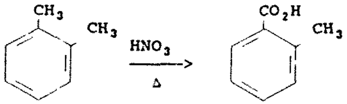
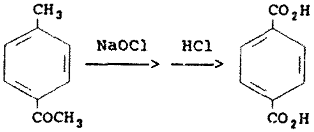
The microcrystallite height parameters, L_c, remain approximately constant for all treatments, corresponding to two graphitic layers per microcrystallite. However, the microcrystallite diameters, L_a, decrease upon oxidation, which is also consistent with the pore-widening effects discussed above.

c) Activated Carbon Surface Chemistry

The extent of oxidation correlates well with the decreasing carbon content and increasing oxygen content of the activated carbon, as shown in Table 6.9. The trend is again repeated as an increasing reduction potential, and a more negative pH shift in water. All of these facts are consistent with the presence of acidic functional groups on the carbon. Reactions such as the following are well known[270] in organic chemistry:



(6.21)



(6.22)

This type of reaction with pendant hydrocarbon groups, is consistent with the observed structural and electronic changes that were discussed in the previous section.

Table 6.9

Effect of surface oxidation on the chemical characteristics of Le Carbone G210 activated carbon

Oxidation conditions	Elemental analyses, %			E V (vs SHE)	Phenol Adsorption after 24h %	ΔpH in water
	C	H	O			
None	92,5	0,9	1,7	-0,054	92,7	+3,76
Boiled in 1M NaOCl for 1h	85,2	1,6	3,2	-0,046	57,5	+3,48
Boiled in 1M HNO_3 for 1h	84,8	1,5	4,0	+0,153	73,1	+0,45
Boiled in 1:1 HNO_3:H_2SO_4 for 2h	71,7	1,9	6,9	+0,289	20,3	-2,43
Soaked in 20% H_2O_2 for 1 week at 25°C	84,4	1,4	2,3		92,2	+0,92

The phenol adsorption activity once again parallels that for gold, which is consistent with the premise that the adsorption mechanisms for both species are inherently similar. There are both chemical and physical changes that occur in the activated carbon due to oxidation, and both of these types of changes have a profound effect on adsorption of aurocyanide. The widening of the micropores reduces the number of adsorption sites bordered by two surfaces, thereby reducing the adsorption potential at these sites. The abundance of carboxyl groups ensures a negatively-charged surface, that is not conducive to the adsorption of anions. In the evaluation of a range of polymeric adsorbents for gold adsorption[80], a polystyrene matrix with carboxylate groups has been found to display the poorest affinity for aurocyanide.

Infrared spectra of the oxidation products are compared with that of the untreated G210 carbon in Figure 6.13. All the carbons oxidized under mild conditions showed a slight enhancement in the C-O stretch band at 1000-1300 cm^{-1}, with the HNO_3 oxidized carbon showing the greatest enhancement, which is consistent with the elemental analyses for oxygen. The technique is not sensitive enough to identify the particular functional groups, however.

The carbon that was boiled in 1:1 $HNO_3:H_2SO_4$ showed a marked enhancement in peak intensities at 1724, 1587 and 1228 cm^{-1}, which can readily be attributed to a preponderance of carboxyl groups, thus verifying the fact that reaction (6.21) has occurred.

6.3 Synthesis and Characterization of Polymeric Models for Activated Carbon: Polyxanthenes and Polyquinones

In a further effort to isolate the specific characteristics of activated carbons that are pertinent to adsorption processes, two polymeric compounds were selected as models for activated carbon, having structures chemically similar to those proposed for activated carbon. In both cases, the preparative methods were similar to those described in the literature, so as to benefit from the knowledge that has already been gained regarding these materials. The proposed structure for the polyxanthene is as follows[63]:

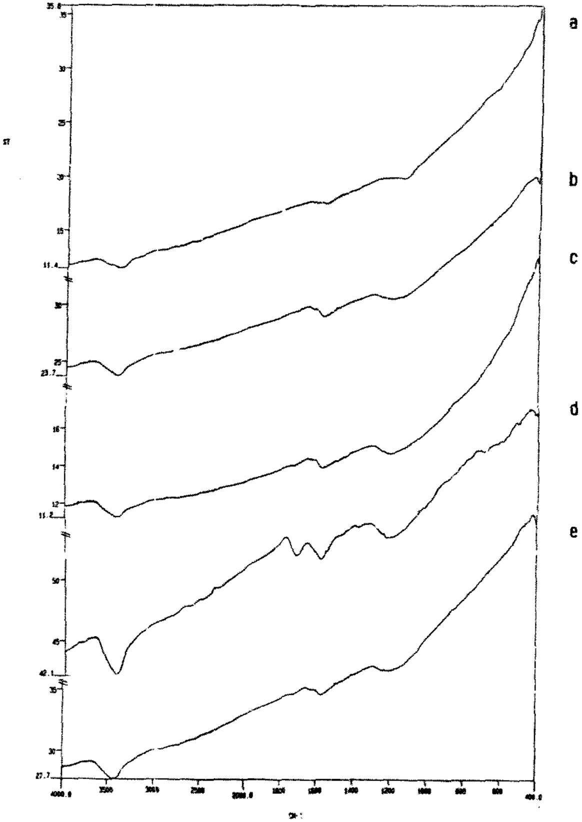
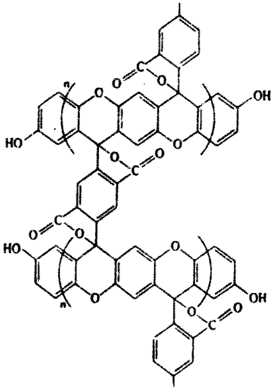
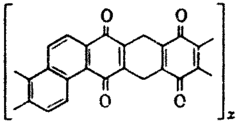


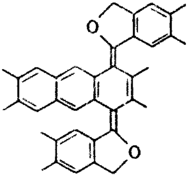
Fig. 6.13 Infrared spectra of Le Carbone G210 activated carbon after different oxidation treatments:

(a) None
(b) Boiled in 1M NaOCl, 1h
(c) Boiled in 1M HNO_3, 1h
(d) Boiled in 1:1 HNO_3:H_2SO_4, 2h
(e) Soaked in 20% H_2O_2 for 1 week at 25°C

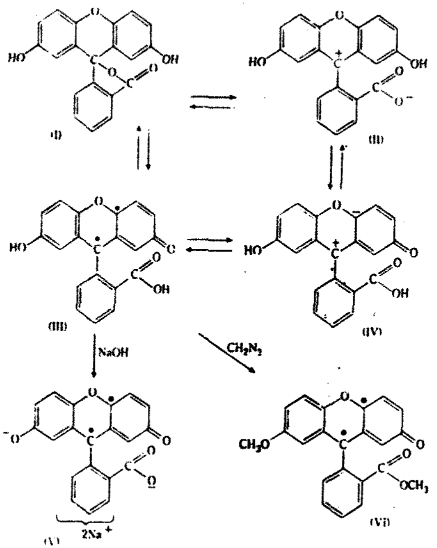


and that for the polyquinone is as follows[64]:





Both of these polymers are reported to behave as electrical conductors. This conductivity is electronic in nature in the case of the polyquinone[64]; however, for the polyxanthene the conductivity has been postulated[63] as being due to a resonating carbonium cation arising from partial ionization of the xanthylium-lactone bond. Some reactions of quinolphthalein, the analogous monomer, are as follows:



Scheme 1

It is interesting to note the presence of cationic, anionic and diradical sites on these structures, all of which could be conducive to adsorption.

a) *Gold Adsorption Activity*

Under acidic conditions, high gold adsorption activities are obtained for both the polyxanthene and the polyquinone. It is remarkable that in the presence of no additives, gold adsorption activities approaching those of activated carbons are attained, despite the fact that the surface areas of the polymers (about 5 m^2/g) are a small fraction of that of a typical activated carbon (about 1000 m^2/g). The fact that a rather different trend is obtained for the effect of extraction medium, than in the case of activated carbon, suggests that a different adsorption mechanism is operative in the case of the model polymers. This aspect will be examined in more detail later in this Chapter. It is noteworthy also that XAD-8, a polymeric acrylic ester (surface area 109 m^2/g), displays virtually no gold activity.

Another interesting anomaly occurs due to the crushing of the carbon. It is well known that the kinetics of adsorption are enhanced by decreasing the particle size, and this is borne out by comparing the results for the G210 and oxidized G210 powders, with those for the granular carbons (Tables 6.10, 6.1 and 6.6, respectively). The gold activities are slightly enhanced, and the fact that the magnitude of the enhancement is small is probably because a pseudo-equilibrium has been reached in the twenty hour contact period. The anomalous result is the marked enhancement in the gold activity of powdered Norit C, over the granular carbon. A possible explanation for this phenomenon is given in the following section.

Table 6.10

Extraction of aurocyanide by powdered polymers, adsorbents and activated carbons under various conditions

Adsorbent	Gold extraction, %		
	No additives	0,033M $CaCl_2$	0,1M HCl
polyxanthene	13,0	5,68	12,6
polyquinone	10,7	5,68	11,9
XAD-8 (P)	0,00	0,00	1,20
G210 (P)	16,8	34,1	82,8
Norit C (P)	12,2	35,2	80,8
G210 OX* (P)	15,2	14,9	20,0
Graphite	0,00	0,00	21,8

*Boiled in 1:1 HNO_3:H_2SO_4 for 2h, then powdered.
(P) powdered

Finally, under the conditions of the experiment, no adsorption of aurocyanide onto graphite was observed from neutral solutions. However, a large amount was extracted from acidic solution. The X-ray diffractogram of the graphite after contact reveals polymeric AuCN to be present, as shown in Figure 6.14. This is confirmed by the infrared spectrum, shown in Figure 6.15, where the CN stretch band of AuCN at 2239 cm^{-1} is clearly evident. The AuCN was found by EDS to be uniformly distributed on the surface of each graphite particle. The invisibility of the AuCN layer in the micrograph in Figure 6.16 shows that this layer must be less than 0,01 μm in thickness. Preferential adsorption of AuCN from acidified aurocyanide solutions

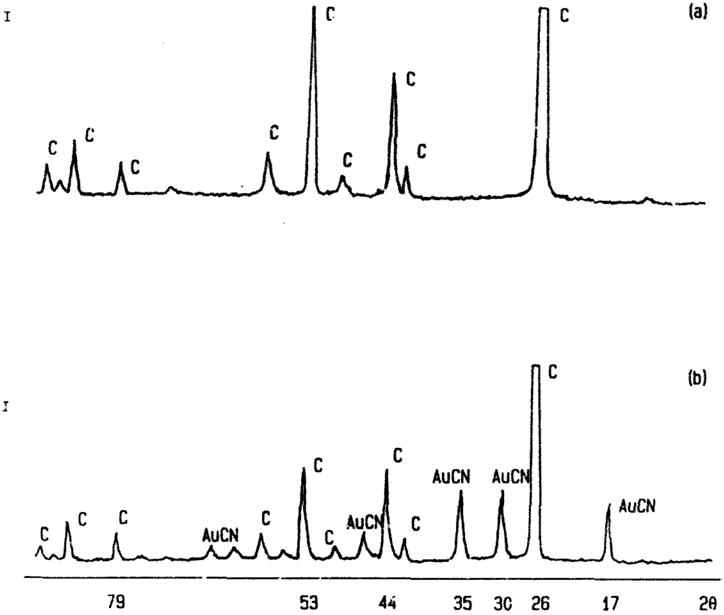


Fig. 6.14 X-ray diffractograms of graphite before and after contact with an aurocyanide solution containing 0,1M HCl

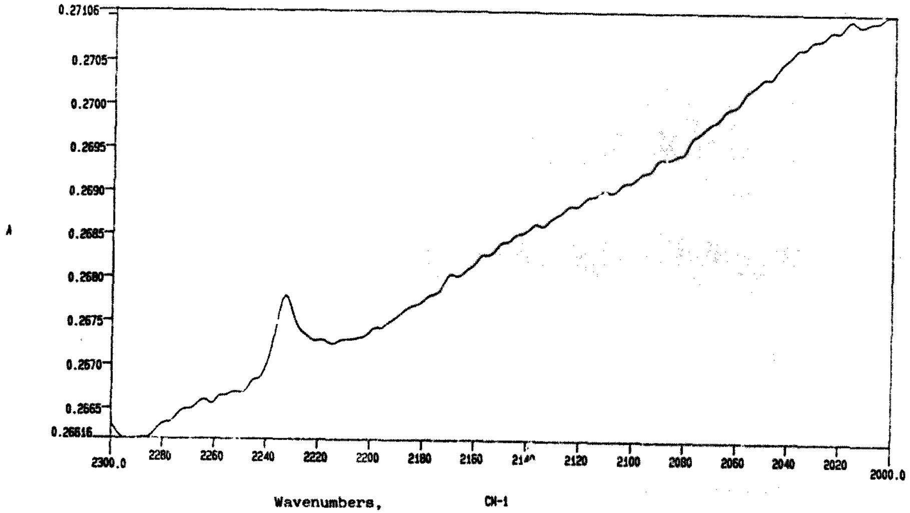
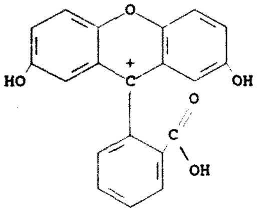


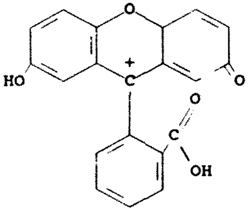
Fig. 6.15 Infrared spectrum of graphite after contact with an aurocyanide solution containing 0,1M HCl

Fig. 6.16 Scanning electron micrograph of graphite after contact with an aurocyanide solution containing 0,1M HCl

onto hydrophobic surfaces has been demonstrated previously for polystyrene[80].

Extraction of aurocyanide by polyxanthene and polyquinone, under various conditions, is shown in Table 6.11. The decrease in gold extraction with increasing chloride concentration suggests that $Au(CN)_2^-$ is extracted by ion exchange in both cases. In the case of the polyxanthene, structures (II) and (IV) in Scheme 1 above provide positively-charged sides where ion exchange can occur, and these structures are both stabilized in the presence of acid, forming the structures





The similar gold adsorption activities both when no additives are present and in acidic solution, results from the acid wash given to the polymers in the final stage of preparation. Subsequent washing with copious amounts of de-ionized water did not increase the pH value of the solution significantly above 3, indicating the presence of cationic sites with carboxylic acid groups, as shown above.

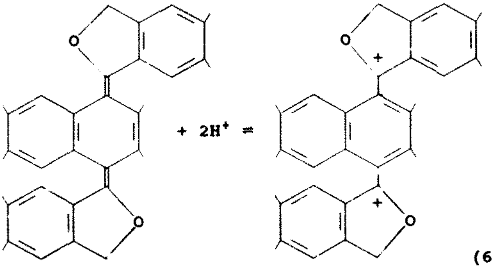
The effect of alkaline solutions of NaCN or NaOH is to drastically depress gold loading, as shown in Table 6.11. This effect must be due to the formation of structure (V) in Scheme 1, where the cationic site is essentially replaced by two anionic sites.

Table 6.11

Extraction of aurocyanide by polyxanthene and polyquinone under various conditions

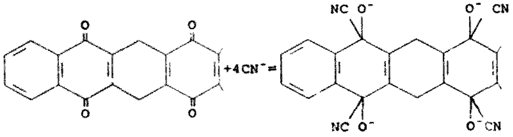
Experimental conditions	Gold extraction, %	
	Polyxanthene	Polyquinone
No additives	13,0	10,7
0,033M $CaCl_2$	5,68	5,69
0,1M HCl	12,6	11,9
0,1M NaCl	1,88	1,00
0,1M $NaClO_4$	1,52	1,68
0,1M NaCN	0,00	0,52
0,1M NaOH	0,00	1,40

In the case of the polyquinone, two structures are likely to be formed, as shown above, and the polymer probably contains a mixture of quinone, hydroquinone, semiquinone and lactone structures. It is the lactone structures that could provide positively-charged ion-exchange sites:



(6.23)

The fact that alkaline solutions do not result in a decrease in gold adsorption activity, suggests that these cationic sites are relatively stable, and that the equilibrium in reaction (6.23) lies well towards the right. The fact that some decrease in gold activity is observed in 0,1 M NaCN solution could be due to cyanohydrin formation, as was postulated in Chapter 5 to occur on activated carbon surfaces:

 (6.24)

The resultant negatively-charged surface repels the $Au(CN)_2^-$ anion.

b) *Polymer Structure*

Table 6.12 shows that the polymers all have skeletal densities of about 1,5 g/cm^3, which is lower than that of high-temperature activated carbon (2,1 g/cm^3) and graphite (2,3 g/cm^3). No significant differences between the skeletal densities of the granular and the crushed adsorbents are evident (cf. Table 6.2).

The micropore volumes for the polyxanthene and polyquinone products are extremely small, and comparable with that of graphite, being about fifty times smaller than that for G210 activated carbon. This is remarkable in terms of the relatively high gold adsorption activities displayed by these polymers (Table 6.10). Another feature is the fact that the micropore volume of the powdered Norit C carbon is double that of the granular Norit C, and this is perhaps the reason for the increase in gold adsorption activity displayed by the powder, over that of the granular carbon. It is possible that the highly interconnected pore network that is present in high-temperature activated carbons, is absent in this case, and fine crushing of this soft material has opened up blind pores in the centre of the particle. It is also noteworthy that the mesopore and macropore volumes are rather invariant for all these adsorbents, both powdered and granular.

Table 6.12

Structural properties of powdered polymers, adsorbents and activated carbons

Adsorbent	Skeletal density g/cm^3	Pore Volume, cm^3/g				Surface Area m^2/g
		micro-pore	mesopore	macropore	total	
polyxanthene	1,5593	0,0123	0,0614	0,1335	0,2029	3,41
polyquinone	1,3986	0,0659	0,0467	0,6847	0,7973	5,05
XAD-8 (P)	1,2767	0,1259	0,3755	0,8516	1,3530	109
G210 (P)	2,1259	0,4690	0,0631	0,7160	1,2481	1200
Norit C (P)	1,5959	0,3233	0,5594	1,4514	2,3341	1310
G210 OX* (P)	1,7596	0,5774	0,1275	0,3047	1,0086	770
Graphite	2,3496	0,0901	0,0019	0,8545	0,9465	2,[illegible]0

*Boiled in 1:1 $HNO_3:H_2SO_4$ for 2h, then powdered
(P) powdered

The surface areas of these polymers are very small, as mentioned earlier, comprising about 0,2 per cent of the surface area of G210 activated carbon. The powdered activated carbons have all increased in surface area relative to the granular carbons, for reasons discussed above.

The conductivities of XAD-8 polymeric adsorbent and Norit C carbon are both very low, as shown in Table 6.13. However, measurable conductivities are apparent for the polyxanthene and polyquinone. This effect has been reported previously[63,64], and serves to support the evidence that these polymers were formed during the synthesis. The polyquinone is postulated[64] to undergo electronic conduction via the conjugated aromatic system, in a manner akin to that in graphite, whereas the polyxanthene is postulated[63] to conduct via an oscillating carbonium ion of the type shown in Scheme 1 above. G210 activated carbon displays a markedly higher conductivity, and that of graphite is still higher. It is noteworthy that only the high-temperature activated carbon and graphite displayed any sign of graphitization in their X-ray diffractograms.

Table 6.13

Conductivities of powdered polymers, adsorbents and activated carbons

Adsorbent	κ, S/cm
polyxanthene	$3{,}0 \times 10^{-7}$
polyquinone	$9{,}7 \times 10^{-8}$
XAD-8 (P)	$<7 \times 10^{-8}$
G210 (P)	3,8
Norit C (P)	$<7 \times 10^{-8}$
G210 OX* (P)	0,14
Graphite	603

*Boiled in 1:1 HNO_3:H_2SO_4 for 2h, then powdered
(P) Powdered

(c) Polyxanthene and Polyquinone Surface Chemistry

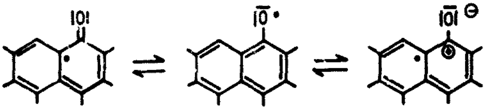
Much of the surface chemistry of these polymers has been discussed earlier. However, Table 6.14 provides some additional information. Elemental analyses of the two polymers are consistent with their proposed structures, with the polyquinone containing more carbon than the polyxanthene, and the polyxanthene containing more oxygen than the polyquinone. The reduction potentials were not easily determinable for powders using the graphite rod method, and are therefore not reported.

Table 6.14
Chemical characteristics of powdered polymers, adsorbents and activated carbons

Adsorbent	Elemental analyses, %			Phenol adsorption after 24h, %	ΔpH in water
Polyxanthene	65,6	2,9	9,6	i	-3,21
Polyquinone	88,6	3,6	2,5	19,6	-2,99
XAD-8 (P)	62,6	7,6	-	9,8	+1,98
G210 (P)	92,5	0,9	1,7	85,1	+2,47
Norit C (P)	69,4	3,4	4,6	41,2	-3,93
G210 OX (P)*	71,7	1,9	7,8	40,4	-3,44
Graphite	95,8	0,5	0,0	0,0	-1,92

*Boiled in 1:1 HNO_3:H_2SO_4 for 2 hrs, then powdered.
(P) powdered
- Not determinable
i interference

The polyquinone was found to adsorb twice as much phenol as XAD-8 polymeric adsorbent, despite the fact that XAD-8 has a surface area that is twenty times as large as the polyquinone. Mattson and Mark[24] have postulated that adsorption of phenol onto activated carbon occurs by means of a charge-transfer interaction, with exchange of electrons from carbonyl groups on the carbon surface to the aromatic ring of phenol. The preponderance of such groups on the polyquinone is consistent with this mechanism. It is possible that the active site for the adsorption of many species, including phenol and aurocyanide, is the free-radical semiquinone group, which exists as a resonance state:



No data could be obtained for the adsorption of phenol onto the polyxanthene due to interfering species in the solution; however, the results for the powdered activated carbons are included for the purpose of comparison. The results for G210 and Norit C and close to those for the granular carbons, whereas that for the powdered oxidized G210 is double that for the granular carbon. No explanation for these effects is immediately apparent. It is noteworthy also that no phenol was adsorbed by graphite, which once again suggests, by comparison with the results for the polyquinone, that carbonyl functional groups play an important role in the adsorption of phenol.

The infrared spectrum of the polyxanthene is shown in Figure 6.17a. The predominant features are the O-H band at 3509 cm^{-1}, and the lactone[266] C=O band at 1719 cm^{-1} and C-O-C band at 1245 cm^{-1}. Figure 6.17b shows a spectrum of the polyxanthene after contact with 0,1M HCl for 24 hours. The two spectra are identical, suggesting that the polymer is in the form of structure (I) in Scheme 1.

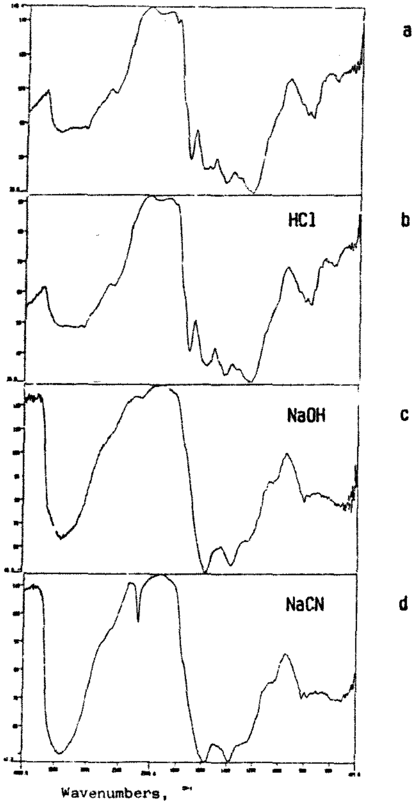


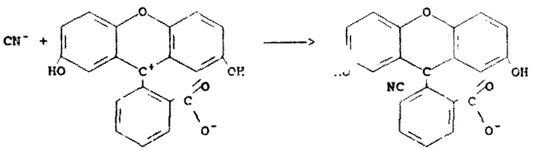
Fig. 6.17 Infrared spectrum of polyxanthene product

(a) untreated
(b) after contact with a 0,1M HCl solution for 24 hours
(c) after contact with a 0,1M NaOH solution for 24 hours
(d) after contact with a 0,1M NaCN solution for 24 hours

Figure 6.17c shows a spectrum of the polyxanthene after contact with 0,1M NaOH for 24 hours. The lactone bands at 1719 and 1245 cm^{-1} have disappeared, and the presence of adsorbed water (bands at 3300 and 1600 cm^{-1}) are now evident. This is consistent with the stabilization of the structure (V) in Scheme 1. The adsorbed water is probably present as the hydration layer for the sodium ions.

The effect of contacting the polyxanthene with 0,1M NaCN solution for 24 hours is similar to that of the hydroxide, since both solutions are alkaline. The spectrum is shown in Figure 6.17d. In addition to these changes, there is a sharp CN stretch band at 2233 cm^{-1}, characteristic[272] of nitrile groups, and not of free CN^-, which absorbs[126] at 2081 cm^{-1}. The cyanide most likely reacts at the carbonium ion in structure (II) of Scheme 1, which also results in the breakage of the C-O-C band and the presence of hydrated sodium ions.

The mechanisms of gold cyanide adsorption and desorption are substantiated by the infrared spectral results. The stabilization of the polyxanthene in the lactone from results in the cationic sites in structures (II) and (IV) of Scheme 1 being present, and the aurocyanide is adsorbed by ion exchange. In alkaline solution, structure (V) is stabilized, which contains no cationic sites, but has two anionic sites that repel the aurocyanide anion, resulting in desorption. In the presence of cyanide, a nitrile is formed by the reaction



(6.25)

Once again, no cationic sites are available in the resultant structure, and the aurocyanide anion is repelled by the anionic site that forms.

The infrared spectrum of the polyquinone is shown in Figure 6.18a. The predominant features are the O-H stretch between 3500 and 3600 cm^{-1}, the strong aromatic C-H stretch at 3030 cm^{-1}, the C=O band at 1592 cm^{-1} and the strong C-O-C band at 1284 cm^{-1}. Strong C-H bending bands are evident between 600 and 900 cm^{-1}. These features are consistent with the postulated structure described above. Once again, the spectrum of the acid-washed polymer is identical with that of the untreated polyquinone, as shown in Figure 6.18b. This is consistent with the fact that aurocyanide is adsorbed to a similar extent from both neutral and acidic solutions. The lack of effect of alkaline washing on the spectrum of the polyquinone is shown in Figure 6 18c, and Figure 6.18d shows that cyanide also has no apparent effect on the spectrum, with no nitrile or cyanohydrin bands being observed. There is a slight depressant effect on gold adsorption activity, however, and it is possible that some degree of cyanohydrin formation does occur, but is easily reversed upon removal of the 0,1M NaCN solution. The fact that no decrease in gold adsorption activity is observed in alkaline solution, is consistent with these results.

6.4 Summary and Conclusions

The most important parameter in the carbon activation process with regard to gold adsorption activity of the product, is activation temperature. The activation atmosphere and the starting material used are of secondary importance. This effect manifests itself in two ways - structurally and chemically.

Micropore volume is the structural parameter of greatest significance to adsorption of gold, because micropores

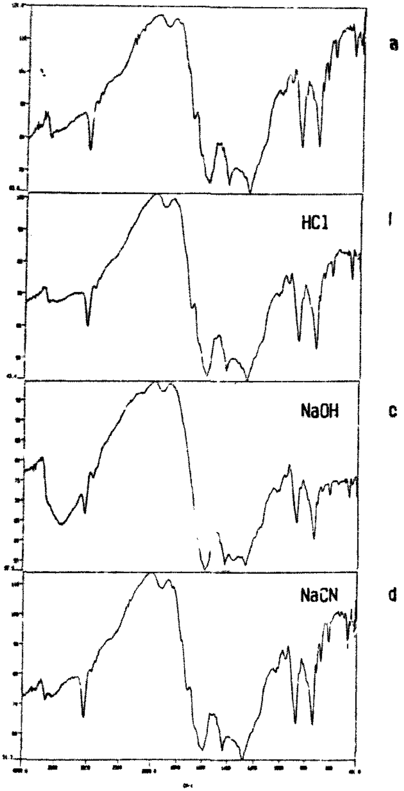


Fig. 6.18 Infrared spectrum of polyquinone product

(a) untreated

(b) after contact with a 0,1M HCl solution for 24 hours

(c) after contact with a 0,1M NaOH solution for 24 hours

(d) after contact with a 0,1M NaCN solution for 24 hours provide adsorption sites that can snugly wrap around the adsorbate. Activated carbon surface area is not a good measure of the adsorption affinity for species. A high degree of microporosity is obtained when graphitization has occurred, and temperatures greater than 750°C are a prerequisite for this phenomenon. The high conductivity of graphitic carbons is a by-product of the activation process, but it may also play a role in the adsorption of various species, where a charge-transfer interaction may be important.

The correct structural characteristics alone are not sufficient to produce an activated carbon with a high activity for adsorption of aurocyanide - the surface chemistry also plays an important role. Surface oxygen-containing functional groups impart a polar character to the inside of the micropore, and aid in the solvation of the adsorbate. Oxidants such as nitric acid result in a proliferation of surface carboxyl groups which are not conducive to the adsorption of gold. Both oxygen and hydrogen peroxide enhance the adsorption of gold under certain conditions. It is postulated that this occurs due to the oxidation of specific functional groups that result in the formation of cationic sites on the carbon surface.

There is a marked correlation between the adsorption of aurocyanide onto activated carbon and that of phenol. It is postulated that a similar adsorption mechanism is present in both cases, viz. solvation by surface groups within micropores of the ideal size, with a possible charge-transfer contribution from the delocalized electron cloud of the carbon, possibly at semiquinone sites.

Two organic hydrocarbon polymers, a polyxanthene and a polyquinone, display particularly high gold adsorption capacities. Gold is adsorbed via an ion-exchange mechanism rather than a solvation adsorption such as that occurring in the case of activated carbon. The quinone functionalities are postulated to be important in the adsorption of phenol onto the polyquinone, and probably also play a role in its adsorption onto activated carbon.

CHAPTER 7 CONCLUSIONS AND RAMIFICATIONS

This Thesis has endeavoured to address the main aspects of the chemistry of the carbon-in-pulp process where disagreement existed between different researchers. For the first time, there is now some understanding as to the reasons for this disagreement. The work has also provided fundamental knowledge of the chemistry of gold species, activated carbon and other adsorbents that may be of benefit to existing and future processes for the selective recovery of gold from its ores.

7.1 The Mechanism of Adsorption of Aurocyanide onto Activated Carbon

It was unequivocally shown, using a variety of techniques, that under the alkaline conditions typically encountered in a CIP plant, gold is extracted as an ion pair of the type $M^{n+}[Au(CN)_2^-]_n$, (where $M^{n+} = Ca^{2+}$, Na^+, etc). At low pH values (below 3) gold is loaded onto activated carbon predominantly as the aurocyanide acid $HAu(CN)_2$ while, at intermediate pH values, the ion pair and the acid are loaded simultaneously. Partial decomposition of the $HAu(CN)_2$ to an AuCN-type species was shown to occur.

When loaded carbon is heated in strongly acidic solution, aurocyanide decomposition to AuCN is more complete. Evidence from elemental analyses, X-ray diffractometry and Mössbauer spectroscopy is consistent with the AuCN being present in the form of short-chain oligomers. When the carbon is treated subsequently with hydroxide solution, the following reaction occurs:

$$2AuCN + e^- \rightarrow Au + Au(CN)_2^-$$

The standard reduction potential for this reaction was calculated to be 0,252V (vs SHE).

No evidence was found of the formation of AuCN during loading under conditions normally encountered in CIP operations. This reaction would occur to some extent, however, during a high-temperature acid-washing step prior to elution.

These reactions were also studied in aqueous solution in the absence of carbon. The kinetics of AuCN precipitation from acidified aurocyanide solutions were found to be first order, with activation energy 73,5 kJ/mol. Polymeric AuCN was found to be unstable in alkaline solutions, particularly at elevated temperatures. The analysis of the solution for $Au(CN)_2^-$ and CNO^-, and the investigation of the resultant solid phase by XRD enabled the following overall reaction mechanism to be derived:

$$3AuCN + 2OH^- = 2Au^0 + Au(CN)_2^- + CNO^- + H_2O$$

This reaction probably also occurs on the carbon surface to some extent.

Aurocyanide adsorbed onto activated carbon from neutral and alkaline solutions is found to remain relatively stable at temperatures up to about 240°C, as concluded from the results of elemental analyses, scanning electron microscopy, X-ray diffractometry and Mössbauer spectroscopic measurements. At higher temperatures the aurocyanide is reduced to the metal, with evolution of gaseous HCN. A portion of the aurocyanide decomposes via an intermediate AuCN-type species. Aurocyanide loaded under acidic conditions decomposes by this mechanism at lower temperatures.

The controversy between different research workers regarding the mechanism of adsorption of aurocyanide onto activated carbon was shown to be due to differences in the experimental conditions employed by different research groups. The present work has shown that several different adsorption mechanisms are possible under varying conditions of ionic strength and pH, and in the presence or absence of oxygen. No evidence for any decomposition of $Au(CN)_2^-$ to AuCN, NH_4^+, HCO_3^-, or CNO^- species in neutral or alkaline solutions could be found. The effects of oxygen and ionic strength, and the pH shift that occurs upon adsorption, were found to be interrelated, and can be explained in terms of a dual adsorption mechanism which becomes more prevalent under low ionic strength conditions.

The important conclusions reached in the present work with regard to the mechanism of adsorption, from neutral and alkaline solutions, are summarized below.

Under all practical conditions (high ionic strength), *adsorption of aurocyanide onto activated carbon occurs via an ion pair mechanism in which ion pairs of the type* $M^{n+}[Au(CN)_2^-]_n$ *are adsorbed onto the carbon surface without chemical change. Oxygen has an insignificant effect on gold adsorption under these conditions.* Oxygen effects associated with operating carbon-in-pulp plants are more likely due to (i) catalytic oxidation of free cyanide, which results in more favourable conditions for gold adsorption, and (ii) enhancement of gold leaching, should this be incomplete.

Under conditions of low ionic strength, adsorption of aurocyanide onto activated carbon occurs via two mechanisms, the relative contributions of which depend on the presence of oxygen:

(i) adsorption of $M^{n+}[Au(CN)_2^-]$ ion pairs, which occurs to a greater extent in the absence of oxygen, and

(ii) formation of ion-exchange sites that coordinate aurocyanide by simple electrostatic ion-exchange. This mechanism occurs to a greater extent in the presence of oxygen.

The $Au(CN)_4^-$ species was found to adsorb onto activated carbon by a similar mechanism to that postulated for $Au(CN)_2^-$, i.e. as an ion pair of the type $M^{n+}[Au(CN)_4^-]_n$. The affinity of $Au(CN)_4^-$ for adsorption onto carbon is greater than that for $Au(CN)_2^-$, which is also consistent with the ion-pair mechanism.

A Mössbauer spectroscopic investigation confirmed that $Au(CN)_4^-$ is the adsorbed species from both acidic and neutral solutions. A carbon that was loaded with $Au(CN)_4^-$ and subsequently acid-boiled, was found to contain $Au(CN)_2Cl_2^-$, $Au(CN)_2^-$ and AuCN, which are products of the decomposition of $Au(CN)_4^-$ by boiling hydrochloric acid.

Silver is adsorbed onto activated carbon from potassium cyanide solution in the form of the $K^+Ag(CN)_2^-$ ion pair. This species is converted into Ag^+ and $Ag(CN)_4^{3-}$ ions upon adsorption, which are stabilized by complexation with surface functional groups. These species undergo further chemical change to AgCN and AgCl after boiling in hydrochloric acid. Subsequent treatment with hot sodium hydroxide solution results in the reduction of all of the silver on the carbon to the metallic state, with some desorption of $Ag(CN)_2^-$.

When silver is loaded onto activated carbon from a silver nitrate solution, adsorption takes place via a dual mechanism, with reduction to metallic silver and precipitation of AgCl both taking place on the carbon surface.

Mercury adsorbs onto activated carbon in the form of $Hg(CN)_2$ from cyanide solution. The $Hg(CN)_4^{2-}$ species adsorbs to a negligible extent, indicating the possibility of eluting adsorbed mercury with cold caustic cyanide solution. Adsorption of mercury from chloride solution occurs via the reduction to mercury(I) species, with subsequent precipitation of insoluble Hg_2Cl_2 within the carbon pores.

7.2 Ion Association of $MAu(CN)_2$ Salts in Various Solvents

Aqueous solutions of $KAu(CN)_2$ and $NaAu(CN)_2$ were found to display a modest degree of association ($K_A \sim 1$), and aqueous $HAu(CN)_2$ showed a higher degree of association ($K_A \sim 30$). Evidence from infrared spectrophotometric data suggest the presence of contact ion pairs and dimers in anhydrous THF and MEK solutions. Addition of a small amount of water effectively hydrates these species, forming solvent-separated ion pairs and free ions.

Distribution experiments confirmed the presence of associated and free species in water-saturated solvents. Correlations with organic phase water content were found to exist for association constant K_A as well as extraction constant K_{ex} for distribution of aurocyanide into various solvents from H^+, Li^+ and K^+ solution. For larger, less hydrated cations such as Cs^+ and NEt_4^+, however, other solvent properties such as dielectric constant and hydrogen-bonding ability begin to play a role.

Aurocyanide ion pairs are also extracted efficiently into organic phases by long-chain polyethers. The polyether coordinates to the alkali metal cation via ether oxygen atoms, wrapping around the ion in a helical configuration. High extraction efficiencies are obtained with high-dielectric solvents, which stabilize the helical polyether-cation complex. *Preferential secondary solvation of the aurocyanide anion by high-dielectric solvents is also an important factor that influences the extraction efficiency.*

The mechanism of extraction of aurocyanide by activated carbon has been established in the present work to involve the adsorption of $M^{n+}[Au(CN)_2^-]_n$ ion pairs under practical conditions. The work presented in this Thesis serves to provide a fundamental confirmation of this hypothesis, the presence of $MAu(CN)_2$ ion pairs in both aqueous and organic solutions having now been established. It is suggested that the interior of a micropore in activated carbon functions in a similar manner to a polar solvent or a poly(oxyethylene) helix, and acts by solvating the adsorbed ion pair. This confirmation also extends to other systems in which $MAu(CN)_2$ ion association has been postulated to play a role, for example in extraction of aurocyanide by polymeric adsorbent resins[80,132], as well as by new weak-base ion exchange resins under high pH conditions[134]. The specific effect of cation on the adsorption of aurocyanide by carbon can now be confirmed as being due to ionic association effects and solvation effects discussed in this Thesis.

7.3 The Mechanism of Elution of Aurocyanide from Activated Carbon

Evidence has been presented which suggests that the mechanism of elution involves ionization of the phenolic-type groups on the surface of activated carbon in strongly alkaline solution. This causes the carbon surface to be *negatively charged, hydrophilic, and incompatible with* adsorption of the aurocyanide ion pair. The catalytic effect of cyanide on the elution process is ascribed to a similar mechanism, but one in which the cyanide ion reacts with surface carbonyl groups, resulting in the formation of additional negatively charged O^- sites on the surface.

A kinetic model was developed for elution of aurocyanide from activated carbon, and was shown to successfully describe the kinetics of elution for several configurations, including recirculation of depleted eluate and flow through a carbon column.

Several chemical influences on the Zadra elution were also examined. Hot acid-washing of the carbon prior to elution was shown to slow down the elution kinetics (when no cyanide is present) due to the formation of metallic gold on the carbon. The extent of acid-washing is a compromise between maximum calcium removal and minimum formation of metallic gold. Decomposition of cyanide during elution was shown to be extensive; however, this was shown to have a significant deleterious effect on the elution only after long time periods not normally experienced in plant operations.

The elution step is an important one in the CIP process as a whole, and it is only relatively recently that an understanding of it is being gained on a fundamental level. A knowledge of how the important factors influence elution, viz. temperature, ionic strength, cyanide and hydroxide concentrations, organic additives and gold in the eluant feed, is essential to the effective utilization of the principles.

There are without doubt, many improvements that can be made to the relatively lengthy, energy-inefficient methods currently used for elution of gold from activated carbon, and the need for a fast, low temperature elution procedure has never been greater.

7.4 Influence of Activated Carbon Surface Chemistry and Structure on the Process

The most important parameter in the carbon activation process with regard to gold adsorption activity of the product, is activation temperature. The activation atmosphere and the starting material used are of secondary importance. This effect manifests itself in two ways - structurally and chemically.

Micropore volume is the structural parameter of greatest significance to the adsorption of gold, because the micropores provide adsorption sites that can snugly wrap around the adsorbate. Activated carbon surface area is not a good measure of the adsorption affinity for species. A high degree of microporosity is obtained when graphitization has occurred, and temperatures greater than 750°C are conducive to this phenomenon. The high conductivity of graphitic carbons is a by-product of the activation process, but it may also play a role in the adsorption of various species.

The correct structural characteristics alone are not sufficient to produce an activated carbon with a high activity for the adsorption of aurocyanide - the surface chemistry also plays an important role. Surface oxygen-containing functional groups impart a polar character to the inside of the micropore, and aid in the solvation of the adsorbate. Oxidants such as nitric acid result in a proliferation of surface carboxyl groups that are not conducive to the adsorption of gold. Both oxygen and hydrogen peroxide enhance the adsorption of gold. It is postulated that this occurs due to oxidation of specific functional groups that result in the formation of cationic sites on the carbon surface.

There is a marked correlation between the adsorption of aurocyanide onto activated carbon and that of phenol. It is postulated that a similar adsorption mechanism is present in both cases, viz. solvation by surface groups within micropores of the ideal size, with a possible charge-transfer contribution from the delocalized electron cloud of the carbon.

Two organic hydrocarbon polymers, a polyxanthate and a polyquinone, display particularly high gold adsorption capacities. Gold is adsorbed via an ion-exchange mechanism rather than a solvation adsorption such as that occurring in the case of activated carbon. The quinone functionalities are shown to be important in the adsorption of phenol onto the polyquinone, and probably also play a role in its adsorption onto activated carbon.

7.5 Ramifications for Existing Carbon-in-Pulp Operations

The research presented in this Thesis has several ramifications for existing carbon-in-pulp operations that have a more practical application than the improved understanding of the chemistry of the process, and these are summarized below.

a) Cyanide-free Elution

It is evident that the addition of cyanide is not a prerequisite for complete elution, which can be achieved using a hydroxide solution. The elution kinetics are somewhat slower with hydroxide than with cyanide; however, addition of a small amount of cyanide is sufficient to increase the elution kinetics significantly.

b) *Acid Treatment of Loaded Carbon Followed by Cyanide-free Elution*

Acid treatment was shown to convert the gold into short-chain $HAu_x(CN)_{x+1}$ oligomers that subsequently undergo a reduction reaction on contact with alkaline solution, with about half of the gold being converted to the metallic form, which cannot be eluted by hydroxide alone. The addition of a small amount of cyanide to the eluant is necessary to prevent this reaction from occurring.

c) *Effects of Oxygen and Ionic Strength*

Oxygen enhances the adsorption reaction in solutions of low ionic strength, but not significantly in solutions of high ionic strength. This fact has ramifications in choosing the most suitable test for carbon activity, which should include conditions of high ionic strength if the effect of oxygen is to be avoided.

d) *Kinetics of Elution*

A model has been developed which can adequately predict the fraction of gold eluted at any time. Successful application of the model to practical plant data will probably require a high degree of computerized process control.

7.6 Ramifications for Future Process Options

The advent of carbon-in-pulp has paved the way for the development of other adsorbents for gold, such as aurocyanide-specific ion-exchange resins. Certain other options are highlighted as possibilities from the results of the present research.

a) *Modification of Dielectric Constant within the Ion-exchange Resin*

The extraction of large anions such as aurocyanide will probably be enhanced, both in capacity and selectivity, by means of the modification of the dielectric constant within the pores of the resin, by chemical modification of the resin matrix.

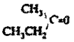
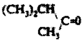
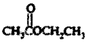
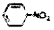
b) *Alternative Functional Groups and Matrices for Ion-exchange Resins*

The present research has raised several intriguing possibilities for the application of alternative adsorbents to the extraction of gold. One such adsorbent would contain poly(oxyethylene) functional groups, and the matrix would be modified in such a way as to improve the dielectric properties. Possible advantages are ease of elution using de-ionized water and enhanced selectivity for aurocyanide. A foreseeable disadvantage is the likelihood of organic compounds poisoning the resin.

A second possibility involves exchanging the conventional polystyrene matrix and amine functional groups for a polyquinone or polyxanthene matrix with carbonium-ion functional groups. These adsorbents promise to have high capacities; however, extensive fundamental and developmental research would be required before their viability could be established.

APPENDIX 1

SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE ORGANIC SOLVENTS STUDIED

Solvent	Structure	ε[a]	μ[b](D)	DN[c]	AN[d]	Solubility[e] of solvent in aqueous phase		Solubility[e] of water in solvent		MW (g/mol)	bp (°C)	ρ (g/cm³)	η (cP)	δ
						wt%s	$100x_s$	%w	$100x_w$					
1-Butanol (B)	$CH_3(CH_2)_3OH$	17.8	1.68	19.5 24.0		7.31	1.88	20.4	48.3	74.1	117.7	0.81	2.46	13.6
1-Pentanol (P)	$CH_3(CH_2)_4OH$	13.9	1.63			2.19	0.45	7.5	28.3	88.2	137.9	0.814	3.31	11.6
1-Hexanol (H)	$CH_3(CH_2)_5OH$	13.28	1.64			0.56	0.10	7.2	42.1	102.2	157.8	0.82	5.44	10.7
1-Octanol (O)	$CH_3(CH_2)_6OH$	10.3	1.68			0.03	0.05	4.6	25.8	130.2	195.2	0.82	8.31	
Methyl ethyl ketone (MEK)	 $CH_3(CH_3CH_2)C{=}O$	18.0	2.74	17.4		22.6	6.8	9.9	28.9	72.1	79.6	0.805	0.42	
Methyl isobutyl ketone (MIBK)	 $(CH_3)_2CH(CH_3)C{=}O$	13.1	2.79			1.7	0.31	1.9	9.8	100.1	115.9	0.804	0.55	
Cyclohexanone (CX)		18.3	2.80	17.8		5.0	0.94	8.7	34.1	98.1	156.7	0.948	2.30	9.9
Ethyl acetate (EA)	 $CH_3C({=}O)OCH_2CH_3$	6.4	1.85	17.1		7.48	1.63	3.20	13.9	88.1	77.1	0.902	0.45	
Diethyl ether (DE)	$CH_3CH_2OCH_2CH_3$	4.2	1.25	19.2	3.9	6.04	1.54	1.26	4.97	74.1	34.6	0.715	0.22	7.4
Tributyl phosphate (TBP)	$(BuO)_3P{=}0$	6.8	3.07	23.7		0.04	0.003	6.4	105	266.32	289	0.973		
Nitrobenzene (NB)		34.82	4.03	4.4	14.8	0.19	0.028	0.25	1.71	123.1	210.7	1.198	1.63	10.0
Tetrahydrofuran (THF)		7.4	1.7	20.0	8.0	S	S	S	S	72.12	67	0.889		
Benzene (BZ)		2.28	0.0	0.1	8.2	0.178	0.042	0.072	0.31	78.12	80.1	0.879		
Cyclohexane (CH)		2.02				0.705	0.107	0.072	0.48	84.16	80.74	0.775		
1:1 Pentanol: Benzene		9.3[f]	-	-	-				5.4	-	-	0.794[g]		
1:1 Pentanol: Cyclohexane		5.5[f]	-	-	-				4.0	-	-	0.841[g]		

[a] Dielectric constant; data from refs 214 and 216.

[b] Dipole moment; data from refs 214 and 216.

[c] Gutmann's[212,213] donor number, from refs 215 and 216

[d] Gutmann's[212,213] acceptor number, from refs 212 and 214.

[e] Data from ref. 49. (All other data from ref. 65).

[f] This work.

[g] Measured for water-saturated solvents; this work. (Theoretical densities for pure 1:1 mixtures are 0,797 and 0,847 g/ml respectively).

APPENDIX 2

CALCULATION OF ESTIMATED EFFECTIVE IONIC RADII FOR $Au(CN)_2^-$ AND $Ag(CN)_2^-$

$Au(CN)_2^-$

			Ref.
Au - C	Bond distance in $KAu(CN)_2$	2,12 Å	119
C - N	Bond distance in $KAu(CN)_2$	1,17 Å	119
CN	Radius	1,96 Å	222
C - N	Bond distance in NaCN; KCN	1,05 Å	273
∴ N	Atomic radius	1,44 Å	
∴ $Au(CN)_2^-$	½ length	4,73 Å	
Au^+	Radius	1,37 Å	274
∴ $Au^+ + 2CN^-$	Volume	73,85 $Å^3$	
∴ $Au(CN)_2^-$	Effective radius	2,60 Å	
$Au^+ + 2CN^-$	Sum of radii	5,29 Å	
	% deviation from crystallographic ½ length	10,6 %	
∴ $Au(CN)_2^-$	Effective radius corrected for bond lengths	2,33 Å	

$\underline{Ag(CN)_2^-}$

				Ref.
	Ag - C	Bond distance in $KAg(CN)_2$	2,13 Å	275
	C - N	Bond distance in $KAg(CN)_2$	1,15 Å	127
	CN	Radius	1,96 Å	222
	C - N	Bond distance in NaCN; KCN	1,05 Å	273
∴	N	Atomic radius	1,44 Å	
∴	$Ag(CN)_2^-$	½ length	4,72 Å	
	Ag^+	Radius	1,26 Å	221
∴	$Ag^+ + 2CN^-$	Volume	65,75 $Å^3$	
∴	$Ag(CN)_2^-$	Effective radius	2,50 Å	
	$Ag^+ + 2CN^-$	Sum of radii	5,18 Å	
		% deviation from crystallographic ½ length	8,9 %	
∴	$Ag(CN)_2^-$	Effective radius corrected for bond lengths	2,28 Å	

APPENDIX 3

DISTRIBUTION AND ASSOCIATION DATA FOR $MAu(CN)_2$ IN VARIOUS SOLVENTS

Solvent	Constant	H	Li	K	Cs	NEt_4
1-Pentanol	K_A	2418	1045	1004	377,1	9949
	$10^4.K_{ex}^{TOT}$	185347	2821	330,5	489,0	2052
	$10^4.K_{ex}^{ION}$	875,5	164,3	57,39	113,9	45,11
	K_{ex}^{IP}	211,7	17,17	5.76	4,29	44,88
	n	0,70	0,67	0.60	0,63	0,87
MIBK	K_A	2188	2364	14186	4724	701,1
	$10^4.K_{ex}^{TOT}$	156,7	1,04	5,25	2,87	234,8
	$10^4.K_{ex}^{ION}$	26,76	2,10	1,92	2,47	57,87
	K_{ex}^{IP}	5,86	0,50	2,73	1,16	4,06
	n	0,79	0,66	0,81	0,63	0,59
Ethyl acetate	K_A	[a]	856486	20165		34736
	$10^4.K_{ex}^{TOT}$	[a]	0,00892	0,459		0,658
	$10^4.K_{ex}^{ION}$	[a]	0,102	0,477		0,434
	K_{ex}^{IP}	[a]	0,874	0,962		1,51
	n	1,0	0,37	0,92	0,88	0,76
TBP	K_A	806,9	4184	1160	2053	1457
	$10^4.K_{ex}^{TOT}$	$2,80 \times 10^8$	497415	4134	3555	6077
	$10^4.K_{ex}^{ION}$	58850	1090	188,8	131,6	204,2
	K_{ex}^{IP}	4749	456,2	21,90	27,01	29,96
	n	0,74	0,68	0,63	0,70	0,67
Nitrobenzene	K_A	[a]	7210	20403	-451,9	-22,03
	$10^4.K_{ex}^{TOT}$	[a]	$4,29 \times 10^{-9}$	0,203	-0,638	-234522
	$10^4.K_{ex}^{ION}$	[a]	0,00771	0,315	3,76	10318
	K_{ex}^{IP}	[a]	0,00556	0,643	-0,170	-22,73
	n	1,0	0,56	0,99	0,50	0,50

[a] Data unobtainable due to an insufficient degree of extraction. Value for n refers to data obtained in the region of ion-exchange with $\overline{HCl}$. Higher aqueous $HAu(CN)_2$ concentrations could not be studied due to decomposition to AuCN.

APPENDIX 4

The Reduction Potentials of AuCN and AgCN.

	E^0(V)[a]		
$AuCN = Au^+ + CN^-$		$(K_{so} = 6{,}04 \times 10^{-32})$[b]	
$Au^+ + e^- = Au^0$	1,68[c]		
$AuCN + e^- = Au^0 + CN^-$	-0,166		(1)
$AuCN + CN^- = Au(CN)_2^-$		$(K = 1{,}205 \times 10^7)$[d]	
$2AuCN + e^- = Au^0 + Au(CN)_2^-$	0,252		(2)
$AgCN = Ag^+ + CN^-$		$(K_{so} = 2{,}291 \times 10^{-16})$[e]	
$Ag^+ + e^- = Ag^0$	0,7996		
$AgCN + e^- = Ag^0 + CN^-$	-0,125		(3)
$AgCN + CN^- = Ag(CN)_2^-$		$(K = 1{,}622 \times 10^5)$[f]	
$2AgCN + e^- = Ag^0 + Ag(CN)_2^-$	0,183		

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[a] All standard reduction potentials are reported as measured against the standard hydrogen electrode (SHE)

[b] Kuzminykh and Tyurin[273]

[c] All data, unless specified otherwise, are from Weast[65]

[d] Based on log $\beta_2 = 38{,}3$ (Sillen and Martell[83,84])

[e] Sillen and Martell[83,84]

[f] Based on log $\beta_2 = 20{,}85$ (Sillen and Martell[83,84])

APPENDIX 5

List of Publications Arising from this Thesis

1. Adams, M.D. and Fleming, C.A., The Mechanism of Adsorption of Aurocyanide onto Activated Carbon. *Metall. Trans. B*, 1989, **20B**, 315-326.

2. Adams, M.D. and Wagner, F.E., Reactions of Adsorbed Aurocyanide Species on Activated Carbon Surfaces. 1989. Paper in preparation.

3. Adams, M.D., The Mechanism of Adsorption of Aurocyanide onto Activated Carbon. 1. Relation between the Effects of Oxygen and Ionic Strength. *Hydrometallurgy*, 1989. Submitted for publication.

4. Adams, M.D. and Wagner, F.E., The Mechanism of Adsorption of Aurocyanide onto Activated Carbon. 2. Thermal Stability of the Adsorbed Species. *Hydrometallurgy*, 1989. To be submitted.

5. Adams, M.D., Innes, D.E. and Copperthwaite, R.G., Adsorption of Aurocyanide onto Activated Carbon Surfaces by Charge-transfer Interaction. 1989. Paper in preparation.

6. Adams, M.D., Fourier Transform Infrared Spectroscopic Study of Adsorbed Aurocyanide Species on Activated Carbon. 1989. Paper in preparation.

7. Adams, M.D. and Wagner, F.E., The Mechanism of Adsorption of $Au(CN)_4^-$ onto Activated Carbon. 1989. Paper in preparation.

8. Adams, M.D., The Mechanisms of Adsorption of $Ag(CN)_2^-$ and Ag^+ onto Activated Carbon,

Hydrometallurgy, 1989. To be submitted.

9. Adams, M.D., The Mechanisms of Adsorption of $Hg(CN)_2$ and $HgCl_2$ onto Activated Carbon, *Hydrometallurgy*, 1989. Submitted for publication.

10. Adams, M.D. Wade, P.W. and Hancock, R.D., The Extraction of Aurocyanide Ion Pairs by Poly(oxyethylene) Extractants, *Talanta*, 1989. Submitted for publication.

11. Adams, M.D., The Kinetics of the Elution of Gold from Activated Carbon by the Zadra Method. *Trans. Inst. Min. Metall., Sect. C*, 1989. Submitted for publication.

12. Adams, M.D., *Elution Theory. In:* Thatcher, L.M., (ed.), 1990. Monograph on the carbon-in-pulp process, to be published.

APPENDIX 6

DIRECTORY OF ANALYTICAL DATA LOCATED ON MICROFICHE

Table A1	Elution of gold from activated carbon after acid treatment
Table A2	AuCN precipitation kinetics
Table A3	Effect of O_2 on gold loading
Table A4	Extraction of $Au(CN)_4^-$ and $Au(CN)_2^-$ by activated carbon
Table A5	Effect of $[CN^-]$ on the extraction of Ag and Hg by activated carbon
Table A6	Potentiometric titration of $HAu(CN)_2$
Table A7	Distribution data
Table A8	Extraction of gold by Triton X-100
Table A9	Effect of flowrate on elution
Table A10	AARL type elution
Table A11	Effect of [Au] in feed on elution
Table A12	Simulated Zadra elution
Table A13	Column elution ; not pre-equilibrated
Table A14	Column elution ; pre-equilibrated
Table A15	Column elutions (5 ml)
Table A16	Effect of temperature on elution

Table A17 Effect of ionic strength on elution

Table A18 Effects of [NaOH] and [NaCN] on elution

Table A19 Effect of CN^- and OH^- at I = 1,2 M

Table A20 *Effect of [NaCN] at [NaOH] 0,2 M*

Table A21 Gold extraction data

Table A22 Extraction of phenol by activated carbon

APPENDIX 7

COMPUTER PROGRAMS DEVELOPED DURING THIS RESEARCH, LOCATED ON MICROFICHE

XPSFIT	Program for fitting Gaussian curves to 2 overlapping sets of Au(4f 7/2) and Au(4f 5/2) XPS peaks. Adapted from PARAFIT[48].
SHEDLOVSKY	Program to calculate association constant and limiting ionic conductance from conductivity data using the Shedlovsky[193] equation.
ELUTION	Program for the calculation of gold loading on carbon from data of gold concentration in eluate.
ZADRASIM	Program for the calculation of gold loading on carbon from data of gold concentration in eluate from Zadra elution with electrowinning cell simulated by dilution.
BED	Program to model the elution of gold from activated carbon by the Zadra process incorporating a fixed bed of carbon and an electrowinning cell.
COLUMN	Program to model the elution of gold from activated carbon by the Zadra process incorporating a column and electrowinning cell. (Modified version of a program written by M.J. Nicol, Mintek).
COLEQUIL	Program to model the elution of gold from activated carbon by the Zadra process incorporating a column and electrowinning cell - assuming equilibration is reached prior to elution commencing.

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