

**Reversible and irreversible adsorption of gold  
from cyanide solutions onto carbonaceous adsorbents  
measured by flow microcalorimetry**

J. Zając\*

*Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques  
Université des Sciences et Techniques du Languedoc  
pl.E.Bataillon, 34095 Montpellier Cedex 05, France*

The thermodynamic reversibility of gold adsorption on carbonaceous adsorbents from aqueous solutions of potassium aurocyanide at room temperature has been studied. A flow adsorption microcalorimetry method was used to measure the amounts of aurocyanide adsorbed and desorbed in one adsorption-desorption cycle, as well as the corresponding integral molar enthalpies, at a  $\text{KAu}(\text{CN})_2$  concentration of  $5 \text{ mmol L}^{-1}$  for a graphitised carbon black (Graphon), three coconut-based active carbons (G209, G210, AC3) and two G210 samples subjected to chemical pre-treatments with 30 mass% hydrogen peroxide solution and 0.5 M solution of hydroquinone. For active carbon G210 the adsorption experiments were carried out with five types of solvent: deionised water, aqueous phase with pH 11.5 adjusted by the addition of KOH, 0.01 M KCl or 0.0033 M  $\text{CaCl}_2$  aqueous solutions, and a 5 mass% solution of ethanol in water. Based on the adsorption and enthalpy values obtained in adsorption and desorption cycles, estimates could be made of the reversible and irreversible contributions to the total adsorption capacity and the integral molar enthalpy of adsorption. With deionised water used as a solvent, the degree of adsorption irreversibility ranges from 25% for Graphon to 61% for the most polar active carbon AC3. The irreversible and reversible enthalpy components have values of about  $-50 \text{ kJ mol}^{-1}$  and  $-25 \text{ kJ mol}^{-1}$ , respectively. Treatment of active carbon G210 with hydrogen peroxide or hydroquinone in a liquid stream at room temperature leads to the neutralisation of all active sites responsible for irreversible adsorption. For this active carbon, the degree of irreversibility changes with the addition

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\* Permanent address: Wydział Paliw i Energii, Akademia Górniczo-Hutnicza, Al. Mickiewicza 30, 30-059 Kraków, Poland.

of various substances to the adsorption medium and is as follows: 44% in deionised water, 51% in 0.01 M KCl solution, 63% in 0.0033 M  $\text{CaCl}_2$  solution, and 46% in 5 mass% ethanol solution. These results suggest that the aurocyanide is extracted as  $\text{Au}(\text{CN})_2^-$  by an anion-exchange mechanism and as an ion-pair or neutral molecule  $\text{M}^{\text{nt}}[\text{Au}(\text{CN})_2^-]_n$  by physical adsorption at the various edge defects in the graphite crystal structure of the carbon surface.

## 1. INTRODUCTION

The recovery of gold using active carbons to concentrate the gold by preferential adsorption from cyanide leach liquors is widely used on a commercial basis [1]. However, the very small gold adsorption capacity of the commonly used active carbons is a serious drawback of the method since it greatly reduces the efficiency of gold extraction. It is clear that the accessibility of the microporous carbon structure to gold adsorption is very limited and that only a small proportion of the total surface area of active carbons adsorbs gold from dilute aqueous solutions. There is still considerable scope for improving the current understanding of the adsorption mechanism. In particular, it is necessary to characterise the important carbon interfacial properties relevant to gold adsorption and also to relate carbon structure to the dynamics, kinetics and selectivity for gold adsorption. Further advances could lead to the production of a carbon with improved gold adsorption capacity and faster extraction kinetics.

Very extensive fundamental studies have been performed on the subject over the years and a number of mechanisms have been proposed in the literature [2]. It is difficult to attain a consensus of opinion on the real mechanism of gold adsorption because the phenomenon is simultaneously influenced by too many factors, which are not easy to assess and control. The confusion which exists in the literature may to a great extent be ascribed to the fact that investigations are often conducted from solutions of different compositions and on poorly defined substrates. The current knowledge concerning surface chemistry of carbon adsorbents is by no means complete and many problems have not yet been satisfactorily solved. In these circumstances, different interpretations of the results are possible. Furthermore, the possibility that gold is extracted by carbon via different adsorption pathways under different experimental conditions cannot be completely excluded.

The prevailing current view is that the mechanism of gold loading on active carbons from aqueous solutions of potassium or sodium aurocyanide involves adsorption of the aurocyanide complex without any chemical change. This may include adsorption of unpaired aurocyanide anions,  $\text{Au}(\text{CN})_2^-$ , and adsorption of  $\text{M}^{\text{nt}}[\text{Au}(\text{CN})_2^-]_n$  as an ion-pair or as a neutral molecule, with  $\text{M}^{\text{nt}}$  depending



on the pH, electrolyte content of the bulk phase, or ash content of the carbon. Sometimes the cation and anion of the neutral ion-paired species are believed to adsorb at separate nearby sites. There is much controversy about the nature of the adsorption sites in carbon adsorbents. Some researchers have concluded that the adsorption of aurocyanide involves oxygen functionalities in the carbon structure [3-6]. The identity of these polar groups, which are produced during the formation of active carbons by oxidation and activation of various carbonaceous materials, remains a mystery. It is often emphasised that the most desirable polar sites should have a basic character. Among those explicitly suggested are carbonium or oxonium cationic sites related to the chromenol or benzopyran groups on the carbon surface [2,3]. Since the surface oxides taking part in aurocyanide adsorption are not known with certainty, another view is that most of the favoured sites are localised either on the graphitic basal planes [7-9] or at edge defects in the graphite structure [10].

In previous work [11], a two-stage adsorption model has been proposed to describe the adsorption of gold complexes on a coconut based active carbon from a solution of  $\text{KAu}(\text{CN})_2$  in deionised water at initial pH 6 and at 298 K. Gold cyanide adsorption follows two mechanisms, one irreversible which is present at all concentrations, and one reversible which occurs only when the equilibrium concentration of aurocyanide becomes sufficiently high. In both cases, the adsorbed species is most likely the aurocyanide complex, which does not undergo a chemical change. Irreversible adsorption has been found to be accompanied by an increase in pH of the aqueous phase and a release of chloride ions into the bulk solution. The potassium counterion remains in solution at this stage. As the loading of gold on the carbon surface is increased, the electrophoretic mobility of charged carbon particles does not change at all. This leads to the postulate that the adsorbate is an aurocyanide anion and that a large part of these ions are extracted by anion-exchange with  $\text{Cl}^-$  ions. Interpretation of the increase in pH is somewhat ambiguous because several different adsorption pathways may produce this effect (e.g., adsorption of  $\text{Au}(\text{CN})_2^-$  at positively charged surface sites accompanied by surface charge regulation, direct ion-exchange between  $\text{Au}(\text{CN})_2^-$  and  $\text{OH}^-$ , or chemisorption of  $\text{HAu}(\text{CN})_2$  by basic oxides on the carbon surface [3,4,11]). Reversible adsorption is thought to be a physisorption of neutral  $\text{KAu}(\text{CN})_2$  species. Here an equimolar amount of aurocyanide anion and potassium cation has been observed to adsorb over the related concentration range.

It is obvious that the determination of the reversible and irreversible adsorption capacities of carbon adsorbents may be of great importance to the estimation of their practical performance. The present paper describes application of flow adsorption microcalorimetry to study the reversibility of gold adsorption on graphite, graphitised carbon black, and some active carbons



in different aqueous media at room temperature. This method has already been shown to be a reliable and fast procedure to measure simultaneously the enthalpy changes and amounts of adsorption in flow adsorption systems and has been successfully used to quantify the reversible and irreversible adsorption components [12-16]. Moreover, similar calorimetry equipment allows determination of the specific areas of surface sites having certain common chemical characteristics in a variety of carbonaceous and mineral adsorbents [17,18]. It has been used in this study to obtain estimates of the polar and accessible basal plane surface areas in the carbon adsorbents. Nevertheless, the exact chemical nature of the carbon surface sites responsible for aurocyanide adsorption has not been addressed.

## 2. MATERIALS AND EXPERIMENTAL METHODS

G209 and G210, two commercial active carbons with BET  $N_2$  surface areas of 1118 and 1150  $m^2 g^{-1}$ , respectively, were supplied by PICA (Vierzon, France). They were derived from coconut shells and prepared by physical activation with water vapour at 1173 K. Their analytical properties have been reported previously [11,19]. For example, the micropore volume for both samples is about 0.27  $cm^3 g^{-1}$ , and the meso/macropore volume is: 0.38  $cm^3 g^{-1}$ , G209; 0.34  $cm^3 g^{-1}$ , G210. Random samples of the carbons were sieved to obtain 40- to 400- $\mu m$  diameter fractions.

Graphitised carbon black (Graphon), well-ordered natural graphite flakes (SP-1 graphite), and another coconut-based powdered active carbon (AC3) were kindly supplied by Dr A. J. Groszek (Microscal Ltd., London). They had BET surface areas of 82, 2, and 1010  $m^2 g^{-1}$ , respectively.

Water used in the adsorption experiments was deionised and purified with a Millipore Super Q system. Ethanol, *n*-heptane, *l*-butanol and *n*-dotriacontane were Aldrich HPLC grade materials with a purity exceeding 99%. Pure potassium dicyanoaurate was supplied by Métaux-Précieux-Industrie (Bagneux, France). All other inorganic chemicals were of ACS Reagent grade.

Potentiometric titrations were performed in Chemical Department of the New York City College with the use of a 665 Dosimat (Brinkmann) combined with a Accumet pH meter model 50 equipped with a combination glass electrode (Corning) [20]. Prior to titration experiment, solid samples of about 0.1 g in 50 mL of a 0.01 N  $NaNO_3$  solution were placed in a thermostated container and equilibrated overnight. The solid suspension was stirred during experiment and a slow stream of nitrogen passed over the sample in order to eliminate the influence of atmospheric  $CO_2$ . Standardised 0.1 N solutions of NaOH and  $HNO_3$  were used as titrants. The titration curves were transformed into proton binding isotherms and the proton affinity distributions were

subsequently calculated basing on the numerical procedures detailed elsewhere [21,22].

Figure 1 shows proton affinity distributions calculated for three active carbons (G209, G210, AC3). It should be noted in general that each sample possesses a variety of surface acidic groups. G209 and G210 have very similar surface properties within the experimental pH range (between 3 and 10). Both carbons contain significant amounts of stronger and moderate surface acids with pK ranging between 5.5 and 7.5. For example, the pK value of 5.8 is usually attributed to a carboxylic group. Some quantitative differences may be ascribed to different proportions between the corresponding acidic groups. In comparison with these two active carbons, AC3 contains much more surface sites with relatively strong (pK 4.5 – 5.2) and relatively weak (pK 8.4 – 9.1) proton-donating power to water. Such distributions may be used in conjunction with other techniques for the identification of surface chemical groups. This would provide significant characterisation of the acid-base properties of carbon surfaces. Nevertheless, it is beyond the scope of this paper to assign the observed peaks to particular chemical species.

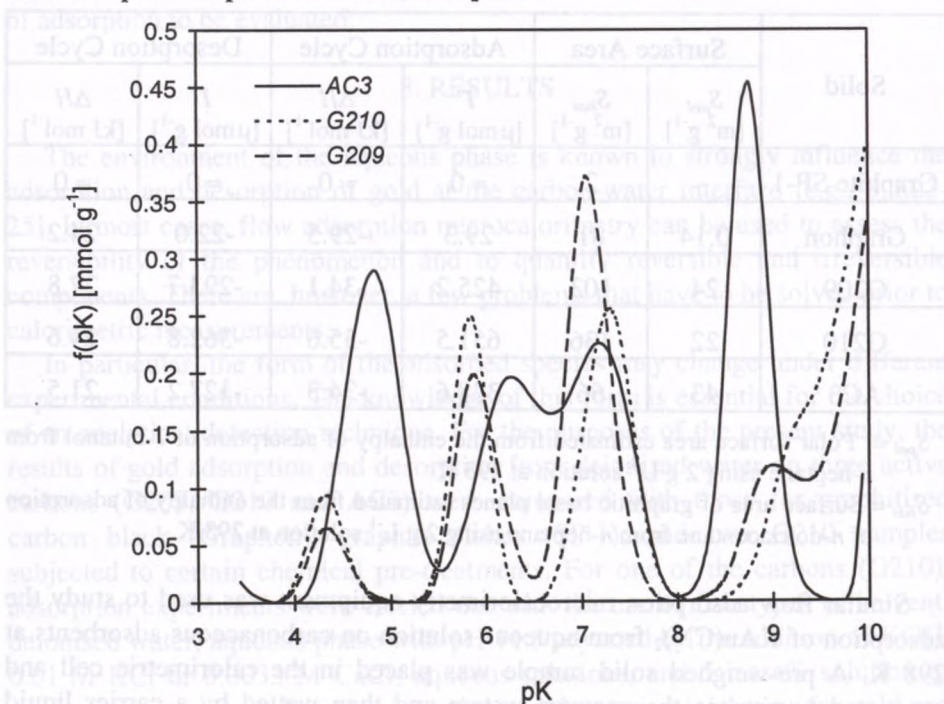


Figure 1. Distributions of surface acidity constants for samples of active carbons G209, G210 and AC3



The enthalpy changes accompanying interfacial phenomena were determined using a Mark IV Microcal Flow Microcalorimeter. The Flow Microcalorimeter itself has been described previously [12]. The area of polar sites on the surfaces of powdered carbonaceous adsorbents was estimated from the enthalpies of *l*-butanol adsorption from *n*-heptane, the relationship between the surface area and the enthalpy value being  $6.7 \text{ m}^2 \text{ J}^{-1}$ . The graphitic character of the surfaces was investigated by determining the preferential adsorption of *n*-dotriacontane from *n*-heptane solution. The relationship between the basal plane surface area and the related enthalpy of displacement was equal to  $19.3 \text{ m}^2 \text{ J}^{-1}$ . A detailed description of the experimental procedure and the principles of the flow calorimetric method can be found in papers [17,18]. The resulting values of polar surface area,  $S_{pol}$ , and basal plane surface area,  $S_{bas}$ , are given in the first two columns of Table 1.

Table 1. Important carbon surface parameters relevant to aurocyanide adsorption and results of adsorption-desorption cycles for the carbonaceous adsorbents used in the study (adsorption from  $5 \text{ mmol L}^{-1}$  solution of  $\text{KAu}(\text{CN})_2$  in deionised water at 298 K)

Solid	Surface Area		Adsorption Cycle		Desorption Cycle	
	$S_{pol}$ [ $\text{m}^2 \text{ g}^{-1}$ ]	$S_{bas}$ [ $\text{m}^2 \text{ g}^{-1}$ ]	$\Gamma$ [ $\mu\text{mol g}^{-1}$ ]	$\Delta H$ [ $\text{kJ mol}^{-1}$ ]	$\Gamma$ [ $\mu\text{mol g}^{-1}$ ]	$\Delta H$ [ $\text{kJ mol}^{-1}$ ]
Graphite SP-1	-	2	$\approx 0$	$\approx 0$	$\approx 0$	$\approx 0$
Graphon	0.14	81	29.3	-29.5	-22.0	24.2
G209	24	103	425.2	-34.1	-293.7	27.8
G210	22	136	651.5	-35.6	-362.8	24.6
AC3	43	66	328.6	-34.3	-127.2	21.5

$S_{pol}$  = Polar surface area estimated from the enthalpy of adsorption of *l*-butanol from *n*-heptane using  $2 \text{ g L}^{-1}$  solution at 293 K

$S_{bas}$  = Surface area of graphitic basal planes estimated from the enthalpy of adsorption of *n*-dotriacontane from *n*-heptane using  $2 \text{ g L}^{-1}$  solution at 293 K

Similar flow adsorption microcalorimetry equipment was used to study the adsorption of  $\text{KAu}(\text{CN})_2$  from aqueous solution on carbonaceous adsorbents at 298 K. A pre-weighed solid sample was placed in the calorimetric cell and evacuated *in situ* via the vacuum system and then wetted by a carrier liquid (i.e., solvent) supplied at a constant rate of  $3 \text{ mL h}^{-1}$  from a syringe pump. For active carbons, the carbon sample was mixed with PTFE powder so as to shorten the time of adsorption and desorption. Once a steady baseline had been obtained, the flow of carrier fluid was switched to the  $5 \text{ mmol L}^{-1}$  solution of



$\text{KAu}(\text{CN})_2$  in a given aqueous solvent and the resulting integral enthalpy of adsorption (displacement of the solvent by the adsorbing solute molecules) recorded. The quantity of gold adsorption was determined by analysing the effluent from the adsorbent placed in the flow cell. An on-line UV detector (wavelength  $\lambda = 248$  nm) was used to monitor the concentration of the adsorbing or desorbing aurocyanide complex in the effluent.

The provision of two independent channels of digital processing capability permitted the storage and subsequent processing of the solute concentration data with reference to the enthalpy of adsorption. The amount of aurocyanide adsorbed on the adsorbent surface was calculated by matching the concentration profile for a given sample with the corresponding profile obtained on an inert PTFE powder in a blank run carried out under the same experimental conditions. The adsorbent and the solution were allowed to remain in contact until no further change in the effluent composition was detected (about 90 min). Solvents and solutions could be interchanged sequentially, allowing the integral enthalpy of desorption (displacement of the solute molecules by the adsorbing solvent) to be measured and the reversibility of adsorption to be evaluated.

### 3. RESULTS

The environment of the aqueous phase is known to strongly influence the adsorption and desorption of gold at the carbon-water interface [e.g., 3,4,23-25]. In most cases, flow adsorption microcalorimetry can be used to assess the reversibility of the phenomenon and to quantify reversible and irreversible components. There are, however, a few problems that have to be solved prior to calorimetric measurements.

In particular, the form of the adsorbed species may change under different experimental conditions. The knowledge of this form is essential for the choice of an analytical detection technique. For the purposes of the present study, the results of gold adsorption and desorption from deionised water on three active carbons (G209, G210 and AC3) were compared with those for graphitised carbon black (Graphon), graphite flakes (SP-1), and two G210 samples subjected to certain chemical pre-treatments. For one of the carbons (G210), adsorption experiments were carried out with the use of five types of solvent: deionised water, aqueous phase with pH 11.5 adjusted by the addition of KOH, 0.01 M KCl or 0.0033 M  $\text{CaCl}_2$  aqueous solutions, and 5 mass% solution of ethanol in water. In each case, adsorption and desorption isotherms for gold and cyanide groups could be constructed using the solution depletion technique [19,26]. The supernatant liquid was analysed for cyanide groups by UV



spectroscopy (in a wavelength range from 210 to 300 nm) and for gold by AA spectroscopy (wavelength  $\lambda = 242.8$  nm, in an air-acetylene flame).

For all the adsorption systems considered here, the loadings of gold and cyanide groups were exactly equal to the stoichiometric values required for the adsorption of an aurocyanide complex in the  $\text{Au}(\text{CN})_2^-$  form and/or as a part of the  $\text{M}^{\text{nt}}[\text{Au}(\text{CN})_2^-]_n$  species, with  $\text{M}^{\text{nt}} = \text{H}^+$ ,  $\text{K}^+$ , or  $\text{Ca}^{2+}$ . Nevertheless, it was not possible to establish whether the metal dicyanoaurate complex represented an ion-pair or a neutral molecule. The same formula  $\text{M}^{\text{nt}}[\text{Au}(\text{CN})_2^-]_n$  will be thus used to designate both adsorbing species.

Simultaneously, the molar ratios of Au to CN in the equilibrium bulk phase after desorption were 1:2, indicating that the gold was desorbed also as the aurocyanide complex. In addition, no free cyanide was detected in the bulk solution, so that UV spectroscopy could be used with the flow microcalorimeter for determining the change in the effluent concentration.

The adsorption of aurocyanide complexes was measured at a  $\text{KAu}(\text{CN})_2$  concentration of  $5 \text{ mmol L}^{-1}$ . Determining the gold capacity at the same solute concentration in the stock solution ensures that uniform adsorption conditions prevail for all carbonaceous adsorbents. The use of such concentrated solutions might seem unreasonable because the leach slurry in a real process for large-scale recovery of gold by active carbon never contains so much gold. Nevertheless, the aurocyanide concentration in the solution percolating through the flow calorimetric cell corresponds to the concentration of the equilibrium bulk phase in the batch adsorption system. Below the above-mentioned concentration, each of the adsorption isotherms,  $\Gamma = \Gamma(c)$ , measured under equilibrium batch conditions [11,19,26] reaches a limiting steady value  $\Gamma_{\text{max}}$  which does not change with further increase of  $c$ . Both reversible and irreversible adsorption progress with increasing concentration until the plateau adsorption region. It is thus clear that reversible and irreversible adsorption components determined at sufficiently high solute concentrations in adsorption-desorption cycles with the use of Microscal Flow Microcalorimeter will be equal to the maximum gold adsorption capacities of the carbonaceous adsorbents.

At the beginning, the adsorption-desorption cycles were conducted for Graphon, SP-1 and three active carbons (G209, G210, AC3) at room temperature with the use of deionised water as a solvent. The amounts of aurocyanide adsorbed at the solid-solution interface,  $\Gamma$ , and the integral molar enthalpies of displacement,  $\Delta H$ , for both adsorption and desorption cycle are presented in Table 1.

The adsorption of aurocyanide species from deionised water on the carbonaceous adsorbents at room temperature was partly irreversible, because the amount of aurocyanide removed by the solvent from the carbon surface in



the desorption cycle was markedly less than the amount adsorbed in the adsorption cycle. The difference between the two values may be considered as a direct measure of aurocyanide species irreversibly retained on the carbon surface. By analogy, the enthalpy of desorption taken with the opposite sign is identified with the average enthalpy of reversible adsorption. Hence the reversible ( $\Gamma_R, \Delta_{ads}H_R$ ) and irreversible ( $\Gamma_{IR}, \Delta_{ads}H_{IR}$ ) components of the amount adsorbed and integral molar enthalpy of adsorption can be calculated as follows,

$$\Gamma_R = -\Gamma_2, \quad \Gamma_{IR} = \Gamma_1 - \Gamma_R \quad (1)$$

$$\Delta_{ads}H_R = -\Delta H_2, \quad \Delta_{ads}H_{IR} = \frac{\Gamma_1 \cdot \Delta H_1 - \Gamma_R \cdot \Delta_{ads}H_R}{\Gamma_1 - \Gamma_R} \quad (2)$$

where  $\Gamma_j$  is the amount of aurocyanide adsorbed/desorbed in the  $j$ th cycle and  $\Delta H_j$  is the molar enthalpy evolved/absorbed during the  $j$ th cycle. The adsorption and enthalpy values obtained with four carbonaceous supports are given in Table 2.

Table 2. Reversible and irreversible components of the amount adsorbed and integral molar enthalpy of aurocyanide adsorption calculated from the results reported in Table 1

Solid	Irreversible Adsorption		Reversible Adsorption	
	$\Gamma$ [ $\mu\text{mol g}^{-1}$ ]	$\Delta H$ [kJ mol $^{-1}$ ]	$\Gamma$ [ $\mu\text{mol g}^{-1}$ ]	$\Delta H$ [kJ mol $^{-1}$ ]
Graphon	7.3	-45.5	22.0	-24.2
G209	131.5	-48.2	293.7	-27.8
G210	288.7	-49.4	362.8	-24.6
AC3	201.4	-42.4	127.2	-21.5

In an effort to explain the role of the polar nature of the adsorbent in adsorption, two samples of carbon G210 were purified by continual washing with cold deionised water and then subjected to different chemical treatments. The first sample was brought into contact with 30 mass% hydrogen peroxide solution, whereas the second one was treated with a 0.5 M solution of hydroquinone. Both chemical treatments were carried out at room temperature in a liquid stream with the use of the flow microcalorimeter, in which a given solution was percolated through a bed of adsorbent at a rate of 3 ml h $^{-1}$  over a period of 9 h. The resulting solid sample in the calorimetric cell was washed



again with deionised water. Unfortunately, determining the polar surface area for the washed samples was no easy task. Calorimetric measurements with the use of *l*-butanol and *n*-heptane required water to be removed carefully from the system by washing with acetone. Such treatment would modify the surface properties of G210 to a great extent. An adsorption-desorption cycle was then performed using a 5 mmol L<sup>-1</sup> solution of KAu(CN)<sub>2</sub> in deionised water at 298 K. The related adsorption and enthalpy data are compared in Table 3 with those for the original carbon sample.

Table 3. Results of adsorption-desorption cycles for active carbon G210 subjected to different chemical pretreatments (adsorption from 5 mmol L<sup>-1</sup> solution of KAu(CN)<sub>2</sub> in deionised water at 298 K)

Carbon Sample	Adsorption Cycle		Desorption Cycle	
	$\Gamma$ [ $\mu\text{mol g}^{-1}$ ]	$\Delta H$ [kJ mol <sup>-1</sup> ]	$\Gamma$ [ $\mu\text{mol g}^{-1}$ ]	$\Delta H$ [kJ mol <sup>-1</sup> ]
Original G210	651.5	-35.6	-362.8	24.6
Treated with 30 mass% H <sub>2</sub> O <sub>2</sub>	399.6	-24.5	-397.9	23.9
Treated with 0.5 M p-C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	254.2	-24.8	-245.5	21.2

The reversibility of aurocyanide adsorption has been studied in the presence of certain organic and inorganic additives in the aqueous phase. KCl and CaCl<sub>2</sub> were used to investigate the effect of the nature of the cation. Here solutions containing potassium aurocyanide in a background electrolyte of either 0.01 M KCl or 0.0033 M CaCl<sub>2</sub> were percolated through a solid sample. The concentration of sodium chloride three times as high as that of calcium salt allowed the comparison to be made at the same ionic strength. Prior to the second series of experiments, the pH of the aqueous phase was adjusted to 11.5 by the addition of KOH. The resulting KOH solution was subsequently utilised as a mean solvent for preparing a stock solution of KAu(CN)<sub>2</sub>. Lastly the adsorption of potassium aurocyanide from 5 mass% ethanol aqueous solution was studied. In all cases, the concentration of KAu(CN)<sub>2</sub> in the stock solution was 5 mmol L<sup>-1</sup>. Contrary to the experiments previously discussed, here the desorption cycles were carried out in appropriate background solutions and not in deionised water. The results of the flow microcalorimetry measurements conducted on active carbon G210 at room temperature are summarised in Table 4. The reversible and irreversible contributions to the adsorption quantity for the four adsorption systems were calculated by means of Eqs (1) and (2). They, too, are given in Table 4.



Table 4. Effect of different additives in the aqueous phase on aurocyanide adsorption from 5 mmol L<sup>-1</sup> solution of KAu(CN)<sub>2</sub> on active carbon G210 at 298 K

Solvent	Adsorption Cycle		Desorption Cycle		Adsorption	
	$\Gamma$ [ $\mu\text{mol g}^{-1}$ ]	$\Delta H$ [kJ mol <sup>-1</sup> ]	$\Gamma$ [ $\mu\text{mol g}^{-1}$ ]	$\Delta H$ [kJ mol <sup>-1</sup> ]	$\Gamma_{IR}$ [ $\mu\text{mol g}^{-1}$ ]	$\Gamma_R$ [ $\mu\text{mol g}^{-1}$ ]
Deionized water	651.5	-35.6	-362.8	24.6	288.7	362.8
0.01 M KCl	681.8	-37.8	-333.3	31.2	348.5	333.3
0.0033 M CaCl <sub>2</sub>	863.6	-39.2	-318.2	42.9	545.4	318.2
KOH (pH 11.5)	646.1	-32.9	-492.3	16.8	153.8	492.3
5 mass% EtOH	178.5	-16.8	-96.9	25.8	81.6	96.9

#### 4. DISCUSSION

The comparison of aurocyanide adsorption on three active carbons with that for Graphon and SP-1 from deionised water gives some idea of the nature of active sites which can adsorb aurocyanide complexes.

Neither adsorption nor enthalpy effects were detected for graphite SP-1. This adsorbent is a non-porous graphite composed of well-ordered natural graphite flakes which have been purified by the manufacturer to a minimum content of impurities [27]. It may be that extensive, ideal graphite-like structures are completely inactive with respect to aurocyanide adsorption. Nevertheless, it seems more probable that the experimental method applied simply fails to detect aurocyanide adsorption because of the small specific surface area of the adsorbent.

For the other carbon adsorbents, the maximum quantity of aurocyanide adsorption increased with increasing total BET specific surface area. The average surface area per adsorbed species on all the adsorbents ranged between 3 and 5 nm<sup>2</sup> and was far from the 0.21 nm<sup>2</sup> estimated for a linear and non-hydrated Au(CN)<sub>2</sub><sup>-</sup> ion adsorbed in a horizontal orientation [28] or from the 0.4 nm<sup>2</sup> obtained for an ion-pair K<sup>+</sup>...Au(CN)<sub>2</sub><sup>-</sup> lying flat on the surface [10]. Partial hydration of the adsorbed species and repulsive interactions in the adsorbed layer decrease the packing density of the adsorbate, but even these



effects cannot account for the low densities of adsorption. This is in agreement with the suggestion that only a small proportion of the total surface area of carbonaceous adsorbents, as determined by the BET N<sub>2</sub> method, adsorbs aurocyanide complexes from aqueous solution.

The adsorbate molecules or ions seem to be localised on some active areas and the isotherm plateau arises from the saturation of all these accessible sites. In the case of active carbons, the aurocyanide adsorption seems to occur mostly in the relatively large meso- and macropores [1]. Penetration of the microporous structure by the adsorbate is greatly limited, on the one hand, by the adsorbate size and, on the other hand, by low kinetics of the process. Much longer times of contact between the adsorbent and the solution may be required to saturate the total surface area available for aurocyanide adsorption. However, long contact times are of little relevance to the practical performance of active carbons in gold extraction.

The integral molar enthalpies of adsorption and desorption obtained with the different samples were very similar, which implies that the interactions between the aurocyanide adsorbate and active sites in the carbon adsorbents were of the same type. This is a clear indication that the adsorption of aurocyanide involved similar surface structures. The presence of aromatic condensed ring systems in the carbon surface is a common feature of the substrates studied. For active carbons G209, G210 and AC3, the maximum amount adsorbed appears to be proportional to the surface area of the graphitic basal planes,  $S_{bas}$ . However, the values of  $S_{bas}$  should be interpreted with caution because the accessibility of the microporous carbon structure to the aurocyanide adsorbate differs from its accessibility to the titrant molecules (C<sub>32</sub> aliphatic hydrocarbon). Until adsorption is claimed to occur mainly on the external carbon surface, the quantity of adsorption may be correlated with  $S_{bas}$ .

Unexpectedly, Graphon gave the lowest density of adsorption per unit surface area of the accessible basal planes (about 0.4 μmol m<sup>-2</sup>), although its basal surface area was virtually identical to the BET specific surface area. Since it was a non-porous and highly graphitised sample, its surface should contain extended contiguous areas of graphitic basal planes. Perhaps such uniform structures cannot provide many active sites for adsorption. The adsorption sites are thus expected to be associated with the graphite-like structures containing non-ideal aromatic rings. Such non-ideality may be due to the presence of some structural imperfections or impurities in the graphite crystal structure. This is in line with the view represented by Sibrell and Miller [10] that the adsorption of aurocyanide complex on graphitic carbons is much greater at edges defects of the graphite planes than on the planes themselves. In the structure of active carbons, the heterogeneity of aromatic rings is much higher and, consequently, the number of surface sites responsible for aurocyanide adsorption certainly increases.



The surface of active carbons also contains polar groups which are located at the edges of broken graphite sheets or which can form heterocyclic ring systems [29]. Even graphitised carbon blacks heated to 3000°C retain a small amount of polar sites on their surfaces [30]. Surface sites of this type may interact with polar molecules by their Lewis acidic or basic functionality. From the analysis of polar surface area in Table 1, it is clear that the overall adsorption of aurocyanide does not correlate directly with this parameter. However, there is not enough evidence to neglect the role of polar sites in the phenomenon, especially when certain polar groups attached to the graphite structure could be the source of edge defects.

The analysis of the adsorption and enthalpy effects collected in Table 2 indicates that the carbonaceous substrates differ widely from one another in the degree of adsorption reversibility. At least a quarter of the total amount of aurocyanide was irreversibly adsorbed on Graphon. Among the three active carbons, AC3 having the greatest polar surface area and the smallest graphitic basal plane area yielded the smallest reversible adsorption and the highest degree of irreversibility (61%). For 209 and 210, the degree of irreversibility was 31% and 44%, respectively. The values of  $\Delta_{ads}H_{IR}$  and  $\Delta_{ads}H_R$  are still believed to reflect similar mechanisms of the phenomena both on a non-porous graphitised carbon black and on microporous active carbons. It should be noted that the value of  $\Delta_{ads}H_{IR}$  obtained under dynamic conditions with active carbon G210 was only a little greater than the  $-55 \text{ kJ mol}^{-1}$  measured in the batch microcalorimetry experiment [11].

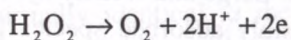
Although the irreversible aurocyanide adsorption was more exothermic than the reversible one, the absolute values of  $\Delta_{ads}H_{IR}$  were much smaller than those expected for a typical chemisorption. The discrepancy may be explained by a competitive character of the phenomenon, which argues in favour of the anion-exchange mechanism. Large and weakly hydrated aurocyanide ions, such as the form of the irreversibly adsorbed species [11,19], displace interfacial water molecules and are capable of exchanging with some simple anions previously retained at the carbon-water interface. The process was irreversible because desorption was carried out in deionised water. The enthalpy change gained on adsorption of  $\text{Au}(\text{CN})_2^-$  will be diminished by the enthalpy necessary to release water molecules and exchangeable anions from the carbon surface. The more polar the active sites involved in the irreversible adsorption, the greater will be both desorption components and, hence, the smaller the total enthalpy of the displacement process. The moderate values of  $\Delta_{ads}H_{IR}$  estimated for the carbonaceous adsorbents seem to show that the active sites are the graphite structures linked to a certain kind of polar groups. The reversible



adsorption of aurocyanide in the  $\text{KAu}(\text{CN})_2$  form is also competitive: the adsorbate has to displace solvent molecules from the interface. The loss of enthalpy related to the desorption of interfacial water should not be great because the absolute values of  $\Delta_{\text{ads}} H_R$  are not small at all. Therefore, the surface sites responsible for reversible adsorption are less active and more hydrophobic in nature. Following the idea of Sibrell and Miller [10], the unsymmetrical charge distribution at defects in the graphite structure and the non-parallel orientation of the potassium aurocyanide ion-pair could well account for the physical adsorption of the aurocyanide adsorbate on the defect sites of the graphitic planes.

Chemical treatment of carbon G210 caused aurocyanide adsorption to undergo much alteration (see Table 3). Firstly, the total adsorption capacity was markedly depressed, especially that for active carbon G210 treated with hydroquinone. Secondly, the absolute adsorption and enthalpy values measured in adsorption and desorption cycles were identical within experimental error, which means that the phenomenon became fully reversible.

Treatment with hydrogen peroxide solution caused the irreversible adsorption component to disappear completely, whereas the quantity of reversible adsorption increased a little. It is probable that the oxidising action of  $\text{H}_2\text{O}_2$  on the carbon surface at room temperature is not efficient in regard to aurocyanide adsorption. Even if the graphite crystal structure were oxidised at the edges of microcrystallites during such mild oxidation, the resulting carbon-oxygen surface structures would be of little relevance to the adsorption of  $\text{Au}(\text{CN})_2^-$  ions. Most likely, hydrogen peroxide acts as a reductant on positively charged surface sites, which, in accordance with an anion-exchange mechanism, should be involved in the irreversible adsorption. These sites would become electrically neutral by acquiring the electrons from the oxidation of hydrogen peroxide to molecular oxygen:



The protons liberated in this reaction are removed in the effluent together with the exchangeable anions, i.e.,  $\text{Cl}^-$ ,  $\text{OH}^-$ , etc. Similarly, the loss of the irreversible adsorption capacity observed after treatment with hydroquinone may be associated with the reducing power of this substance. Furthermore, neutral hydroquinone molecules have some capability to adsorb chemically on the carbon surface, which could account for a significant decrease in the reversible adsorption component.

As found by previous investigators [23,31], the presence of salt in solution enhanced the maximum capacity of the carbon for adsorption of aurocyanide (see Table 4). This result is due rather to the nature of cation than to a simple



ionic-strength effect. When potassium ions were added to the adsorption medium, the total adsorption capacity was increased by only  $30 \mu\text{mol g}^{-1}$  in comparison with the system without electrolyte and the degree of irreversibility increased from 44% to 51%. The irreversible and reversible components of the integral molar enthalpy of adsorption attained values of  $-44 \text{ kJ mol}^{-1}$  and  $-31 \text{ kJ mol}^{-1}$ , respectively, thereby indicating that the enthalpy difference between both adsorption pathways was somewhat diminished. With  $\text{Cl}^-$  as the common anion, a divalent calcium cation at the same ionic strength produced a much higher total capacity than an univalent potassium ion. The degree of adsorption irreversibility rose to 63%, whereas the two enthalpy components were almost the same.

The addition of an electrolyte to the aqueous phase containing  $\text{K}^+$ ,  $\text{Au}(\text{CN})_2^-$  and other ions may induce several new effects which influence adsorption and desorption. Some of these effects will be competing. The proportion between the different forms of the adsorbed species, i.e.,  $\text{M}^{\text{n}+}[\text{Au}(\text{CN})_2^-]_n$  and  $\text{Au}(\text{CN})_2^-$ , is believed to undergo some subtle changes under different experimental conditions. The reversible adsorption of aurocyanide can no longer be ascribed only to the ion-paired or molecular species, while the irreversible component cannot be identified exclusively with the unpaired anion. At higher  $\text{K}^+$  concentrations, more  $\text{K}^+[\text{Au}(\text{CN})_2^-]$  will be adsorbed from solution. During desorption, there are potassium counterions in the bulk phase and, consequently, some of the  $\text{K}^+[\text{Au}(\text{CN})_2^-]$  adsorbed species may be difficult to remove from the interface. In other words, the adsorption of neutral complex becomes partially irreversible. By analogy, addition of  $\text{Cl}^-$  ions to the solution during adsorption and desorption cycles reduces the adsorption of  $\text{Au}(\text{CN})_2^-$  by an anion-exchange mechanism and renders it more reversible. In the presence of  $\text{Ca}^{2+}$ , one part of aurocyanide may be adsorbed in the  $\text{Ca}^{2+}[\text{Au}(\text{CN})_2^-]_2$  form and this large complex will have much higher affinity for the carbon surface than that of potassium aurocyanide species [31]. The reduction in the adsorption reversibility could simply be due to a competition between both types of neutral complex for adsorption on the carbon. Furthermore, the hypothesis that  $\text{Ca}^{2+}$  is specifically involved in the electrostatic adsorption of the aurocyanide anion cannot be excluded. Divalent calcium counterions may be adsorbed via a charge-transfer-complexation mechanism on the graphitic basal planes [32], where they constitute additional positively charged surface sites for the adsorption of the anionic species  $\text{Au}(\text{CN})_2^-$ . Other factors to be considered in relation to the addition of electrolyte ions are the moderation of electrostatic interactions in the system (both attractive and repulsive), variations of the pH-dependent charge of the carbon surface, modification of the structure of interfacial water, or lowering of the solubility of  $\text{Au}(\text{CN})_2^-$  ions in the aqueous phase. Since the equilibrium of adsorption and desorption results



from the interplay of all the above competing effects, it is almost impossible to extract information from the net effect.

In agreement with the results of other workers [23,31], increasing the pH value of the solution from 6 to 11.5 scarcely influenced the total adsorption capacity of active carbon. Nevertheless, the degree of irreversibility was diminished to a great extent and attained 24%. As already mentioned in the Introduction, the adsorption of aurocyanide anions is accompanied by a rise in pH, which is consistent either with the chemisorption of  $\text{HAu}(\text{CN})_2$  or with anion-exchange (direct or indirect) between some  $\text{Au}(\text{CN})_2^-$  ions and hydroxyl anions. At high pH values, all the aurocyanide is in the ionic form and the ability of  $\text{Au}(\text{CN})_2^-$  to ion exchange is obviously lowered. Other exchangeable anions, like  $\text{Cl}^-$ , are freed in the adsorption cycle and, hence, are not present in the bulk phase during desorption. Percolating a concentrated KOH solution through the adsorbent in the desorption cycle results in the removal of many aurocyanide anions previously adsorbed on the carbon surface.

Both reversible and irreversible contributions to the amount adsorbed decreased by about 4 times in the presence of ethanol. The degree of irreversibility remained practically the same (about 46%). Several effects may combine to yield such results.

Firstly, alcohol molecules can decrease the relative permittivity of the medium, thereby disfavours the ionic dissociation of  $\text{KAu}(\text{CN})_2$ . Under such conditions, only the irreversible adsorption of aurocyanide would have been lowered.

Secondly, alcohols like ethanol and *n*-butanol adsorb on hydrophobic graphite-like structures from aqueous solutions at room temperature [26,33]. The effect is more pronounced for *n*-butanol, which at the concentration of 1 mass% saturates the hydrophobic surface of Graphon. A much greater concentration of ethanol, i.e., about 5 mass%, is needed to saturate most of the adsorption sites [33]. Therefore, aurocyanide adsorbate has to compete with the ethanol molecules. This result supports the conclusion that both reversible and irreversible adsorption of aurocyanide on active carbons is to a great degree associated with the graphite crystalline structure. It may be that the unpaired and ion-paired (undissociated or solvent-shared) aurocyanide species, retained at edge defects in the graphite structure by electrostatic and physical forces, are also stabilised by attachment to the adjacent basal planes. Blocking some of the basal plane sites by adsorbing ethanol molecules diminishes the amount of aurocyanide adsorbate.

## 5. CONCLUSIONS

Flow microcalorimetry, applied to gold adsorption on graphitised carbon black and coconut-based active carbons from aqueous solutions of  $\text{KAu}(\text{CN})_2$  at room temperature, appears to be particularly useful for the study of thermodynamic reversibility of the phenomenon. The maximum gold capacity of the carbonaceous adsorbents is composed of two parts corresponding to the amounts of aurocyanide reversibly and irreversibly retained on the carbon surface. For a given composition of the adsorption medium, the proportion between these two adsorption components is a complex function of both the polar and graphitic nature of the solid support. The degree of adsorption irreversibility ranged from 25% for a highly graphitised Graphon sample to 61% for the most polar active carbon. The irreversible and reversible contributions to the integral molar enthalpy of adsorption from deionised water have been estimated for  $-50 \text{ kJ mol}^{-1}$  and  $-25 \text{ kJ mol}^{-1}$ , respectively. Since the density of adsorption on Graphon is very low, the postulate that aurocyanide adsorption occurs mainly at some edge defects in the graphite crystal structure is supported in this paper. One part of the aurocyanide is believed to adsorb as an unpaired anion  $\text{Au}(\text{CN})_2^-$  by an anion-exchange mechanism on the very active surface sites having polar character. The less active sites are occupied by the ion-paired or undissociated species of the type  $\text{M}^{\text{H}^+}[\text{Au}(\text{CN})_2]_n$  through the action of intermolecular forces.

The addition of  $\text{KCl}$  or  $\text{CaCl}_2$  to the aqueous phase enhanced both the total and irreversible capacity of active carbon G210 for aurocyanide adsorption, the effects being strongly marked in the presence of calcium cation at the same ionic strength. The degree of adsorption irreversibility was 51% for  $\text{K}^+$  and 63% for  $\text{Ca}^{2+}$ . An increase in the pH value of the aqueous phase from 6 to 11.5 did not affect the total capacity of carbon G210, but the degree of irreversibility was depressed to 24%. When ethanol molecules were added to the aqueous phase, both adsorption components were greatly reduced to the same extent and the proportion between them did not change.

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### CURRICULUM VITAE



**Jerzy J. Zajac** was born in Poland in 1957. He received his M.Sc. in Physical Chemistry from the University of Mining and Metallurgy in Krakow. He then joined the Faculty of Fuels and Energy at the same university, where his early research was in the area of adsorption at different interfaces. Subsequently, he turned his attention to the adsorption from solution onto solid substrates, focusing on thermodynamic aspects and modelling of the phenomenon. He received a Ph. D. in chemistry from

the Maria Curie-Skłodowska University in Lublin in 1988 under the supervision of Władysław Rudziński. In 1988 he became a lecturer in the Department of Physical Chemistry at the University of Mining and Metallurgy in Kraków. A 1991 French Government Fellowship supported a stay at the University of Montpellier, where he collaborated with Stan Partyka on thermodynamics of micellization and adsorption of surfactants in aqueous media. He has been continuing his theoretical and experimental studies of adsorption at the solid-liquid interface in France, being involved in several research projects supported financially by the European Community. Currently, he is a temporary Research Fellow at the French Research Centre in Montpellier. His research interests encompass interfacial phenomena, surface characterisation of solid materials, as well as heterogeneous catalysis. He utilises a variety of experimental techniques, with special attention focused on calorimetric measurements (immersional, titration and flow microcalorimetry). He has been collaborating with Microscal Ltd in London for many years. Altogether he has over 18 years of experience in surface science.



