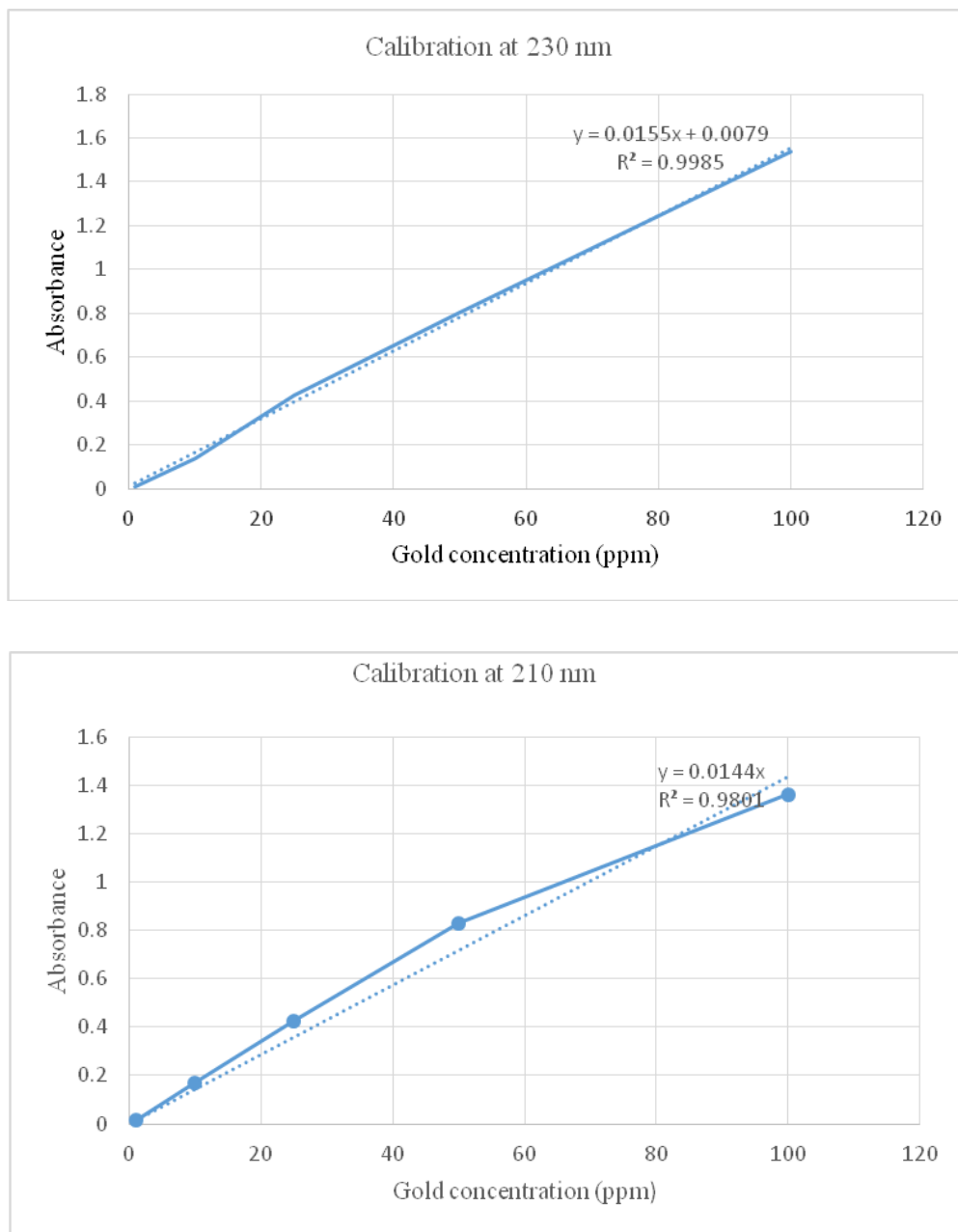


Figure 3-3 UV-Vis wavelength calibration at 210 nm and 230 nm

3.2.2 Raman

Raman spectroscopy is a spectroscopic technique used to observe and measure rotational, vibrational, and other low-frequency vibration modes in a material. It relies on inelastic (Raman) scattering generated from mono-chromatic light (usually a laser) in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular

vibrations (or other excitations in the system), resulting in an energy shift of the laser photon which provides information on the vibrational modes in the material examined. These measured vibrational shifts are used in chemistry to provide structural fingerprints and by comparison to known spectra various species can be identified.

One of the most suitable methods to characterize carbonaceous materials is Laser Raman spectroscopy. Since the Raman signal is sensitive to short range disorder, it can also reveal different forms of amorphous carbons. Also, Raman spectroscopy has a higher spatial resolution and so provides less averaged information [6,7, 8].

The technique uses the shape and width of the detected Raman peaks to provide information on the nature of the carbon bonds. The degree of symmetry (or asymmetry) of characteristic Raman peaks combined with their shift in wavelength provides information on the structure (maturity) of the carbonaceous material. The characteristic Raman peaks for carbon used in this study are from the first order region, 1100-1800 cm^{-1} . The spectra of carbon in this region are characterized by four distinct lines around 1150, 1350 (D peak), 1500 and 1620 (G peak) cm^{-1} . The G and D peaks provide the most valuable information on the microstructure of the carbonaceous material [6,7, 8].

The instrument used in this study is a Renishaw InVia Reflex Raman Spectrometer operated with a 633nm laser and grating of 1800 1/mm. In order to provide a statistical evaluation, for the testing >10 grains of CN material were analyzed.

The structure of carbonaceous material ranges from amorphous carbon to crystalline graphite. The distance between the interlaying spacing decreases as the organic material becomes mature (amorphous C to graphite) and the carbonaceous material becomes more ordered. In this study, Raman spectroscopy examined the degree of disorder (structural deviations from the structure of crystalline graphite of carbonaceous materials) of activated carbon prior to and after oxidation, since it has previously been associated with its ability to adsorb gold from solution [9,10].

3.2.3 SEM-EDX

Scanning electron microscopy (SEM) is a surface analysis technique which produces images of a sample, observed in either high or low vacuum, by scanning the surface with a high energy electron beam. The electrons interacting with atoms in the sample, produce secondary electrons which are collected by a detector providing information about the

sample's surface morphology. Coupled energy dispersive x-ray spectroscopy (EDX) is a semi-quantitative x-ray analytical technique used to identify the elemental composition of the sample [11].

SEM analysis was performed on the samples before and after oxidation. The concentration of oxygen and carbon (before and after oxidation) were measured with a LEO 440 SEM equipped with a Gresham light element detector and a Quartz XOne EDX system operated at 20 keV. Secondary evaluation of carbonaceous material after oxidation was also performed on the Hitachi SU 3500 variable pressure SEM couples with an Oxford X-Max 50mm X-ray detector.

3.2.4 XRD

Two ore samples were examined for mineralogical content by XRD. The ore samples were ground to a fine powder using a mortar and pestle and mounted on a clean XRD slide. The powder mounts were then placed in the Rigaku RTP 300 RC X-ray diffractometer. EVA software (version 16.0) (Bruker-AXS 1996-2010) was utilized for phase identification and peak analysis.

XRD is a versatile, non-destructive technique that reveals detailed information about the mineral phases present and crystallographic structure of natural and manufactured materials by measuring the average distance between layers or rows of atoms called d-spacings. When a monochromatic X-ray beam with wavelength (λ) is projected onto a powdered crystalline material at an angle (θ_1), and certain conditions are met to satisfy Bragg's Law ($n\lambda=2d\sin\theta$) diffracted rays are detected at another angle (θ_2). Since $\theta_1+\theta_2=2\theta$, by varying the angle (θ_1), the Bragg's Law conditions are satisfied by different d-spacings in polycrystalline materials at different diffracted angles (θ_2) maintaining the 2θ . The resulting diffraction patterns are characteristic and can be used to identify the crystalline materials [12].

3.2.5 TOF-SIMS

Time of flight secondary ion mass spectrometry (TOF-SIMS) is an extremely sensitive surface analytical method which provides detailed qualitative elemental and molecular information about the surface.

The method has a high detection sensitivity in the ppm range for most elements and all the elements including H, can generally be detected from the uppermost 1-2 nm of the surface. For analysis, clustered packets of an ion beam (Cs, Ga, Au, Bi Ar) impact the surface of the analyte. The ion energy of the incident beam removes positive and negative secondary ions and molecular species from the very outermost surface layers. The removed species are accelerated in a flight tube reflected and collected on a detector. The mass spectra reflects the time of flight of the various species with different mass to reach the detector, lightest (H^+) first, large molecular species last [13,14].

Samples before and after oxidation along with companion samples before and after Au(CN)- adsorption were analyzed using Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and processed using the methods outlined in [15]. The samples were mounted on indium foil and placed in the TOF-SIMS instrument, pumped down and analysed. Regions or individual grains of CM were analysed.

The analysis provides a comprehensive survey of the surface species on the grains of interest in the various samples. The analytical approach was to conduct comparative surface analyses of CM grains before and after various treatments. Differences will then be evaluated with respect to the testing parameters that may provide insight as to the role of the particular treatment under investigation.

The instrument used in this work is an ION-TOF, TOFSIMS IVTM secondary ion mass spectrometer. An isotopically enriched $^{209}\text{Bi}^{3+}$ (bismuth) primary ion beam is rastered across an area of interest on the sample surface. The data were recorded with full mass spectra in 256x256 pixels using a hybrid focused bunched mode $^{209}\text{Bi}^{3+}$ ion beam, 25 kV Bi^{3+} ion source and 1 μm of beam size. The raster size used was variable depending upon the size of the CM grains and data was with an acquisition time of 125 scans. The bombardment of the surface with the bismuth primary ion beam induces the emission of positively and negatively charged secondary ions from the sample surface. These secondary ions are extracted from the sample surface and mass analyzed using a time-of-flight secondary ion mass spectrometer. A plot of secondary ion intensity versus mass results in a traditional first order mass spectrum, with a resolution of 10,000 above 200 atomic mass units (amu). TOF-SIMS can detect species with concentrations in the ppm range.

3.2.6 XPS

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that can provide information about the elemental composition, its atomic abundance and chemical state [16,17]. For XPS, an X-ray of known energy, in this case Al K α at 1486.7eV, interacts with atoms of the sample and as a result photoelectrons are emitted. The kinetic energy of the emitted electrons is measured and the atomic core level binding energies of the sample are calculated. These binding energies observed in a spectrum can be used to identify most of the elements in the periodic table (not hydrogen and helium) and chemical state information can be determined since binding energies are sensitive to the chemical environment of the atom (Beisinger 2015) .

In this study, XPS analysis was employed as a quantitative technique for the investigation of the oxygen containing surface functionalities to examine the variability in surface chemistry of activated carbon following, and prior to, oxidation. The aim of the study is to link the gold adsorption decrease as a result of oxidation to changes in surface oxygen content and the formation of functional groups as determined by chemical state information. Moreover, the analysis served to verify results obtained from TOF-SIMS technique.

For the analyses the treated samples were mounted on indium foil and transferred to the introduction chamber of the X-Ray Photoelectron Spectrometer (XPS). The analyses were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al K α source (15 mA, 14 kV). The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f_{7/2} line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p_{3/2} line of metallic copper. The binding energy accuracy is ± 0.025 eV. The Kratos charge neutralizer system was used on all specimens. Survey spectra were collected with a pass energy of 160 eV on an analysis area of $\sim 300 - 700 \mu\text{m}$. High-resolution spectra were obtained using either a 20 eV or 40 eV pass energy and an analysis area of $\sim 300 - 700 \mu\text{m}$. Spectra were analysed using CasaXPS software (version 2.3.14) (Fairley, 1999–2005) with relative sensitivity factors (R.S.F.) derived for the Kratos Axis Ultra at Surface Science Western. Peak fitting parameters used to interpret the spectra were derived from X-ray Photoelectron Spectroscopy (XPS) Reference Pages by M. Biesinger (www.xpsfitting.com).

3.3 Ore preg-robbing characterization

3.3.1 Experimental Design and selection of testing criteria

3.3.1.1 Sample preparation for oxidation experiments

To determine the surface characteristics of AC prior to any treatment, AC was hand ground to +75-150 micron, washed with deionized water and dried overnight. The sample was divided into three portions. A portion of the fresh untreated sample was preserved for TOF-SIMS, SEM and Raman analysis with the remained treated by HNO_3 and H_2O_2 as oxidants.

3.3.2 Oxidation treatment

In order to reduce the PR capacity, oxidative treatment as a potential effective process was selected. A literature evaluation of the various oxidation methods [21,22,23,24,25,26,27,28] identified that wet oxidation may be a significant and promising method for reducing the PR capacity of carbonaceous Au ores. Treatment with HNO_3 and H_2O_2 results in changes to surface characteristics which may lead to a reduction in gold adsorption on the surface of carbonaceous matter. The oxidation experimental set up (Table3-1) was designed based on the review of the studies that have been previously conducted.

The oxidation experiment on separate batches of activated carbon was carried out using 10M HNO_3 (supplied by Sigma-Aldrich) and 10 molar H_2O_2 (Sigma-Aldrich). The contact time for each mixture was 2 hours. Subsequent to the oxidation, the residue was repeatedly washed to reduce the pH to neutral and air dried for 12 hours. To investigate the influence of oxidation on the AC in terms of surface chemistry as well as structural alteration, samples of each treated activated carbon were analyzed by TOF-SIMS, SEM and Raman spectroscopy.

Table 3-1 Oxidation experimental conditions

Factors	Oxidation By HNO ₃	Oxidation by H ₂ O ₂
Size fraction	+75-150 micron	+75-150 micron
Solid/Liquid ratio	1 g/ 10 ml	1 g/ 10 ml
Solution concentration	10 Molar	10 Molar
Time	2 hours	2 hours
Rotation (stirring with magnet)	600 rpm	600 rpm
Temperature	80-90 °C	Ambient
Pressure	Ambient	Ambient

3.3.2.1 Adsorption test (Cyanidation)

To assess the gold uptake on AC prior to oxidation and after cyanidation, experiments were conducted on 3 samples: fresh AC, AC treated by HNO₃ and AC treated by H₂O₂ as described in Table 3-2.

Table 3-2 Adsorption experimental conditions

Factors	Fresh AC Sample	Treated sample with H ₂ O ₂	Treated sample with HNO ₃
Solid/Liquid ratio	0.25 g/ 50 ml	0.25 g/ 50 ml	0.25 g/ 50 ml
Gold concentration	1000 ppm	1000 ppm	1000 ppm
Time	2 h (shaking rotator)	2 h (shaking rotator)	2 h (shaking rotator)
Temperature	Ambient	Ambient	Ambient

Following the experiment, the solutions were filtered and analyzed by UV-VIS for Au uptake. However, the solutions weren't clear enough to be accurately analyzed by UV-VIS despite secondary filtration (Figure 3-4). The samples were then submitted for Au analyses by AAS. The filtration residue was dried overnight and analyzed by TOF-SIMS.

**Figure 3-4 Adsorption test solution**

In order to investigate the determinative factors in adsorption, a series of tests was designed. Based on the preliminary tests, 4 factors (listed in Table 3-3) were chosen to be

considered as effective. The series of tests consists of 20 experiments including random 2^4 tests (A full factorial) as well as two center points all of which were designed by Design-Expert ® version 7 software (DX7) (Table 3-3,3-4). To compare the results achieved prior and after oxidation, two tests (number 21 and 22) using fresh AC at two different concentrations of gold were added to the series. After the adsorption tests, solutions were filtered and submitted for gold analysis by AAS (Perkin Elmer AA-800). The residue sample was dried overnight and then was studied by TOFSIMS.

Design-Expert is statistical software that performs design of experiments and provides test matrices for screening up to 50 parameters. Statistical significance of these parameters is provided by analysis of variance (ANOVA). Based on the validated predictive models, a numerical optimizer determines the optimum values for each of the parameters. The software defines the main effects of each parameter and the interactions between them [29]. In the tables below the selected level (Table 3-3) and results (Table 3-4) are presented.

Table 3-3 Selected Factors and levels of adsorption test

Factor	Low	High
Time (min)	30	120
Oxidant Type	H ₂ O ₂	HNO ₃
Oxidant Concentration (molar)	4	10
Gold concentration (ppm)	6.8	0.68

Table 3-4 Adsorption tests experiments

N	Time (min)	Oxidant type	Oxidant concentration (molar)	Primary Au Concentration (ppm)	Au concentration in solution (ppm)
1	30	H ₂ O ₂	4	0.68	0.08
2	120	H ₂ O ₂	4	0.68	0.04
3	30	HNO ₃	4	0.68	0.03
4	120	HNO ₃	4	0.68	0.02
5	30	H ₂ O ₂	4	6.8	0.11
6	120	H ₂ O ₂	4	6.8	0.06
7	30	HNO ₃	4	6.8	0.68
8	120	HNO ₃	4	6.8	0.21
9	30	H ₂ O ₂	10	0.68	0.06
10	120	H ₂ O ₂	10	0.68	0.03
11	30	HNO ₃	10	0.68	0.06
12	120	HNO ₃	10	0.68	0.31
13	30	H ₂ O ₂	10	6.8	0.36
14	120	H ₂ O ₂	10	6.8	0.02
15	30	HNO ₃	10	6.8	2.54
16	120	HNO ₃	10	6.8	1.38

17	75	H ₂ O ₂	7	3.7	0.01
18	75	HNO ₃	7	3.7	0.11
19 R	75	H ₂ O ₂	7	3.7	0.03
20 R	75	HNO ₃	7	3.7	0.15
21	120	-	-	0.68	0.004
22	120	-	-	6.8	0.006

The results from the adsorption tests with fresh activated carbon show that only 0.004 ppm gold remained in the solution from the initial concentration of 0.68 ppm. This indicates that 0.67 ppm gold was adsorbed on the fresh AC surface. In the test with the higher solution concentration, only 0.006 ppm gold didn't adsorb on the fresh AC indicating that 6.79 ppm gold was preg-robbed (Table 3-4).

By comparison with the treatment data (Figures 3-5a, 3-5b), oxidation made a considerable decrease in gold adsorption on the AC resulting in more gold remaining in the solution.

The stages performed in the activated carbon Au adsorption testing program are presented in Figure 3-6.

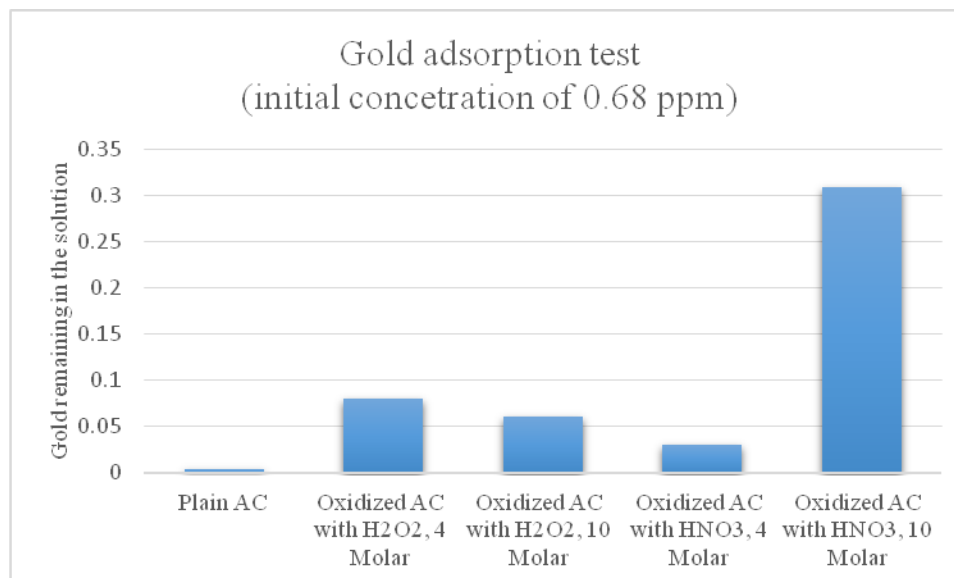


Figure 3-5 (a) Comparison between plain AC, oxidized AC with H₂O₂ and HNO₃ in gold adsorption

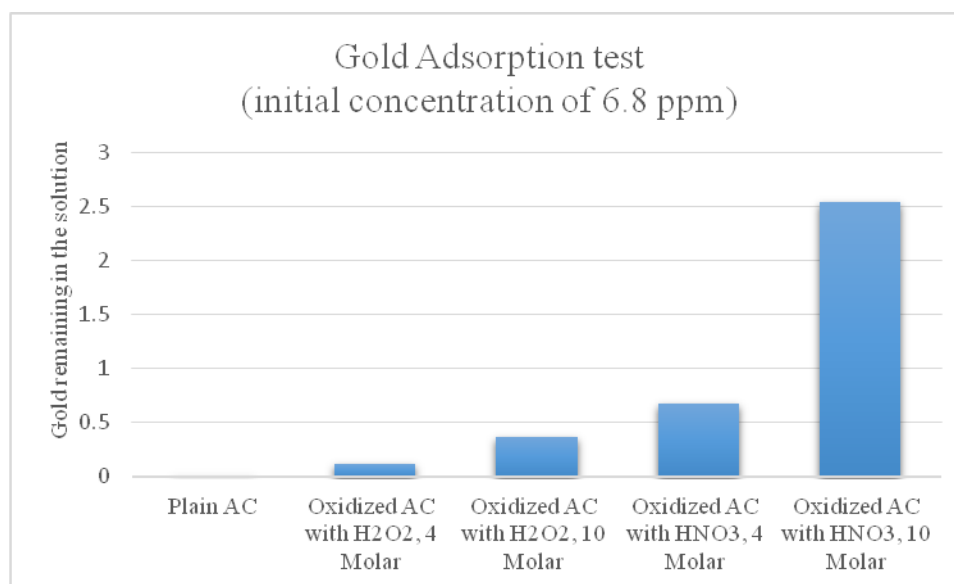


Figure 3-5(b) Comparison between plain AC, oxidized AC with H₂O₂ and HNO₃ in gold adsorption

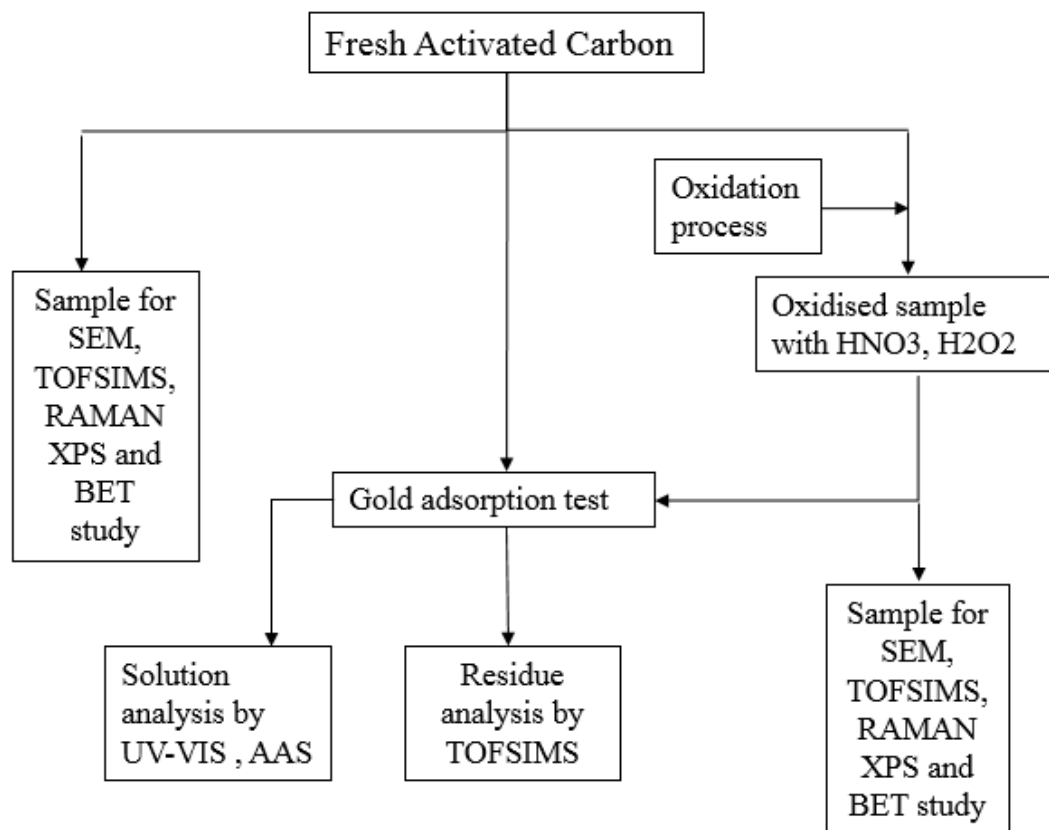


Figure 3-6 Graphical representation of the steps performed in the activated carbon Au adsorption testing program

3.3.2.2 Fitting a model and statistical analysis

From the adsorption tests, the oxidized AC adsorbed less Au from solution. Hence, the gold concentration remaining in solution was identified as a measured response to the tests and was used to develop a model to identify significant test factors. A power transformation mathematical operation was chosen to obtain the best fit for the data. To identify the significant factors on half normal plot, the ones which had not followed the trend were selected (Figure 3-7).

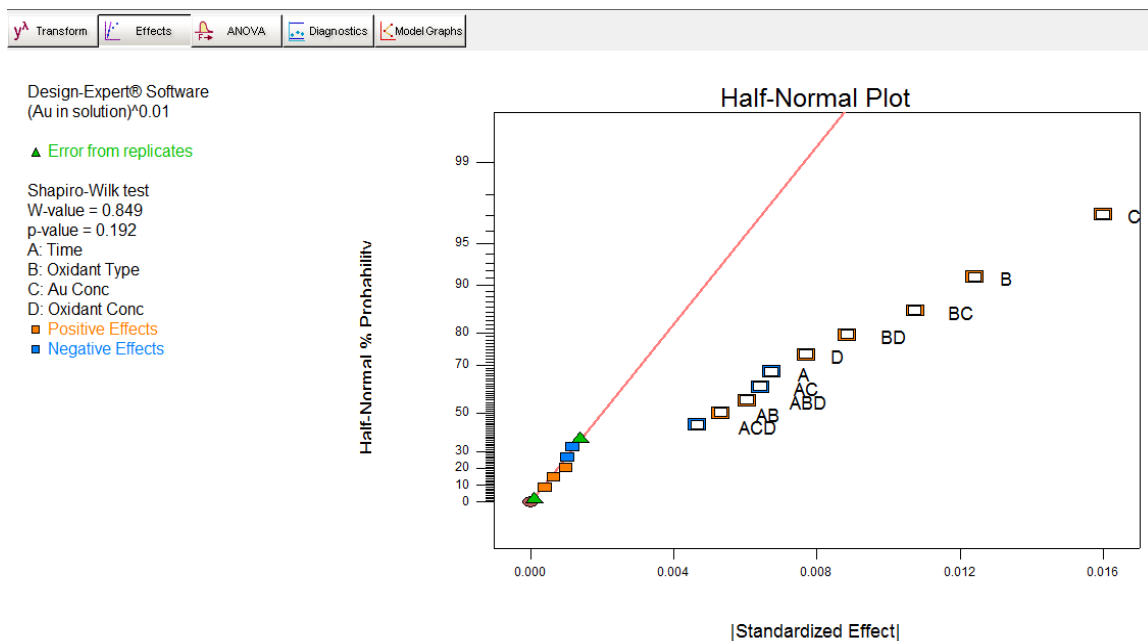


Figure 3-7 Probable significant factors in adsorption test

In accordance with the probable effective factors, the model was validated and statistical analysis was carried out. As is presented in Figure 3-8 as well as Table 3-5, Au concentration, oxidant type, their interaction and oxidant concentration are the most significant effective factors in adsorption test efficiency.

Table 3-5 Analysis of variance of the model

Source	F-Value	P-Value	
Response	1 Au in solution		
ANOVA for selected factorial model			
Model	33.11	< 0.0001	significant
A-Time	16.28	0.0050	
B-Oxidant Type	55.32	0.0001	
C-Au Conc	91.77	< 0.0001	

D-Oxidant Conc	21.32	0.0024	
AB	10.16	0.0153	
AC	14.77	0.0063	
BC	41.40	0.0004	
BD	28.16	0.0011	
ABD	13.15	0.0084	
ACD	7.81	0.0267	
Curvature	13.93	0.0036	significant
Lack of Fit	0.10	0.9807	not significant

The Model F-value of 33.11 implies the model is significant. There is only 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AB, AC, BC, BD, ABD, ACD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The "Curvature F-value" of 13.93 implies there is significant curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space. There is only a 0.36% chance that a "Curvature F-value" this large could occur due to noise. The "Lack of Fit F-value" of 0.10 implies the Lack of Fit is not significant relative to the pure error. There is a 98.07% chance that a "Lack of Fit F-value" this large could occur due to noise.

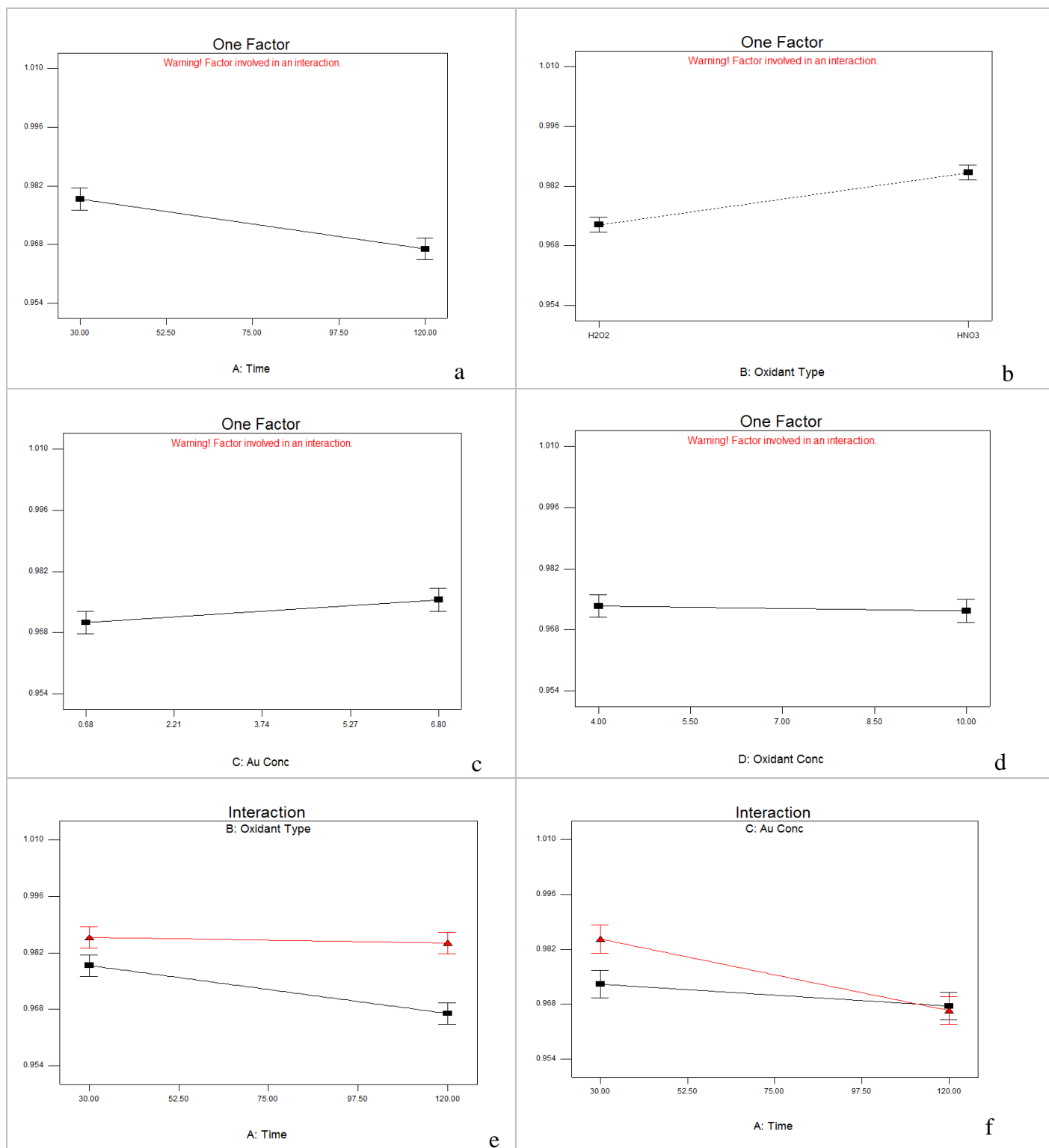
Table 3-6 Evaluation of model accuracy

R-Squared	0.9793
Adj R-Squared	0.9497
Pred R-Squared	0.8989
Adeq Precision	18.605

The "Pred R-Squared" of 0.8989 is in reasonable agreement with the "Adj R-Squared" of 0.9497. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 18.605 indicates an adequate signal. This model can be used to navigate the design space.

3.3.2.2.1 Significant factors effect

Following the ANOVA and evaluation of the model graphs obtained from the software, the effect of each factor on the gold concentration remaining in solution after the adsorption test was studied (Figure 3-8). The horizontal axes are the effective factors and the vertical axes are the gold remaining in solution. Figures (a, b, c, d) indicate the effective factors on the adsorption test. Figures (e, f, g, h) indicate the interaction of two parameters on each other in two levels of each factor. For instance, for Figure (e), the red line shows the HNO₃ and the black line shows H₂O₂ as the oxidants. In Figures (f and g) the red line represents higher concentration of Au and the black line shows the lower one. In Figure (h) the red line shows 10 molar concentration of the oxidant and the black line shows 4 molar concentration. The Y axis represents Au in solution.



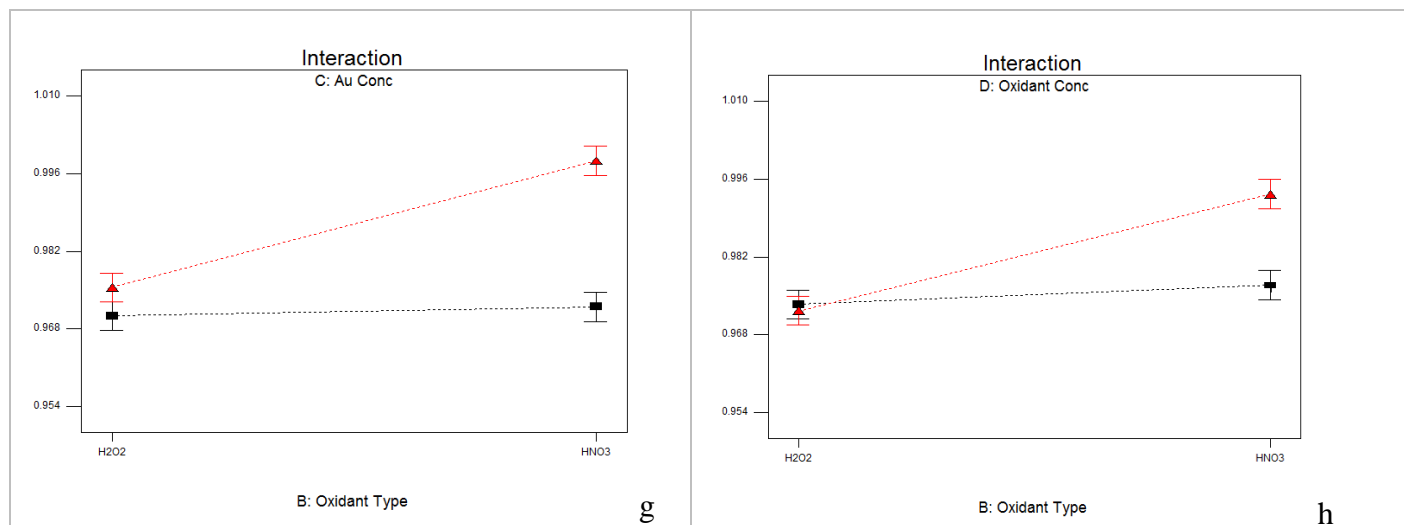


Figure 3-8 Significant factors in process efficiency and their relations

Effective factors on the adsorption:

Time: According to Figures 3-8a, as adsorption time increased, the gold content decreased specifically at higher concentration which indicates that adsorption decreased at longer times. Therefore 30 minutes would be used for the following experiments.

Oxidant type: Comparing H_2O_2 to HNO_3 higher gold content remained in solution with HNO_3 (Figure 3-8b) specifically at the higher concentration of Au. However, at the lower concentration, figure (3-8g), the oxidant type didn't appear to influence the adsorption. Since in this study a higher concentration of gold will be used, HNO_3 was chosen for the final experiments.

Oxidant concentration: In general, the gold concentration in solution didn't change with an increase from 4 molar to 10 molar H_2O_2 to HNO_3 . However, in terms of using HNO_3 as oxidant, higher concentrations play a significant role in lower gold adsorption.

Gold Concentration: According to the figures, gradual increase of gold concentration from 0.68 ppm to 6.8 ppm led to a higher amount of gold in remaining solution regardless of oxidation treatment efficiency.

3.4 Final experiments on Activated Carbon

Given the results presented in the previous sections, a series of experiments was designed which include choosing a high concentration of HNO_3 as the oxidant, performing tests over shorter periods of time with higher concentrations of gold.

3.4.1 Oxidation treatment

In the preliminary testing, the solutions were analysed for Au content by AAS. For the subsequent testing the Au analyses was performed using UV-Vis spectroscopy. In order to perform UV-Vis spectroscopy the solution needed to be clear enough for analysis. The possible contributions to an unclear solution include the high concentration of HNO_3 , high rotation speed (resulting in particle breakage) and high solid/liquid ratio. Since a high concentration of HNO_3 is essential for proper oxidation, the solid/liquid ratio had to be decreased to 1 g/100 ml. Also, the rotation speed was lowered. The final oxidation conditions are given in Table 3-7.

Table 3-7 Final experimental conditions for oxidation

Factors	Oxidation treatment
Size fraction	-75+38 micron
Solid/Liquid ratio	1 g/ 100 ml
Solution concentration	HNO_3 10 Molar
Time	2 hours (stirring with magnet)
Temperature	80-90 °C
Pressure	Ambient

Subsequent to the oxidation the residue was repeatedly washed to reduce the pH to neutral. The material was then resized, sieved and washed, to -75+38 micron to remove any fine particulates generated by the process and air dried for 12 hours.

3.4.2 Adsorption tests

For the adsorption tests, 0.1 g of the sized dried fresh and oxidized activated carbon were added to 15 ml of a 6mM NaOH solution with 100 ppm Au as $\text{Au}(\text{CN})_2^-$. The samples were then placed on an oscillating table. Shaking tray rotation speed was set to avoid either spill or settlement. The final adsorption conditions are given in Table 3-8.

Table 3-8 Final experimental conditions for adsorption

Factors	Adsorption test
Size fraction	-75+38 micron
Solid/Liquid ratio	0.1 g/ 15 ml
Solution concentration	$\text{Au}(\text{CN})_2^-$ 100 ppm
Temperature	Ambient
Time	30 min
Pressure	Ambient
pH	Above 10

After a 30 minute adsorption, the solid and liquid were separated by filtration. The solid was rinsed with 10 ml DI water and the filtrate was brought up to 25mL with DIW for analysis by UV-VIS.

3.5 Tests with a composite preg-robbing carbonaceous gold ore

As the results achieved from oxidation/adsorption tests on activated carbon were promising, the same procedures were conducted on a composite sample of preg-robbing carbonaceous gold ore from the Cortez Mine, Nevada. Treatment of the composite ore sample however introduced a number of other factors potentially linked to the preg-robbing performance outside those related to the inherent CM. A number of factors which would potentially affect the treatment and adsorption process and the overall results from the testing program include ore mineralogy, gold minerals, gold distribution and gold liberation.

3.5.1 Experiments for the composite sample of preg-robbing carbonaceous gold ore

3.5.1.1 Micro flotation

Given the carbon content of the sample was on the order of 3.5% it was decided that the carbon content be upgraded to in order to provide a better opportunity to monitor changes to the preg-robbing capacity of the CM in the ore. Flotation is a physicochemical process for mineral separation based on the difference in surface wettability of different minerals. In general, the easily wettable minerals are defined as hydrophilic and those that are water-repellent are hydrophobic. When air is sparged through the pulp, the hydrophobic particles tend to attach to the air bubbles and float whereas the hydrophilic particles remain in the pulp [30]. Collectors are used to induce mineral surface hydrophobicity and depressants are used to make the mineral surface hydrophilic.

Microflotation was performed on the ore sample in order to concentrate carbonaceous material. The microflotation method is similar to conventional flotation, however in the process, microbubbles (10–40 μm) are generated by passing air, at a very low flow rate, through a frit rather than by a rotating sparger. The microflotation tests were performed using a modified Siwek micro flotation cell [31].

Although the carbonaceous matter is hydrophobic by nature, to enhance recovery diesel oil was used as a collector. Since the sample is dominated by quartz, sodium silicate was used to depress the silicates and methyl isobutyl carbinol (MIBC) was added as a frothing agent. To determine the optimum conditions for high recovery of carbonaceous matter, a series of four flotation tests were completed; the test conditions resulting in the highest carbon recovery and grade is presented in Table 3-9.

Table 3-9 Experimental conditions for micro flotation

Flotation test	Conditions
Sample amount	10 g
Sample size	-38 micron
Collector	Diesel (5 drops (2'))
Frother	MIBC (150 μ l)
Depressant	NaSiO ₃ (500g /ton)
PH	Neutral

Subsequent to the flotation, the concentrate and tail samples were filtered, air dried for 12 hours and weighted. The result is shown in the Table 3-10.

Table 3-10 Flotation results

Sample	Description	Mass (g)	Recovery (%)
Without adding depressant	Concentrate 1	2.13	22.08
	Tail 1	7.53	77.92
Adding depressant	Concentrate 2	1.38	16.13
	Tail 2	7.21	83.87

The concentrate of each test represents the upgraded carbon rich portion of the sample. To determine the carbon content of the samples, each concentrate and tail along with the feed (as received untreated sample) were ashed in a muffle furnace at 400°C for 24 hours. Prior to the ashing, the sample was oven dried at 100°C to determine moisture content. Moisture and carbon contents are determined by weight loss in the various stages. The results from the tests indicate that the feed ore contains ~3.8 % carbon while the concentrate sample showed ~7.8% C. The microflotation resulted in upgrading the sample carbon content by 100% (Table 3-11).

Table 3-11 Carbon content in the sample

Sample	Description	Moisture (%)	Carbon (%)
Without adding depressant	Concentrate 1	0.54	7.7
	Tail 1	0.19	2.28
Adding depressant	Concentrate 2	0.19	7.88
	Tail 2	0.04	2.96
	Feed ore	0.44	3.78

3.5.1.2 Oxidation treatment

The oxidation treatment on the flotation concentrate of the sample was performed in the same manner as that for the activated carbon. Details of the treatments are given in Table 3-12. The experiment used the same conditions as AC oxidation with the exception of a smaller particle size as the feed size for the microflotation needs to be significantly finer (-38 um).

Table 3-12 Experimental conditions for the oxidation of the preg-robbing gold ore

Factors	Oxidation treatment
Size fraction	-38 micron
Solid/Liquid ratio	1 g/ 100 ml
Solution concentration	HNO ₃ 10 Molar
Time	2 hours (stirring with magnet)
Temperature	80-90 °C
Pressure	Ambient

3.5.1.3 Adsorption tests

For a comparative study and an evaluation of the oxidation efficiency, a series of adsorption tests were performed. The first series involved contacting the sample with a cyanide solution, void of gold and the second series with a cyanide solution containing 50 ppm Au. The first series of tests were performed to evaluate the effect of leachable Au in the test samples. The second series were performed to determine the preg-robbing capacity of the fresh (untreated) sample and the oxidized samples.

The flotation pH was set between (4-6) to dissolve the carbonates in the pulp as their presence are not desirable in the oxidation process.

Subsequent to the adsorption, the samples were rinsed by 15ml DI water, filtered and the remaining solution was analyzed by UV-VIS. The residues were studied by TOFSIMS, XPS and SEM. The experimental stages which performed are shown in Figure 3-9.

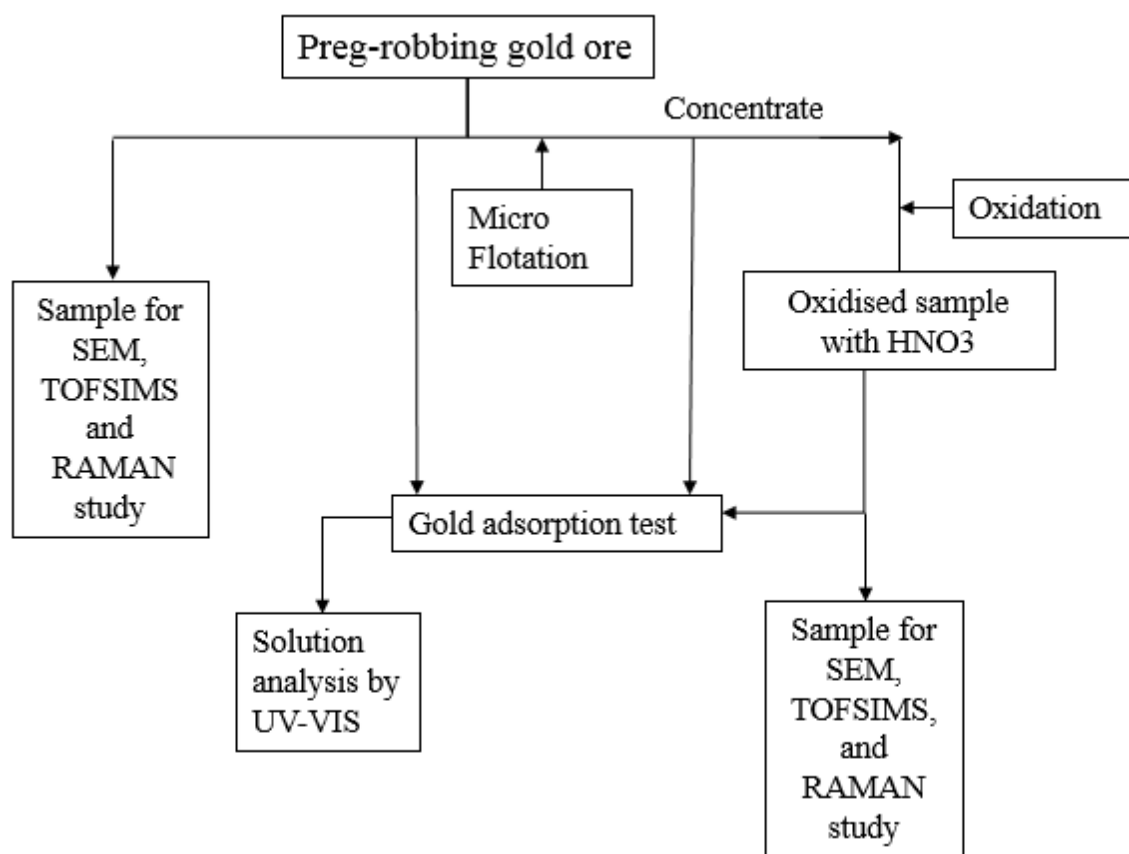


Figure 3-9 Graphical representation of the steps performed in the ore sample Au adsorption testing program

3.6 References

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Chapter 4

4 Analytical results and evaluation

The objective of this study is to determine the contributing factors of carbonaceous material in the preg-robbing capacity of carbonaceous gold ores in order to minimize loss related to gold adsorption.

In order to better understand the role of CM in preg-robbing, a series of experiments with activated carbon were performed to determine the preg-robbing capacity of CM before and after oxidation. The results from the tests were evaluated by a variety of analytical techniques. Adsorption capacity was determined by UV-Visible spectroscopy. Information regarding the structural nature of the CM was performed by SEM/EDX and Raman spectroscopy, surface analyses was performed by TOFSIMS and XPS analysis. The final results of this investigation may provide the industry with an improved tool to better estimate the PR capacity of an ore which, in turn, would help define strategies for its further reduction.

4.1 Measurement of Au adsorption by UV-VIS spectroscopy

4.1.1 Results

The adsorption tests were carried on -75+38 sized activated carbon before and after oxidation with an estimated 100 ppm concentration of gold (as AuCN) in a stock solution. In order to establish an optimal contact time for adsorption, tests were performed at several intervals over a 3 hour period (Figure 4-1). The testing indicated that most of the adsorption occurred within a 30-minute contact time which is in agreement with the results from the test development experiments discussed in chapter 3.

The results of the adsorption experiments to determine the preg-robbing capacity of the plain activated carbon and oxidized activated carbon showed that, compared to the fresh activated carbon, the gold attachment to oxidized activated carbon decreased significantly (Figure 4-2). The fresh activated carbon was able to adsorb ~80 ppm Au, on the order of 85% of that in solution. After oxidation however the activated carbon was only capable of adsorbing 20 ppm representing an approximate 75% reduction in the relative proportion of that adsorbed. Clearly the oxidation process had a significant effect on the Au adsorption

capacity of the CM. The following series of analyses were performed in order to evaluate factors responsible for this reduction in adsorption capacity.

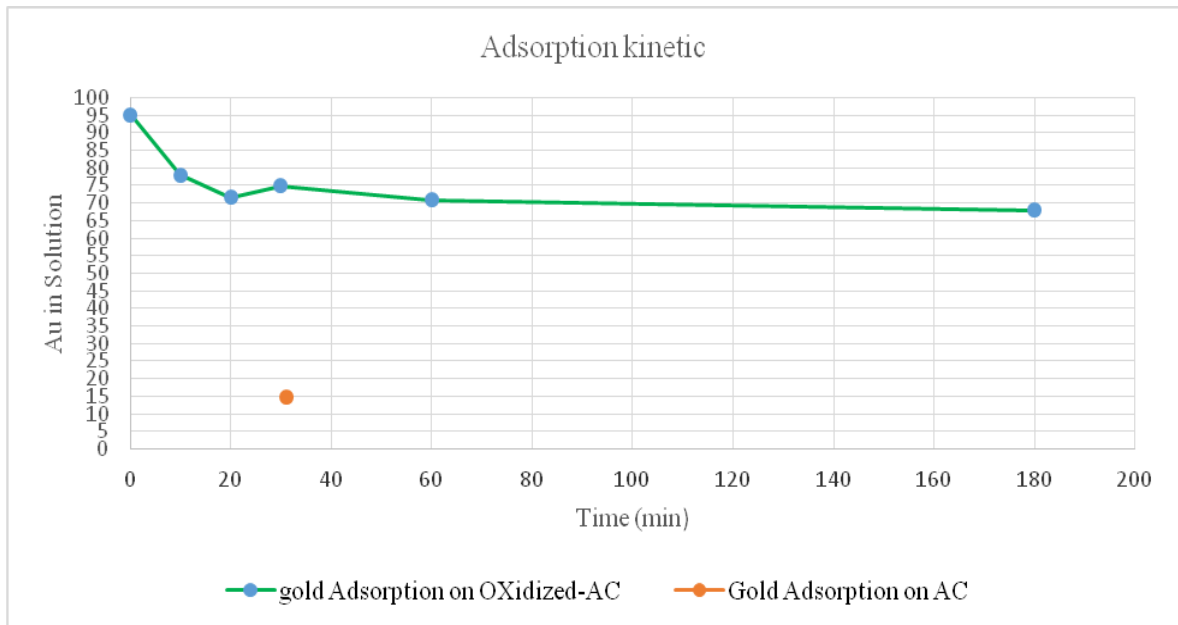


Figure 4-1 Au (CN)₂⁻ adsorption over a 3-hour period

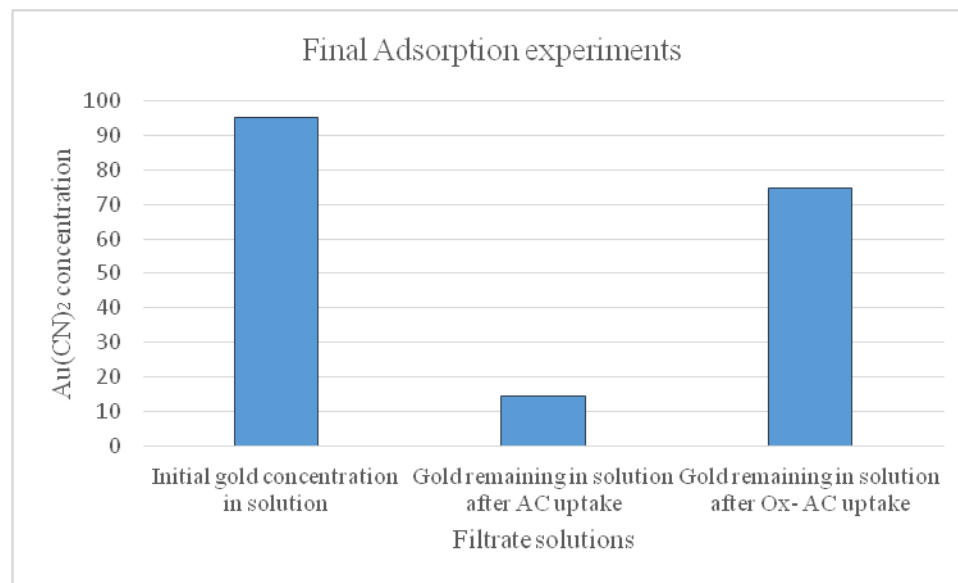


Figure 4-2 Au(CN)₂⁻ adsorption for the plain AC and oxidized AC

4.2 Raman

Subsequent to the carbon oxidation, the AC (activated carbon) and OAC (oxidized activated carbon) samples were analysed by Laser Raman spectroscopy in order to determine if the process of oxidation affected the organization of the carbonaceous material. Raman analysis has been used as a diagnostic tool capable of predicting and differentiating the preg-robbing properties of C-matter [1]. Changes in the degree of C disorder has been shown to have some influence on the ability of the carbonaceous material to adsorb Au(CN) [2].

4.2.1 Results

The samples generated from primary oxidation were analyzed. The Raman spectra of the samples (plain activated carbon, plain activated carbon + gold, oxidized activated carbon + gold) are plotted in Figure 4-3. The fitting parameters for the deconvolution in the first order region are based on the spectral variability in the degree of amorphous character. Given this, the fitting model then is based on the deconvolution of the spectra for activated carbon. In all cases the fit parameters defined here were used for all other analyses in the data set. The spectral fit parameters are characterized by four distinct lines around, 1350 cm^{-1} , (D band) and 1580 cm^{-1} (G band) along with broad Gaussian bands at 1620 cm^{-1} and 1150 cm^{-1} , the latter are assigned to amorphous carbon. The fit constraints were defined by analyzing and fitting the spectra from +10 activated C grains. For accuracy in the determination of the spectroscopic parameters, curve fitting was performed for all spectra. The best curve fit parameters were identified as mixed Gaussian-Lorentzian. The results of these line fit parameters are given in Figure 4-3.

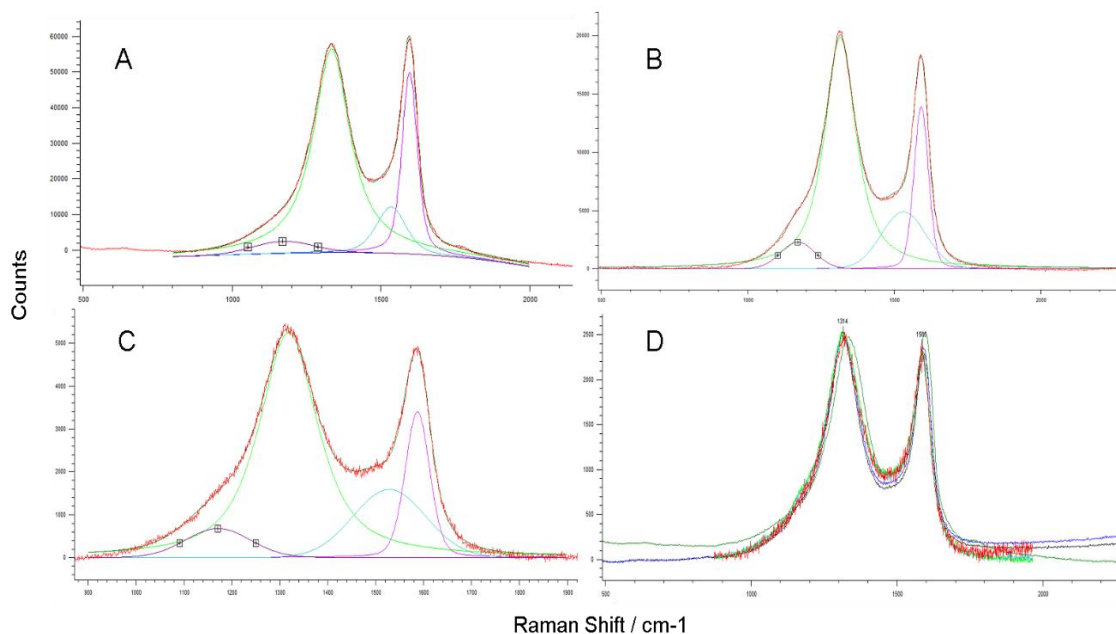


Figure 4-3 Raman spectra showing the characteristic G (1585) and D (1315) bands for the samples; fresh activated carbon (A), fresh activated carbon + gold (B), oxidized activated carbon + gold (C), overlay of Raman spectra of from [(A),(B),(C)] D

It is clear from the overlay of the Raman spectra that there appears to be no great change in the peak position, shape or their relative intensities between the AC and the OAC. In order to comparatively evaluate the degree of disorder of the C-matter in each sample, the Raman ratio (Intensity of D band / the Intensity of G band), which reflects the measured degree of disorder in the carbon structure and its potential for preg-robbing, is calculated and displayed on a scatter plot. The ratio is calculated from the deconvoluted Raman spectra. Literature and research evaluations have shown that the preg-robbing capacity of the carbonaceous matter is positively correlated with increasing degree of disorder [3].

The Raman ratio in Figure 4-4 shows that the fresh activated carbon (ACT C) and oxidized activated carbon (OAC) appear in the same area of the plot. The data indicate that the organization of activated carbon hasn't been significantly affected by the oxidation process. Therefore the reduction in the ability of the oxidized activated carbon to adsorb $\text{Au}(\text{CN})_2^-$ does not appear to be linked to changes in the degree of carbon maturity as a result of the oxidation process.

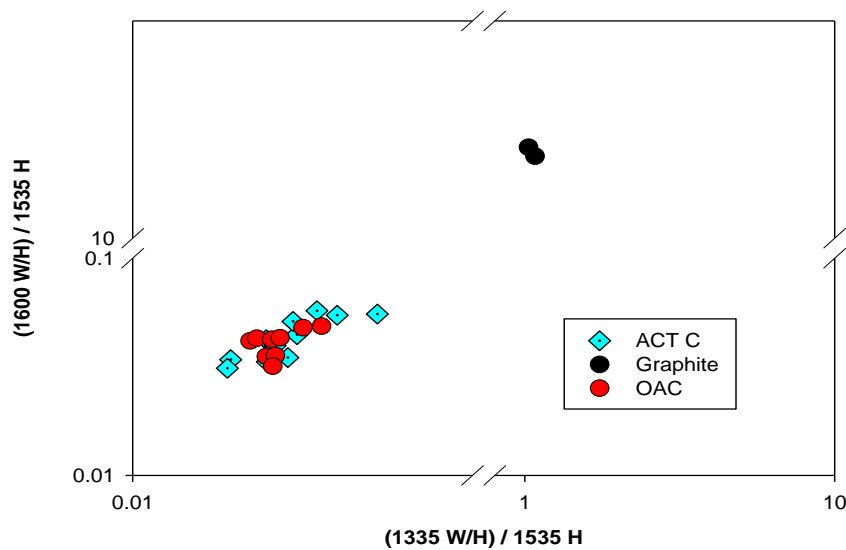
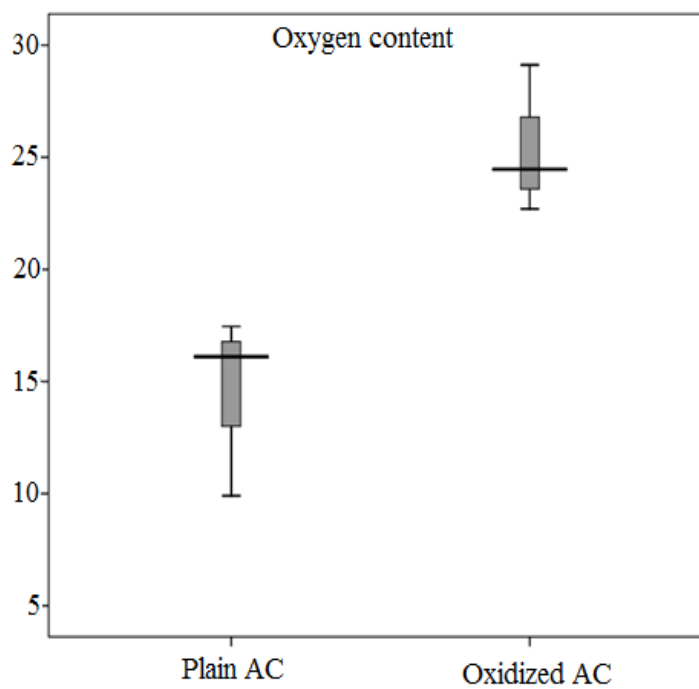
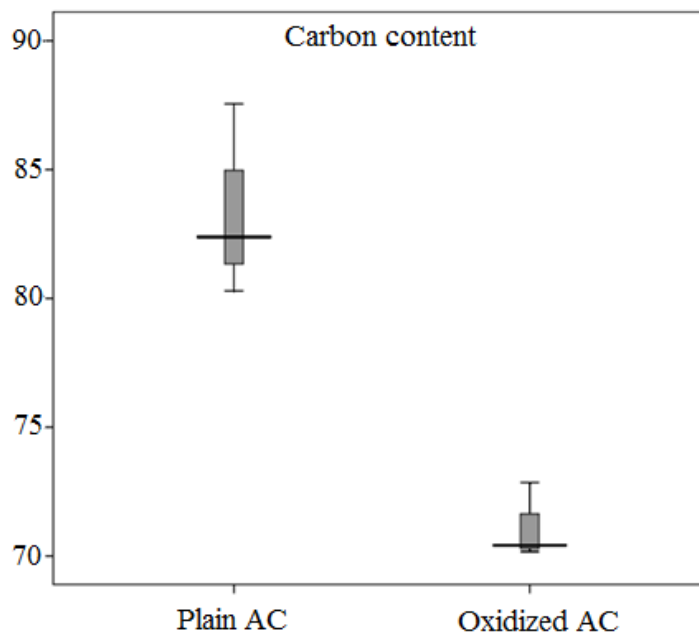


Figure 4-4 Raman ratio for activated carbon (ACT C), oxidized activated carbon (OAC) and graphite

4.3 Surface structure and chemical analysis by SEM/EDX

4.3.1 Composition analysis

The SEM analysis was performed on the samples AC and OAC prior to adsorption testing. The carbon and oxygen data from the analyses of AC and OAC grains are given in Figure 4-5. The data indicate that there is a reduction in the relative concentration of carbon combined with an increase in oxygen on the OAC grains (Figure 4-5). The oxidation process resulted in a significant decrease in the C/O ratio.



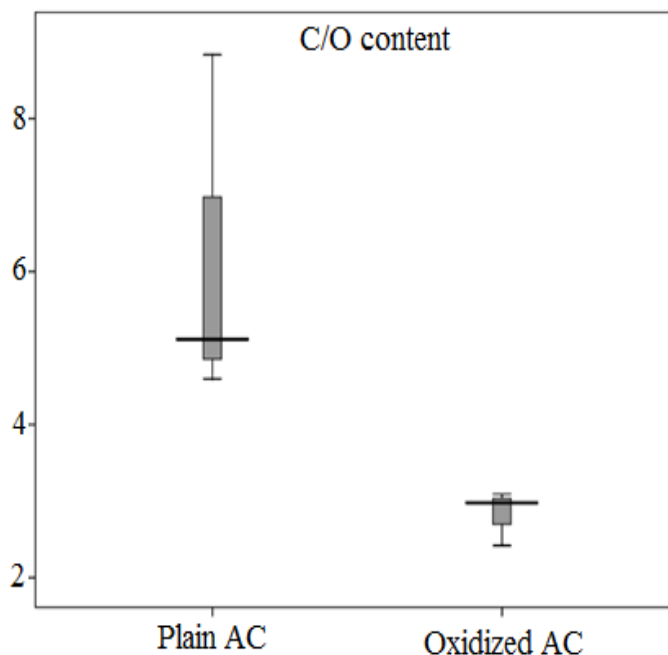


Figure 4-5 EDX surface analyses data. Box plots illustrating the concentration of oxygen (%), carbon(%) and C/O on the surface of plain AC and oxidized AC.

4.3.2 Surface Morphology

Previous research using HNO_3 to oxidize AC has shown that the total surface area and total pore volume decreased after the oxidation. Jaramillo et al, (2010) showed that [4] the oxidation of activated carbon resulted in a decrease in total surface area and microporosity while mesoporosity increased. They linked the oxidation temperature and HNO_3 concentration to the reduction of microporosity and long oxidation times to significant changes in surface area. Conversely, in other studies a greater surface area and porosity in activated carbon after the oxidative treatment was been reported. Acid particle dissolution could result in opening of some blocked pores which would result in a higher surface area [5,6,7].

The decrease in the pore volume is believed to be due to the generation of oxygen functional groups on the walls or at the entrances of micro pores. The generation of oxygen functional groups, and the decrease in the C/O ratio, was cited as a link to pore wall thinning and collapse resulting in an overall decrease in pore volume [6,7,8,9,10,11].

In this study, SEM analysis was performed on 685 areas of fresh and oxidized activated carbon. An example of SEM images showing areas marked as pores and their analyses are given Figure 4-6. The data from the analyses are presented in Figure 4-7. The data shows a slight increase in the pore size indicating that the oxidation generated greater proportion of larger macropores. Literature however has shown that, as a rule, the oxidation treatment develops mesoporosity whereas macroporosity remains unaffected. Thus, in order to link the $\text{Au}(\text{CN})_2$ adsorption capacity of carbonaceous matter to porosity modification with the higher level of certainty, the overall surface area of the samples was determined by BET analyses (section 4-4).

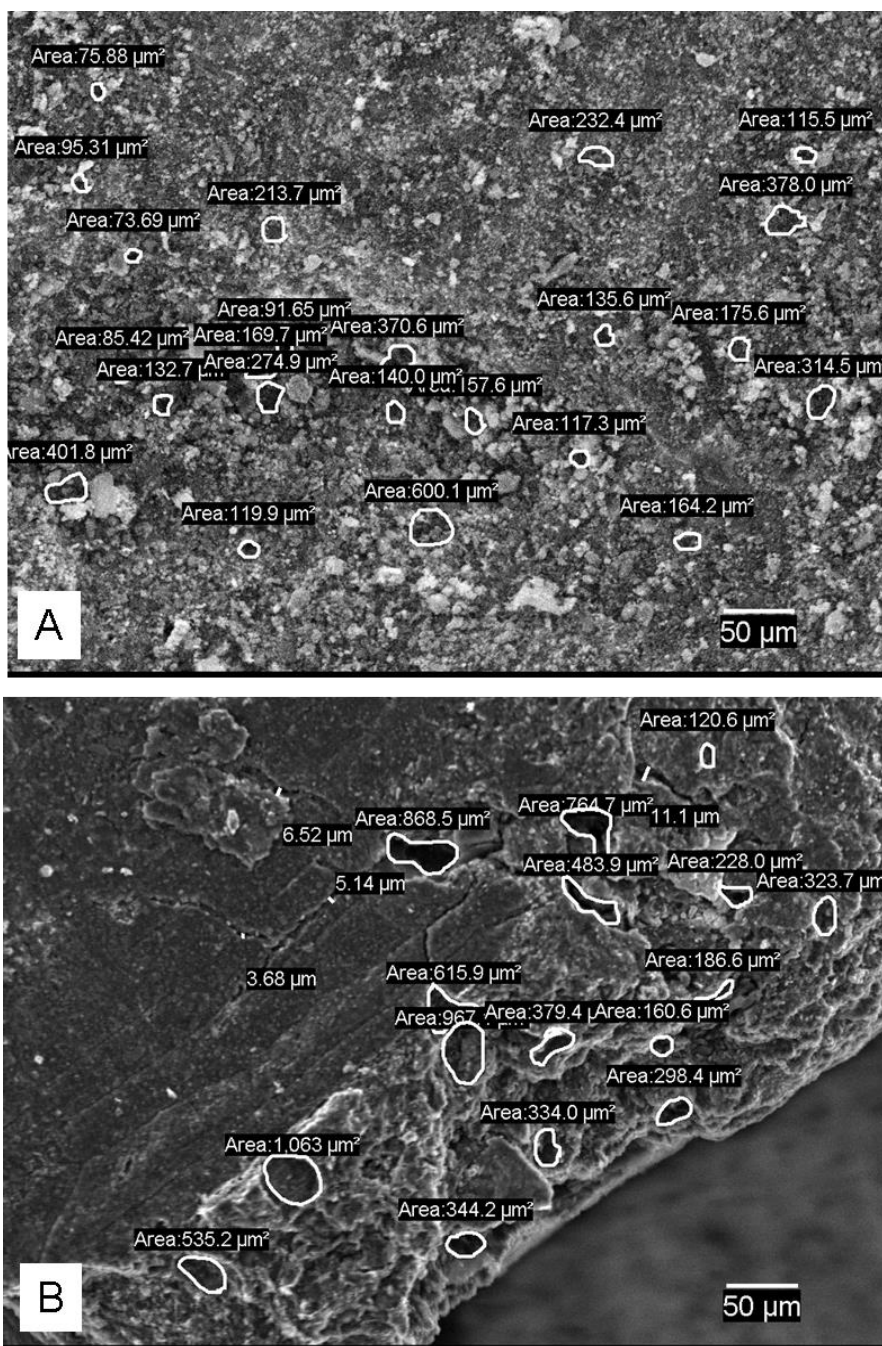


Figure 4-6 SEM images with pore size measurements of plain activated carbon (A), oxidized activated carbon (B)

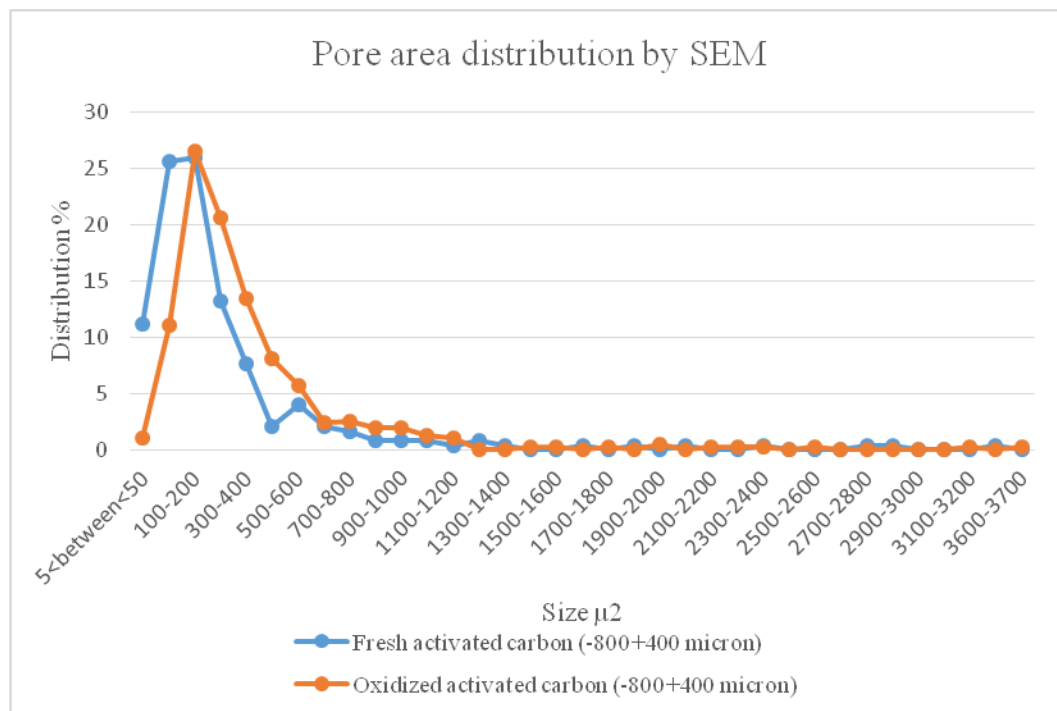


Figure 4-7 Pore size distribution of plain activated carbon and oxidized activated carbon

4.4 BET surface area analyses

Brunauer–Emmett–Teller (BET) is a technique for measurement of the specific surface area by the adsorption of gas molecules onto a solid surface. The gasses most commonly used are argon and nitrogen [12]. As discussed in the section earlier, oxidation with nitric acid has a strong influence on total surface area. In this study, the BET surface area analysis shows that the oxidation treatment results in a significant increase in total surface area, Table 4-1. This would suggest that oxidation provides a greater surface area for $\text{Au}(\text{CN})_2$ adsorption, however results from the adsorption tests indicate gold uptake on the oxidized sample decreased. Given this, it appears that surface chemistry may play a key role in reduction of $\text{Au}(\text{CN})_2$ adsorption on activated carbon after the oxidation treatment.

Table 4-1 BET analysis on AC and OAC

	Size	Surface Area (BET) (m ² /g)
Plain AC	-75 + 38 micron	423.6
Oxidized AC	-75 + 38 micron	699.3

4.5 Surface chemical analysis of activated carbon subjected to oxidation by TOF-SIMS

4.5.1 Primarily TOF-SIMS study

The instrument used in this study is ION-TOF, TOF SIMS IV. All spectra were processed by IONTOF software. Peaks in the calibrated spectra were assigned to specific isotopes based on their atomic mass and similarly peaks showing molecular species of the Au(CN)₂⁻ were assigned mass positions. To compare intensities between different areas, corrected intensities were normalized to the total number of counts for the areas studied. The analysis provides a broad survey of the surface species on the activated carbon.

To assess the impact of oxidation on the surface chemistry of activated carbon, TOF-SIMS analysis was performed on 3 samples: activated carbon, activated carbon after Au(CN)₂ adsorption and oxidized activated carbon after Au(CN)₂ adsorption.

Table 4-2 Primary samples studied by TOF-SIMS

Sample	Description	Size (micron)	Initial gold concentration
1	Activated carbon (AC)	-841 +400	0
2	AC + adsorbed Au	-841 +400	250
3	Oxidized AC + adsorbed Au	-841 +400	250

Previous studies revealed that oxygen surface complexes are formed on activated carbons when they are treated with oxidizing agents [8,9,13,14]. The modification would occur through the changes in surface chemistry of CM by formation of oxygen functional groups potentially resulting in less gold uptake on the surface of activated carbon. TOF-SIMS images for oxygen (O), carbon (C) and Au(CN)₂ species potentially linked to variability in Au adsorption are shown in Figure 4-8.

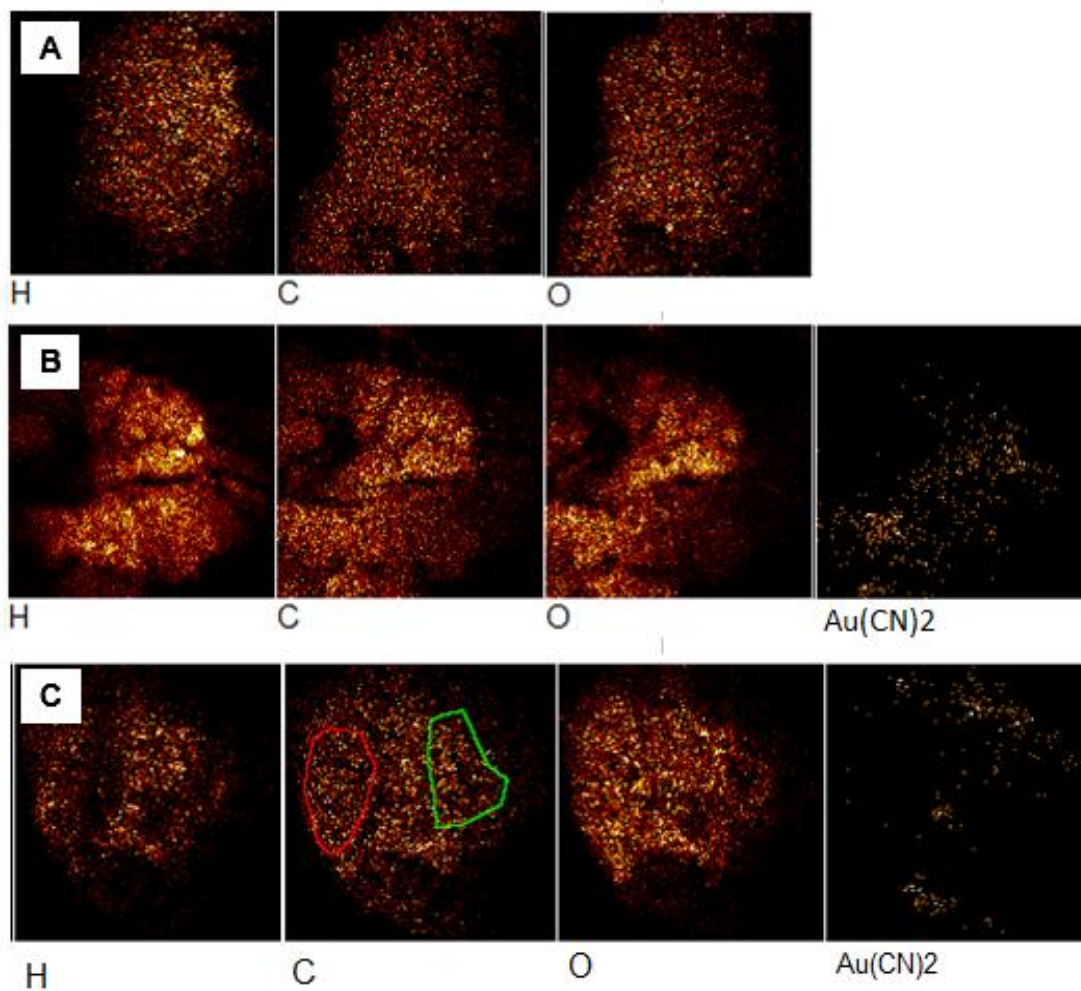
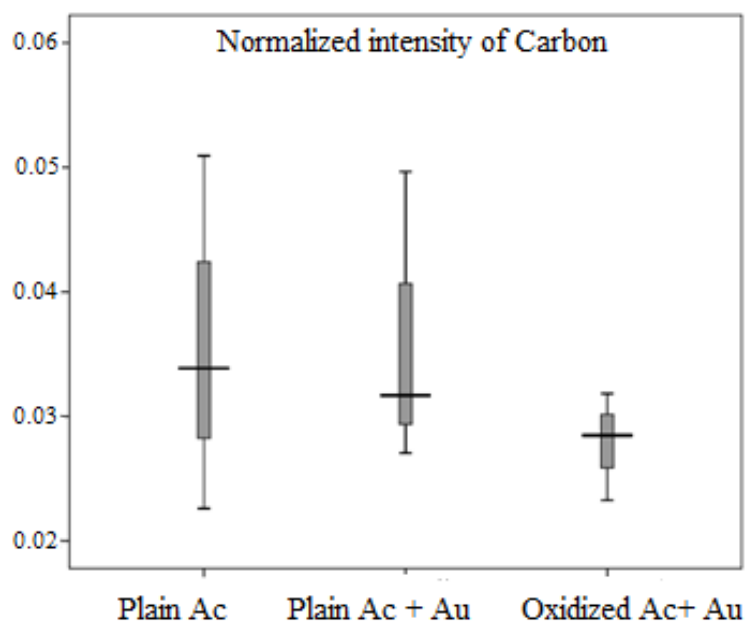
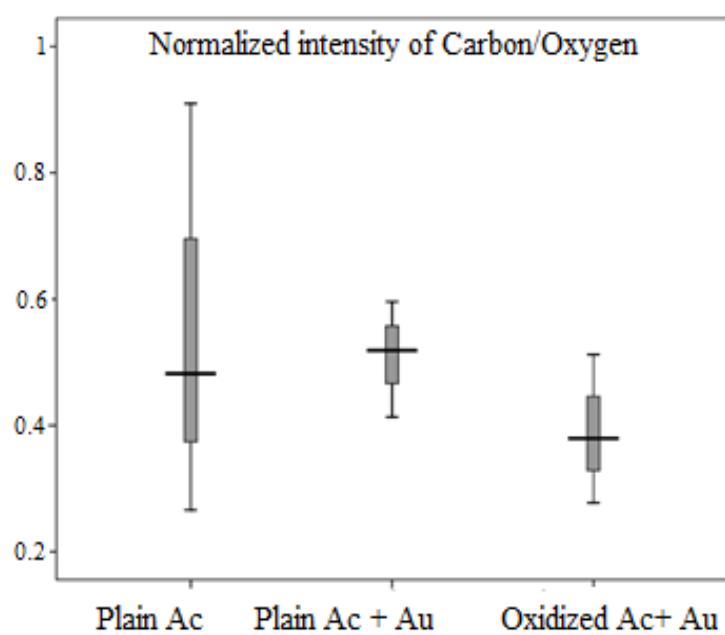
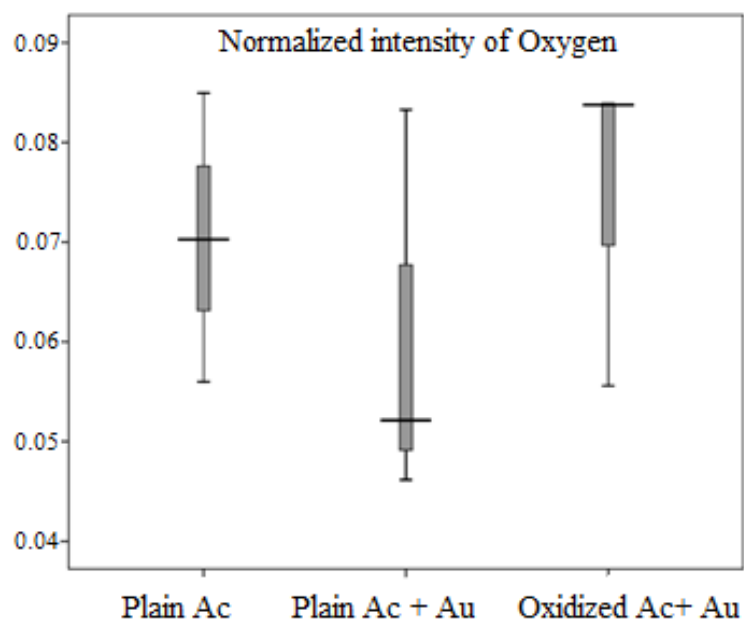


Figure 4-8 : TOF-SIMS surface analyses image. Distribution of elements H, C, O and Au(CN)₂ in a grain of activated carbon (A) , activated carbon +gold (B), oxidized activated carbon + gold (C) (Field area: 500*500 μm^2)

To assess the oxidation efficiency regarding the generation of oxygen functional groups and consequently reduction of gold uptake on the surface of activated carbon, the relative proportion of surface C, O, C/O and Au(CN)₂ were examined. Comparing the AC with the OAC shows that the surface C content decreases considerably in the OAC whereas the relative proportion of O increases in the same sample pair. This change is similarly reflected in the C/O ratio. Most importantly, the gold uptake on the oxidized activated carbon dramatically decreased (Figure 4-9).





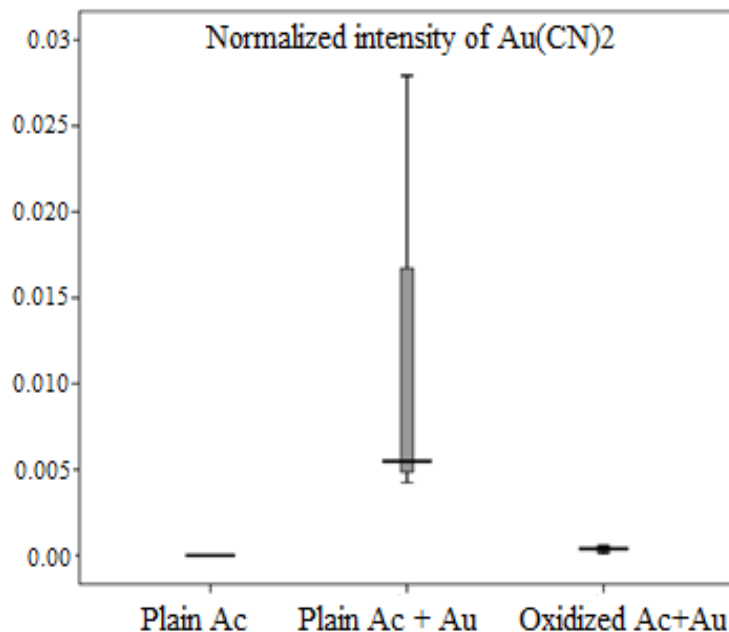


Figure 4-9 TOF-SIMS surface analyses data. Box plots illustrating the normalized intensity of carbon , oxygen, carbon oxygen ratio (C/O) and Au(CN)₂ on the surface of plain activated carbon (AC), plain AC + gold and oxidized activated carbon + gold

4.5.2 Detailed TOF-SIMS surface evaluation of oxidized carbon

As it was described in chapter 3 the final series of oxidation and gold adsorption tests were carried out on 1g of -75+38 micron sized activated carbon oxidized with HNO₃. These samples were analyzed by TOF-SIMS in order to identify surface molecular species linked to changes in the relative proportion of O and C after oxidation which resulted in the decrease in Au(CN)₂⁻ adsorption. The relative intensity of C and O on the FAC (Fresh activated carbon) and OAC in Figure 4-10 illustrates a similar behavior as that observed previously, that the decrease in Au(CN)₂⁻ adsorption appears to be linked to a decrease in the C/O ratio.

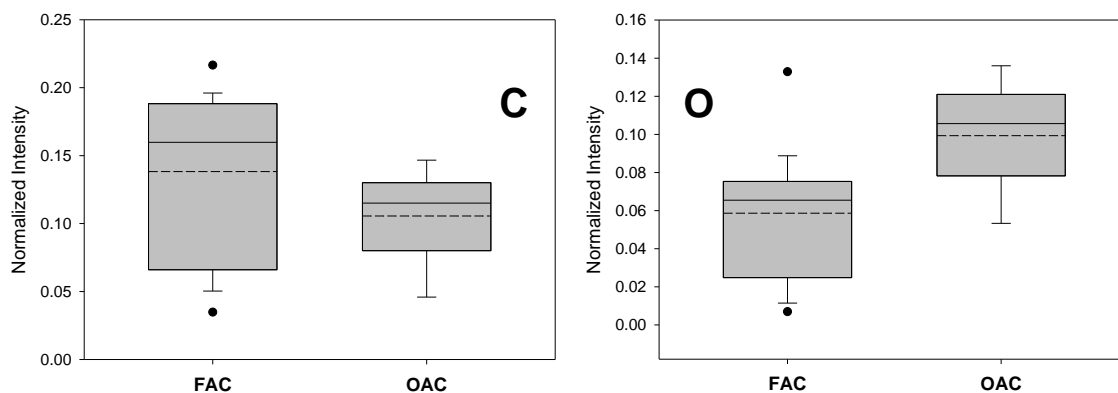


Figure 4-10 TOF-SIMS surface analyses data. Box plots illustrating the normalized intensity of carbon (C) and oxygen (O) on the surface of fresh activated carbon (FAC) and oxidized activated carbon (OAC)

Detailed evaluation of the TOF-SIMS spectra from the surface of oxidized activated carbon revealed peaks representative of the parent molecule and the first mass fragment (parent - OH) of carboxylic acid (Figure 4-11). The relative proportion of these species measured on the grains shows a significant build up on the surface of the activated carbon as a result of the HNO_3 oxidation (Figure 4-12). Comparative analysis reveals that the oxidation treatment with 10 molar nitric acid leads to highest relative proportion of these surface acid functional groups.

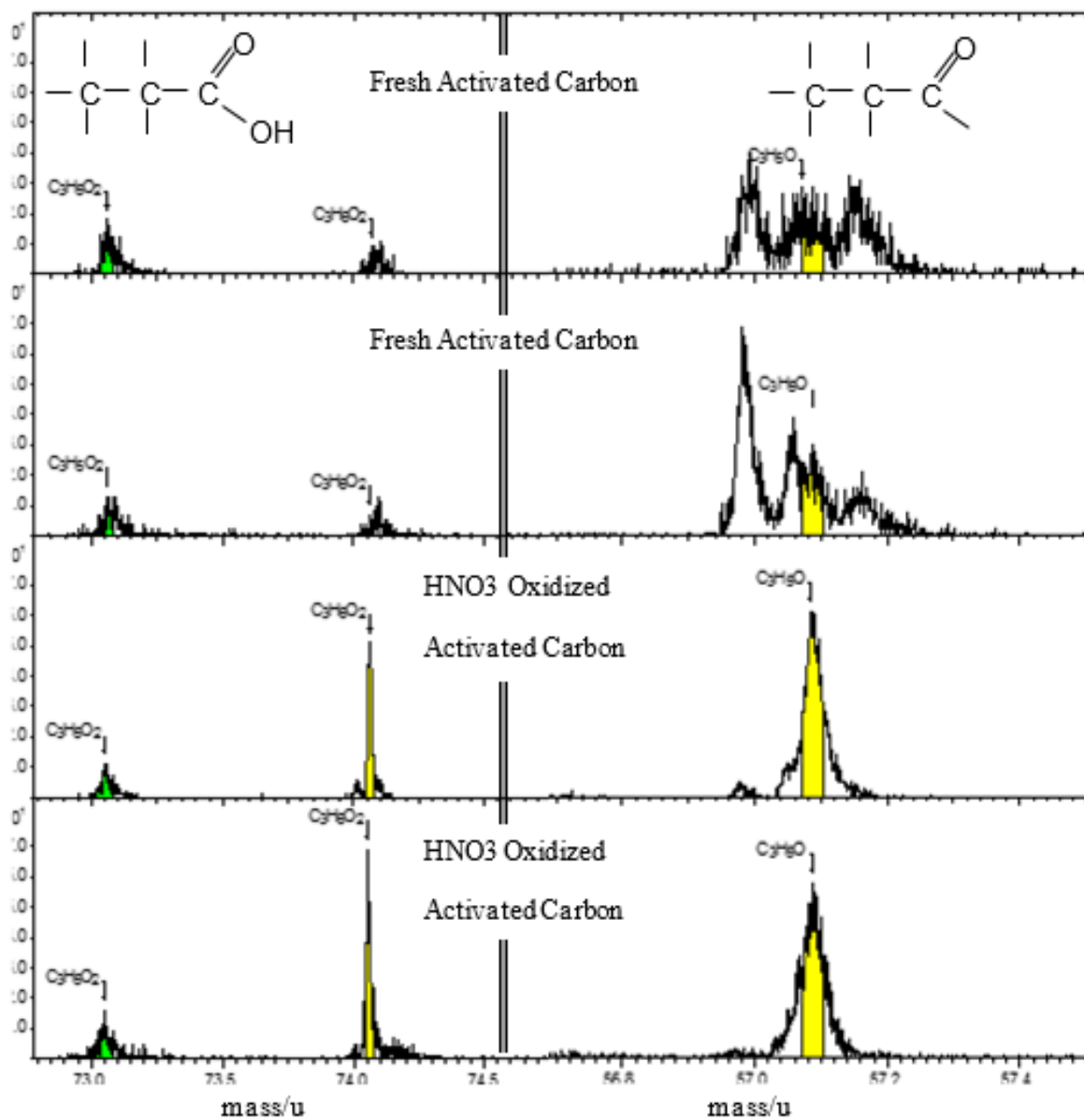


Figure 4-11 TOF-SIMS spectra in the mass regions of carboxylic acid. The left of the double line shows the peak position for the parent molecule, to the right, first mass fragment (parent –OH).

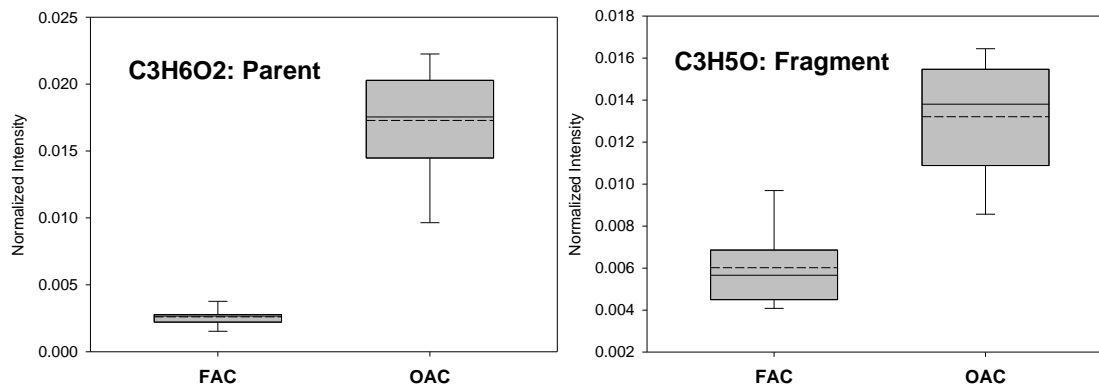


Figure 4-12 normalized intensity of mass positions representative of the carboxylic parent molecule and the first mass fragment (parent – OH) on the surface of (FAC) and (OAC)

Carboxylic acid, represents a class of organic compounds where a carbon (C) atom is double bonded to an oxygen (O) atom and to a hydroxyl group (–OH) by a single bond. These together are referred to as the carboxyl (COOH) group as they contain both the carbonyl group (C=O) and a hydroxyl group (OH). A fourth bond links the carbon atom to a hydrogen (H) atom or to some other combining group.

The general formula of a carboxylic acid is R–COOH, with R referring to the remainder of the molecule. Carboxylic acid can be considered a polar compound; partially positive and partially negative; [8, 15, 16], the general formula is given in Figure 4-13.

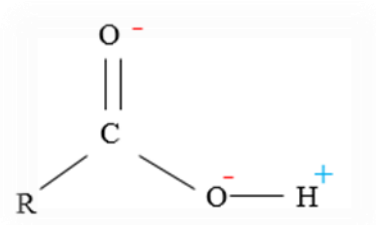


Figure 4-13 General formula of carboxylic acid illustrating the polar nature of the compound. R represents the C-H chain

4.6 Surface chemical analysis of activated carbon subjected to oxidation by XPS

The XPS analysis was used to corroborate the TOF-SIMS results and further investigate the surface chemical changes to the organic material before and after oxidation with HNO₃. The analysis would aid in the interpretation of the factors linked to the observed gold adsorption decrease as a result of chemical oxidation.

4.6.1 Results from the XPS analysis

In this study, the sample (1g of -75+38 micron sized activated carbon, oxidized with HNO₃), similar to that prepared for TOF-SIMS, was examined. Quantitative analytical results from survey scans showed a remarkable change (almost twice) in the relative proportion of oxygen after the treatment along with a decrease in the carbon content (Table 4-3). This is reflected in the C/O ratio drop from the plain activated carbon to the oxidized activated carbon.

Table 4-3 Surface carbon and oxygen content of plain and oxidized activated carbon as determined by XPS analysis

	Carbon %	Oxygen %	C:O ratio
Plain activated carbon (PAC)	91.1	7.0	13
Oxidized activated carbon (OAC)	83.9	13.6	6

High resolution XPS spectra collected on the surface of the PAC and OAC showed a distinct increase in the O-C=O, C*-C-O and C-OH bonds along with a decrease in the proportion C=C bonds (Figure 4-14). The results which show an overall increase in surface oxygen content, suggests that a variety of surface functional groups containing oxygen are formed during the HNO₃ oxidation process. The increase in relative proportion of C=O bonds reflects the development of surface carboxylic acid groups (identified by TOF-SIMS). The later were not defined but a significant increase in repeated patterns commonly separated by a masses 17 (-OH) or 16 (O) were observed in the high mass regions of the

TOF-SIMS spectra of the oxidised activated carbon. The development of carboxylic groups and lactones and the formation surface C-O groups result in the relative proportional decrease in of C-C, C-H bonds representative of the plain activated carbon surface. The development of carboxylic groups and lactones is also seen (identified by TOF-SIMS) in the relative decrease in C=C bonds likely reflective of the fresh activated carbon in direct response to oxidation and formation C-O groups (Table 4-4).

Table 4-4 Relative proportion of the assigned peaks as measured by XPS on the surface of (PAC) and (OAC).

%	O-C=O	C=O	C-OH, C-O-C	C=C
PAC	3.2	2.6	7.6	85.5
OAC	5.3	4.4	8.7	67.5

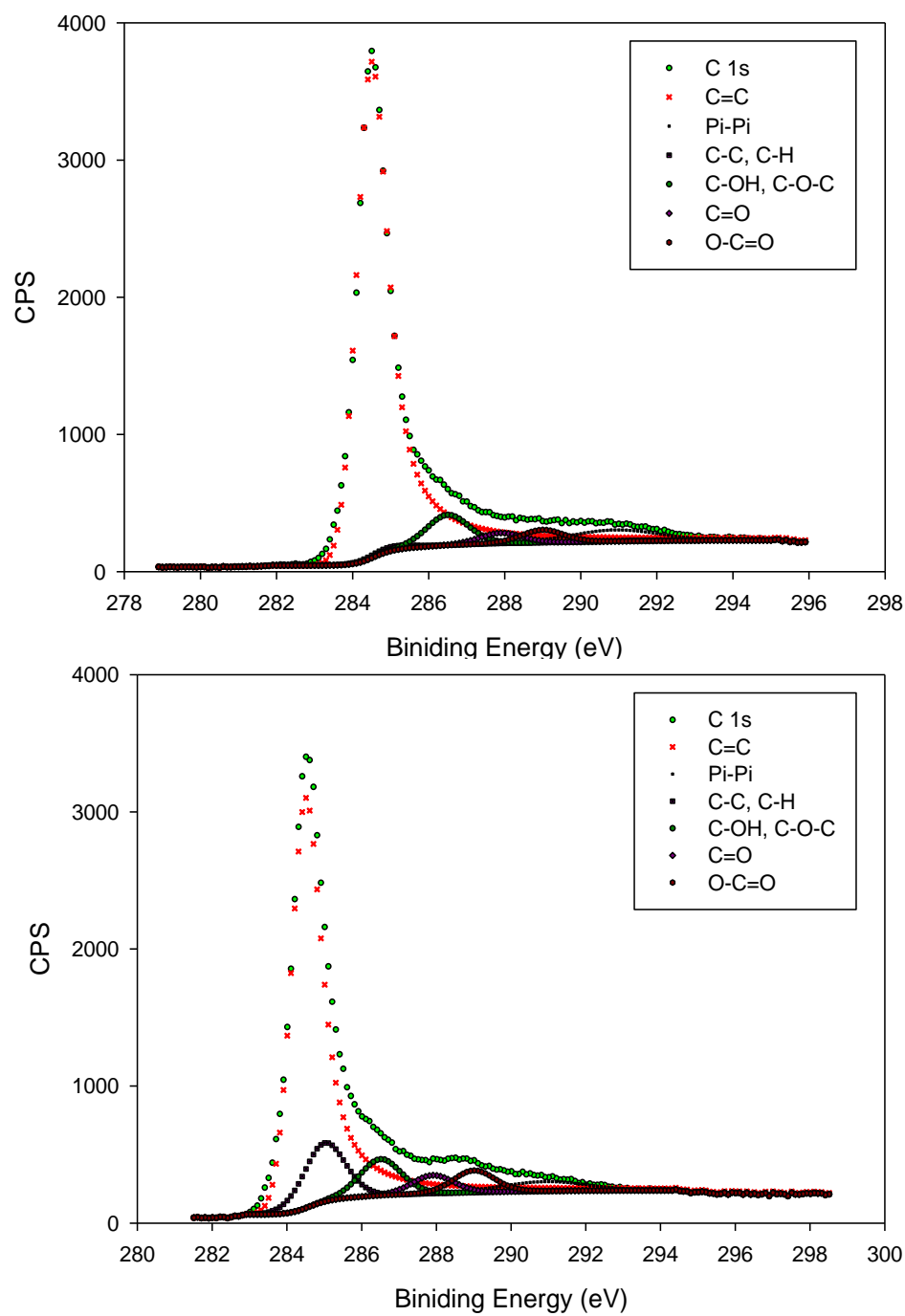


Figure 4-14 High resolution C 1s XPS spectra showing peak fits and their assignment as measured on the surface of plain activated carbon (upper), oxidised activated carbon (lower).

In a recent review by Miller et al (2016), for Au adsorption on carbon, it has been proposed that [17] there is a combined electrostatic and chemical interaction between the gold-cyanide anion and the carbon surface. Currently, the most accepted theories regarding the mechanism of gold adsorption include the adsorption of ion pairs $Mn^{n+} [Au(CN)_2^-]_n$ onto active sites of activated carbon. In addition, adsorption of the unpaired anion $Au (CN)_2^-$ resulting from a weak donation of electrons from the carbon to the Au has been identified. It has also been established that, basic surface functional groups are favored for $Au (CN)_2^-$ on the surface of activated carbon.

Based on the overall results of this study, surface oxidation of the activated carbon has resulted in decrease in C/O ratio reflecting a decrease in surface C along with the development of surface acidic functional groups. The shifting from a basic to a more acidic surface along with a reduction in the surface proportion of C would then likely interfere with the ability of the surface of the carbonaceous material to adsorb the $Au (CN)_2^-$ complex; a phenomenon clearly identified in this testing.

4.7 Results from oxidation investigations on a carbonaceous gold ore

Given the promising results achieved from the treatment on the activated carbon, the same procedures were conducted on a preg-robbing carbonaceous gold ore sample (BR-20) provided by Barrick.

4.7.1 Sample characterization

The chemical composition of the sample was characterized by X-ray fluorescence spectroscopy (XRF). The sample is dominantly composed of SiO₂ with significant amounts of CaO, MgO, Al₂O₃ and Fe₂O₃ along with minor proportions K₂O, TiO₂, P₂O₅ and BaO. The total S content is ~0.9 wt%, total C content 5.5 wt % with the organic carbon making up ~1.8%. The Au content of the sample is 3.16 ppm (Table 4-5,4-6).

Table 4-5 Major oxide concentration for sample BR-20 before oxidation.

%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	P ₂ O ₅	BaO	LOI	S (t)	C(T)	C (Org)
BR-20	59.86	3.74	2.3	10.27	5.82	0.69	0.16	0.11	0.16	15.3	0.87	5.5	1.75

Table 4-6 Trace element results for sample BR-20 before oxidation. All data in ppm

ppm	Au	Cu	As	Zn	Ni	Sb	Mo	Ag
BR-20	3.16	878	411	304	250	87	33	<0.5

4.7.2 Mineralogical analysis

The dominant mineral phases in the sample pre and post oxidation were determined by X-ray powder diffraction (XRD). Prior to the mineralogical analysis the samples were ground to 80% passing 38 microns to ensure sample homogeneity.

The analysis indicates that the dominant minerals in sample BR-20 are quartz, carbonates (calcite and dolomite) along with gypsum and the sheet silicates kaolinite and muscovite (Figure 4-15). The minerals present after oxidation include quartz, kaolinite and muscovite.

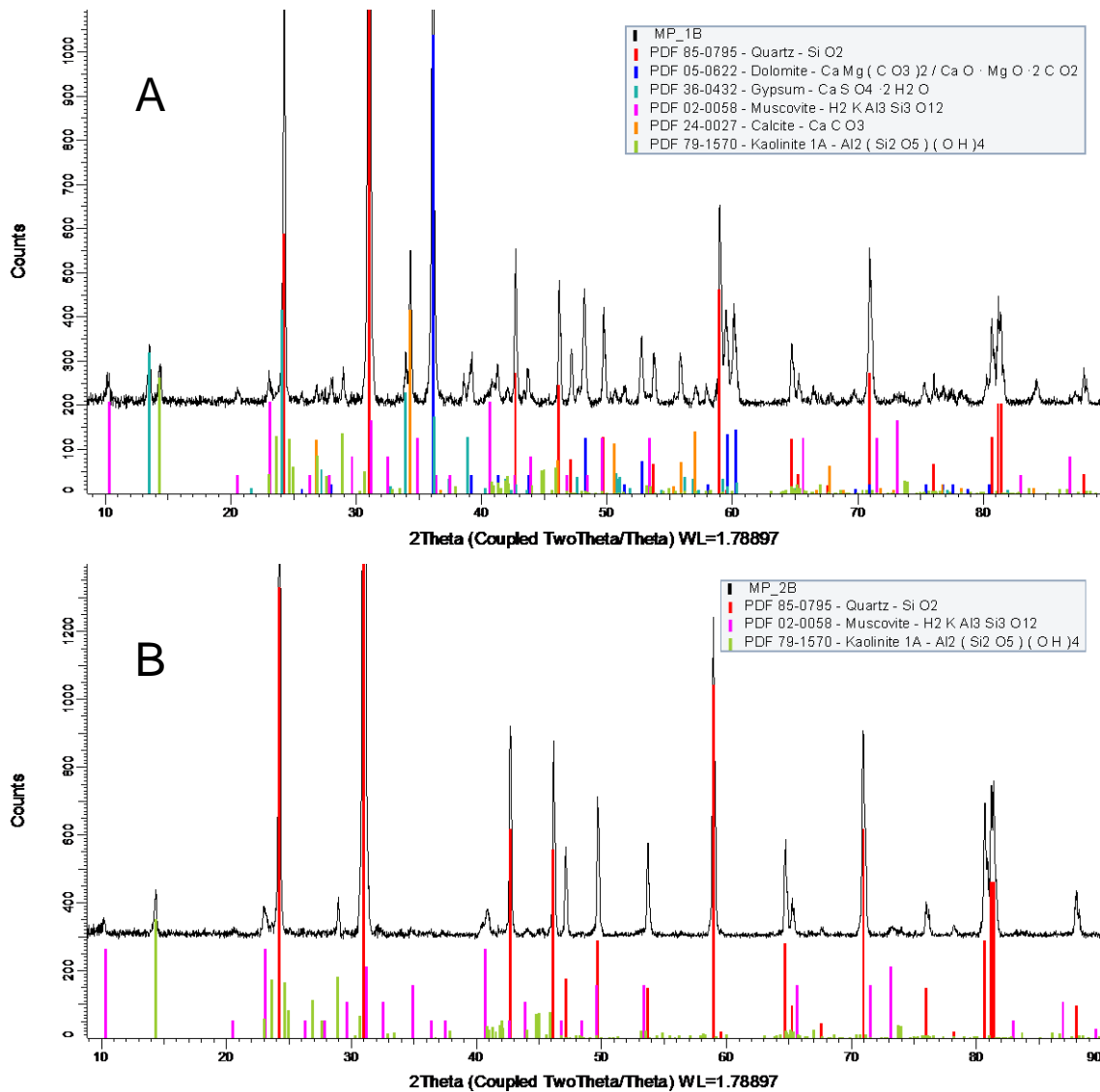


Figure 4-15 Stacked XRD patterns for BR-20. A: the fresh un-oxidized sample, B the HNO₃ oxidized sample.

A detailed mineralogical breakdown of the sample was performed by the QEMSCAN (quantitative evaluation of mineralogy by scanning electron microscopy) technique (Figure 4-16). The analysis, provided by Barrick, gives information on the major, minor and trace minerals present in the sample. The analysis also indicates that dominant minerals include quartz, calcite, dolomite, kaolinite, and muscovite. Other significant phases identified include organic carbon, chlorite, K-feldspars, pyrite and Fe-oxides.

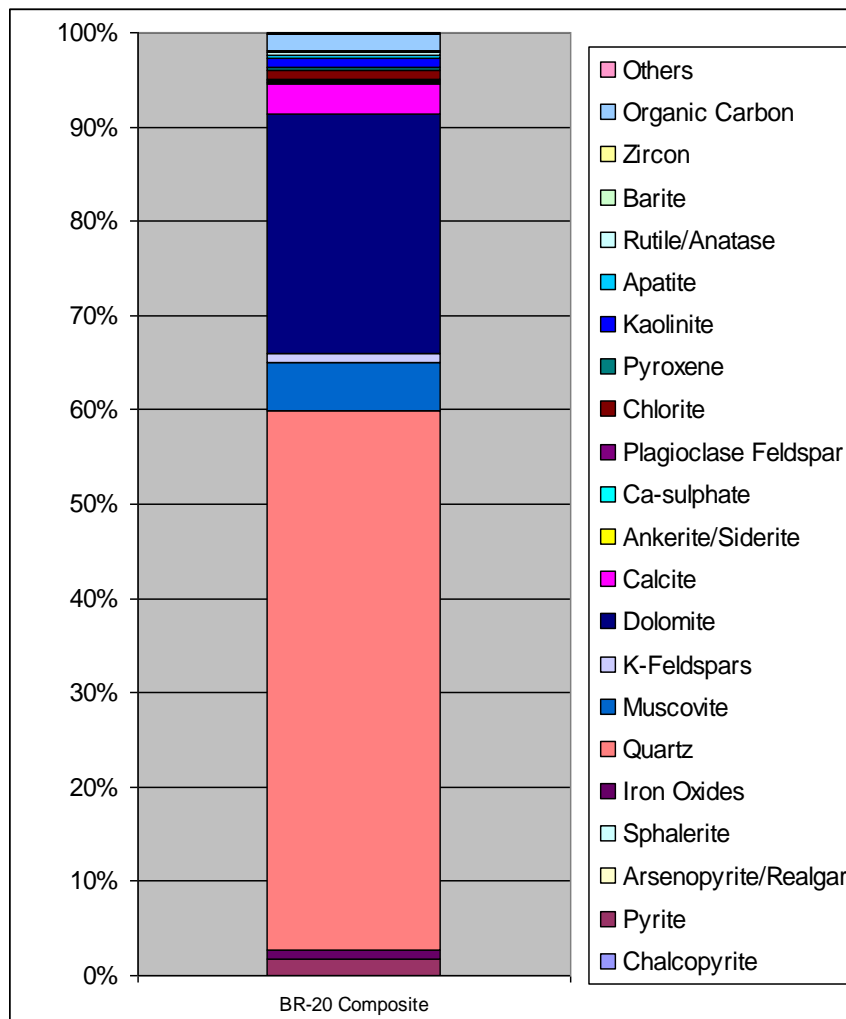


Figure 4-16 Relative proportion (%) of all minerals identified by the QEMSCAN (quantitative evaluation of mineralogy by scanning electron microscopy) technique. Data was provided by Barrick.

4.7.3 Au deportment

A full gold deportment study was performed on sample BR-20 by Barrick. Below is a summary of the information provided.

- Minor amounts of pyrite (1.69 %) were noted in the sample. Morphologically, most of the pyrite grains were porous, fine and micro-crystalline/disseminated pyrite aggregates. Greater than 95% of the pyrite is liberated. Note: the gold content of the sulphide grains was not provided.
- A minor amount of organic carbonaceous material was identified (1.75% to 1.85%).
- Visually 21 native gold grains were identified in the sample; the Au content varying from 86% to 100%. The majority of the gold grains were liberated and fine to medium grained (5 μ m to 12 μ m). A few locked grains in sulfides and silicates were noted.

4.7.4 Carbonaceous material characterization

A detailed evaluation of the carbonaceous material from sample BR-20 was performed by SEM/EDX. The carbonaceous materials varied from irregular flake like materials to blocky grains (Figure 4-17). The grains identified range in size from 5 to > 150 microns in length. For the most part the grains are liberated.

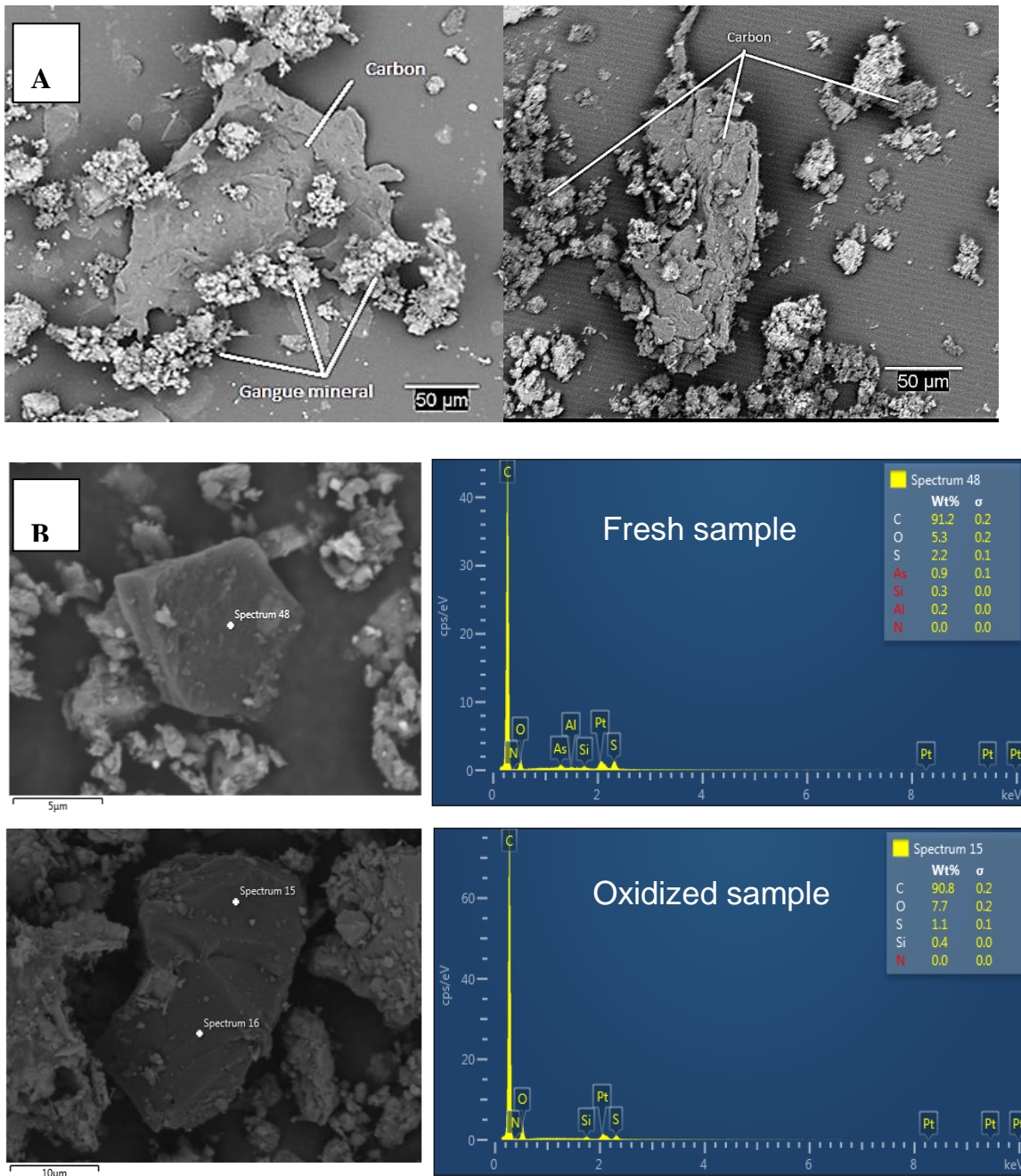


Figure 4-17 SEM images of carbonaceous materials accompanied with numerous fine silicate particles and agglomerates in sample BR-20

As discussed in Chapter 3, in order to provide a more appropriate sample for testing, the C content of the sample was increased by collecting a microflotation concentrate. The SEM evaluation of the flotation concentrate showed that there is a significant proportion of fine silicates associated with the carbonaceous material (Figure 4-17). Although most of the carbonaceous particles are well liberated, numerous fine silicate minerals and agglomerates still remain attached to the carbonaceous material surface. In order to potentially further exclude some of the fine silicates from the sample a second flotation test was performed using Na-silicate as a depressant for the silicate gangue. As the relative proportion of gangue in the concentrate did not decrease in these tests, the oxidation testing was performed on the flotation concentrates without the inclusion of Na-silicate.

4.7.5 BR-20 Au adsorption results and discussion

The concentrate sample was oxidized with two different HNO_3 concentrations; 4 and 10 molar HNO_3 . Adsorption tests using a solution of $\text{NaCN}+\text{NaOH}$ (no added AuCN) were performed on both the fresh and oxidised samples. Sample BR-20 has an inherent Au content of ~3 ppm, which occurs mostly as free liberated Au grains. A second series of tests were performed using the same methodology but with an additional 50 ppm Au (Figure 4-18).

The adsorption data indicate that oxidation with HNO_3 does not appear to be efficient in terms of reducing the PR capacity of the carbonaceous material in the BR-20 sample. For both the 4 and 10 molar oxidation, $\text{Au}(\text{CN})_2$ adsorption was less than that for the untreated concentrate sample.

Furthermore, oxidation with 10 Molar HNO_3 is not as effective as the oxidation with 4 molar HNO_3 . A study by McDougall et al (1980) identified that at higher gold concentrations increasing the nitrogen content of the carbon leads to an increase in gold attachment. In the testing work here increasing the surface nitrogen content by oxidation with 10 molar nitric acid could potentially result in an increase in gold adsorption on the surface of CM, particularly when extra gold is added to the solution [18].

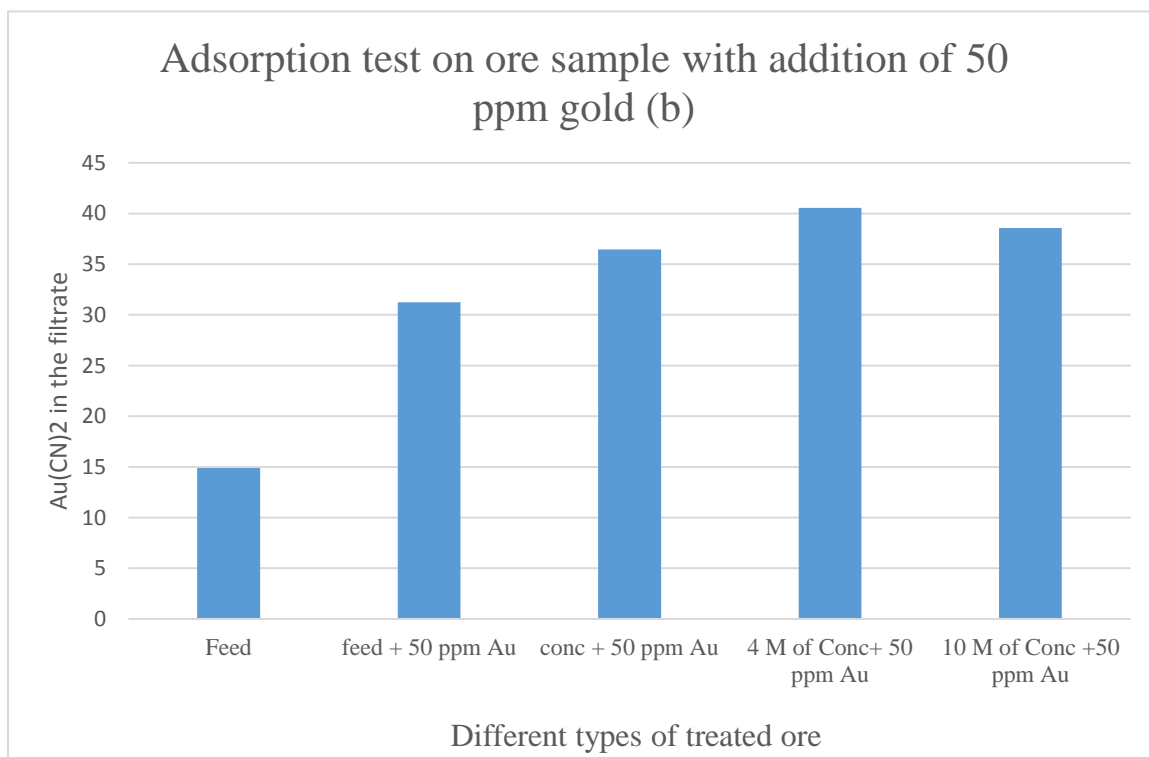
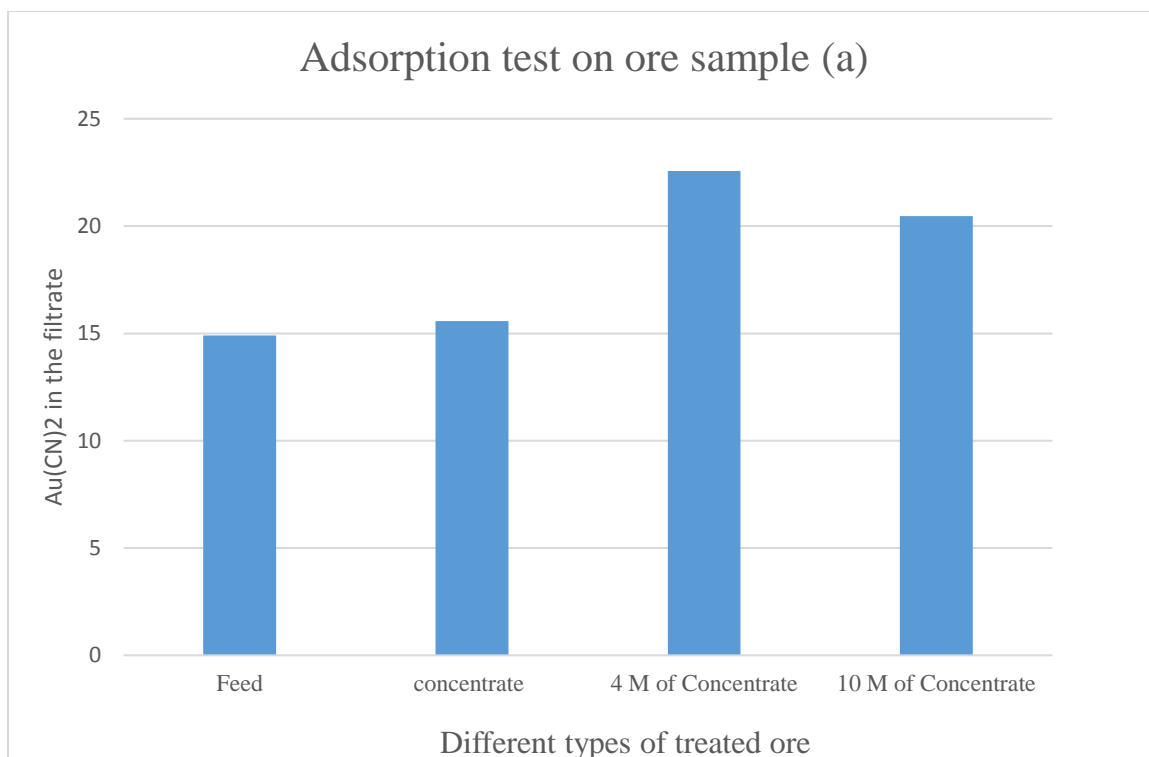


Figure 4-18 Au (CN)₂ adsorption on plain ore and different types of treated ore (a) and with 50 ppm gold added (b)

In order to determine factors potentially responsible for the observed reduction in the efficiency of oxidation in terms of gold adsorption CM from the samples before and after oxidation were examined in detail by SEM, Raman and TOF-SIMS.

SEM/EDX analysis of the carbon grains before and after oxidation was performed. Examples of carbon grains from both samples along with their EDX analysis are shown in Figure 4-17. EDX analyses for carbon and oxygen are given in Figure 4-19. The data illustrate that, at the EDX detection limits (0.5wt%), the carbon contents in both before and after oxidation are very similar but the oxygen content is slightly higher in the oxidized samples. This was similarly observed in the treated activated carbon samples by TOF-SIMS however the magnitude of the EDX determined oxygen increase on the surface of the oxidized BR-20 carbon grains is significantly less. This is likely related to the sampling volume of the two systems; the EDX analyses is derived from 3-4 um whereas the TOF-SIMS data is generated in the upper 100 nm.

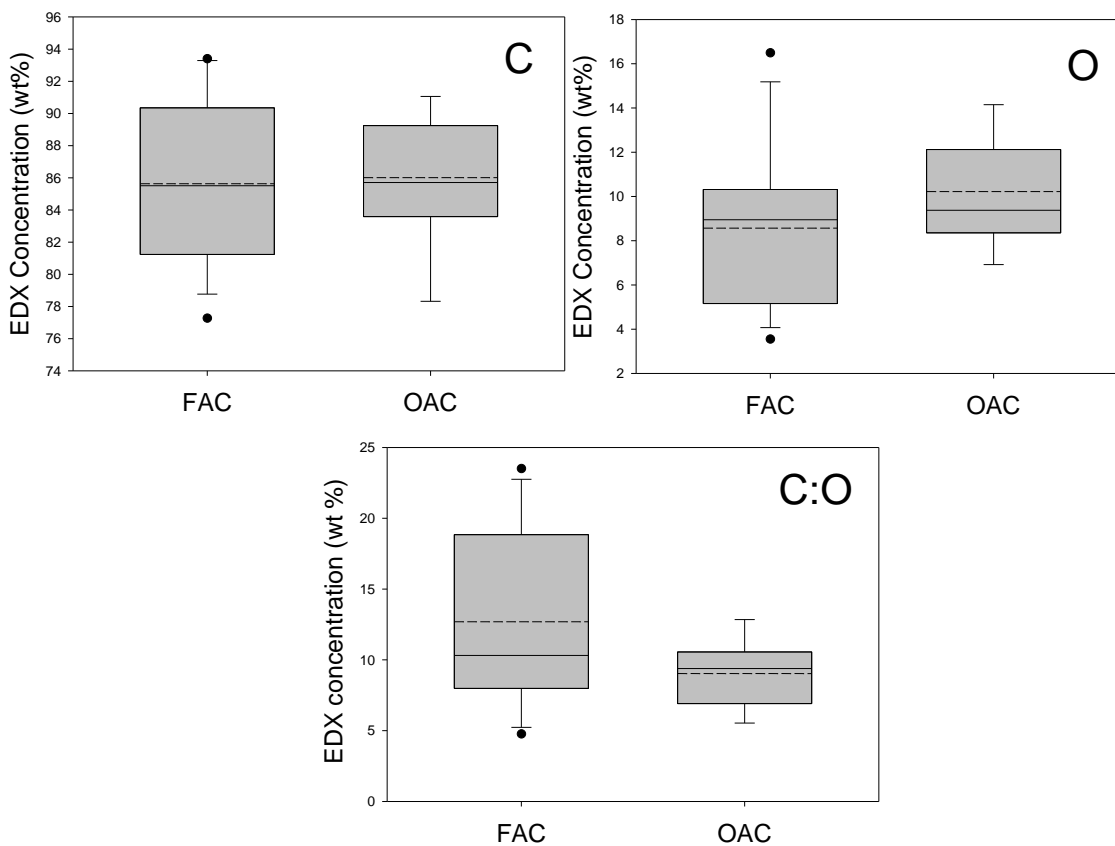


Figure 4-19. EDX analysis for C, O along with the C:O ratio for grains from sample BR-20. The Boxes show outliers, 95th and 5th percentiles along with the mean (solid line) and the median (dashed line). Data shown is for all grains with >80% carbon in the analysis.

As part of the CM assessment before and after oxidation the samples were analysed by Raman spectroscopy in order to determine if the oxidation process altered the carbon internal organization. The data in Figure 4-20 illustrates that the Raman ratio of the CM after oxidation did not vary significantly from that before oxidation, indicating that oxidation did not modify the structural organization of the CM.

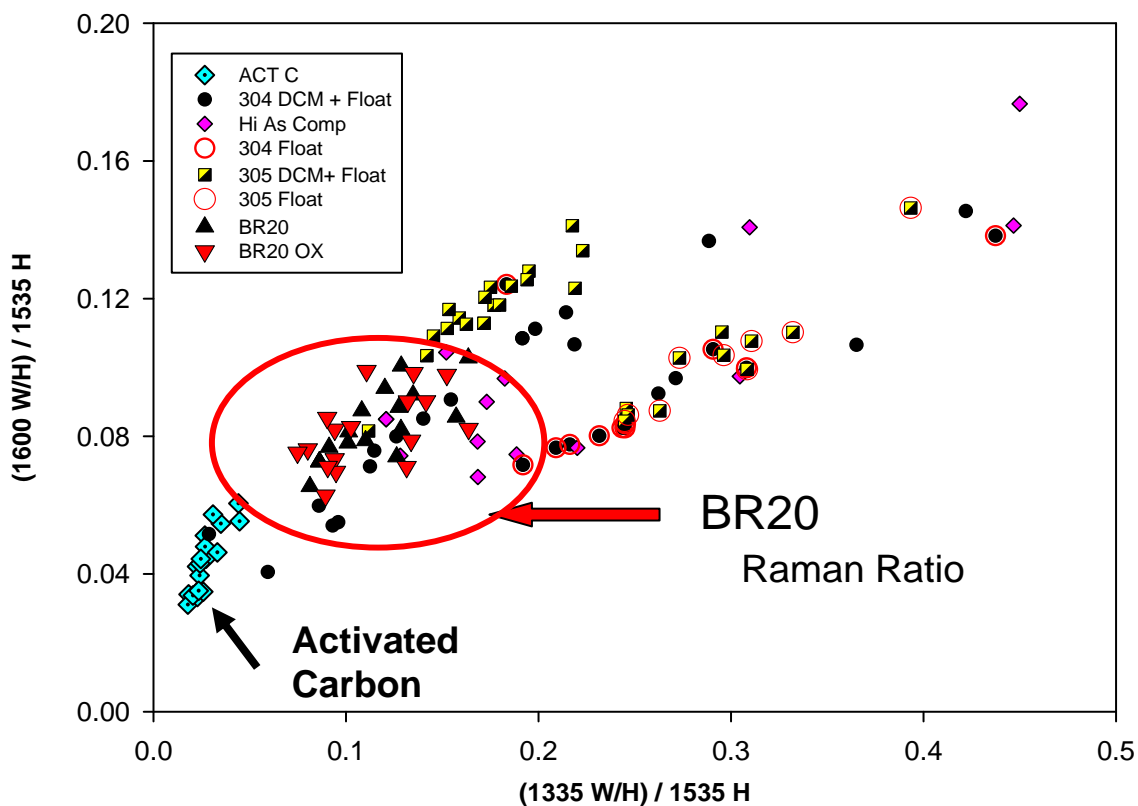


Figure 4-20 Raman ratio for carbonaceous materials in the BR-20 samples before and after oxidation along with carbonaceous materials from a number of other carbonaceous gold ores within Nevada.

The ore sample consists mostly of quartz, carbonates, such as dolomite and calcite, as well as the Aluminosilicate minerals kaolinite and muscovite. The HNO_3 treatment resulted in the removal of the carbonate and other minerals leaving behind quartz and silicates as indicated by the XRD analysis. The adsorption results which are different from the testing with activated carbon are therefore likely linked to changes in the mineralogy and chemical composition of the ore sample during the oxidation process.

An idealized schematic of the oxidation process operating on sample BR-20, based on the analyses performed in this work, is given in Figure 4-21. As discussed earlier, the HNO_3 oxidation of carbonaceous material produced oxygen rich functional groups, in the case of the activated carbon sample carboxylic acid. During the oxidation the breakdown of various minerals, cations such as Ca^{2+} and Mg^{2+} (carbonates) along with Al^{3+} and K^+ (clays and other soluble phases) are released to solution (shown as the oxidation stage in Figure 4-21). As the sample is washed to remove residual acid and increase the pH for the adsorption testing, the cations in solution adsorb onto the surface of the carbonaceous material. Evidence for this is provided by the TOF-SIMS surface analyses of carbon grains in the BR-20 sample before and after oxidation which shows a clear increase in the proportion of these species on the carbon grains after oxidation (Figure 4-22).

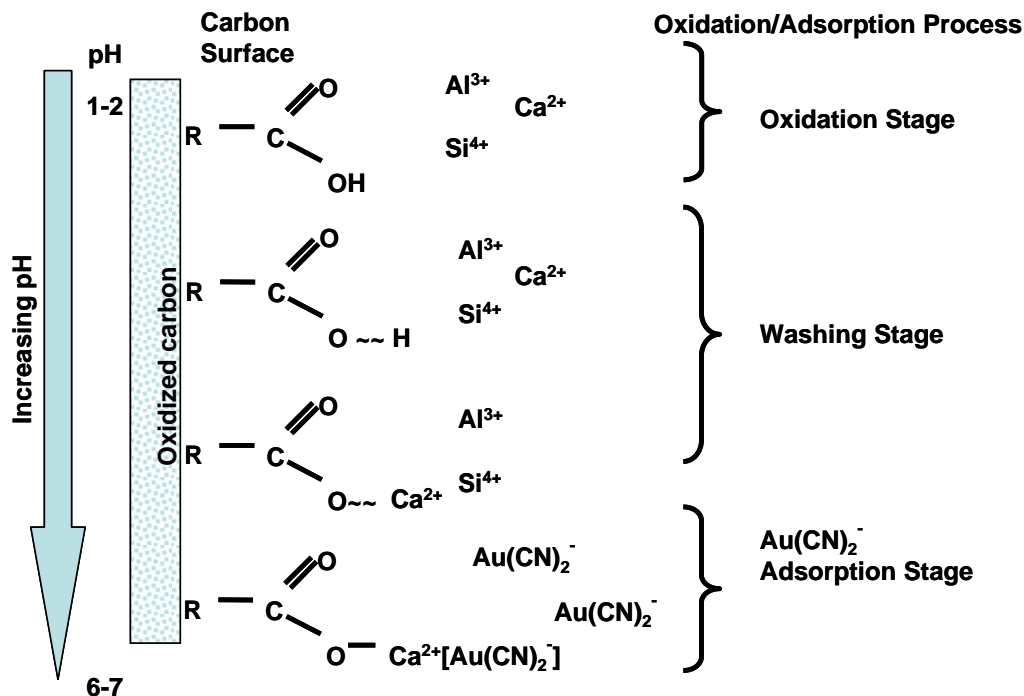


Figure 4-21 Process schematic of the HNO₃ oxidation results and process of potentially increasing the preg-robbing capacity of the oxidized carbonaceous material in sample BR-20.

During the adsorption testing in a neutral or alkaline environment, the Au(CN)₂⁻ anion is adsorbed onto the carbon, likely together with an alkali cation such as Ca⁺, and is held electrostatically as a metal dicyanoaurate complex Mⁿ⁺[Au(CN)₂]_n (adsorption stage Figure 4-21). Davidson et al, (1947) investigated the alkaline metal, Mⁿ⁺[Au(CN)₂]_n, ion pair complexes and determined that the attachment to activated carbon is stronger than the Au(CN)₂⁻ anion alone. They also determined that the adsorption follows the order ; Ca²⁺ > Mg²⁺ > H⁺ > Li⁺ > Na⁺ > K⁺ [19].

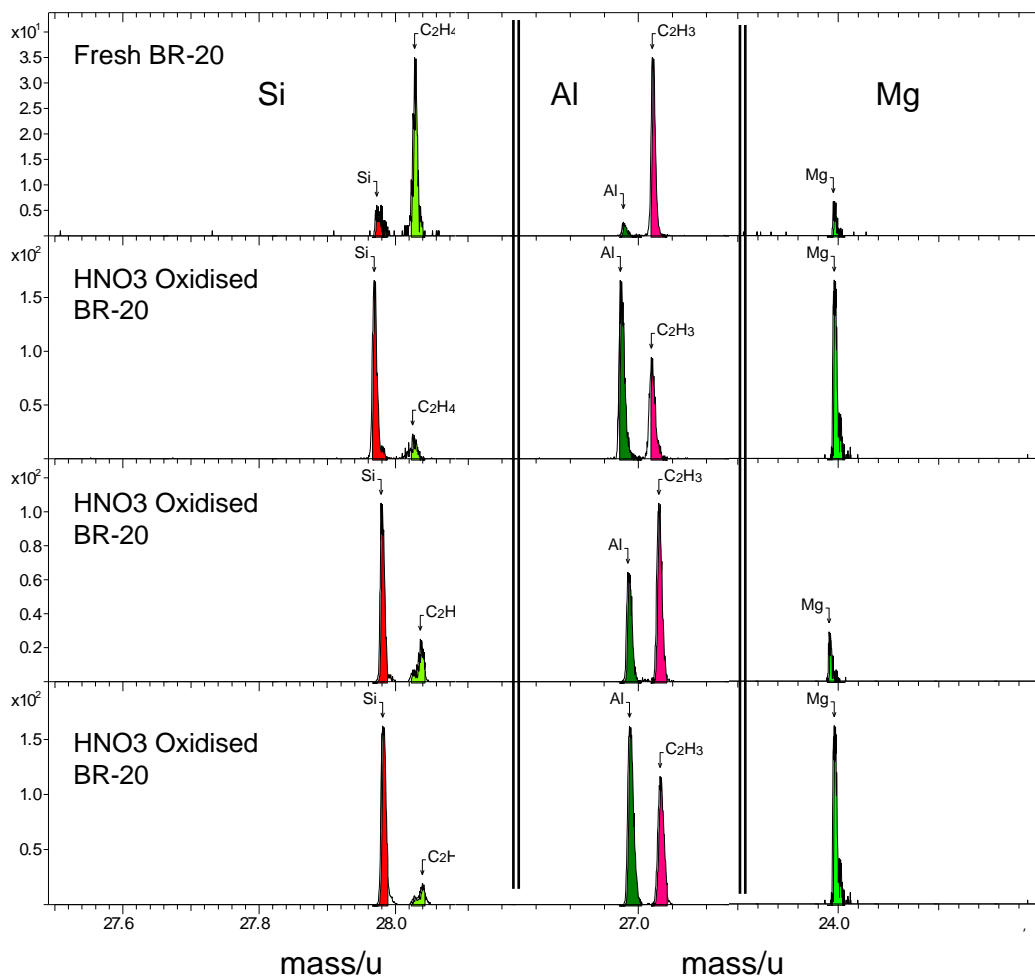


Figure 4-22 TOF-SIMS spectra in the mass regions of Si, Al and Mg on the surface of no oxidized and oxidized carbon grains from sample BR-20. The data show an increase in proportion of Si, Al and Mg on the surface of the oxidized carbon.

The resultant formation of the $M^{n+}[Au(CN)_2^-]_n$ complex, then fixes the gold on the surface of CM resulting in a decrease in the gold content in the filtrate solution.

This phenomena is likely responsible for the lack of improvement in lowering the pre-grobbing efficiency of carbonaceous material by oxidation in the BR-20 sample as compared to that determined for activated carbon.

4.8 References

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Chapter 5

5 Conclusion and future work

5.1 Conclusion

Preg-robbing (PR), is responsible for poor recoveries as the carbonaceous materials (CMs) in the ore compete with activated carbon used during the leaching and adsorption phase of processing. In this study, chemical oxidation of CM by different reagents was employed to investigate and compare the mechanism of Au (CN)₂ adsorption onto CM prior to and following the treatment.

Results revealed that the oxidation of activated carbon with HNO₃ and H₂O₂ resulted in decrease in gold adsorption on the activated carbon. However, HNO₃ is more efficient compared to H₂O₂. A summary of the results from testing at the following conditions, given below, are listed

Test conditions: oxidation of activated carbon at 80°C, 10 molar HNO₃ for two hours. Au(CN) adsorption on activated carbon before and after oxidation, contact time is 30 minutes.

- UV-VIS analysis of the solutions indicated that the Au(CN) uptake on the oxidized activated carbon showed a five fold reduction compared to the plain activated carbon.
- Raman spectroscopy was performed on the residues prior and after oxidation. The Raman analysis indicated that the organization of activated carbon hasn't been significantly affected by oxidation so the changes in the degree of C disorder were likely not involved in the observed reduction of the oxidized activated carbon to adsorb Au(CN)₂⁻.
- In terms of total surface area and macro porosity, SEM analyses from 685 areas of fresh and oxidized activated carbon showed a slight shift in average macropore area on the oxidized CM suggesting that oxidation generated greater diameter macropores. Surface area analysis by BET reveals a significant increase in surface area as a result of oxidation. This potentially created more available area for

Au(CN)₂ adsorption. However, results from the adsorption tests showed that regardless of the increased surface area, gold uptake decreased.

- The SEM study on the residues established the link between the change in surface chemistry and the decrease in Au(CN) adsorption. Increase in oxygen content and decrease in carbon content, both resulted in reduction of C/O ratio. This was used as an indicator of degree of surface oxidation which led to reduction of gold uptake on the surface of activated carbon by formation of oxygen functional groups.
- TOF-SIMS spectra identified a significant build up of carboxylic acid on the surface of the activated carbon due to oxidation.
- The XPS study of the residues showed a distinct increase in the O-C=O, C*-C-O and C-OH bonds along with a decrease in the proportion C=C bonds. From the results obtained, showing an overall increase in surface oxygen content, it would appear that a variety of surface functional groups containing oxygen are formed during the HNO₃ oxidation. The increase in relative proportion of C-O bonds reflects the development of surface carboxylic acid groups which is in agreement with TOF-SIMS results.
- Basic surface functional groups are favored for adsorption of Au (CN)₂⁻ on the surface of activated carbon. The shifting from a basic to a more acidic surface along with a reduction in the surface proportion of C would then likely interfere with the ability of the surface of the carbonaceous material to adsorb the Au (CN)⁻ complex. Since carboxylic is a highly polar functional group the overall surface of the charge of the oxidized carbonaceous material would shift to more negative and thus would repel the gold-cyanide ions ultimately decreasing gold adsorption.

Therefore, considering all the effective factors, it appears that changes in the surface chemistry of the activated carbon due to the oxidation play a significant role in reducing the capacity for gold cyanide complex adsorption.

Based on the results obtained for the activated carbon similar tests were performed on a preg-robbing carbonaceous gold ore, BR-20

- The sample contains 3 ppm gold, total C content 5.5 wt % with the organic carbon making up ~1.8%, total S content is ~0.9 wt% . The dominant mineral is quartz along with carbonates (calcite and dolomite) and clay minerals.
- The test conditions for the oxidation procedure and adsorption tests were performed on the BR-20 ore sample in a same manner as those for the activated carbon.
- UV-VIS analysis of contact solutions indicate that the Au(CN) uptake on the oxidized sample is similar to or less than that for the un-oxidised sample. This indicates that the oxidation process did not reduce or inhibit the capacity of the CM in the sample to adsorb Au.
- SEM/EDX analysis showed that the surface carbon content in plain and treated sample remain similar but the oxygen content is slightly higher in the oxidized samples. A lower proportion of oxygen functional groups after oxidation on the surface of the sample may be linked to a lower efficiency of surface oxidation by HNO₃. As the sample contain a significant proportion of carbonates (~30%) the buffering capacity of the sample is likely high enough to lessen the effect of HNO₃ oxidation. Testing with a higher concentration of HNO₃ did not diminish the adsorption capacity as higher concentrations of HNO₃ could also lead to an increase in surface nitrogen species which have been linked to increased gold adsorption on carbon.
- TOF-SIMS analysis on the sample before and after oxidation showed the presence of acidic functional groups on the surface of the oxidised carbon along with an increase in the proportion of cations such as Al³⁺ and Mg⁺. Their presence is believed to result from the oxidation process where cations such as Ca⁺ and Mg⁺ , from carbonates, along with Al³⁺ and K⁺, from clays and other soluble phases, are released to solution. As the pH increases with successive washing of the sample after oxidation, they adsorb onto surface of the carbonaceous material in the sample. During the Au(CN)- adsorption phase of the tests these elements form relatively stable metal aurocyanide complexes on the carbonaceous matter resulting in the observed increased Au adsorption capacity of the carbonaceous material as a result of oxidation.

- Given the results obtained from the testing on sample BR-20, oxidation treatment with nitric acid appears to be not as successful as the treatment on the activated carbon in terms of gold adsorption. The minerals in this particular ore sample intensify the mechanism complexity linked to the surface chemical modification of carbonaceous material and its capacity for gold adsorption.

5.2 Future work

- Oxidation treatment with chlorine could be considered. After oxidation, remnant ClO^- or Cl^- in solution may combine with free cations forming stable salts interfering with their adsorption on the carbonaceous surface limiting their ability form stable metal aurocyanide complexes on carbon surfaces. However Cl^- has been shown to interfere with AuCN in solution, potentially inhibiting Au adsorption on CM (Miller et al. 2016).
- Since the treatment with nitric acid was problematic in the ore sample, H_2O_2 could be tested as an oxidant. Performing tests with H_2O_2 may determine the optimum conditions for achieving the efficient oxidation
- In order to link the $\text{Au}(\text{CN})_2$ adsorption capacity of carbonaceous matter to porosity modification with the higher level of certainty, mesoporosity, microporosity and total pore volume of the samples also need be investigated.
- As surface chemistry is the key factor for gold adsorption, more evaluation of the surface functional groups such as lactone or quinone will support the importance of surface chemical role. This may be important when evaluating the preg-robbing capacity and potential methods for reduction in other carbonaceous ores.

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