

Chapter 32

FUNDAMENTAL ASPECTS OF GOLD CYANIDE ADSORPTION ON ACTIVATED CARBON

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ABSTRACT

The carbon-in-pulp process for gold processing depends on the adsorption of dissolved $\text{Au}(\text{CN})_2^-$ from solution onto activated carbon. Our work shows that coconut and peat based carbons have the same mechanism and kinetics of adsorption. There is no contribution to the bonding from carbon-oxygen functionalities on the carbon surface, as has been invariably supposed in all previous theories for the mechanism of the reaction. It is shown that $\text{Au}(\text{CN})_2^-$ is reversibly adsorbed intact on, and parallel to, the graphitic planes of the carbon. The physicochemical basis of the measurement of carbon reactivity for gold adsorption is discussed.

INTRODUCTION

The Carbon-in-Pulp (CIP) gold processing technology has enabled a rapid, world-wide growth in gold production. As a result, gold is one of the few winners for the mining industry in the 1980's. The key step in the CIP technology is the adsorption of the gold(I) dicyanide ion, $\text{Au}(\text{CN})_2^-$, onto coarse carbon granules. This adsorption mechanism has been studied since at least 1909 and a number of quite different theories for this step have evolved (Bansal et al., Chapter 6.8, 1988) supposing one of the following essential steps in the process: 1) reduction of $\text{Au}(\text{CN})_2^-$ to Au, 2) adsorption of neutral metal cation-gold(I) dicyanide anion pairs, 3) decomposition of $\text{Au}(\text{CN})_2^-$ to AuCN, 4) adsorption of $\text{Au}(\text{CN})_2^-$ onto charged carbon-sites with partial reduction of $\text{Au}(\text{CN})_2^-$ to cluster-type species; or 5) involving a redox-mechanism in which specific sites on the carbon are oxidized to form a positive site for $\text{Au}(\text{CN})_2^-$ adsorption with a concomitant reduction of quinone sites on the carbon surface (Hughes et al., 1984).

These gold adsorption theories invariably assume that carbon-oxygen surface structures play a direct role in the mechanism. Oxygen is located on the edges of the graphitic planes located randomly on the pore-surfaces of activated carbon and forms specific C-O functionalities such as quinone/hydroquinone, carboxylic acid, chromene etc., although there has not been full characterization of these structures to date.

Conclusive proof of each proposed mechanism has hitherto been lacking but one interesting result is the demonstrated effect of the presence of oxygen on carbon on the gold loading of Norit R2020, which is a peat-based extruded CIP carbon. This result was interpreted as an oxidative reaction in which AuCN was formed, but the applicability of this mechanism to coconut shell carbon was unclear (Tsuchida and Muir, 1986). Similarly, there is no consensus on the factors which determine the carbon-gold adsorption reactivity in a CIP plant and the selection of carbons for use in CIP plants has no broad scientific basis.

We have therefore studied the fundamental aspects of gold adsorption on activated carbon. In this paper we describe $\text{Au}(\text{CN})_2^-$ adsorption/desorption in alkaline solution. Direct X-ray photoelectron spectroscopy (XPS) was used to confirm the state of adsorbed gold on typical coconut shell and extruded peat-based CIP carbon and we discuss the physicochemical basis of the measurement of carbon reactivity for gold adsorption.

EXPERIMENTAL

The procedure for gold adsorption, desorption and kinetic experiments was the same as previously described (Jones et al., 1988).

Norit R2520 and RO3515 are extruded peat-based carbons and samples were ultrasonically water washed of fines to obtain reproducible results for the specific gold loading rate. Calgon GRC22 is a granular coconut shell carbon and was prewashed in 1 M HF - 1 M HCl, followed by extensive ultrasonic water washing and storage in vacuo; but for this carbon, these preconditioning steps had no influence on the specific gold adsorption rate.

XP spectra were obtained using a VG ESCALAB Mk II with MgK_α radiation. The state of adsorbed gold cyanide was inferred from the measured Au 4f and N 1s photoelectron peaks recorded and calibrated as described elsewhere (Klauber, 1988).

RESULTS AND DISCUSSION

Solution Adsorption/Desorption Studies

In a 24 hr. interval, adsorption capacity measurements correspond to an adsorption equilibrium with carbon surfaces accessible via macropores. A key observation is that $\text{Au}(\text{CN})_2^-$ adsorption on carbon is thermodynamically reversible in the absence of CN^- ions in solution, as demonstrated over 7 orders

of magnitude for $[\text{Au}(\text{CN})_2^-]$ (Jones et al., 1988). The same pattern was found when gold adsorbed at 30°C was eluted from the carbon by soxhlett extraction at 95°C. In this test, the carbon was presoaked in cyanide-free alkaline solution and soxhlett extracted over 24 hr. At 95°C, gold desorbs because the adsorption step is exothermic. Subsequently, the test was repeated after presoaking the carbons in 5% NaCN/10% NaOH. The elution efficiency is shown in Table 1 and proves that cyanide ion has no effect on the gold recovery from peat or coconut derived carbon (the residual gold on the carbons in these tests at 95°C would represent the equilibrium isotherm value).

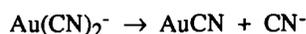
Table 1

% Gold elution efficiency after soxhlett extraction at 95°C from carbons loaded to 20 wt% after presoaking in basic electrolytes.

Electrolyte	Calgon GRC22	Norit R2520
Cyanide-free basic solution*	87	87
5% NaCN/10% NaOH	83	88

*either pH 10, ionic strength 0.1M borate buffer or 10% NaOH.

The absence of any effect of CN^- on the reversibility of adsorption/desorption and on the high elution yields is compelling evidence that no Au-CN bond is broken in the adsorption step. If such a bond was broken, for example, by the proposed reaction on the carbon surface (Tsuchida and Muir, 1986):



then surface CN^- would either desorb from the carbon or be destroyed by surface oxidation, ultimately to NH_3 and CO_3^{2-} . Therefore, since AuCN is insoluble in cyanide-free solution (Anon, 1976) reversible desorption/elution would only be possible in cyanide-containing electrolytes. Similar arguments rule out the supposed presence of Au on the carbon surface. Our experimental facts therefore demonstrate that $\text{Au}(\text{CN})_2^-$ does not undergo any change in structure in the adsorption step.

Gold adsorption on activated carbon appears to be ultimately limited by the solution solubility of $\text{KAu}(\text{CN})_2$ rather than the supply of active carbon sites. Gold loadings of several mmol/g can be readily achieved (Jones et al., 1988) with an extrapolated value of 3 mmol/g (60 wt%) for coconut carbon Calgon GRC22 in 1M $\text{KAu}(\text{CN})_2$ solution (30°C, pH 10). These high values are at odds with the theoretical requirement (Bansal, et al. Chapter 6.8, 1988) that the C-O functionalities on the carbon surface are involved in the adsorption mechanism. The theories all require that the C-O site has an equimolar participation with each mole of adsorbed gold and that it is capable of interaction with H^+ and OH^- . The reported total C-O concentrations in typical CIP carbons measured by pH-titration only give total C-O concentrations in the range 0.05-1 mmol/g (Parentich and Kinsella, 1984). These values are clearly too low not only for the present gold adsorption results but also for the value of ~0.3 mmol/g reported by Tsuchida and Muir (1986) for as-received peat carbon Norit R2020.

XPS Studies

Because much higher carbon-site concentrations are required than available from C-O functionalities on CIP carbons suggests that the graphitic planes, which make up the bulk of the carbon surface, are involved in the gold adsorption mechanism. XPS was used to further investigate this mechanism and Figure 1 shows the observed N 1s and Au 4f peaks for gold adsorbed on coconut and peat-based carbons. These spectra demonstrate conclusively that the state of gold is the same for each type of carbon, in agreement with the solution adsorption/desorption studies described above. The stoichiometry of the adsorbed species was confirmed as Au:CN = 1:2 using the relative areas of N 1s and Au 4f peaks. The spectra show that coconut and peat derived carbons have the same surface geometry for the adsorbed gold species.

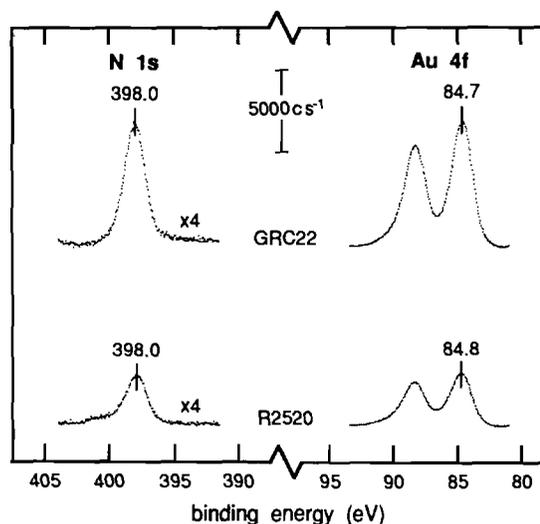


Figure 1. N 1s and Au 4f photoelectron peaks for Calgon GRC22 (gold content 40 wt%) and Norit R2520 (gold content 20 wt%) for gold adsorption from cyanide-free pH10 borate/KCl buffer at 30°C.

The N 1s state is sensitive to the local site environment on the carbon as previously demonstrated when the effect of H^+ on the structure of the adsorbed gold species on carbon was explored (Klauber, 1988). The fact that the N 1s spectrum consists of a single, sharp peak with the same electron binding energy for both carbon types shows that the terminal N atoms in the linear ionic structure $(\text{N}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{N})^-$ experience the same chemical environment on the surface of each carbon. This confirms directly that the geometry of the adsorbed $\text{Au}(\text{CN})_2^-$ species therefore cannot involve C-O centres, because this would result in an asymmetric surface binding state for N. The only alternative adsorption geometry consistent with the symmetry of the N state found for both carbon-types is an interaction between the central gold atom and the graphitic structure, as shown in Figure 2. The geometry of the graphitic plane provides an excellent match to the structure of the $\text{Au}(\text{CN})_2^-$ ion and there is a weak carbon to gold π -donor bond which holds the ion onto the carbon surface. The cations in the system (Na^+ , K^+) coadsorb non-specifically at the carbon-solution interface and do not form identifiable ion pairs $[\text{M}^n+][\text{Au}(\text{CN})_2^-]_n$ on the carbon surface as suggested by McDougall (1988), since this geometry would also remove the observed symmetry of the N interaction.

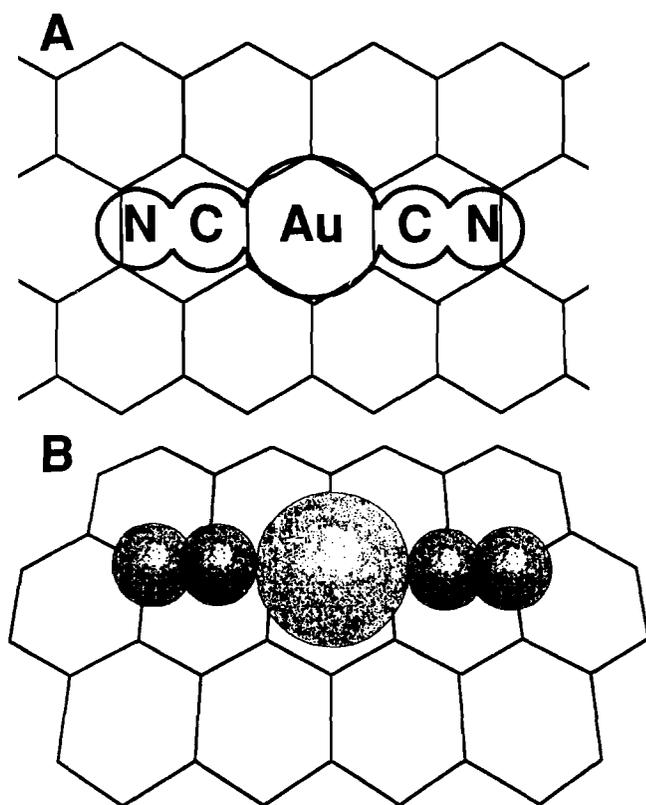


Figure 2. Adsorption geometry of $\text{Au}(\text{CN})_2^-$ on a graphitic plane: A) Geometric match; B) 3-dimensional artistic impression. Sizes are based on the atomic radii for Au, C and N in relation to the graphitic ring size.

The present work on the adsorption mechanism of gold on both coconut and peat-based carbon identified that the most relevant characteristic of activated carbon for gold adsorption in a CIP operation is a high concentration of accessible graphitic planes. The previously reported 50% reduction in the gold adsorption capacity of deoxygenated peat-based carbon (Tsuchida and Muir, 1986) is evidently due to a decreased wetting of the carbon pores since deoxygenation increases the hydrophobicity of the carbon surface. C-O functionalities are not involved in the adsorption mechanism of $\text{Au}(\text{CN})_2^-$ and there is no intrinsic degeneration of the carbon surface as a result of gold adsorption on the carbon surface. Thus, there is no fundamental reason why carbon has to be regenerated in a clean CIP plant, as has been supposed (Muir, 1987).

Carbon Gold Loading Reactivity Measurement

Experimentally, carbon gold loading reactivity is best obtained from a measurement of the initial reaction rate in a baffled batch reactor. The solution should be stirred rapidly to eliminate rate-control by mass-transport of $\text{Au}(\text{CN})_2^-$ to the external surface of the highly reactive activated CIP carbons. In this work, stirring of at least 2000 rpm was required to eliminate diffusion-control in the solution film surrounding the carbon particle. For these conditions, the specific carbon reactivity can be obtained from a first-order expression describing the heterogeneous kinetics of the surface reaction:

$$R = k[\text{Au}(\text{CN})_2^-] \quad \dots(1)$$

where R = gold adsorption rate ($\text{mol g}^{-1}\text{s}^{-1}$) and k ($\text{L g}^{-1}\text{s}^{-1}$) a measurement of the carbon gold loading reactivity. This relationship is demonstrated in Figure 3 showing the initial rate of gold adsorption over at least two orders of magnitude of $[\text{Au}(\text{CN})_2^-]$ for Calgon GRC22.

Equation (1) also holds for batch adsorption on fresh Calgon and Norit carbon for a carbon concentration $\sim 1 \text{ gL}^{-1}$ from CIP-grade gold solutions (e.g. 5 mgL^{-1} concentration) and at least 80% of the gold can be stripped from the solution in such a test without any deviation of the data from equation (1). Lower gold solution concentrations result if the batch-reaction is followed beyond about 1 hr., but for this condition the apparent carbon reactivity decreases continuously because the equilibrium position in the more dilute solution is rapidly approached at such reaction times. To treat this variation requires an equation of the form (Jones et al., 1988):

$$k = k_0[\Gamma_{(\text{eq})} - \Gamma] \quad \dots(2)$$

where Γ (mol g^{-1}) is the gold loading on the carbon and $\Gamma_{(\text{eq})}$ the isotherm value ultimately attained in the experiment. k_0 is a true kinetic measurement of the carbon gold adsorption. However, k_0 is reduced by about one magnitude in the presence of pulp particles (Jones et al., 1988). Although the mechanism of this effect has been identified (Jones and Linge, 1987) there is no available mathematical relationship for the effect and prediction of gold loading rates in a CIP plant requires experimental measurements in the presence of pulp in the reactor.

Previously, Davidson et al. (1982) also recommended that carbon reactivity be tested in a baffled reactor but the authors did not stress that the solution stirring rate dependence of gold adsorption needs to be eliminated from the measurement to ensure that solution mass transport did not control the rate. The authors proposed evaluation of the carbon reactivity from a linear plot of t/Γ versus t (t =time). The full fundamental basis of this equation is unknown and in this work plots of data in this form have always produced curves.

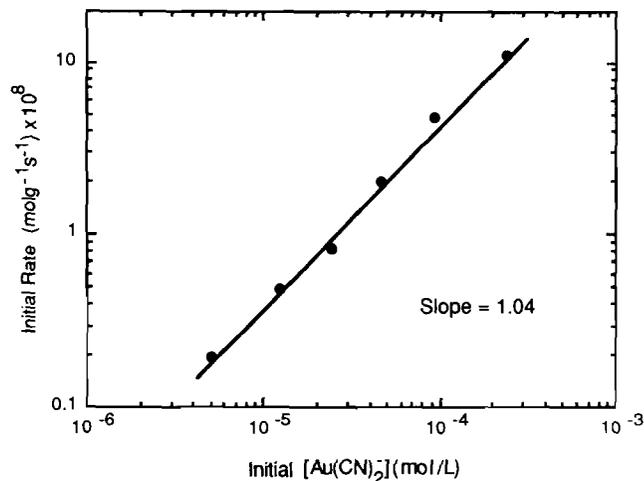


Figure 3. Initial rate of gold adsorption on Calgon GRC22 versus initial gold solution concentration in a baffled reactor for solution stirring of 2000 rpm at 30°C in pH10 borate/KCl buffer. (Note conversion factors: $10^{-11} \text{ mol g}^{-1}\text{s}^{-1} = 7 \text{ gt}^{-1}\text{hr}^{-1}$; $10^{-5} \text{ mol L}^{-1} = 2 \text{ mgL}^{-1}$)

The Mintek-equation involves a plot of $\log \Gamma$ versus $\log t$ and was initially proposed for the analysis of the adsorption rate when the gold solution concentration was constant in the test; but again, these plots curve unless a restricted time interval is chosen for the analysis (Jones et al., 1988).

In Australia, the Murdoch equation (Muir, 1987) has been vigorously promoted for assessing the gold loading reactivity of carbons (Muir 1987, Avraamides 1988a). The Murdoch equation has the same form as the Mintek equation but the gold solution concentration is treated as a variable. Thus, for batch adsorption tests, plots of $\log(\Gamma/[Au(CN)_2^-])$ versus $\log t$ are tested but we have not been able to produce linear plots from our data using this test (Jones et al., 1988).

The Murdoch equation has usually been used for analysing gold adsorption on CIP carbons in rolling bottles (La Brooy and Bax, 1985; Avraamides, 1988a). It has been shown (Hughes and Linge, 1988) that rolling bottles do not provide sufficiently rapid solution mass transport of $Au(CN)_2^-$ to CIP carbon and that the measurement is therefore unable to distinguish the reactivity difference of different reactive carbons. Bottle rolling tests are thus unsuitable to evaluate the reactivation efficiency of kilns, as has been presumed (Avraamides, 1988b). For mass transport controlled gold adsorption tests, the main response difference of different carbons is the specific external carbon surface area, and in the bottle rolling tests the reactivity response of different carbons therefore varies inversely with the carbon particle diameter, as has been observed (Muir, figure 5, 1987).

The Murdoch equation returns apparent first-order rate constants which do not fit the measured half-life ($\ln 2/k$) of the reaction. For example, for bottle rolled Calgon GRC22 the observed half life in the test is about 1.4 hr. whereas the Murdoch equation rate constant is quoted as 1100 hr.^{-1} (La Brooy and Bax, figure 2, 1985) and this inconsistency is confusing.

Users of the Murdoch equation fail to recognize that in a batch test gold adsorption stops when the equilibrium isotherm conditions prevail and this equation is thus fundamentally unsound as a basis of a carbon gold adsorption reactivity assessment.

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REFERENCES

- Anon, 1976, Entry 4358, The Merck Index, M. Windholz editor, Merck and Co. Inc. Rahway N.J. USA. 9th edition, p 586.
- Avraamides, J., 1988a. Selection and testing of activated carbon for gold recovery, Randol Perth International Gold Conference, pp. 261-267.
- Avraamides, J., 1988b. Principles and practice of thermal carbon regeneration, Randol Perth International Gold Conference, pp 294-296.
- Bansal, R.C., Donnet, J.B. and Stoeckli, F., 1988. Active Carbon, (Marcel Dekker, Inc. New York).
- Davidson, R.J., Douglas W.D. and Tumilty, J.A., 1982. The selection of granular activated carbon for use in a carbon-in-pulp operation, In: Carbon in Pulp Technology for the Extraction of Gold, Aus.I.M.M. Parkville, Vic. Australia, pp 199-218.
- Hughes H.C., Muir D.M., Tsuchida N., and Dalton R., 1984. Oxidation reduction potential of activated carbon during anion loading, In: Gold Mining, Metallurgy and Geology, Aus.I.M.M. Regional Conference, Kalgoorlie, Paper 7, Metallurgy Section.
- Hughes, H.C. and Linge H.G., 1988. The kinetics of gold loading from gold(III) chloride solution onto fresh activated coconut carbon, Hydrometallurgy (in press).
- Jones, W.G., and Linge, H.G., 1987. Effect of ore pulp on the adsorption rate of gold cyanide on activated carbon, Aus.I.M.M. Regional Conference, Kalgoorlie and Hydrometallurgy (in press).
- Jones, W.G., Klauber, C. and Linge, 1988. The adsorption of $Au(CN)_2^-$ onto activated carbon, Randol Perth International Gold Conference, pp 243-248.
- Klauber, C., 1988. Acid induced oligomerization of aurocyanide adsorbed on carbon, Surface Science, 203:118-1298.
- La Brooy, S.R., and Bax, A.R., 1985. The fouling of activated carbon by organic reagents, In: Innovation in the Process and Resource Industry, Proc 13th Aust. Chemical Engineering Conference, Perth, E.A. Books, St Leonards, NSW, pp 187 -191.
- McDougall, G.J., 1988. The mechanism of gold cyanide onto activated carbon, Randol Perth International Gold Conference, pp 249-252.
- Muir, D.M., 1987. Recent developments in gold metallurgy from an Australian perspective, Bull Proc. Aus.I.M.M., 292:87-97.
- Parentich, A. and Kinsella, B., 1984. Titrimetric studies on activated carbon, In: Gold Mining, Metallurgy and Geology, Aus.I.M.M. Regional Conference, Kalgoorlie, Paper 6, Metallurgy section.
- Tsuchida, N. and Muir, D.M., 1986. Studies on role of oxygen in the adsorption of $Au(CN)_2^-$ and $Ag(CN)_2^-$ onto activated carbon, Metallurgical Transactions B, 17B:529-533.