

PREG-ROBBING CARBONACEOUS MATTER: AN EVALUATION OF SURFACE CHEMICAL CONTROL

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ABSTRACT

Gold losses related to carbonaceous matter (CM) during processing are a significant problem in the gold processing industry. Inherent CM in gold ores can behave similarly to activated carbon in its ability to adsorb gold cyanide. This phenomenon is termed preg-robbing as the surface adsorbed gold cannot, for the most part, be recovered. Research has identified that gold adsorption by inherent CM is linked to the specific surface area, pore structure, degree of C disorder and surface functional groups. One of the strategies to inhibit CM preg-robbing prior to leaching is a chemical oxidation; a process linked to modification of the surface functionality. In this study, the variability in gold cyanide adsorption due to oxidation with different reagents has been investigated. Variability in gold cyanide adsorption by CM is examined in relation to structural and surface modifications using TOF-SIMS, XPS and Raman spectroscopy.

KEYWORDS

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

INTRODUCTION

A major obstacle for effective gold recovery during carbon in leach (CIL) or carbon in pulp (CIP) processes carbonaceous gold ores is the presence of carbonaceous matter (c-matter) which has the ability to adsorb, or preg-rob gold from the cyanide leach solution. It can be responsible for poor recoveries as the carbonaceous materials (CMs) within the ore competes with activated carbon used during the leaching and adsorption phase of processing (Cay, 2014). Preg-robbing capacity can vary significantly with mild preg-robbing ores showing adsorption capacities of less than 1 g Au/t ore, while severe preg-robbing ores may have CM with the capacity to preg-rob more than 500 g Au/t ore (Dunne, 2007). Research by a number of groups have shown that the degree of C disorder has some influence on the ability of the carbonaceous material to adsorb $\text{Au}(\text{CN})_2^-$ (Miller et al, 2005, Helm et al, 2009, Hart et al, 2010). It is also apparent the adsorption characteristics of carbonaceous material is affected by changes in surface chemistry (Dimov, 2016).

Various treatment including; flotation to remove the carbonaceous material (Wills, 2010), addition of surface blinding agents (for example kerosene) to passivate or blanket the carbon surfaces (Dimov, 2016), addition of strong adsorbents (eg. activated carbon or resin) to compete with the carbonaceous material and passivation or surface coating by oxidation (pressure, roasting, chlorination and biological oxidation), have been employed prior to leaching in an attempt to minimize the gold losses (Dunne, 2013).

The flotation of the carbon can be problematic as Au potentially associated with the CM and sulphides (possible Au carriers), can result in some gold loss. Also, it requires significant a capital expenditure to build a separate C removal circuit (Cay, 2014; Dunne, 2013). The use of higher than normal proportions of AC is only suitable for ores with low to moderate preg-robbing capacity. The drawbacks of adding kerosene, fuel oil or designed blanking agents, is potential fouling of the activated carbon in pulp (Adam, 2006). This can result in a deleterious decrease in gold recovery (fouling of the AC) and may require more frequent or extensive AC thermal regeneration. Research has shown that oxidation pre-treatments are the most effective processes. Oxidation as a pretreatment can be carried out in a number of ways: a) Pressure oxidation for sulphide oxidation and CM passivation; recommended grain sizes should be smaller than 25 microns and autoclave operated at the temperatures of 225°C or greater. The approach is primarily limited to processing double refractory ores with low preg-rob capacity due to limited oxidation effect on CMs (Simmons, 1995). b) Roasting the refractory ore where oxidation 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 currently being phased out, c) chlorination (gaseous chlorine) and sodium or calcium hypochlorite have been used to remove carbonaceous matter (Adam, 2006). Pitfalls here are the potential to create Au-chlorides which can potentially be lost in the processing, d) bio-oxidation of the CM which requires a significant amount of time making it only suitable for specific installations (Yang, 2013). Currently there are no industrial applications of microbial passivation, however, in China significant research has been performed in this field (Dunne, 2013).

In double refractory ores, oxidation of CM can alter the pore structure, produce a reduction in the potential CM volume and change the relative proportion of surface functional groups. The net result is an overall degradation of the CM producing a less adsorbent surface (passivation) and reducing PR capacity (Helm, 2009) Studies on preg-robbing ores and coal have shown that oxidation of CM results in significant changes to the CM surface chemistry which will affect PR potential. Therefore, the chemical oxidation method involving either oxidizing gases (O_2 , O_3) or oxidizing liquids (HNO_3 , H_2O_2 , ammonium peroxydisulfate, etc.) have the potential to be utilized prior to cyanidation.

This paper presents the initial results from a two-part study initiated to better understand the role of surface functionality in the preg-robbing behavior of carbonaceous material in carbon rich Au ores. It describes an experimental study (part 1) on the effectiveness of activated carbon oxidation by nitric acid to minimize the preg-robbing. The goal of part 1 is to evaluate CM surface chemistry before and after chemical oxidation in order to better link the changes to CM surface functionality to variability in preg-

robbing. The study procedure involves chemical oxidation, adsorption testing, CM analyses using several analytical techniques including UV-Visible spectroscopy, time of flight secondary ion mass spectrometry (TOF-SIMS), Laser Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Sample Preparation

The study was carried out using activated carbon prepared from coconut provided by Alpha-Aesar. The study procedure involves performing several $\text{Au}(\text{CN})_2^-$ adsorption tests prior and after oxidation of activated carbon following the conditions as described at Table 1. All water used was de-ionized and all reagents were Anala-R grade. The oxidation treatment was carried out with the 1 g of sized (75+38 micron) activated carbon per 100 mL 10M HNO_3 (Sigma-Aldrich). The mixture was stirred for 2 hours at 80-90°C. 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 and air dried for 12 hours.

For the adsorption tests, 0.1 g of the sized dried fresh or oxidized activated carbon was added to 15 ml of a 6 mM NaOH solution with 100 ppm Au as $\text{Au}(\text{CN})_2^-$. The samples were then placed on an oscillating table. In order to establish an optimal contact time for adsorption tests were performed at several intervals over a 3 hour period (Figure 1a). The testing indicated that most of the adsorption occurred within a 30-minute contact period.

Table 1. Experimental conditions

Factors	Oxidation treatment	Adsorption test
Size fraction	-75+38 micron	-75+38 micron
Solid/Liquid ratio	1 g/ 100 ml	0.1 g/ 15 ml
Solution concentration	HNO_3	$\text{Au}(\text{CN})_2^-$
	10 Molar	100 ppm
Time	2 hours (stirring with magnet)	30 Minutes
Temperature	80-90 °C	Ambient
Pressure	Ambient	Ambient

The change in amount of $\text{Au}(\text{CN})_2^-$ uptake on the fresh activated carbon (FAC) and oxidized activated carbon (OAC) was analyzed after contact and filtration by Ultraviolet-Visible spectroscopy. Changes to the carbon structure and surface chemistry of the FAC and OAC was assessed on the same sample not subjected to $\text{Au}(\text{CN})_2^-$ loading by Laser Raman Spectroscopy (Raman), Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and X-ray Photoelectron Spectroscopy (XPS).

RESULTS

The gold cyanide adsorption results shows that compared to the fresh activated carbon the gold attachment to the activated carbon surface after oxidation has been significantly decreased (Figure 1).

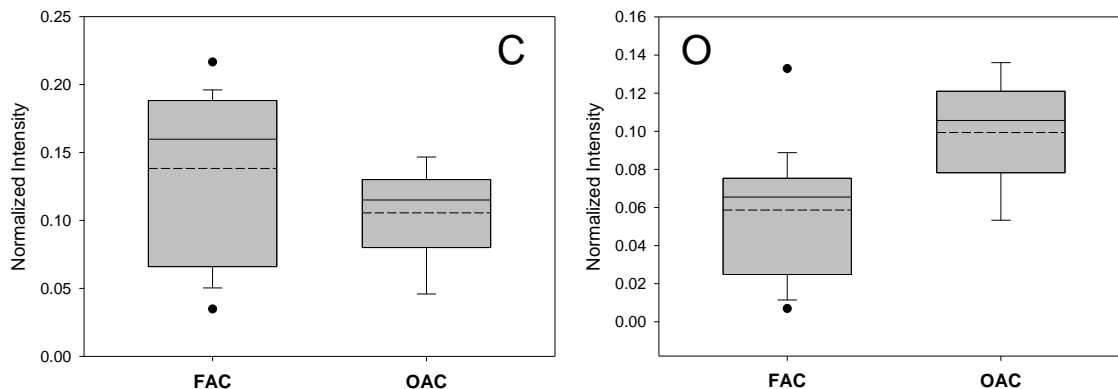


Figure 3. TOF-SIMS surface analyses data. Box plots illustrating the normalized intensity of carbon (C) and oxygen (O) on the surface of fresh activated carbon (FAC) and oxidized activated carbon (OAC).

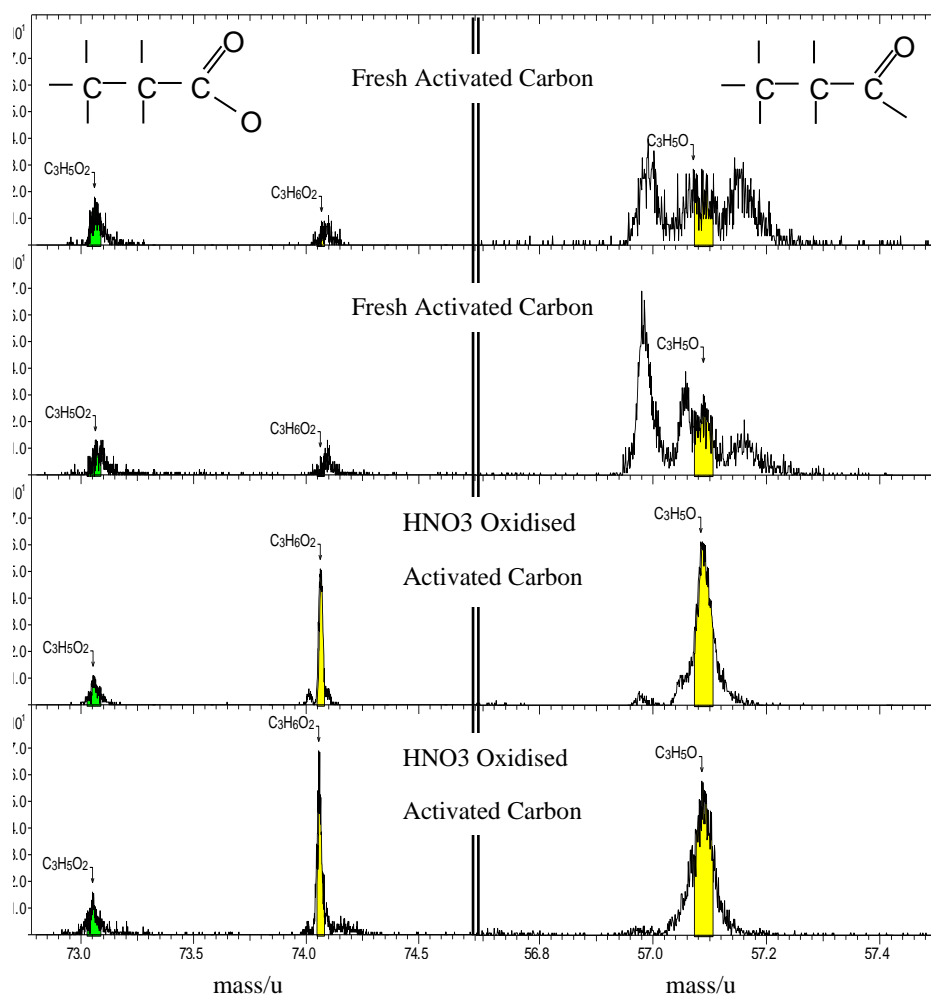


Figure 4. TOF-SIMS spectra in the mass regions of carboxylic acid. The left of the double line shows the peak position for the parent molecule, to the right, first mass fragment (parent -OH).

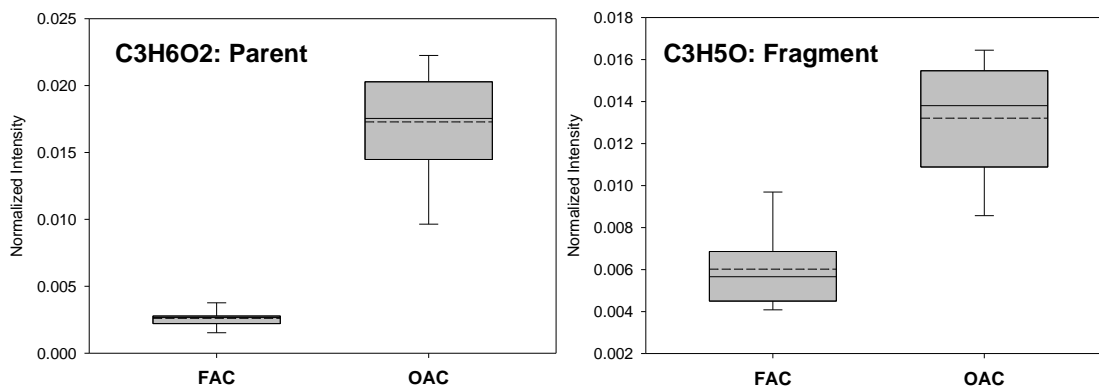


Figure 5. TOF-SIMS surface analyses data. Box plots illustrating the normalized intensity of mass positions representative of the carboxylic parent molecule and the first mass fragment (parent – OH) on the surface of (FAC) and (OAC).

Quantitative XPS analyses results from survey scans shows that the C/O ratio from the fresh activated carbon to the oxidized activated carbon dropped from 13 to 6 (Table 2).

Table 2. XPS determined surface carbon and oxygen content of fresh and oxidized activated carbon

Activated Carbon type	Carbon %	Oxygen %	C:O ratio
Fresh activated carbon	91.1	7.0	13
Oxidized activated carbon	83.9	13.6	6

High resolution XPS spectra collected on the surface of the FAC 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, C-H bonds (Figure 6; Table 3). 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 process. The increase in relative proportion of bonds reflects the development of surface carboxylic acid groups (identified by TOF-SIMS) and lactones. 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 fresh activated carbon surface. The development of carboxylic groups and lactones is also seen (identified by TOF-SIMS) in the relative decrease in of C=C bonds likely reflective of the fresh activated carbon in direct response to oxidation and formation C-O groups (Table 3).

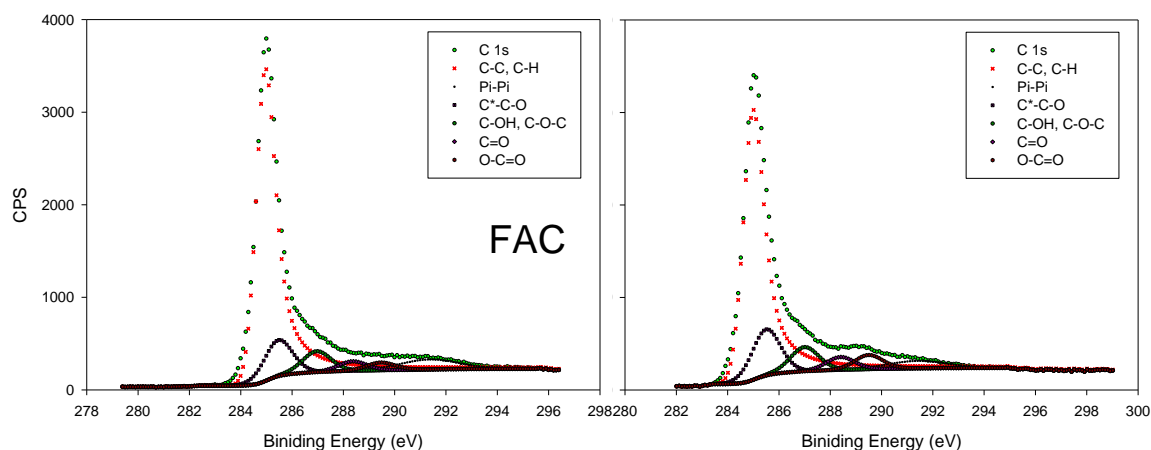


Figure 6. High resolution C 1s XPS spectra showing peak fits and their assignment as measured on the surface of fresh activated carbon (FAC) oxidised activated carbon (OAC).

Table 3. Relative proportion of the assigned peaks as measured by XPS on the surface of (FAC) and (OAC).

%	O-C=O	C=O	C-OH, C-O-C	C-C, C-H	C=C
FAC	3.2	2.6	7.6	1	85.5
OAC	5.3	4.4	8.7	14.1	67.5

DISCUSSION

The oxidation treatment produces a certain amount of oxygen containing surface species such as: carboxyl, lactones, phenols, ketones. The XPS and TOF-SIMS surface analysis of HNO_3 oxidized CM identified a significant decrease in the C:O ratio combined with an increase in the relative proportions of O-C=O, C=O, C-OH and C*-C-O bonds all representing the development of carboxylic acid surface groups. Research by other groups (Moreno-Castilla, 1996; Jaramillo, 2010) have identified similar surface chemical responses as a result of activated carbon oxidation. This research has established the link between the change in surface chemistry and the decrease in $\text{Au}(\text{CN})_2^-$ adsorption. The relative contribution of a potential pore volume decrease or surface area increase, needs still be established however the adsorption decrease appears to be at least partially in response to the increased proportion of acidic surface functional groups. In light of this, it is possible that the preg-robbing capacity of carbonaceous Au ores, which show a departure from the CM structural trend, may similarly be influenced by the surface functionality of the CM. Research from observations made regarding this particular phenomenon is currently underway. Various carbonaceous Au ores showing preg-robbing response based on the CM structural trend will be evaluated in response to oxidation of the carbonaceous components by HNO_3 .

CONCLUSIONS

Oxidation of activated carbon by HNO_3 :

- Resulted in a reduction in preg-robbing
- Did not change the degree of C disorder in the activated carbon
- Resulted in the decrease in the surface C:O ratio
- Increased the content of acidic oxygen surface groups identified as carboxylic acid groups

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