THE ION EXCHANGE PHENOMENON OF ACETYLENE BLACK

BY

JOHANNES WILHELM COETZEE

A THESIS SUBMITTED IN FULFILMENT OF THE
MASTERS DEGREE OF TECHNOLOGY IN CHEMICAL
ENGINEERING AT THE CAPE TECHNIKON

SUPERVISOR : PROF F W PETERSEN

THE CAPE TECHNIKON

JUNE : 1996

ABSTRACT

Acetylene Black (ACB) is a pure form of carbon which is used in the battery, plastics, printing and rubber industries. It is extensively used in the battery industry to absorb electrolyte and to lower the electrical resistance of dry cell batteries. It is the attempt of this thesis to investigate the surface characteristics and structure of ACB by using it as an adsorbent for cyanide complexes, in particular gold cyanide.

The thesis is predominantly aimed at identifying the mechanism of metal cyanide adsorption onto ACB, viz. ion exchange and/or physical adsorption. In order to quantify the mechanism of adsorption, comparative studies with other adsorbents currently used in the mining industry, such as activated carbon, were conducted. These studies revealed various similarities in the metal adsorption process between ACB and activated carbon, thus indicating physical adsorption rather than ion exchange to be the dominant mechanism for metal adsorption from solution.

The rate of metal adsorption onto acetylene black was relatively fast compared to activated carbon. Furthermore, adsorption profiles revealed that intraparticle diffusion was negligible when a metal was adsorbed onto ACB from solution. This indicates that acetylene black has a predominantly amorphous structure, although X-ray diffractrometry indicates a certain degree of graphitisation associated with ACB.

The small surface area of ACB, together with the lack of intraparticle diffusion, resulted in the rapid attainment of the equilibrium metal loading on ACB. Moreover, this equilibrium metal loading was far less than that of activated carbon and ion-exchange resin. While pH, temperature and strong oxidizing agents had a marked effect on the adsorption profile of metal cyanides onto ACB, the effect of oxygen enrichment and organic solvents was negligible. Furthermore, the adsorption of gold onto ACB is best explained by a Freundlich-type isotherm. As is the case with activated carbon and ion exchange resin, gold is eluted from ACB by a NaOH solution. It was also found that the elution efficiency is influenced by a change in temperature.

Changes in operating variables in the production of ACB had an effect on the absorption stiffness of the product. Both an increase in acetylene feed rate and operating temperature reduced the absorption stiffness of the product.

ACKNOWLEDGEMENTS

The work contained in this thesis was carried out in the Department of Chemical Engineering at the Cape Technikon between January 1994 and August 1995.

I wish to thank my supervisor for this project, Prof F W Petersen, not only for his guidance during the project but also for his friendship.

I would like to thank Karbochem for their financial support, and in particular Messr C Brodrick and G Louw who were always willing to assist.

A special thank you to Ms A Lloyd for her assistance with experimental work and, without whom, the smooth running of the project would not have been possible.

I especially would like to thank Lana for her support, love and positive influence, not only throughout the duration of this project but throughout everything I try to achieve.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 ACETYLENE BLACK (ACB) PRODUCTION

As early as the 1860's it was known that carbon can be obtained from acetylene. Since that time many processes, such as explosion under pressure and partial combustion have been used to produce carbon black. The carbon black used for the purpose of this thesis is produced by the thermal decomposition of acetylene gas at temperatures above 800 °C. It is important that this reaction takes place in the absence of oxygen to eliminate a combustion reaction in which carbon dioxide and carbon monoxide is produced.

$$C_2H_2 \rightarrow 2C_{(s)} + H_{2(g)} \qquad \Delta H = -220 \text{ kJ/mole} \qquad (1.1)$$

The average cost of this process in 1986 was 1000 US dollars per tonne (Shakourzadeh *et al.*, 1986)

Acetylene, obtained from the carbide process, is cracked in a cylindrical, refractory lined retort (reactor), fitted with a suitable nozzle to ensure the effective distribution of acetylene as illustrated in Figure 1.1. At start-up, air is allowed into the retort and the acetylene is ignited and allowed to combust until the temperature in the retort reaches a value of above 800 °C. At attainment of the correct temperature for cracking, the air supply is discontinued and the production of ACB commences. The temperature in the retort is then controlled by cooling water circulation in the jacket of the retort and by controlling the acetylene feed rate. ACB is conveyed to the bagging section by means of a pneumatic conveyor and separated from the air stream by means of a cyclone separator. The ACB is then compressed to reduce transport costs. However, compression influences electrolyte absorption negatively. Thus, the degree of compression must be selected carefully.

Although the process described above is still the most commonly used one to supply carbon to the dry cell battery industry, other processes, such as the partial combustion of benzene, have been investigated to replace the classical method (Shakourzadeh *et al.*, 1986). The partial combustion of benzene is given by the following reaction :

$$C_6H_6 + 1.2\ O_2 \rightarrow 0.4(6\ CO + 3\ H_2) \qquad (1.2)$$

$$C_6H_6 \rightarrow 0.6(3\ C_2H_2) \rightarrow 0.6(6\ C + 3\ H_2) \qquad (1.3)$$

Furthermore, the "*MURABLACK PROCESS*" has been developed by MURABLACK LTD (India) and claims to produce a superior product for use in dry cell batteries (Stoeckli *et al.*,1995).

1.2 INDUSTRIAL USES OF ACB

ACB is used extensively in the rubber, plastics and battery industries, and to a lesser extent in the production of printing inks, cables and pigments. However, ACB is more well known for its contribution in the production of dry cell batteries. Although ACB does not play a role in any chemical reaction, it does play a significant role in the overall performance of the dry cell battery. For the purpose of dry cell battery production, ACB is used to absorb electrolyte and to lower the electrical resistance of the cell.

1.3 OBJECTIVES OF THIS STUDY

Although much research has, and still is devoted to the performance of ACB in dry cell batteries and how to improve such performance, there is a general lack of information on the adsorptive behaviour of ACB. In a rapidly changing world, and in view of increasing research being devoted to rechargeable batteries where ACB plays no role, it was decided to launch an investigation into the adsorptive/ion exchange behaviour of ACB in order to find a new application for this substance. The specific objectives were :

- To evaluate the recovery of metal cyanides from solution by ACB.
- To quantify the mechanism of metal cyanide recovery viz. ion exchange and/or adsorption.
- To investigate the possibility of increasing the adsorptive behaviour of ACB.
- To compare ACB as an adsorbent to other adsorbents currently used in the mining industry.
- To evaluate the effect of operating parameters in the retort on the performance of ACB.

Although metal cyanides, and in specific gold cyanide, was used to investigate the adsorptive behaviour of ACB, it is not the attempt of this thesis to specifically investigate ACB as an adsorbent in the mining industry, but rather to shed more light on the surface characteristics of ACB.

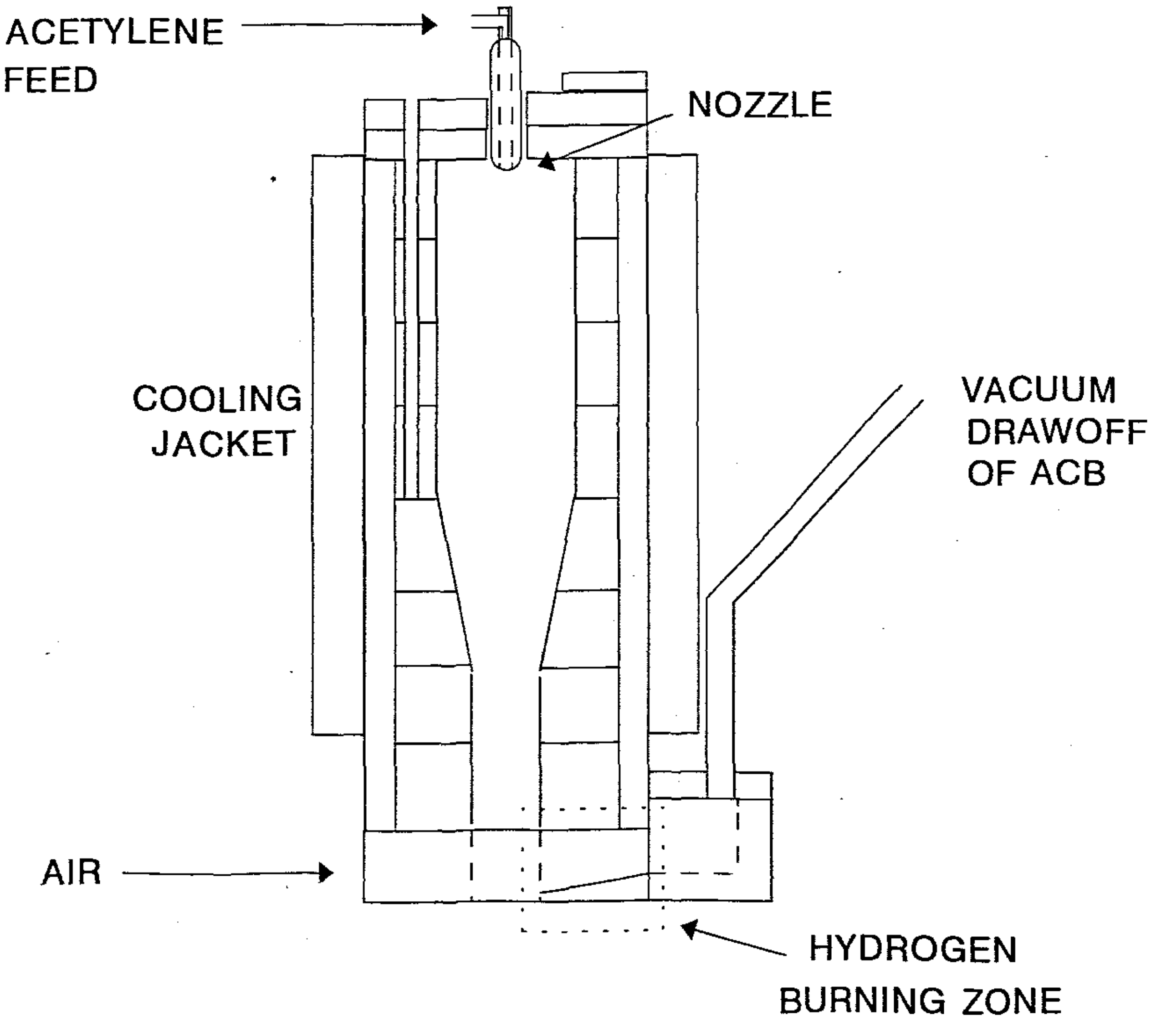

Figure 1.1 : Retort layout

CHAPTER 2

LITERATURE REVIEW

2.1 CHEMICAL AND PHYSICAL PROPERTIES

2.1.1 Carbon Black

Acetylene black belongs to the carbon black family which is characterized by their amorphous or imperfect graphitic structure. However, carbon blacks consist of nuclei surrounded by concentrically deposited carbon layers, and these layers are arranged similarly to that of graphite. Furthermore, these layers are nearly parallel to one another but they are randomly positioned so that there are no *c* direction as found with graphite (Ullmann's Encyclopedia of Industrial Chemistry, 1986). The "crystalline" regions within carbon blacks varies between 60-90%. The specific surface area of carbon blacks varies widely and may be as small as 10 m^2/g and as large as 1000 m^2/g. Furthermore, carbon blacks with a surface area of less than 150 m^2/g are porous with pore diameters of less than 1.0 nm. The global chemical composition of carbon blacks are shown in Table 2.1. Hydrogen and oxygen are bound to the carbon surface as shown in Figure 2.1. Hydrogen is bound to the carbon surface as CH groups and, more importantly, oxygen is bound to the surface as acidic or basic functional groups. Thermal blacks may contain up to 2% by mass oxygen and is found on the surface as almost pure, basic surface oxides (Ullmann's Encyclopedia of Industrial Chemistry, 1986).

2.1.2 Acetylene Black

Acetylene Black (ACB), produced by the thermal decomposition of acetylene, belongs to the carbon black family, but unlike other carbon blacks has a "*chainlike*" structure with void spaces to form an integrated network as depicted in Figure 2.2. Furthermore, these void spaces has an effect on the particle size when ACB is compressed. Petersen *et al.* (1994) showed that 67 % of the ACB particles of a 50 % compressed sample were smaller than 3 μm, whereas only 55 % of the particles were smaller than 8 μm when the sample is compressed by 25 %. Furtermore, ACB has a relatively small surface area of 60 m^2/g.

ACB is neither truly crystalline nor is it truly amorphous. However, ACB is found to be more crystalline than most other carbon blacks with the crystalline structure found internally. At present, the accepted structure is that of graphitic layers stacked together at equidistant intervals slightly greater than that of graphite. However, these layers are arranged randomly in respect to one another (Shawinigan Acetylene Black, 1950).

The structure of ACB is frequently defined by its absorption stiffness value (A.S. value). The A.S. value, which indicates the degree of structure associated with ACB, is the mass of a water/acetone mixture absorbed by a certain mass of ACB. Thus, changes in the structure of ACB can be identified via changes in the AS value (Petersen *et al.*, 1994). Grinding, mechanical mixing and compression were identified as factors which alteres the AS value, hence structure.

Petersen *et al.* found that an inverse relationship exists between the electrical resistance of ACB and the pressure applied to a specific sample. Thus, the higher the density the less the electrical resistance offered by ACB in the dry cell battery. Furthermore, trace impurities of alumina, copper, iron and potassium are present in ACB while aromatics, such as anthracene and naphtalene, are also present.

The ACB used for the purpose of this thesis shows an internal moisture content of 0.08%. Exposure to the atmosphere does however not increase the internal moisture content (Petersen *et al.*, 1994). Moreover, ACB is not readily wetted with water. However, traces of acids, acetone or wetting agents can overcome this resistance to wetting.

2.1.3 Activated carbon

Activated carbon, irrespective of the source material, is characterized by its large surface area, typically 600 to 1500 m^2/g. This large internal surface area together with the high surface activity of activated carbon makes it an effective adsorbent for many organic and inorganic substances. Activated carbon contains a complex network of pores, which can be classified according to their equivalent diameters (McDougal and Hancock, 1980) :

macropores	50	-	2000	nm
mesopores	5	-	50	nm
micropores	0.8	-	5	nm

Furthermore, these pores constitute the largest percentage of the surface area of an activated carbon particle.

2.1.4 Ion-exchange resin

Synthetic ion-exchange resin consists of an inert polymeric hydrocarbon network to which functional groups are chemically attached. Furthermore, ion exchange resins are all cross-linked gels, containing a large percentage of water, irrespective of the method of manufacture (Arden, 1968). Anion-exchange resins contain quaternary ammonium groups for strong-base resins and primary, secondary or tertiary amines for weak-base resins, whereas cation exchange resins contain phenolic, sulphonic, carboxylic and phosphonic acid as ion exchange groups (Kunin, 1972).

Ion-exchange resin can be classified into two main types:

- The gel type resin with high exchange capacity and a pore diameter of 1 nm.
- The macroporous or macroreticular type with its more porous structure and faster loading capacity and a pore diameter of 100 nm.

2.2 THE MECHANISM OF ADSORPTION

2.2.1 Activated carbon

Although much research, resulting in numerous publications, have been devoted to the mechanism of metal complex recovery by activated carbon, full agreement has not been reached between various researchers. It has been suggested (Dixon *et al*, 1978) that an electrostatic interaction exists between $Au(CN)_2^-$ and $Ag(CN)_2^-$ anions and positively charged sites on the activated carbon surface. McDougal *et al.* (1980) suggests that gold cyanide is recovered from solution in the form of an ion pair, $M^{n+}\{Au(CN)_2^-\}$, where M^{n+} is an cation such as Na^+, K^+ or Ca^{2+}. The presence of these cations increases the loading capacity of the $Ag(CN)_2^-$ complex onto activated whereas the presence of competing ions such as CN^- decreases loading capacity (Cho and Pitt, 1979).

The explanation of Tsuchida *et al* (1984) is based on the oxidation of $Au(CN)_2^-$ by chemisorbed oxygen. Neutral AuCN is adsorbed and CN is decomposed to CO_3^- and NH_3. The formation of CO_3^- at the active site of the carbon surface then leads to the precipitation of Ca^{2+} and Mg^{2+}.

In more recent work (Adams, 1990) it was found that several different adsorption mechanisms could be found under varying conditions such as, high or low ionic strength, different pH levels and the presence of oxygen. Under conditions of high ionic strength, the adsorption takes place via a ion-pair mechanism and under conditions of low ionic strength two mechanisms exists, one which involves the adsorption of ion pairs and the other electrostatic ion-exchange.

2.2.2 Ion-exchange resin

Gold, in the form of the anionic $Au(CN)_2^-$ complex, is extracted from solution by an anion-exchange resin. A strong-base resin contains quaternary amine functional groups and extracts aurocyanide as follows (Fleming and Nicol, 1981) :

$$\vdash N^+R_3X^- + Au(CN)_2^- \rightarrow \vdash N^+R_3Au(CN)_2^- + X^- \qquad (2.1)$$

where the symbol $\vdash$ denotes the matrix of the resin. A weak-base resin contains tertiary amine functional groups, and, in the free-base form, the resin is uncharged. Therefore, it is necessary for the resin to be protonated prior to the extraction of aurocyanide. This protonation can only occur at pH levels below the pK_a of the tertiary amine functional group and it is thus essential that the pH of the pulp is below the pK_a of the resin (Fleming and Nicol, 1981).

$$pH < pK_a$$

$$\vdash NR_2 + H^+X^- \rightleftarrows \vdash N^+R_2HX^- \qquad (2.2)$$

$$pH > pK_a$$

$$\vdash NR_2HX^- + Au(CN)^- \rightleftarrows \vdash N^+R_2HAu(CN)^- + X^- \qquad (2.3)$$

The most promising weak-base resins have pK_a values between 9 and 11 with the maximum absorption of anions between pH 7 to 9. These pH values are sufficiently high to eliminate the danger of HCN evolution (Fleming and Nicol, 1981).

2.3 ELUTION

2.3.1 Activated carbon

Temperature is probably the variable which has the greatest effect on elution rate (SAIMM, 1987). Where an increase in temperature decreases the loading capacity of gold onto activated carbon, it increases the elution rate. Furthermore, while the presence of dissolved solids such as Ca^{2+} and Na^+ favours the adsorption stage, the presence of these species decrease elution efficiency. Hence, desorption is favoured by conditions of low ionic strength.

It is postulated that the addition of a hot NaOH solution converts the $Ca^{2+}\{Au(CN)_2\}^-$ ion pair into the less strongly adsorbed $Na^+Au(CN)^-$ ion pair, which is then stripped under conditions of low ionic strength (SAIMM, 1987). This is the basis of the Anglo American Research Laboratories (AARL) elution process. The reduction in the gold loading capacity of activated carbon in the presence of high cyanide concentrations is the basis of the Zadra elution process. It is believed that the cyanide ion is involved in competitive adsorption on the active sites of the carbon.

The effect of various organic solvents on the desorption process have been studied by various researchers. It was found that desorption can occur, even at low temperatures, in the presence of high concentrations of certain organic solvents (SAIMM, 1987). A mechanism whereby the organic solvent greatly increases the activity of small anions, such as CN^-, and has little effect on large complex anions, have been suggested by Muir *et al.*, 1985.

2.3.2 Ion-exchange resin

Gold is easily eluted from weak-base resins using a fairly dilute caustic solution :

$$\vdash N^+R_2HAu(CN)_2^- + OH^- \rightleftarrows \vdash NR_2 + H_2O + Au(CN)_2^- \qquad (2.4)$$

The elution of gold from strong-base ion-exchange resins can be achieved in one of two ways, namely, the displacement of the aurocyanide by another anion or the conversion of the gold to a non-anionic complex. The latter is achieved by the addition of the neutral thiourea ligand in an acidic environment (Fleming and Nicol, 1981) :

$$\vdash N^+R_3Au(CN)_2^- + (NH_2)_2CS + 2HX \rightleftarrows$$
$$\vdash N^+R_3X^- + [Au(NH_2)_2CS]^+ + 2\ HCN \qquad (2.5)$$

The aniodic complex can also be displaced by anions such as chloride or sulphate. However, this process only becomes feasible with the addition of organic solvents which markedly increases the activity of the chloride or sulphate. Zinc cyanide, because it is relatively cheap and compatible with existing gold processes, has been investigated as an anion to displace aurocyanide. This process involves the following reaction :

$$2\ \vdash N^+R_3Au(CN)_2^- + Zn(CH_4)^{2-} \rightleftarrows (\vdash N^+R_3)_2Zn(CN)_4^{2-} + 2\ Au(CN)_2^- \qquad (2.6)$$

During the elution step the resin becomes loaded with zinc cyanide and must be regenerated before use in the adsorption process.

$$(\vdash N^+R_3)_2Zn(CN)_4^{2-} + 4\ HX \rightleftarrows 2\ \vdash N^+R_3X^- + ZnX_2 + 4\ HCN \qquad (2.7)$$

2.4 FACTORS INFLUENCING THE EQUILIBRIUM AND KINETIC PARAMETERS

2.4.1 Activated carbon

An increase in temperature reduces the gold and silver loading capacity of activated carbon as a result of the exothermic nature of this process (McDougall and Hancock 1980). Furthermore, Dixon *et al* (1978) concluded that a reduction in the oxygen concentration in the system reduces the active sites on the carbon surface, and hence, reduces the equilibrium loading of aurocyanide onto activated carbon. Van der Merwe and Van Deventer (1988) found that an increase in the oxygen concentration above atmospheric level increased the gold and silver loading capacities of certain carbons.

Various researchers (McDougall and Hancock, 1980; Fleming and Nicol, 1984) *have shown that a reduction in the* pH *of the system will generally favour the* aurocyanide loading capacity of activated carbon. This effect is the result of the increased adsorption of the neutral $HAu(CN)_2$ species (Adams *et al*, 1987).

Free cyanide in the system adversely affects the adsorption of aurocyanide onto the surface of activated carbon (Fleming and Nicol, 1984). Furthermore, the presence of organic compounds such as ethanol, benzene, acetone and acetonitrile also reduces the equilibrium capacity of activated carbon (Fleming and Nicol, 1984).

2.4.2 Ion exchange resins

The effect of temperature on the loading of aurocyanide onto ion exchange resin is relatively small when compared to the effect it creates on the loading capacity of activated carbon as reported by Fleming and Cromberge (1984). Furthermore, resin performance is almost unaffected by the addition of organic solvents to the system. Clays or shales are also not expected to influence the loading capacity or kinetics of adsorption of ion-exchange resins as resins do not possess large micropores. Finally, the loading of aurocyanide onto resins decreases with increasing ionic strength (Fleming and Nicol, 1984).

2.5 EQUILIBRIUM EXPRESSIONS

2.5.1 The linear isotherm

One of the most frequently used single solute isotherms used is of the form:

$$q_e = AC_e \tag{2.8}$$

However, this linear isotherm is only applicable at very low concentrations of adsorbate.

2.5.2 The Freundlich isotherm

$$q_e = AC_e^n \tag{2.9}$$

This isotherm is widely used to describe single solute adsorption from solution although it does not approach true linearity at low equilibrium concentrations (Morris and Weber, 1962).

2.5.3 The Langmuir isotherm

This isotherm is linear at low concentrations and is of the form:

$$q_e = \frac{AC_e}{B+C_e} \tag{2.10}$$

When molecules are adsorbing onto the adsorbent surface, the rate of adsorption is proportional to the percentage of free space available on the adsorbent surface and also on the concentration of the solution. Equilibrium is reached when the rate of adsorption equals that of desorption (Pergamon, 1991).

2.6 SIGNIFICANCE OF THE LITERATURE REVIEW

From the review of the literature, it is clear that little published information exists on the adsorptive/ion exchange behaviour of acetylene black. Furthermore, little agreement between researchers seems to exist on the actual structure of ACB.

This thesis will investigate the adsorptive behaviour of ACB and an attempt will be made to shed more light on the structure of ACB. Moreover, ACB will be compared to other adsorbents in an attempt to quantify the adsorption mechanism of aurocyanide onto ACB.

TABLE 2.1

GLOBAL CHEMICAL COMPOSITION OF CARBON BLACK

COMPONENT	MASS %
carbon	80 - 99.5
hydrogen	0.3 - 1.3
oxygen	0.5 - 15
nitrogen	0.1 - 0.7
sulphur	0.1 - 0.7

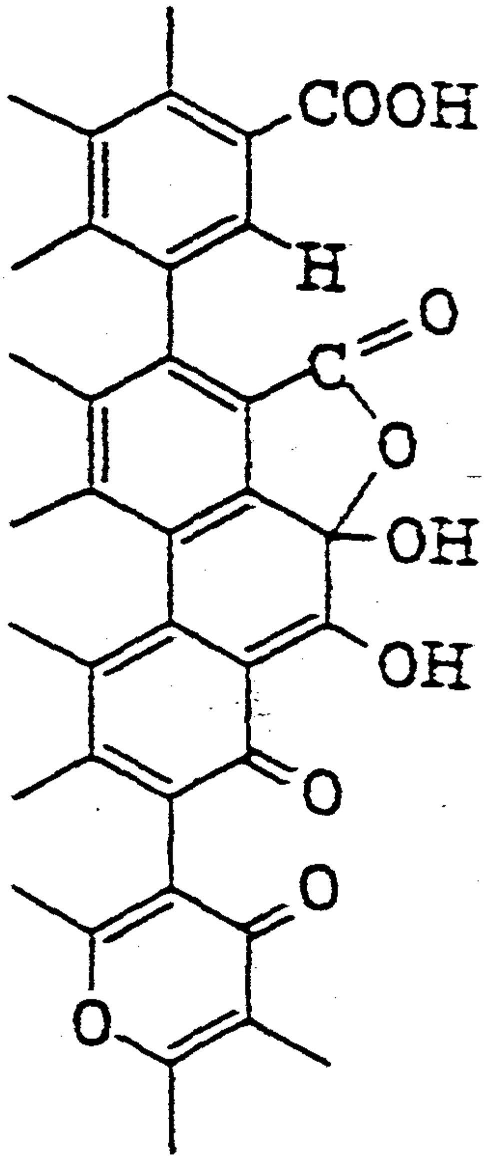

Figure 2.1 : Global carbon black composition

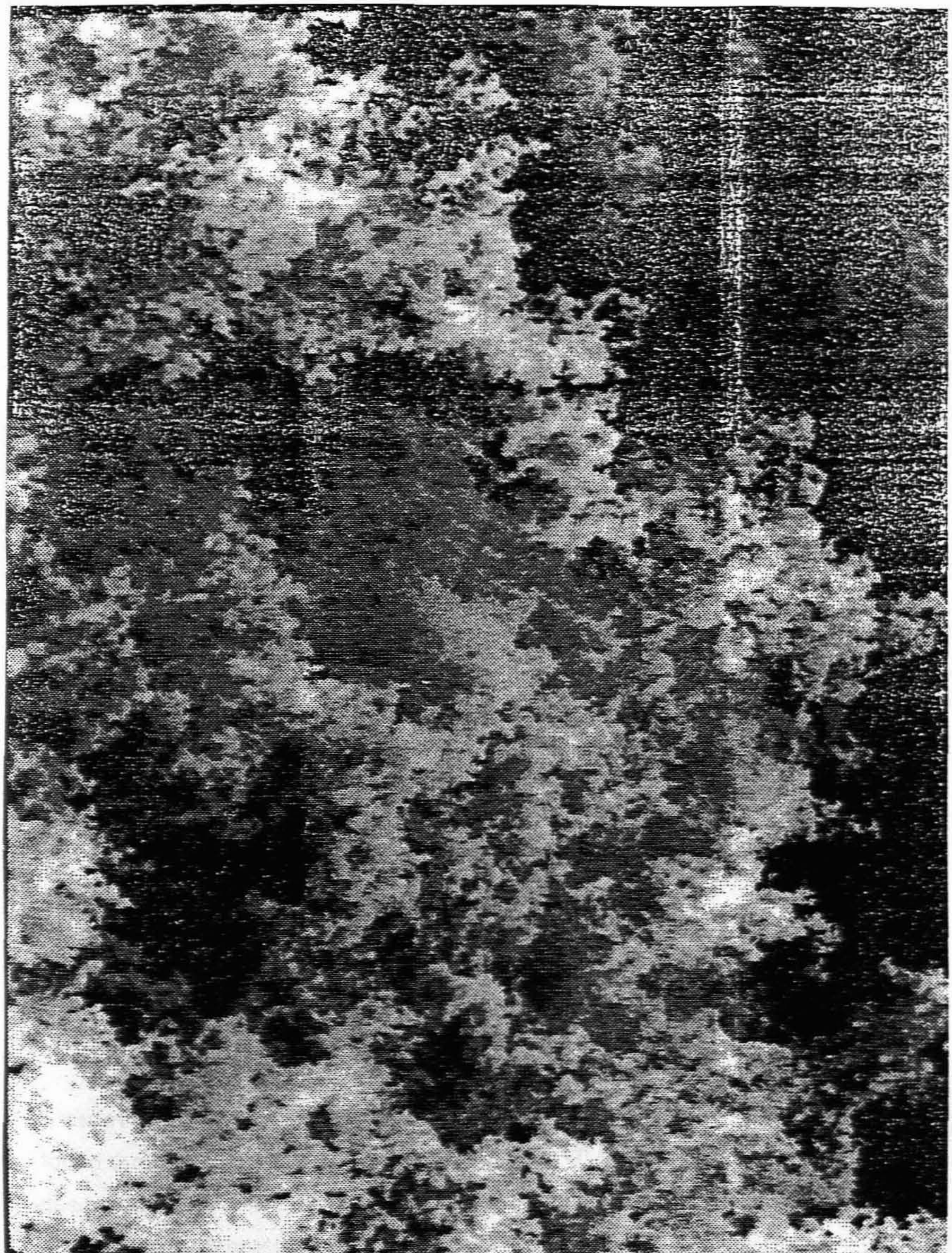

Figure 2.2 : Electron microscope image of ACB

CHAPTER 3

THEORY

A model for gold adsorption onto acetylene black, which involves external film diffusion, but ignores intraparticle diffusion, is described in this chapter. This model is by no means novel and has been used by various researchers in the past (Petersen, 1991 and Petersen and van Deventer, 1990).

3.1 ASSUMPTIONS

The following assumptions applies to the model:

- The ACB particles are treated as equivalent spheres.
- Isothermal conditions are assumed during adsorption.
- Pore diffusion is assumed negligible.
- The adsorption reaction on the ACB surface occurs instantaneously, hence equilibrium exists at the solid-liquid interface.

3.2 MATERIAL BALANCE EQUATIONS

After evaluating the three equilibrium expressions explained in Chapter 2, it was found that the equilibrium between aurocyanide on ACB and that in solution is best described by the Freundlich type isotherm. The values of A and n in this isotherm is obtained by regression analysis performed on Equation 3.1

$$q_s = A\,C_s^n \tag{3.1}$$

If film transfer determines the adsorption rate, diffusion through the liquid film surrounding the ACB particle can be described by Fick's law:

$$n_L = k_f(C-C_s) \tag{3.2}$$

A mass balance over the batch stirred reactor yields:

$$-V\frac{dC}{dt} = n_L\, a_{ACB} \tag{3.3}$$

The ACB particles are assumed spherical so that:

$$a_{ACB} = \frac{6\ M}{\rho\ d_p} \tag{3.4}$$

Substituting equations 3.2 and 3.4 into 3.3 leads to:

$$-V\frac{dC}{dt} = \frac{n_L\, 6\ M}{\rho\ d_p} = \frac{k_f\,(C-C_s)\ 6\ M}{\rho\ d_p} \tag{3.5}$$

Simplifying and substituting equation 3.1:

$$\frac{dC}{dt} = \frac{6\ k_f\ M}{\rho\ d_p\ V}\left[\left(\frac{q_s}{A}\right)^{\frac{1}{n}} - C\right] \tag{3.6}$$

From a mass balance over the reactor:

$$q_s = \frac{(C_i-C)\ V}{M} \tag{3.7}$$

Substituting equation 3.7 into equation 3.6 leads to:

$$\frac{dC}{dt} = \frac{6\ k_f\ M}{\rho\ d_p\ V\ B}\left(\frac{(C_o - C)\ V}{M}\right)^{\frac{1}{n}} - \frac{6\ k_f\ M\ C}{\rho\ d_p\ V} \qquad (3.8)$$

$$WHERE:\ B = A^{\frac{1}{n}}$$

Equation 3.8 can be used to evaluate the value of the external mass transfer coefficient (k_f) by comparing the results obtained to actual experimental results. The BASIC programme, as shown in Appendix A, was written to determine the value of k_f.

3.3 EXTERNAL MASS TRANSFER COEFFICIENT

The liquid phase material balance in a batch reactor yields:

$$\frac{dC}{dt} = \frac{6\ k_f\ M}{\rho\ d_p\ V}(C_s - C) \qquad (3.9)$$

When assuming that film mass transfer determines the adsorption rate in the early stages of the batch process, a linear concentration gradient from the bulk liquid to the adsorbent surface is postulated. Also, when assuming that the adsorbate concentration on the surface of the adsorbent (C_s) is negligibly small as compared to the adsorbate concentration in the bulk liquid, equation 3.9 simplifies to:

$$\frac{dC}{dt} = -\frac{6\ k_f\ M}{\rho\ d_p\ V}C \qquad t \rightarrow 0 \qquad (3.10)$$

Integrating equation 3.10 yields:

$$\ln\left(\frac{C_o}{C}\right) = \frac{6\ k_f\ M}{\rho\ d_p\ V}\ t \qquad t \to 0 \tag{3.11}$$

An expression for k_f is then found:

$$k_f = \frac{\ln\left(\frac{C_o}{C}\right)}{t}\ \frac{\rho\ d_p\ V}{6\ M} \tag{3.12}$$

A plot of $\ln(C_o/C)$ vs. time for the initial stages of the adsorption process is used to estimate the value of k_f experimentally.

The kinetic parameter k_f and equilibrium parameters A and n will be used in Chapters 6 and 7 to explain the adsorption of gold cyanide onto ACB.

CHAPTER 4

EXPERIMENTAL

4.1 MATERIALS

Potassium aurocyanide of an analytical grade was used to evaluate the surface characteristics of ACB. The $KAu(CN)_2$ salt was dissolved in de-ionized water for the purpose of all adsorption experiments. Ferrocyanide and gold-iodide were prepared separately for the purpose of adsorption experiments by respectively dissolving iron metal in a cyanide solution and metallic gold in an iodine/iodide solution. NaOH of an analytical grade, dissolved in de-ionized water, was used throughout in the case of elution experiments.

The acetylene black used in all experiments is produced by the thermal decomposition of acetylene gas, and was supplied by the Ballengeich plant, Newcastle in South Africa. It has a mean particle size of 2.5 μm, is 50% compressed, and has a surface area and density of 60 m^2/g and 95 kg/m^3 respectively.

4.2 ADSORPTION AND DESORPTION EXPERIMENTS

Adsorption experiments were carried out in a baffled stirred tank reactor with dimensions as indicated by Figure 3.1. Agitation was provided by a flat bladed impeller driven by a variable speed motor. The agitation rate was kept constant at 400 rpm in all adsorption experiments. All adsorption experiments were conducted at ambient temperature and commenced at a pH of 7. It was found that the change in pH was small during adsorption. In the case of adsorption experiments with oxygen addition, oxygen was bubbled through the gold cyanide solution for 30 minutes before the addition of the adsorbent and continued until equilibrium conditions were attained.

In the case of elution experiments, a suspension of loaded ACB was heated to various temperatures in a 1 liter glass container on a hot plate, with agitation provided by a magnetic stirrer.

4.3 ION EXCHANGE DETERMINATION

Ion release over a range of pH values were determined by acid/base titrations. The test method used by *EVEREADY Ltd*, as explained in Appendix B, was used to determine the ion exchange capacity of ACB.

4.4 ABSORPTION STIFFNESS DETERMINATION

Absorption stiffness is defined as the amount of an acetone/water mixture absorbed by a given mass of carbon black. The acetone mixture is added to the ACB in an Erlenmeyer flask while continuously swirling the flask by hand. The saturation point is reached when the ACB forms a stable spherically shaped mass. A complete absorption stiffness test method is shown as Appendix C.

4.5 ANALYTICAL METHODS

The amount of aurocyanide adsorbed or desorbed was determined by monitoring the amount of gold cyanide in solution. This was achieved by drawing samples at regular intervals and analyzing the samples on a Varian Techtron AA-1275 atomic absorption spectrophotometer (AA) at an absorbance peak of 242.8 nm. In the presence of organics the AA readings were corrected according to the method used by Petersen and Van Deventer, 1990.

The structure of ACB was evaluated by means of X-ray diffractrometry with a typical profile obtained shown by Figure 4.2. The broad base of the major peak obtained in Figure 4.2 indicates the imperfect graphitic structure of ACB.

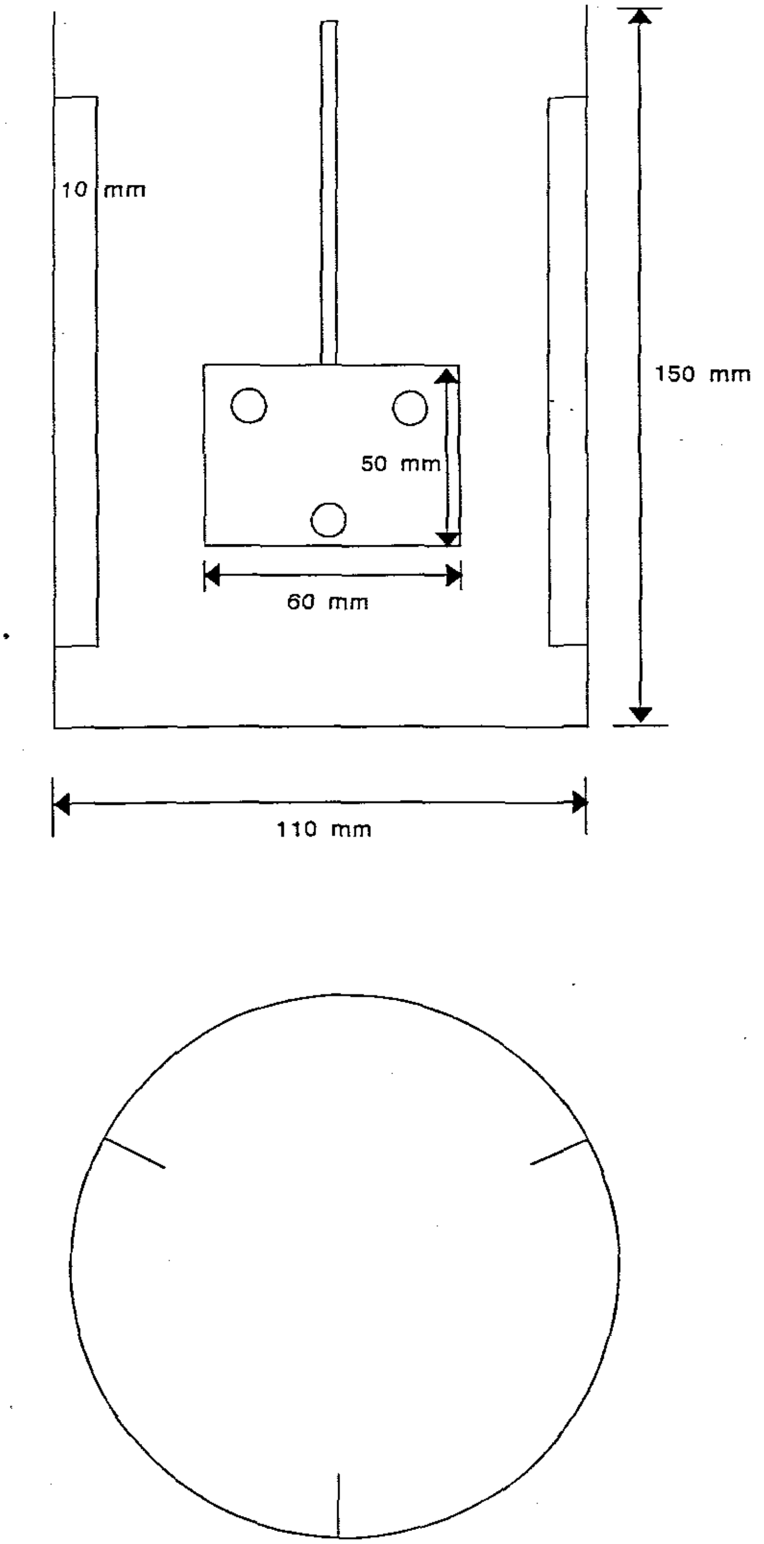

Figure 4.1 : Batch experimental apparatus

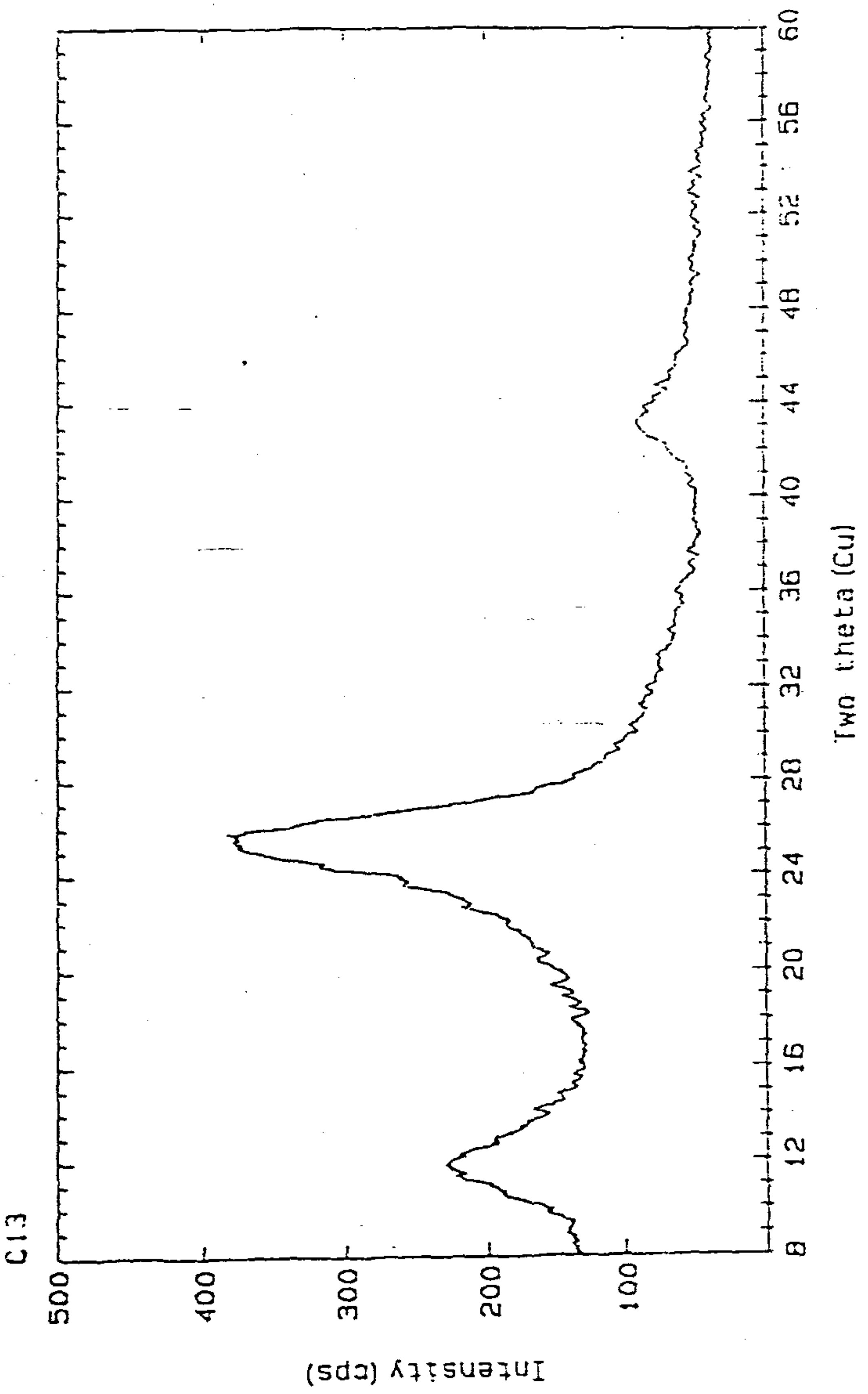

Figure 4.2 : X-ray diffractrometry result

CHAPTER 5

THE EFFECT OF ACETYLENE FLOW RATE AND TEMPERATURE ON THE STRENGTH OF ACB

This chapter is devoted to an understanding of the type of ACB used in this thesis and factors affecting its characteristics. Little information is available on the effect of operating variables on the quality of ACB. If ACB is to be considered for other applications, it is imperitive to investigate factors which could affect the strength and durability. Furthermore, such information could be important to ACB and battery manufacturers.

The absorption stiffness (AS) value, defined as the amount of a 10% acetone in water solution absorbed by ACB, is postulated to be a function of the degree of "*structure*", hence the length of the carbon chains found in ACB. In this chapter, the effects of a change in acetylene flow rate to the reactor and the temperature in the reactor on the AS-value was investigated.

The results obtained by selecting retorts at random over a two day period are shown in Tables 5.1 and 5.2. Due to the sensitive nature of the experiments, that is, the subjective nature of the end point of an analysis (Appendix C), the results obtained were grouped to minimize the effect of experimental errors. The grouped results are graphically illustrated in Figures 5.1 and 5.2.

5.1 THE EFFECT OF ACETYLENE FLOW RATE

It was found that an increase in the acetylene feed rate decreases the absorption stiffness as is graphically shown in Figure 5.1. If the theory of a "*chainlike*" structure for ACB is accepted, and that an increase in the lengths of these chains increases absorption stiffness, it is possible to develop a theory for the decrease in AS value with an increase in the acetylene feed rate. It is postulated that an increase in the acetylene feed rate shifts the reaction zone inside the retort resulting in a decreases in retention time. This decrease in retention time allows less time for chain formation and growth. However, it should be noted that a decrease in feed rate will ultimately result in a reduction of ACB output, and in certain cases lead to difficulties in maintaining the correct operating temperature.

5.2 THE EFFECT OF TEMPERATURE

Whereas acetylene flow rate influences production, it is not foreseen that changes in operating temperature will have the same effect. Furthermore, from Figure 5.2 it is clear that changes in temperature does not provide the same conclusive results as was the case with changes in the acetylene feed rate. However, it does seem that there is a general downward trend in AS value as the temperature is increased. In all except but one case, an increase in temperature reduced the AS value. Using the results obtained as confirmation, it seems that the operating temperature should be kept as low as is practically possible, that is, sufficiently high to ensure cracking.

To develop a theory for the increase in AS value with a change in operating temperature is more difficult as was the case with a change in acetylene feed rate. One possibility is that temperature influences the degree of graphitization of the product and that this degree of graphitization influences the AS value.

TABLE 5.1

THE EFFECT OF ACETYLENE FLOW RATE ON THE AS VALUE

RETORT NUMBER	FLOW RATE [rotameter reading]	AS VALUE [average : ml/5 g]
5	140	69.7
	160	58.7
	180	54.7
8	140	72.5
	160	65.1
	180	60.7
17	140	72.3
	180	62.5

* Grouped data

TABLE 5.2

THE EFFECT OF TEMPERATURE ON THE AS VALUE

RETORT NUMBER *	TEMPERATURE [°C]	AS VALUE [average : ml/5 g]
5	860	56.5
	900	64.7
	940	62.0
8	860	68.4
	900	66.1
	940	59.5
17	860	71.7
	900	69.0
	940	61.5

* Grouped data

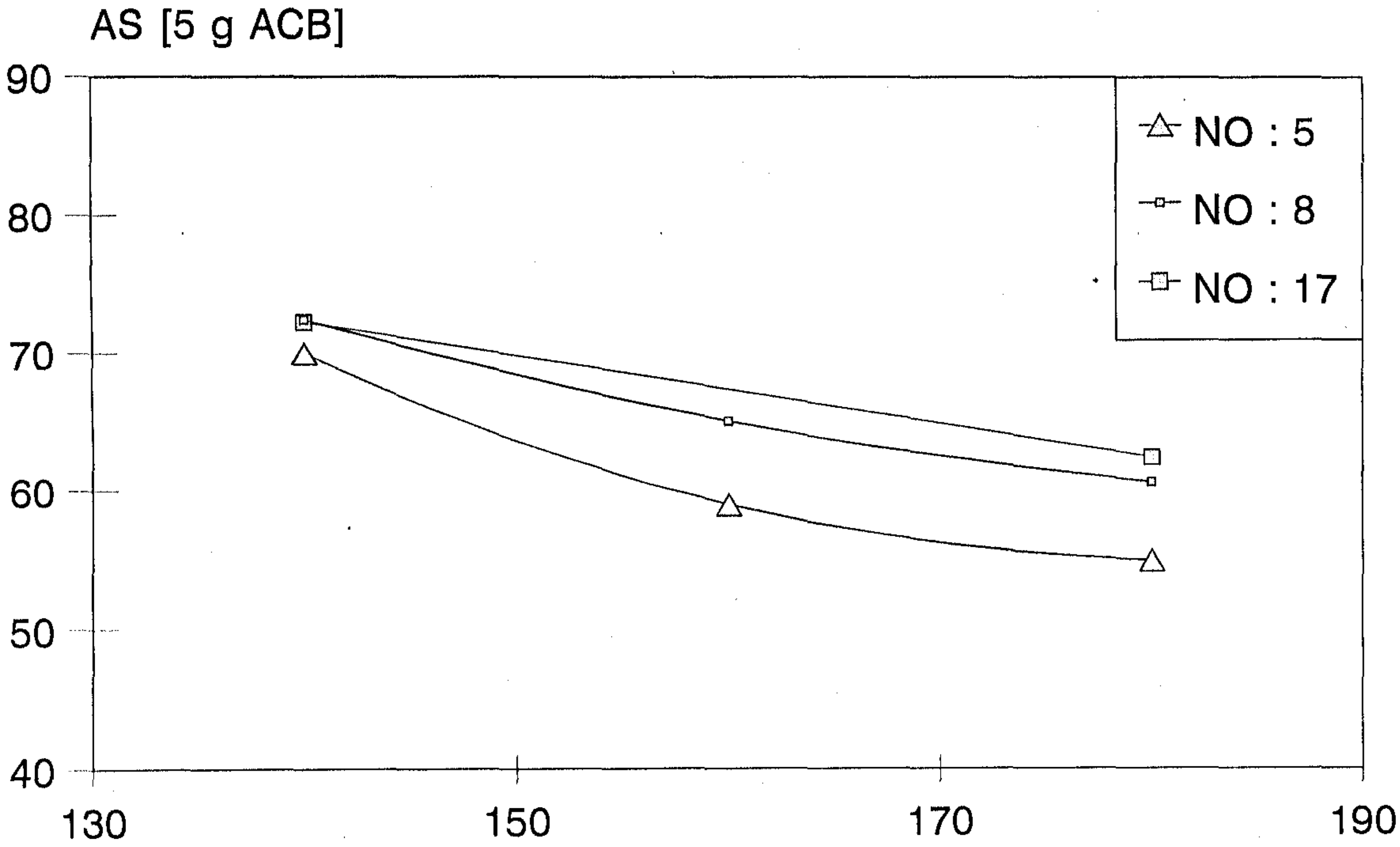

Figure 5.1 : AS as a function of acetylene flow rate
Exp. no. 21

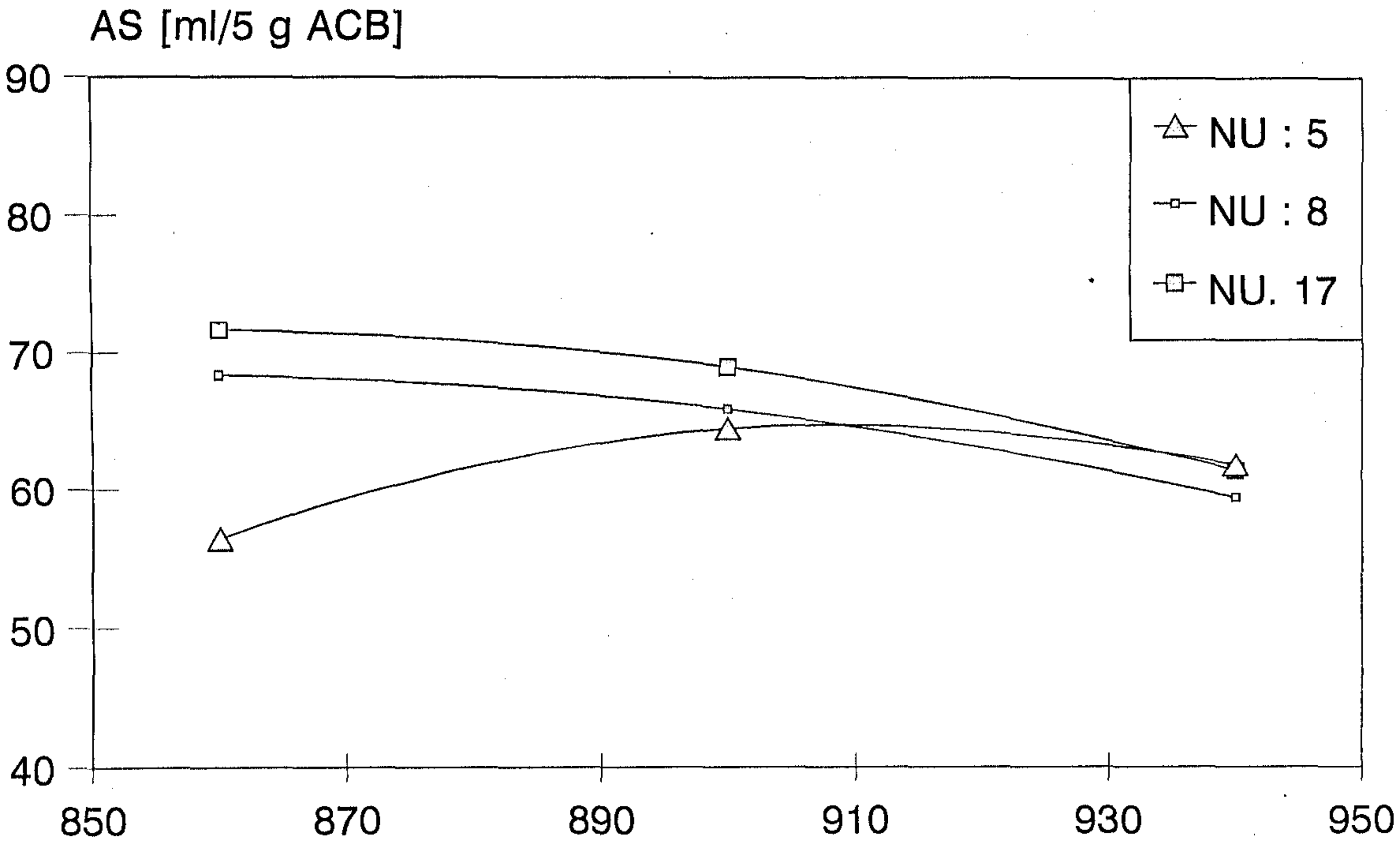

Figure 5.2 : AS as a function of temperature
Exp. no. 21

CHAPTER 6

ADSORPTION AND ION EXCHANGE

No work, as yet, has been published on the recovery of metal cyanides by ACB, although it is believed that ion exchange tests have been conducted by Eveready in the United Kingdom.

The surface characteristics of any material is an important function of the overall behaviour of such material. For ACB, such surface characteristics may play an important part in the absorption stiffness value, and ultimately on the overall performance of the dry cell battery. Furthermore, should ACB be considered for alternative applications, surface characteristics and structure will in all probability play a major role.

In an ideal reactor (system), with no oxygen or water present and a pure feed of acetylene, the product will consist of a pure carbon network, whilst all the hydrogen will be combusted. In reality the feed is neither pure, nor is the reaction complete. Furthermore, oxygen and water vapour is present due to leakages. The presence of these different species and the fact that the reaction is not complete, could result in active groups on the ACB surface. These active groups can participate during gold cyanide adsorption, or can exchange groups via an ion exchange mechanism.

6.1 ION EXCHANGE CAPACITY

The test method described in APPENDIX B was applied to determine the specific ion-exchange capacity of ACB. However, due to the different operating parameters that may be used on different plants, care should be taken in generalizing these results.

The results of the acid/base titrations are tabulated in Table 6.1. From the results it is clear that the ion-exchange capacity of the ACB is negligible at low pH and small under basic conditions where H^+ is exchanged for K^+. This indicates that surface groups such as carboxylic groups are present in low concentrations whereas the concentration of hydroxyl groups on the surface are negligibly small. These results are confirmed by the ion-exchange with K^+ shown in Figure 6.1.

6.2 ADSORPTIVE BEHAVIOUR

The adsorptive behaviour of ACB was evaluated by using three species, gold cyanide, ferro cyanide and gold iodide, with the selection of ferro cyanide and gold iodide based on the common elements gold and cyanide. Typical adsorption profiles of gold cyanide, ferro cyanide and gold iodide onto ACB, under identical conditions, is depicted in Figure 6.2. It was found that the equilibrium adsorption value of gold iodide was higher than that of gold cyanide, with ferro cyanide the lowest of the three species. From the adsorption profiles it is also clear that equilibrium is approached very rapidly and that intraparticle diffusion is minimal, with equilibrium conditions attained within 10 minutes. This rapid attainment of equilibrium conditions emphasises the relatively flat pore structure of ACB as was found from XRD analysis, that is, a low degree of graphitization.

It was found that a Freundlich-type isotherm best explained the adsorption of gold onto ACB as shown by Figure 6.3. The values of A and n were determined experimentally from a plot of the natural log of the various equilibrium loading values versus the natural log of the equilibrium concentration in solution (Figure 6.4). The values of A and n obtained for gold cyanide adsorption are tabulated in Table 7.1. Also, from Figure 6.3, it is clear that the gold cyanide loading capacity of ACB is small when compared to that of activated carbon and ion-exchange resin.

The mass transfer coefficient (k_f) was estimated experimentally by using equation 3.12 and adjusted by using the BASIC programme in APPENDIX A. The experimental value of k_f obtained from gold cyanide adsorption is indicated in Table 7.1 and the adjusted k_f in Table 7.2.

TABLE 6.1

THE ION-EXCHANGE CAPACITY OF ACB

pH	EXCHANGE CAPACITY μ mole.g^{-1}
1.4	negligible
2.4	negligible
3.6	negligible
4.8	negligible
6.9	negligible
11.1	0.102
12.4	0.113

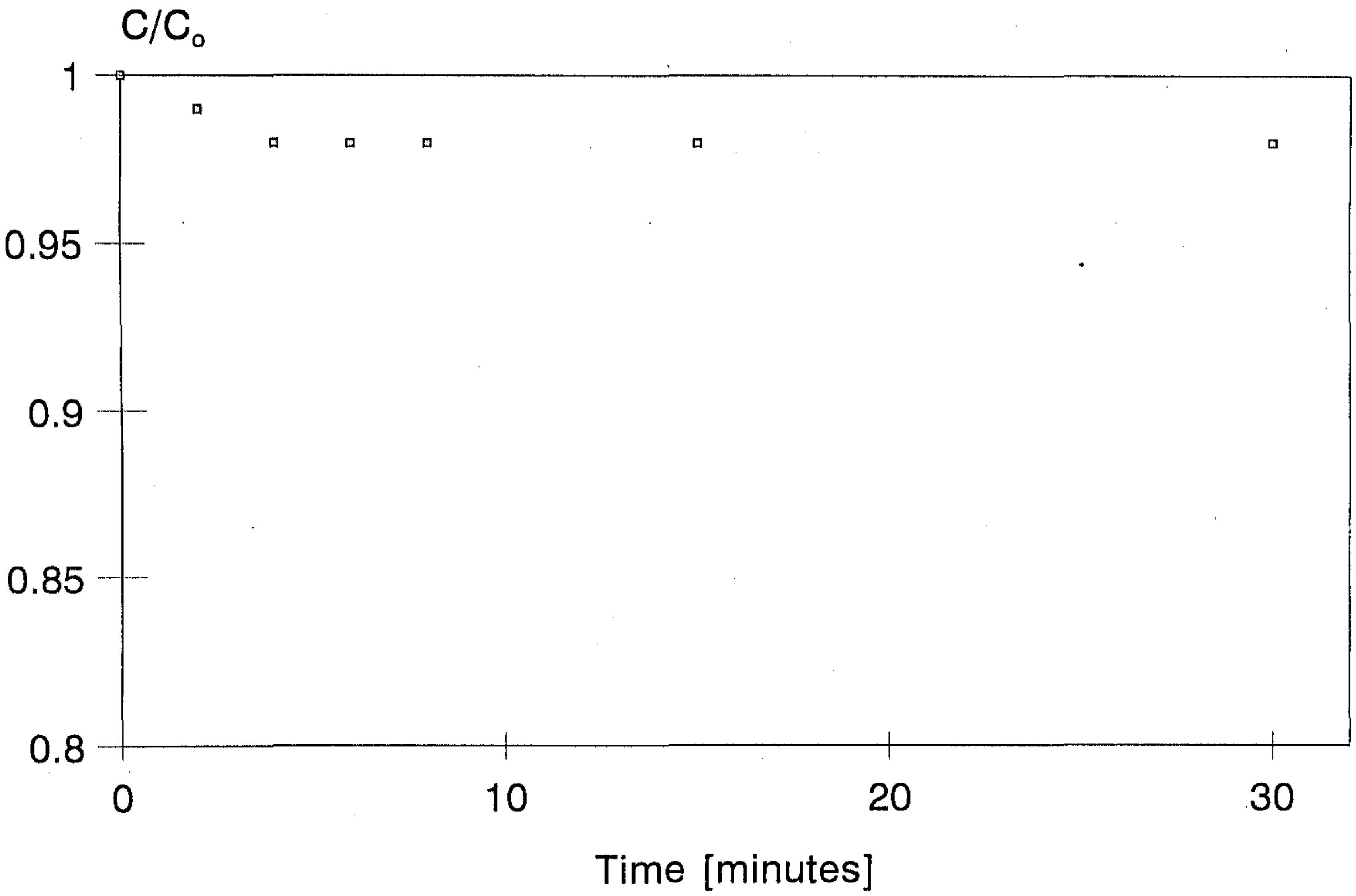

Figure 6.1 : Potassium adsorption onto ACB
C_o = 500 mg/l ; [ACB] = 30 g/l ; Exp. no. 2

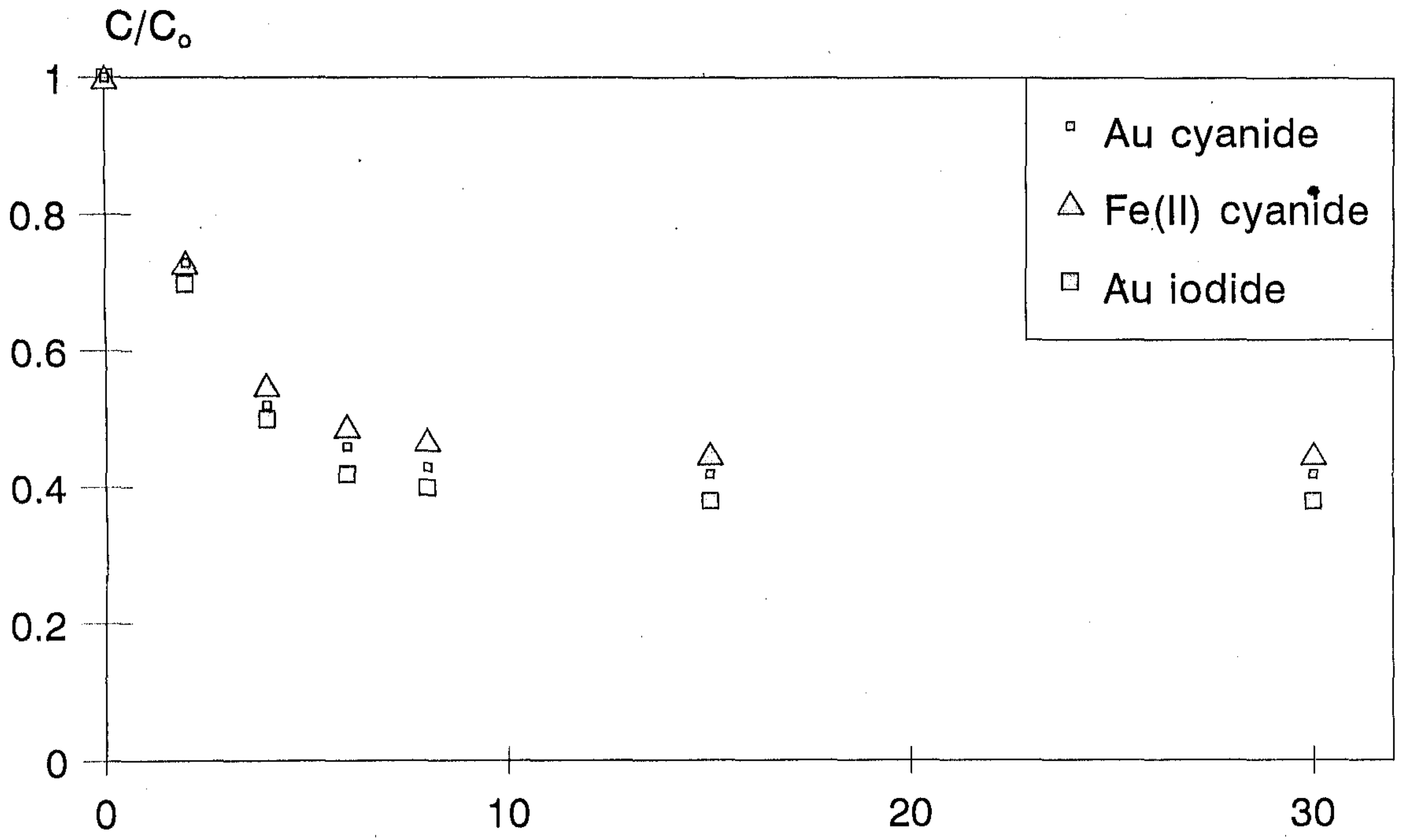

Figure 6.2 : Gold and iron adsorption onto ACB
C_o = 15 mg/l ; [ACB] = 10 g/l ; Exp. no. 3,4,5

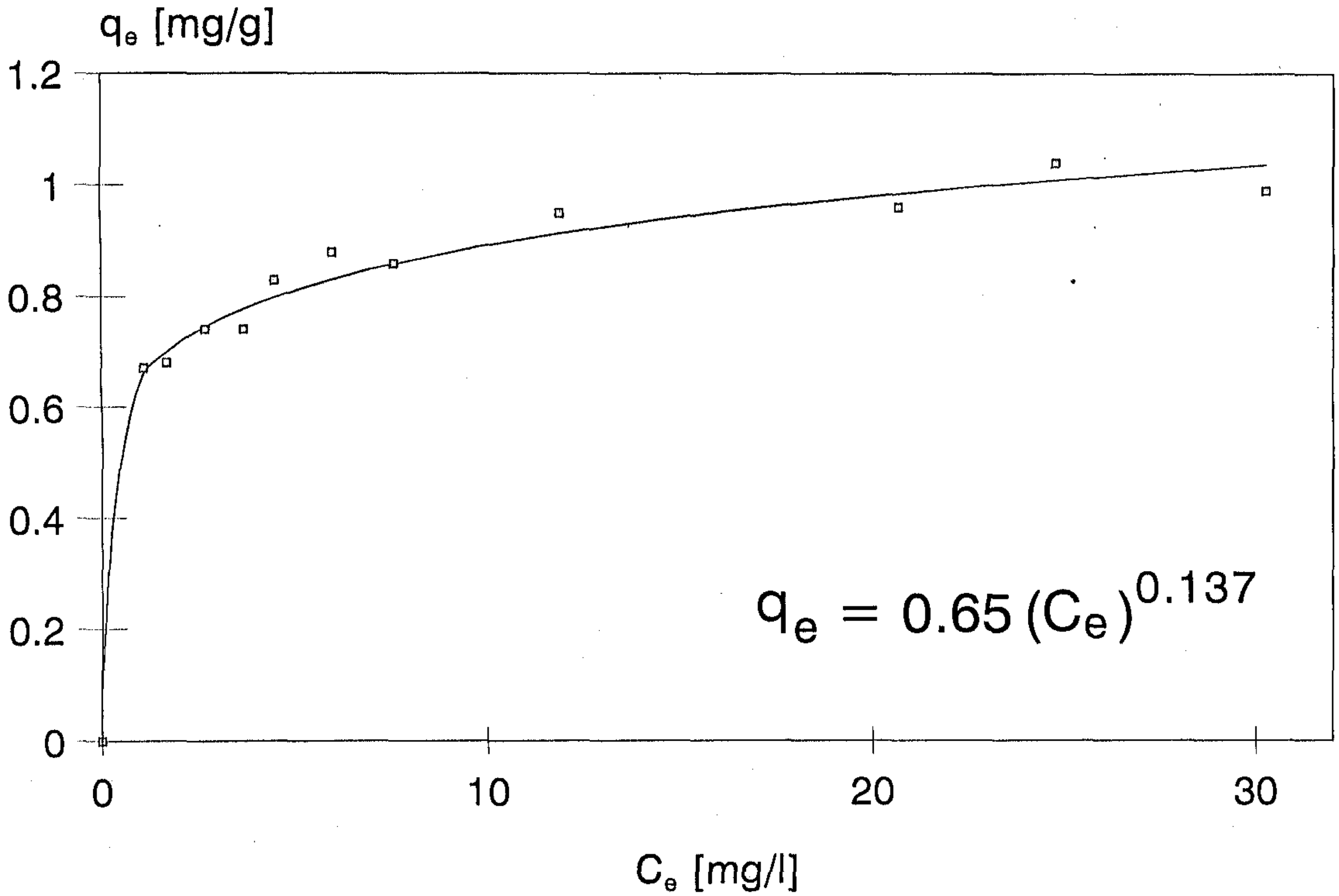

Figure 6.3 : Equilibrium adsorption of gold cyanide onto ACB at pH 7
Exp. no. 6

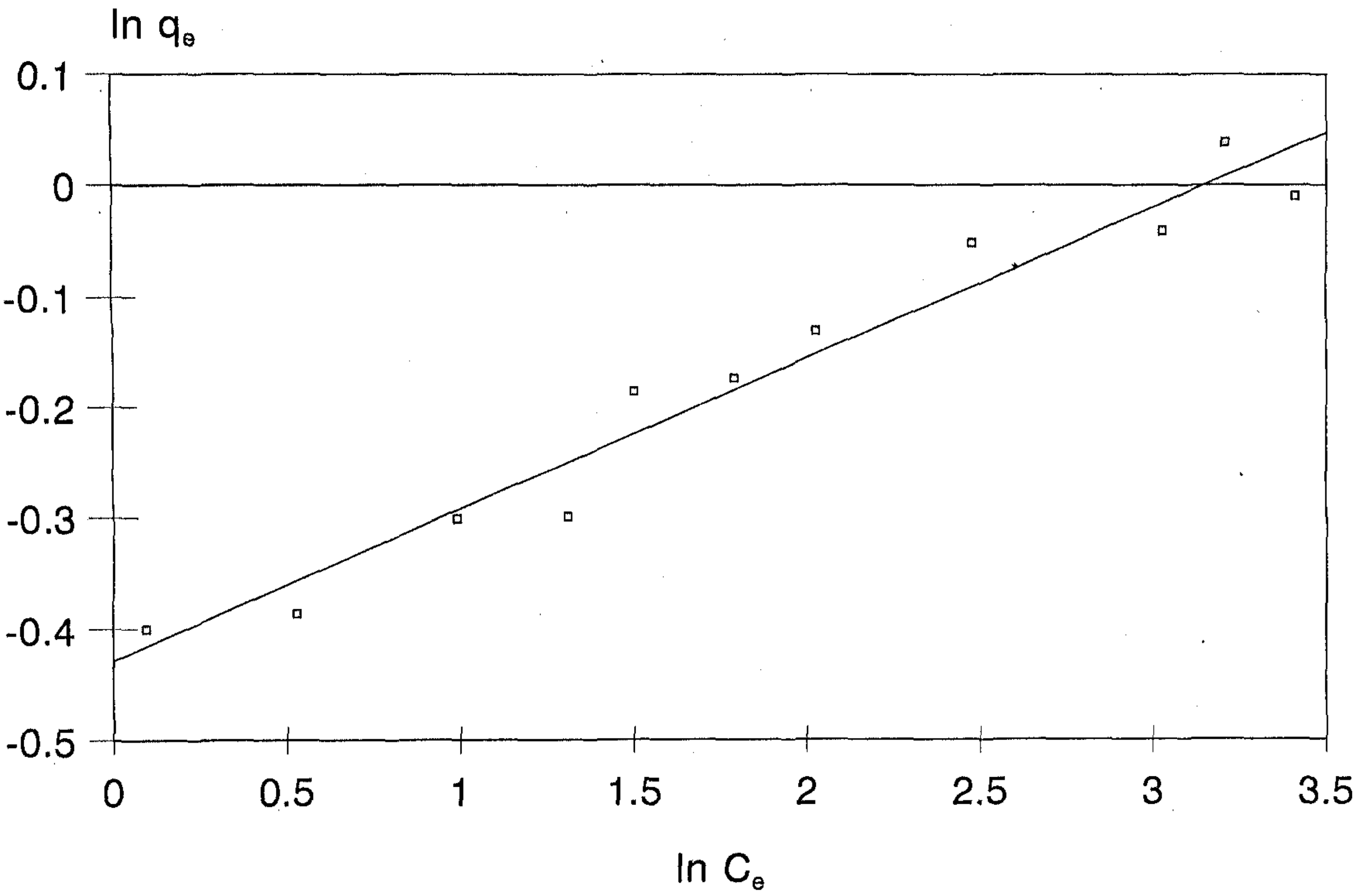

Figure 6.4 : Linearization of gold adsorption data at pH 7
Exp. no. 6

CHAPTER 7

EFFECT OF OPERATING PARAMETERS ON MASS TRANSFER

The effect of various operating conditions, such as dissolved oxygen levels, pH and organic solvents, on the adsorptive behaviour of activated carbon have been studied extensively by various researchers (Van der Merwe and Van Deventer , 1988 ; Adams, 1990). The aim of this chapter is to investigate and evaluate the effect of these variables on the adsorptive behaviour of ACB.

Figures 7.1 to 7.8 show the respective effects of the addition of oxidizing agents, a reduction in pH, the addition of organic solvents, ageing and temperature on the adsorption of gold cyanide onto ACB. The values of A and n under different conditions, obtained by regression analysis as explained in section 6.2, are tabulated in Table 7.1 together with the various mass transfer coefficients obtained experimentally by using equation 3.12. The regression analysis results are compared to experimental data in Figures 7.9 to 7.11. The surface diffusion model, as explained in Chapter 3, was then used to obtain theoretical values for A, n and k_f. These values were obtained by using the BASIC program (APPENDIX A) and tabulated in Table 7.2.

7.1 THE EFFECT OF DISSOLVED OXYGEN

In order to investigate the effect of oxygen on the adsorption of gold cyanide, oxygen was bubbled through a solution of gold cyanide before the addition of ACB. The oxygen supply was continued during the adsorption process until equilibrium was attained.

According to Adams (1990), oxygen oxidises the carbon surface, thereby increasing the equilibrium loading value of gold cyanide onto activated carbon. From Figure 7.1 it is clear that this phenomenon is not present when ACB is used as adsorbent. This suggests that the surface of ACB is not easily oxidised under moderate conditions. From the values of A, n, and k_f depicted in Table 7.1, it is clear that oxygen addition has a negligible effect on gold cyanide adsorption onto ACB.

7.2 THE EFFECT OF STRONG OXIDIZING AGENTS

The effect of the addition of MnO_2, an integral component of the dry cell battery, on the adsorptive behaviour of ACB is depicted in Figure 7.2, whereas the effect of the addition of H_2O_2 is shown in Figure 7.3. From Figures 7.2 and 7.3 it is clear that these oxidizing agents has a marked effect on the rate of adsorption and also on the equilibrium gold loading value. It is postulated that these strong oxidizing agents modify the carbon surface, resulting in a more polar species. This increase in the polarity of ACB increases the contact angle between ACB and the solution, and hence the rate of mass transfer and equilibrium loading. The change in equilibrium loading is manifested by the equilibrium parameter A and the change in the rate of adsorption is indicated by the change in the film diffusion parameter k_f as indicated in Tables 7.1 and 7.2.

7.3 THE EFFECT OF pH

The mixing of the dry cell battery components is a critical step in the manufacturing stage of dry cell batteries. It is thus essential to evaluate the effect of certain operating conditions, such as pH levels, on the characteristics of ACB.

Fleming and Nicol (1984) observed that a decrease in pH enhances the adsorptive behaviour of activated carbon for gold cyanide. Adams (1990) concluded that a decrease in pH should increase the adsorptive behaviour of activated carbon since hydronium ions participate in the half-reactions during the oxidation of the carbon surface.

Similar conclusions are drawn from the graphical representation of results in Figure 7.4. However, it must be emphasised that the increased rate of mass transfer and larger equilibrium loading may also be the result of an increase in the polarity of the ACB surface. Thus, although it is clear that a decrease in pH enhances the adsorptive behaviour of ACB, it is not conclusive that it is the result of an increase in the concentration of hydronium ions. The increase in adsorption kinetics and equilibrium loading is confirmed by the increase of the values of k_f and A (Tables 7.1 and 7.2).

7.4 THE EFFECT OF TEMPERATURE

The loading capacity of activated carbon is reduced with an increase in temperature as a result of the exothermic nature of the reaction when gold or silver cyanide is adsorbed onto activated carbon. The opposite is true when ACB is used as adsorbent as shown graphically by Figure 7.5. The results show clearly that an increase in temperature enhances the adsorptive behaviour of ACB. Furthermore, the rate of mass transfer is increased substantially as indicated by the value of k_f in Tables 7.1 and 7.2.

The results obtained would suggest that the adsorption of gold cyanide onto ACB is endothermic in nature. However, it must be emphasised that an increase in temperature does result in more effective mixing in the batch stirred tank reactor. It is thus likely that the increased adsorptive performance is the result of an increase in the efficiency of mixing, rather than the result of an endothermic nature of the reaction. Should this be the case, the possibility exists that an increase in temperature could lead to more efficient mixing of the dry cell battery components.

7.5 THE EFFECT OF AGEING

From Figure 7.6 it is clear that ageing under atmospheric conditions has an effect on the adsorptive behaviour of ACB. This indicates a loss or modification of surface groups under atmospheric conditions. The changes in adsorption kinetics are manifested by the values of A and k_f in Tables 7.1 and 7.2.

7.6 THE EFFECT OF ORGANIC SOLVENTS

Whereas organic solvents influences the adsorptive behaviour of activated carbon negatively, it has a negligible effect on the adsorption of aurocyanide by ACB as indicated by Figures 7.7 and 7.8. As was the case with the lowering of the pH level, it is not possible to conclude that organic solvents has no effect on the adsorption process. It is expected that organic solvents will increase the wettability of ACB and hence, increase adsorptive behaviour. However, this expected increase in adsorptive performance does not occur, and it is possible that the positive effect of an increase in wettability caused by the addition of organic solvents is counteracted by the negative effect on adsorption.

TABLE 7.1

EXPERIMENTAL VALUES OF k_f, A AND n FOR VARIOUS OPERATING CONDITIONS

Conditions	**k_f [m.s^{-1}] x 10^8**	**A**	**n**
pH = 7	1.08	0.65	0.137
O_2 addition	1.01	0.67	0.131
H_2O_2 addition	1.63	0.91	0.12
pH = 2	1.39	0.79	0.14

TABLE 7.2

VALUES OF k_f, A AND n OBTAINED FROM THE EXTERNAL FILM DIFFUSION MODEL

Conditions	**k_f [$m.s^{-1}$] x 10^8**	**A**	**n**
pH = 7	1.2	0.68	0.137
O_2 addition	1.2	0.67	0.131
MnO_2 addition	1.7	0.9	0.12
H_2O_2 addition	1.8	0.93	0.12
pH = 2	1.6	0.79	0.14
60 °C	1.46	0.74	0.14
Aged	1.05	0.58	0.13

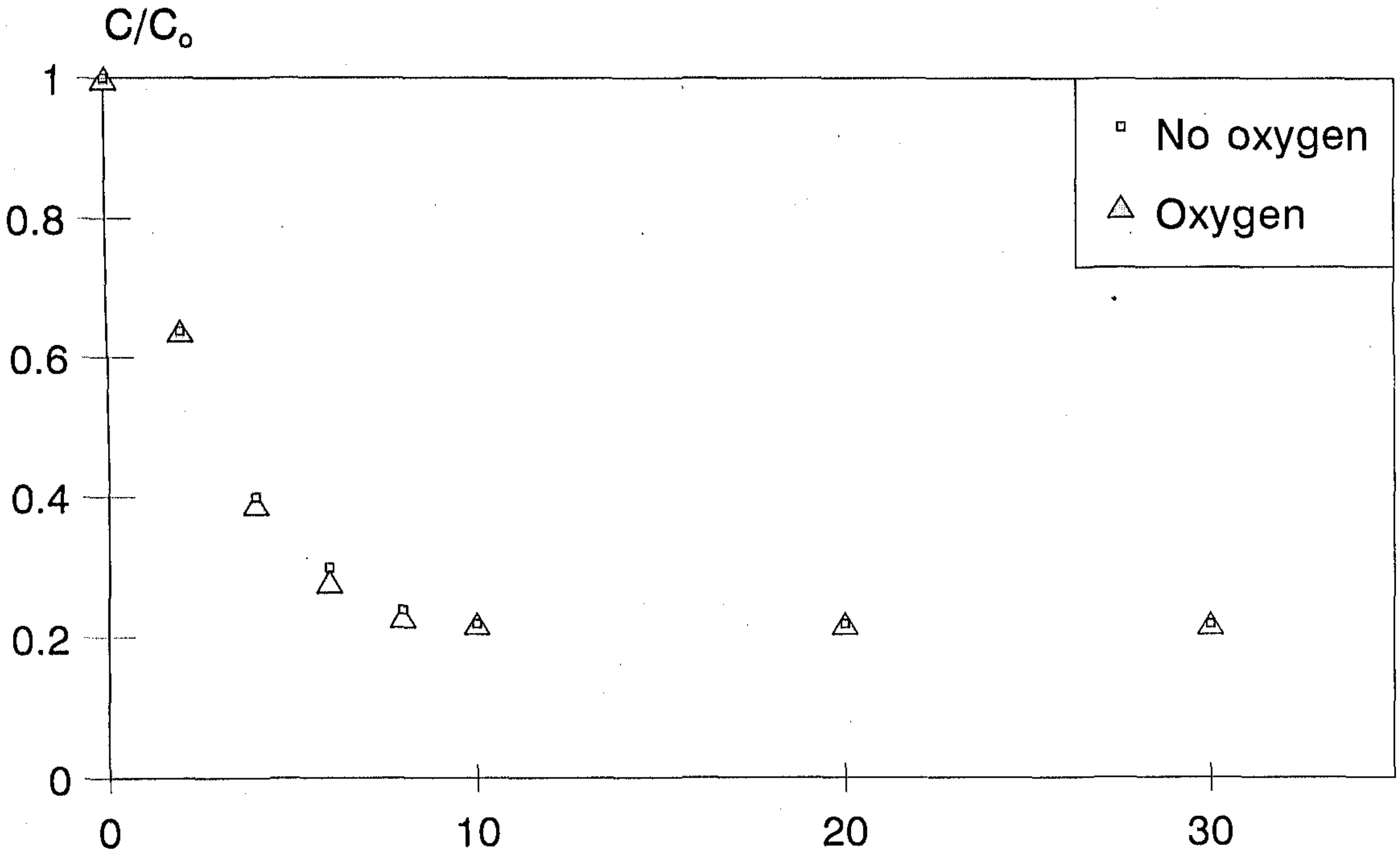

Figure 7.1 : Au adsorption with O_2 addition

C_o = 15 mg/l ; [ACB] = 15 g/l ; Exp. no. 7

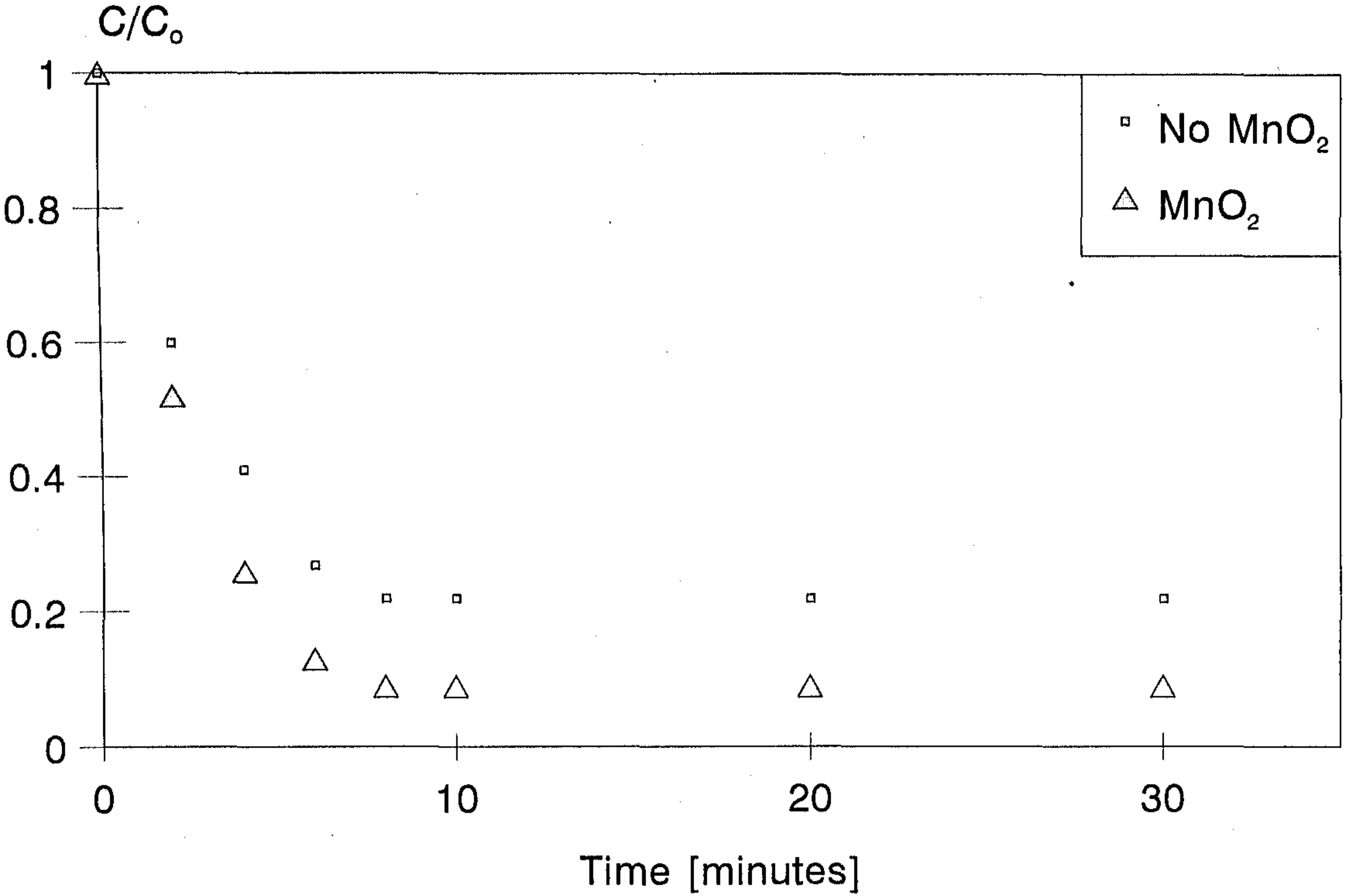

Figure 7.2 : Au adsorption with MnO_2 addition
C_o = 15 mg/l ; [ACB] = 15 g/l ; Exp. no. 8

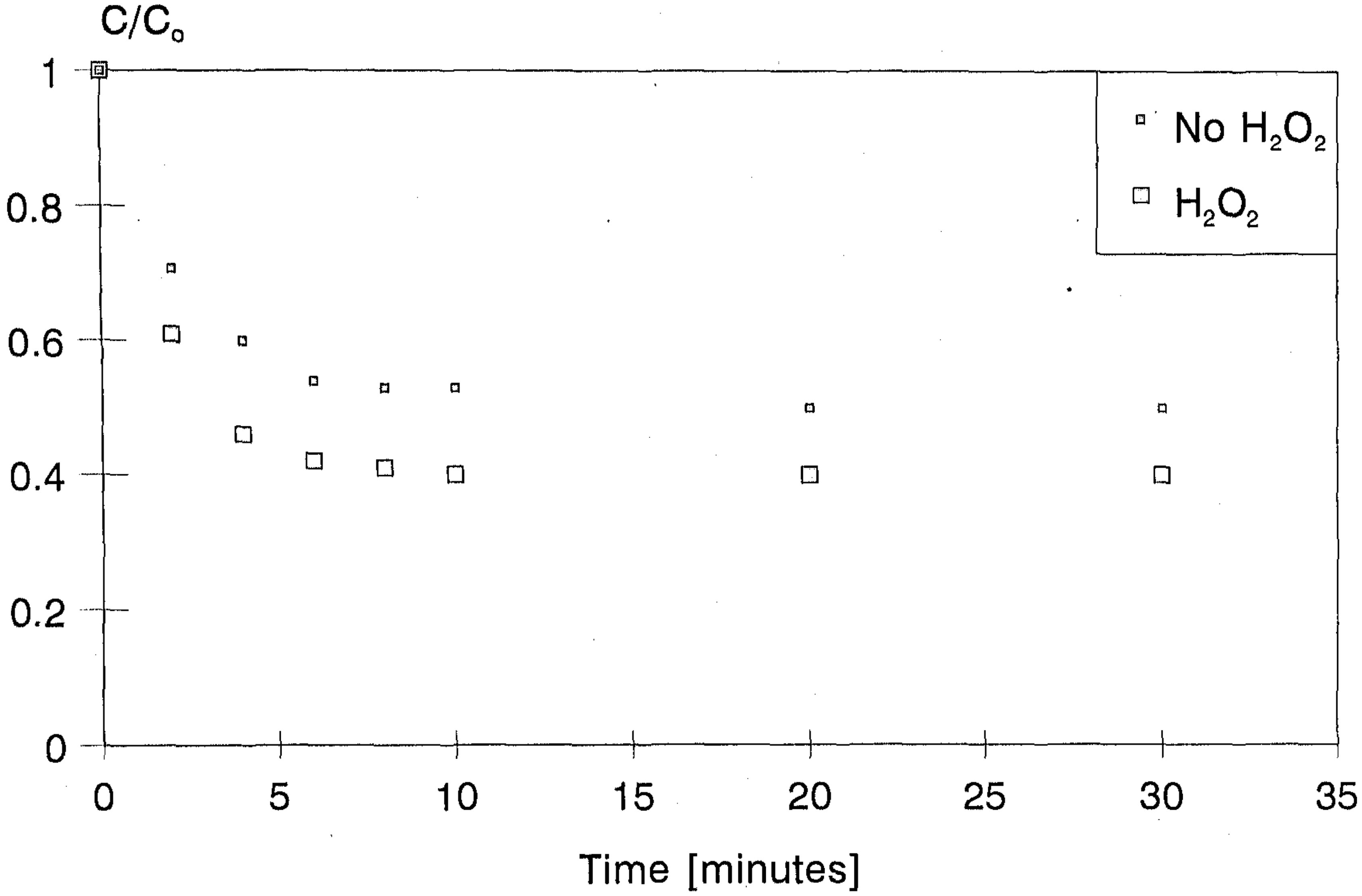

Figure 7.3 : Au adsorption with H_2O_2 addition
C_o = 20 mg/l ; [ACB] = 10 g/l ; Exp. no. 9

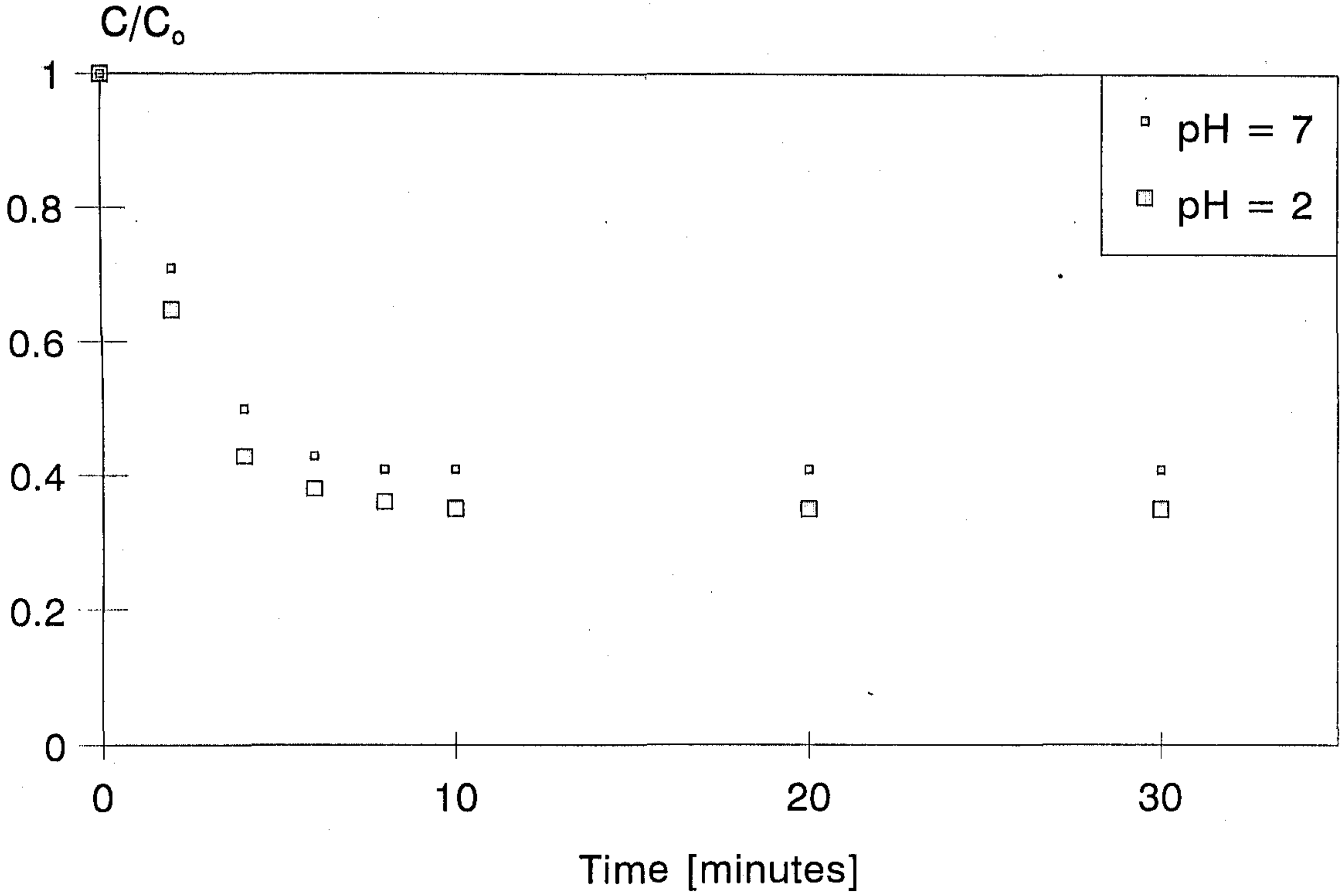

Figure 7.4 : Influence of pH on Au adsorption
C_o = 15 mg/l ; [ACB] = 10 g/l ; Exp. no. 10

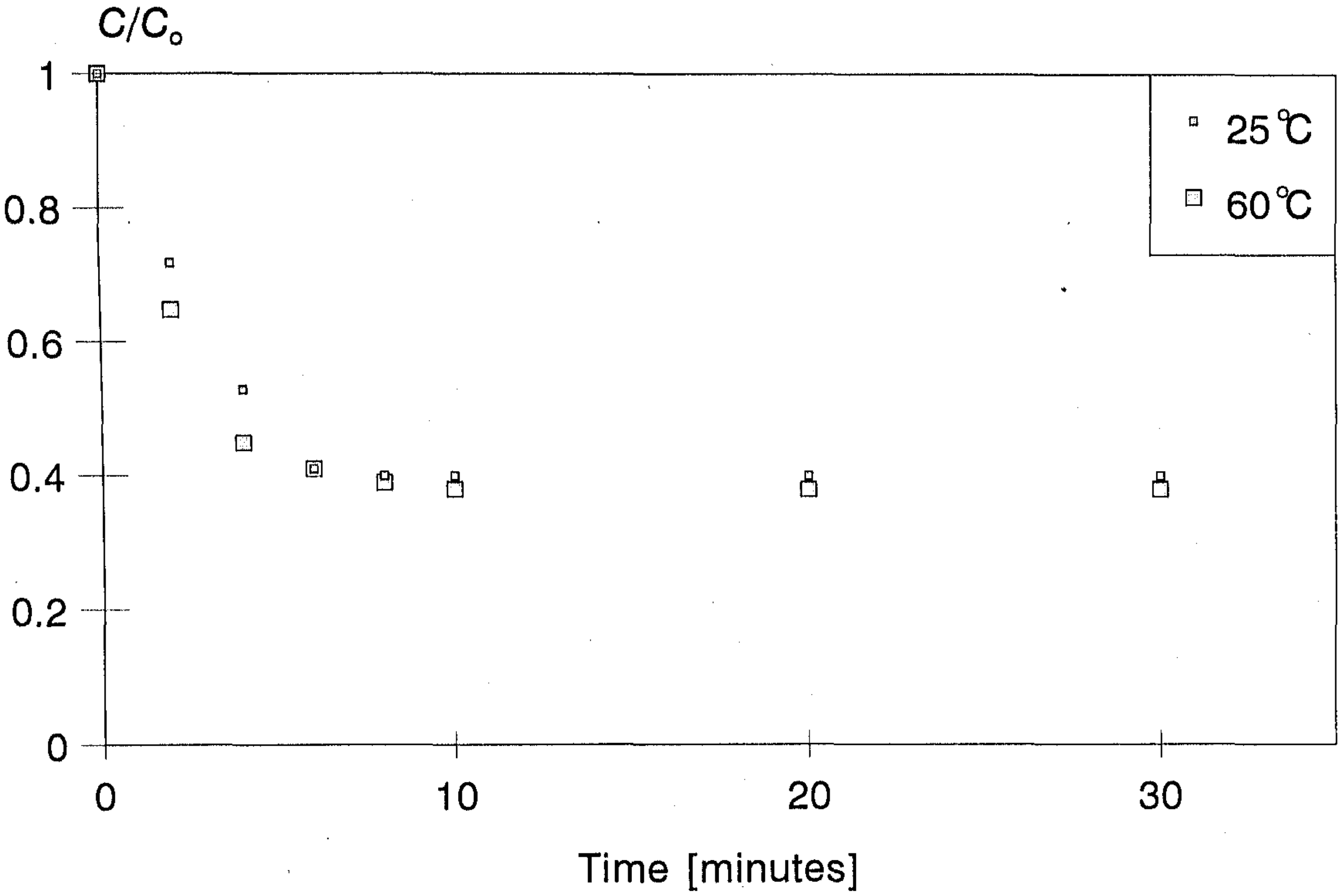

Figure 7.5 : Au adsorption with increased temperature
C_o = 15 mg/l ; [ACB] = 10 g/l ; Exp. no. 11

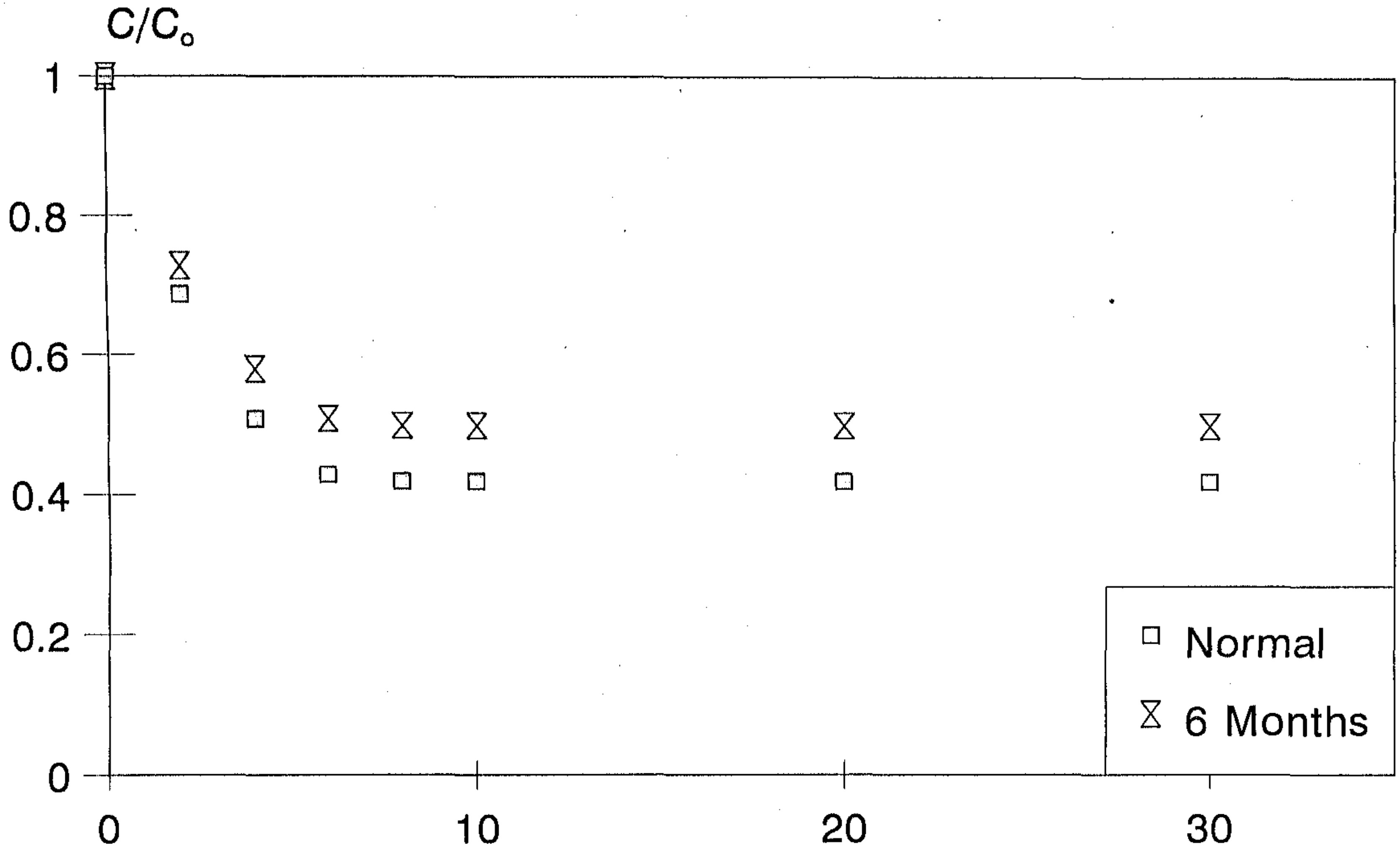

Figure 7.6 : The effect of ageing on Au adsorption
C_o = 15 mg/l ; [ACB] = 10 g/l ; Exp. no. 12

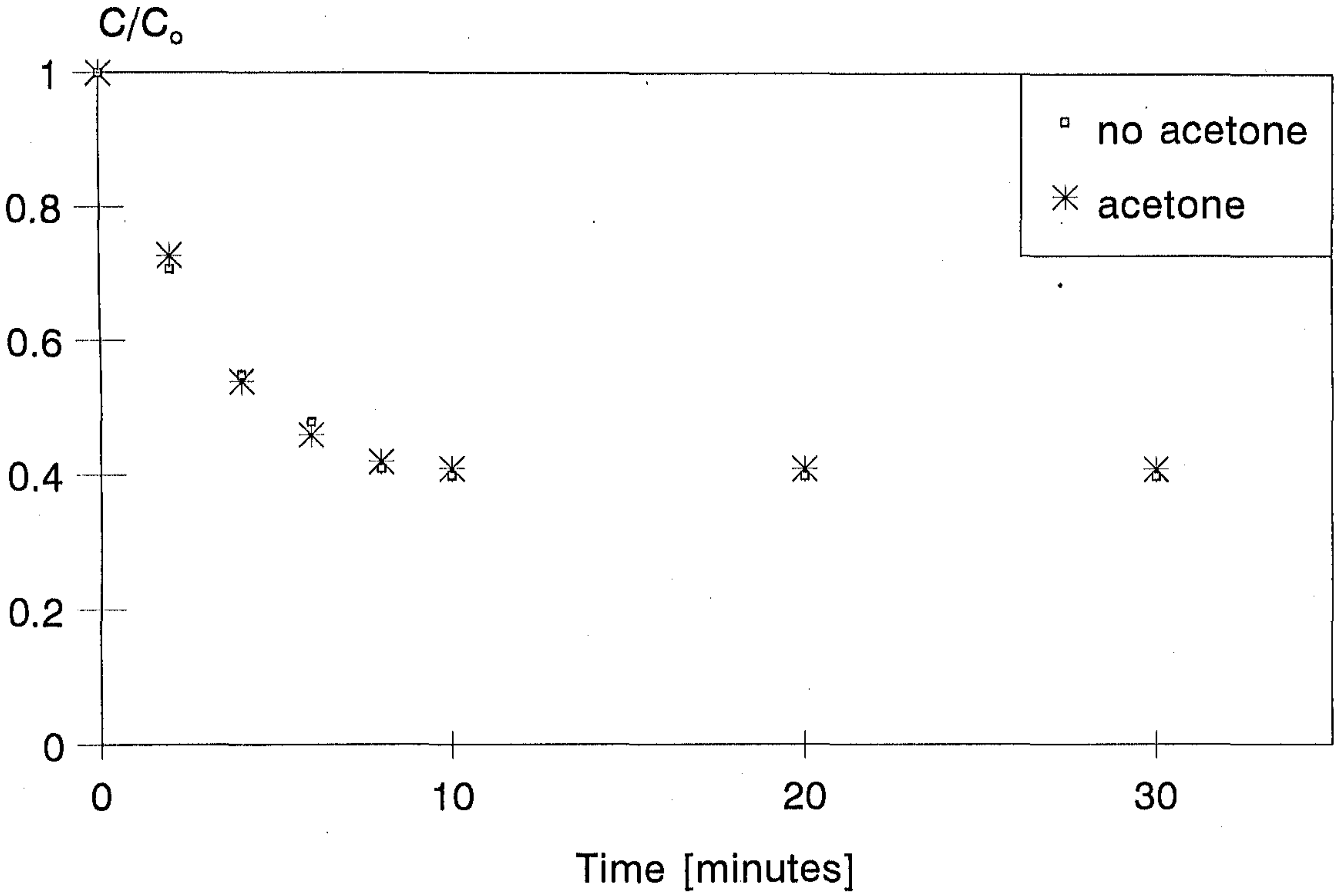

Figure 7.7 : Au adsorption with the addition of acetone
C_o = 15 mg/l ; [ACB] = 10 g/l ; Exp. no. 13

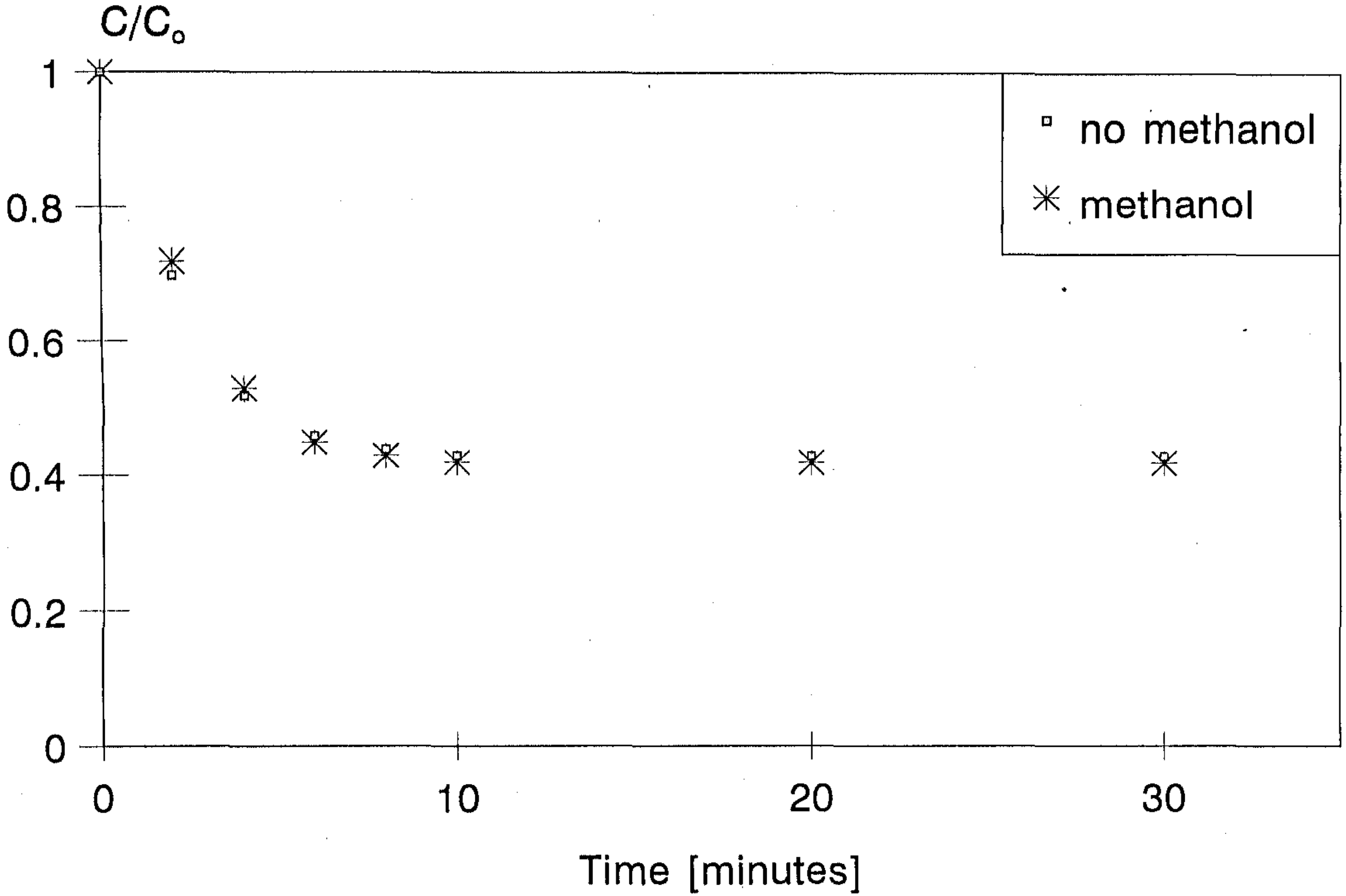

Figure 7.8 : Au adsorption with methanol addition
C_o = 15 mg/l ; [ACB] = 10 g/l ; Exp. no. 14

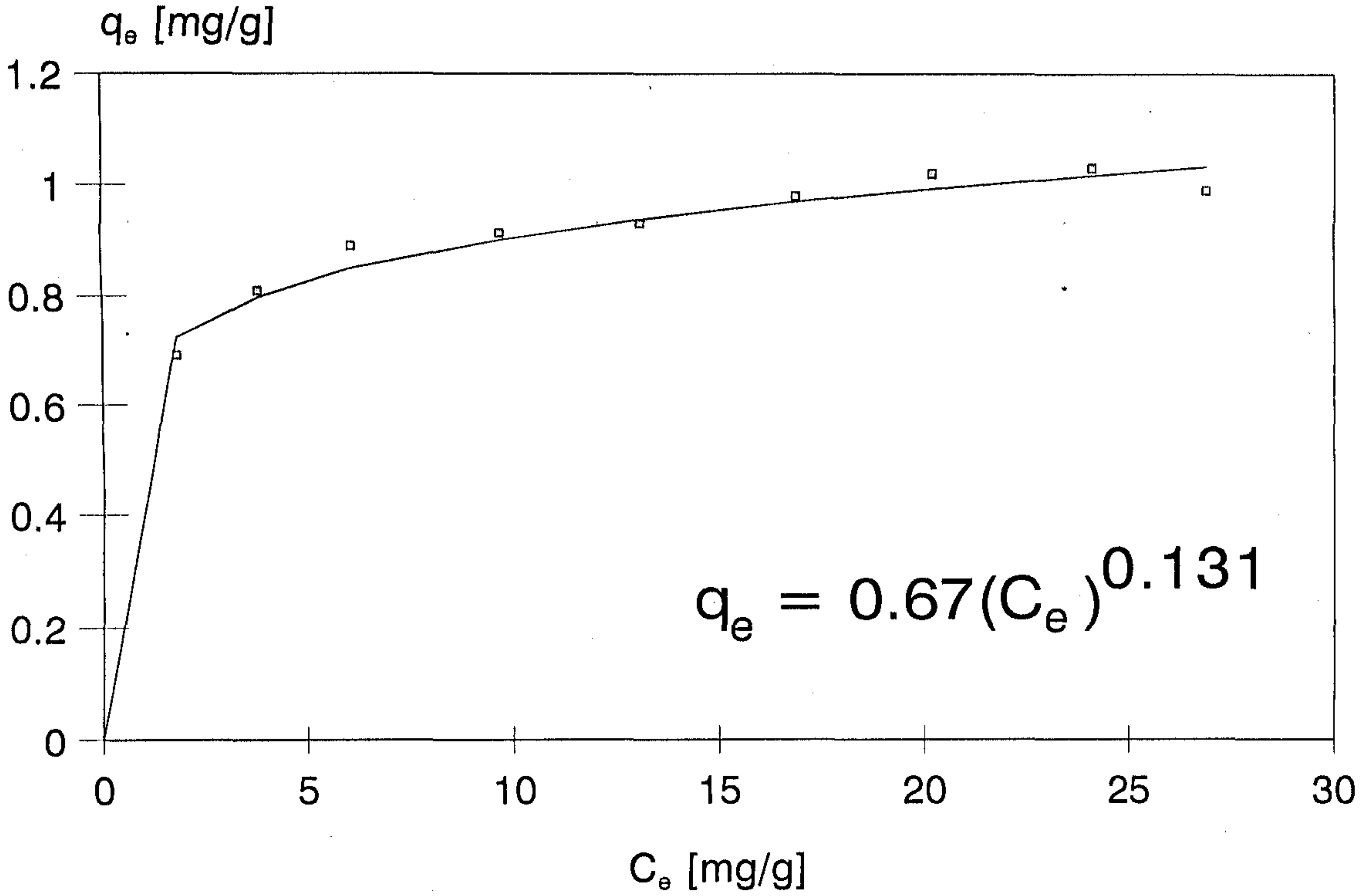

Figure 7.9 : Equilibrium Au loading with O_2 addition
Exp. no. 15

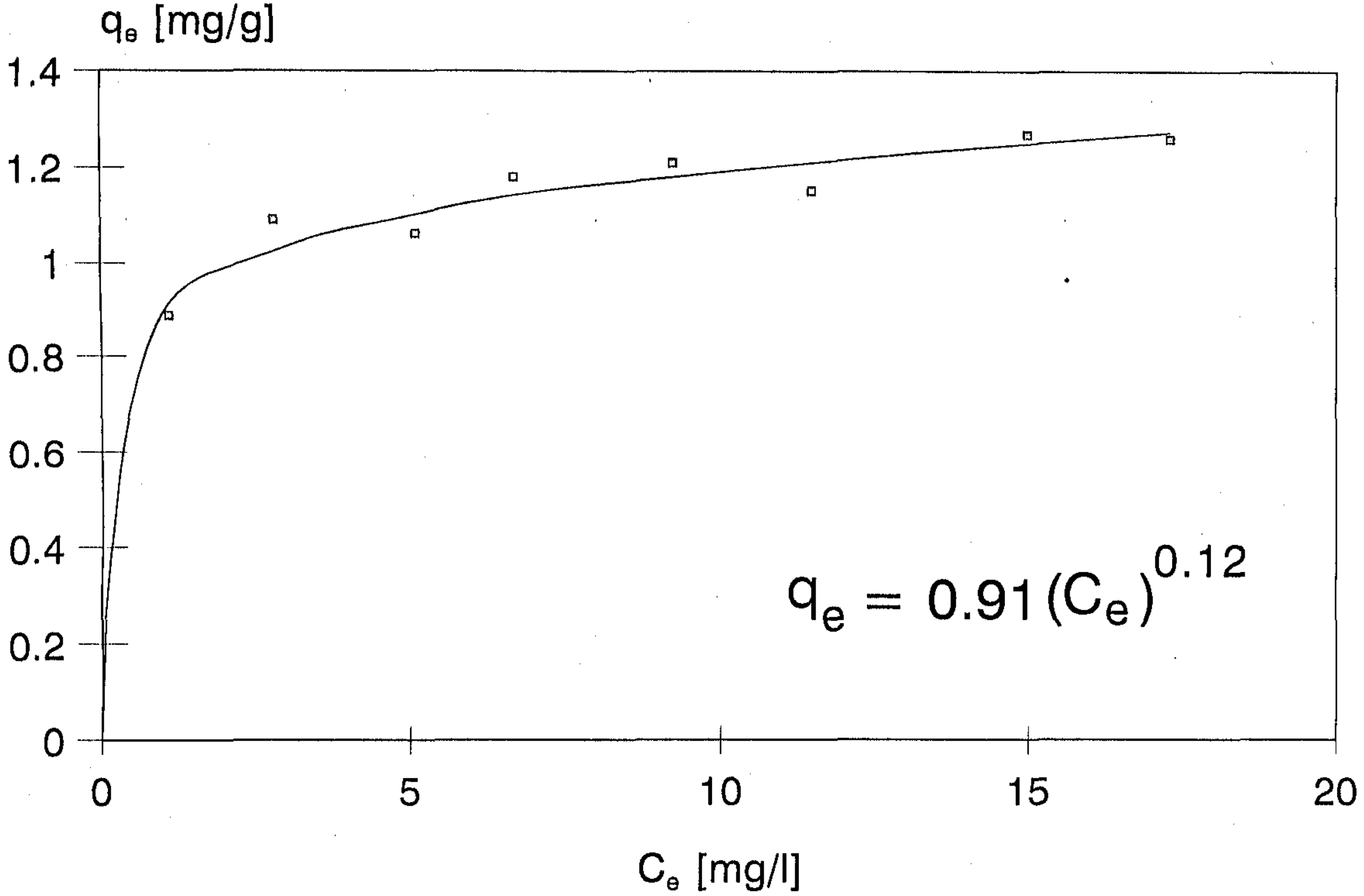

Figure 7.10 : Equilibrium Au loading with H_2O_2 addition
Exp. no. 16

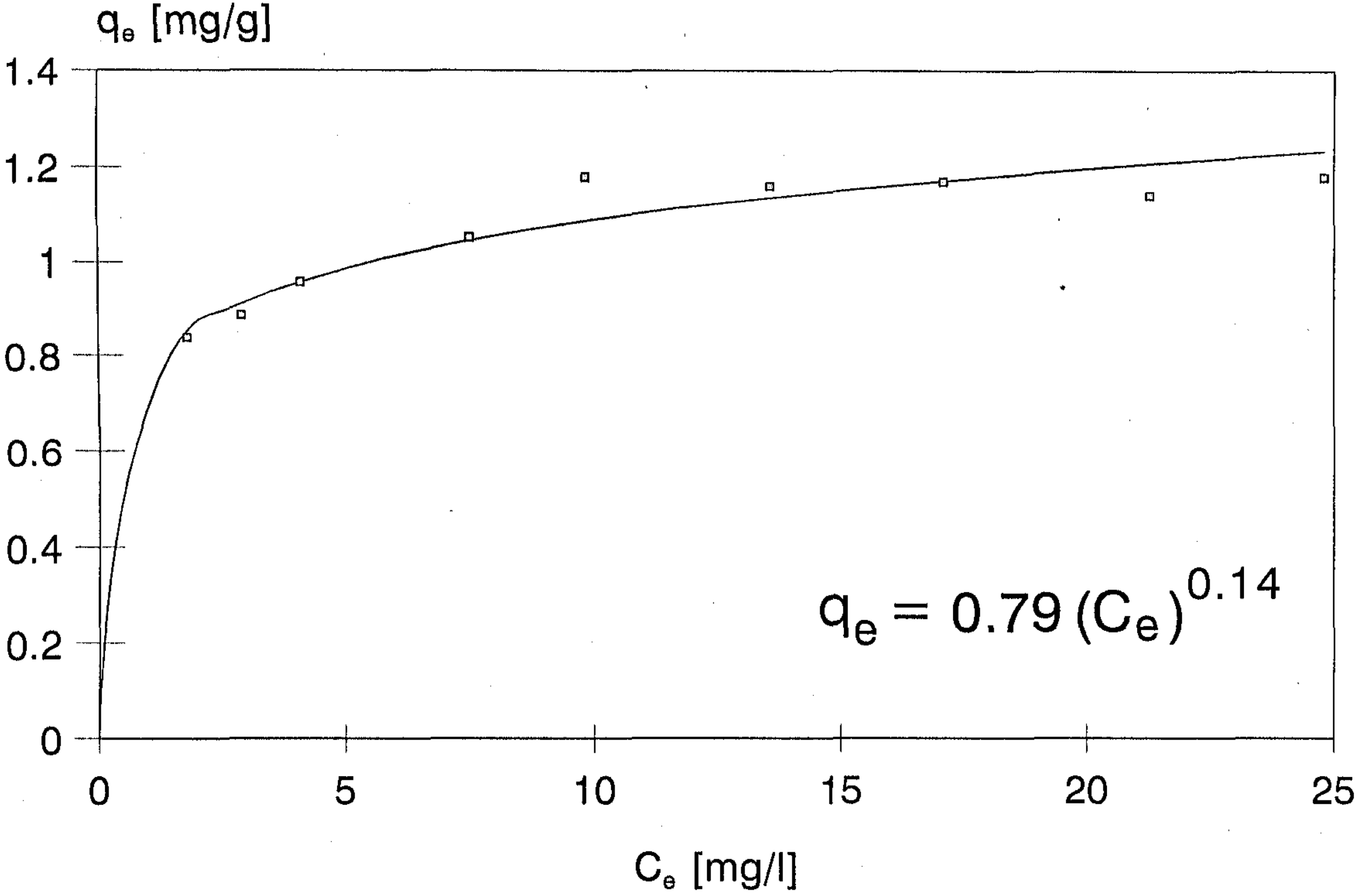

Figure 7.11 : Equilibrium Au loading at pH = 2
Exp. no. 17

CHAPTER 8

ELUTION

Gold is eluted from activated carbon and weak-base resins by a NaOH solution. Furthermore, temperature is considered as having the largest effect on desorption when activated carbon is the adsorbent. Whereas an increase in temperature decreases adsorptive performance of activated carbon, an increase in temperature favours desorption. The basis of the AARL elution process is based on the theory that the addition of a hot NaOH solution converts the $Ca^{2+}\{Au(CN)_2\}^-$ ion pair into the less strongly adsorbed $Na^+Au(CN)^-$ ion pair, which is then stripped under conditions of low ionic strength. The Zadra elution process, on the other hand, is based on the theory of competitive adsorption on the active sites of the carbon in the presence of high cyanide concentrations. (Stanley, 1987). In certain circumstances however, as for example found on the Hartebeestfontein gold mine in South Africa, the addition of cyanide has a negligible effect on desorption efficiency. In these cases a hot NaOH solution is sufficient for effective elution.

As was expected, gold is eluted from ACB by a caustic solution. The results of the desorption of acetylene black with a loading of 0.87 mg Au/g is tabulated in Table 8.1 and is graphically presented in Figure 8.1. Although gold is eluted from ACB at room temperature, the efficiency of desorption increases with an increase in temperature. It is postulated, as is the theory of the AARL process, that the hot NaOH solution converts the $Ca^{2+}\{Au(CN)_2\}^-$ ion pair into the less strongly adsorbed $Na^+Au(CN)^-$ ion pair. In addition to this, it is believed that the larger degree of desorption at higher temperatures is assisted by the fact that the mixing efficiency is favoured by higher temperatures as was illustrated by adsorption in Chapter 7.

As was the case with adsorption, desorption takes place relatively fast. This is graphically illustrated in Figures 8.2 and 8.3, with the respective initial gold loading being 0.76 and 0.81 mg Au/g.

TABLE 8.1

ELUTION EFFICIENCY AS A FUNCTION OF TEMPERATURE

Temperature [°C]	% Eluted
25	22
35	35
45	44
60	61
80	76
95	80

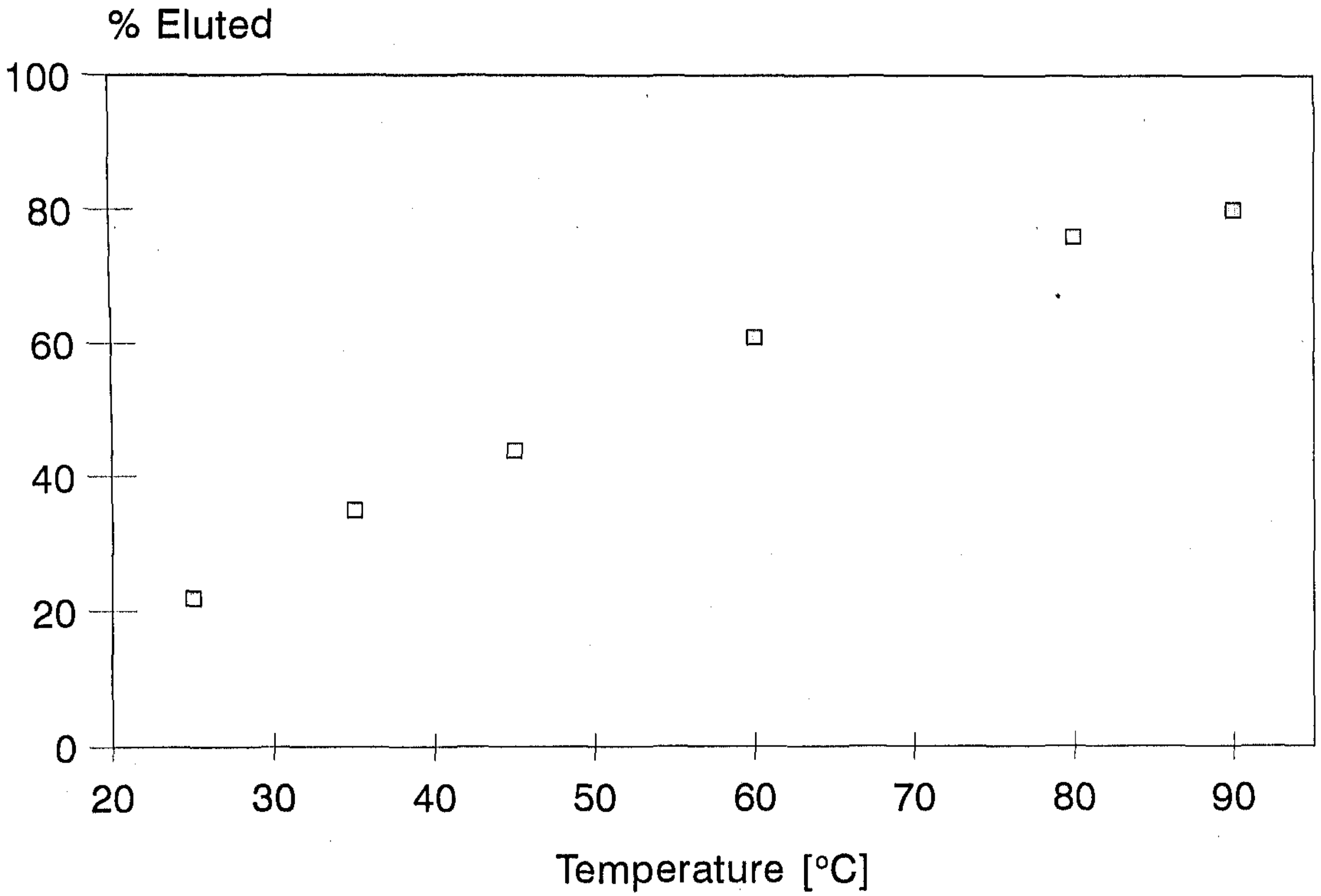

Figure 8.1 : Au elution with a NaOH solution
[NaOH] = 2 % ; Exp. no. 18

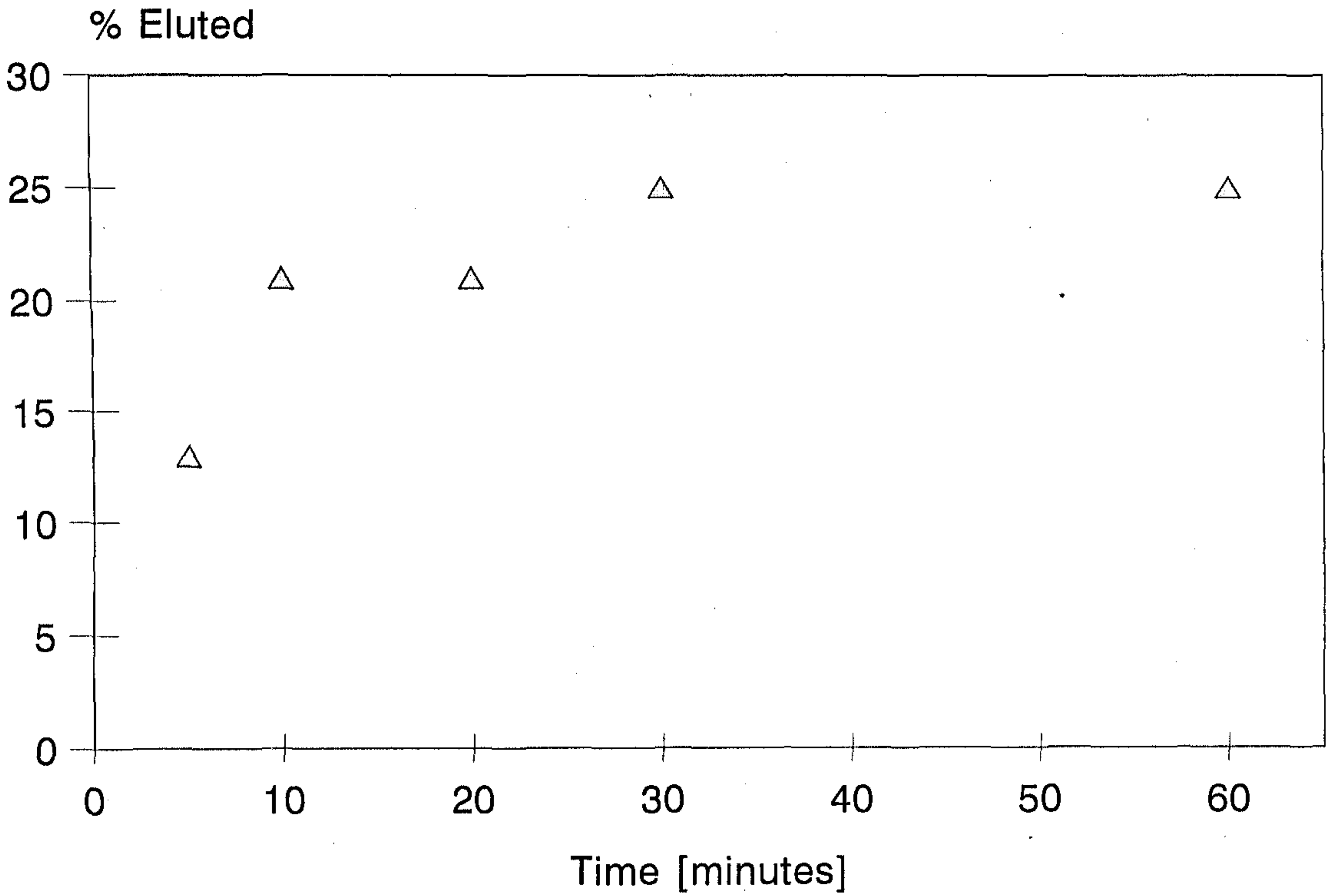

Figure 8.2 : Au elution with NaOH
[NaOH] = 2 % ; Temp. = 25 °C ; Exp. no. 19

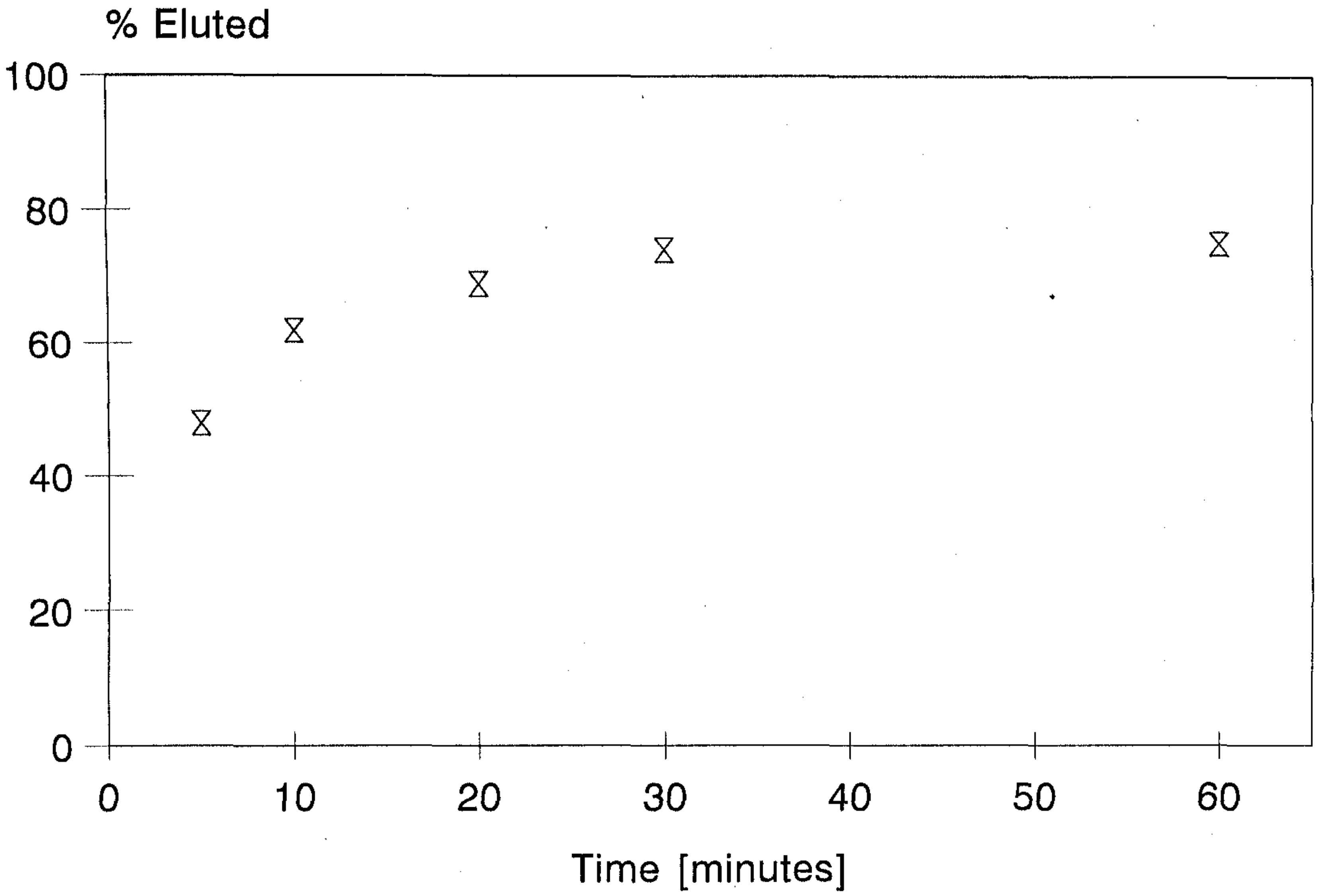

Figure 8.3 : Au elution with NaOH
[NaOH] = 2 % ; Temp. = 80 °C ; Exp. no. 20

CHAPTER 9

CONCLUSIONS

The primary objective of this thesis was to study the surface characteristics of ACB by comparing its behaviour to that of adsorbents currently used in the mining industry. For this purpose the adsorption and desorption of aurocyanide onto and from ACB was studied. The following conclusions may be drawn from the experimental work contained in this study :

- The structure of ACB is not truly graphitic, neither is it truly amorphous. This is manifested by X-ray diffractrometry results and the fact that intraparticle diffusion is negligible when aurocyanide is adsorbed onto ACB.

- The results obtained from acid/base titrations suggests that ACB has a very small ion exchange capacity, especially at low pH.

- The adsorption kinetics of ACB was found to be relatively fast with equilibrium conditions reached in a few minutes. This result is ascribed to the relatively small surface area, flat pore structure and small particle size of ACB. Furthermore, the Freundlich isotherm best explained the equilibrium adsorption of gold cyanide on ACB.

- While changes in pH, the addition of strong oxidizing agents, age and temperature had an effect on the adsorptive behaviour of ACB, variables such as oxygen enrichment and the addition of organic solvents had no noticeable influence on the process.

- Gold is eluted from ACB by a caustic solution. Furthermore, as is the case with activated carbon, an increase in temperature favours the elution process.

- An increase in acetylene feed rate to the retort decreases the performance (AS value) of ACB as applicable to dry cell battery use. Also, an increase in operating temperature in the retort decreases the AS value, although this decrease in AS is not as prominent as the first mentioned effect.

REFERENCES

---

1. Adams, M D, "The mechanism of adsorption of aurocyanide onto activated carbon. Relation between effects of oxygen and ionic strenght" *Hydrometallurgy*, vol 25, 1990, pp 171 - 184.

2. Adams M D, McDougall, G J and Hancock, R D "Models for the adsorption of aurocyanide onto activated carbon, Part III: Comparison between the extraction of aurocyanide by activated carbon, polymeric adsorbents and 1-pentanol", *Hydrometallurgy*, vol 19, 1987, pp 50 - 54.

3. Arden, T V, Water Purfication by ion-exchange, Butterworth & Company (Publishers) Ltd., 1968.

4. Cho, E H and Pitt, C H, "Kinetics and thermodynamics of silver cyanide adsorption on activated carbon", *Metall. Trans. 10B*, 1979, pp 165 -174.

5. Coulson & Richardson, Chemical Engineering, vol 2, Pergamon Press, 1991, pp 746 - 747.

6. Dixon, S, Cho, E H and Pitt, C H "The interaction between gold cyanide, silver cyanide and high surface area charcoal" *A I Ch E Symposium Series*, vol 74, no 173, 1978, pp 75 - 83.

7. The Extractive Metallurgy of Gold in S A, vol 1, SAIMM, 1987, pp 481 - 530.

8. Fleming, C A and Nicol, M J, "Alternative processes to filtration: CIP and RIP in metallurgical industry", *Hydrometallurgy '81*, 1981, pp C2/1 - C2/16.

9. Fleming, C A and Cromberge, G, "The extraction of gold from cyanide solutions by strong- and weak-base anion exchange resins", *J S Afr. Min. Metall.*, vol 84, no 11, 1984, pp 369 - 378.

10. Fleming, C A and Nicol, M J "The absorption of gold cyanide onto activated carbon III. Factors influencing the rate of loading and the equilibrium capacity", *J S Afr. Min. Metall.*, vol 84, no 4, 1984, pp 85 - 93.

11. Keinath, T M, "Design and operation of activated carbon adsorbers used for industrial wastewater decontamination, *A I Ch E Symposium Series*, no 166, vol 73, 1976, pp 1 - 8.

12. Kunin, R, Ion exchange resins, Robbert E Kruger (eds) Publishing Company, Huntington, N.Y., 1972.

13. McDougall, G J and Hancock, R D, "Activated carbon and gold: A literature survey", *Mineral Science and Engineering*, vol 12, no 2, 1980, pp 85 - 89.

14. Morris, J C, Weber, W J Jr, "Removal of biologically-resistant pollutants from waste waters by adsorption", *Proceedings of First International Conference on Water Pollution Research*, Pergaman Press, Ltd., Oxford, England, 1962.

15. Petersen, F W, MSc Thesis (Metallurgical Engineering), University of Stellenbosch, 1991, pp 28 - 33.

16. Petersen, F W and van Deventer, J S J, The influence of organics on the determination gold, silver and copper by atomic absorption spectrophotometry, *Minerals Engineering 3*, 1990, pp 415 - 420.

17 Petersen, F W, Williams, N C and Broquet, H, Report to Karbochem Ltd, Newcastle, South Africa, 1994

18. Shakourzadeh Boulouri, K and Amouroux, J, "Reactor Design and Energy Concepts for a Plasma Process of Acetylene Black Production", *Plasma Chemistry and Plasma Processing*, vol 6, No 4, 1986, pp 335 - 348.

19. Shawinigan Acetylene Black, Gulf Oil Canada Ltd, Chemicals Dept., 2020 University Street, Montreal, 1950.

20. Sheindorf, C H, Rebhum, M and Sheintuch, M, "A Freundlich-type multicomponent isothem", *Journal of Colloid and Interface Science*, vol 79, no 1, 1981, pp 136 - 142.

21. Stoeckli, H F, Laederach, A, Affolter, J and Athalye, A, "On the Physico-chemical properties of Carbon Blacks in relation to the performance of $2N/MnO_2$ batteries", *9th IBA Battery materials Symposium*, Cape Town, South Africa, 20 - 22 March 1995.

22. Tsuchida, N, Ruane, M and Muir, D M, "Studies on the Mechanism of gold adsorption on carbon" *Paper 136/2: Mintek 50th International Conference on recent advances in Mineral Science and Technology*, Sandton, South Africa, March 26 - 30, 1984.

23. Ullmann's Encyclopedia of Industrial Chemistry, vol A5, 1986, pp 140 - 163.

24. Van der Merwe, P F and Van Deventer, J S J, "The influence of oxygen on the adsorption of metal cyanides on activated carbon", *Chemical Engineering Communications*, vol 65, 1988, pp 121 - 127.

NOMENCLATURE

A	parameter in Freundlich isotherm
B	parameter in isotherm
a_{ACB}	external surface area of ACB [m^2]
C	metal concentration in solution [mg/l]
d_p	diameter of particle [m]
ΔH	Heat of reaction [kJ/mole]
k_f	external film transfer coefficient [m/s]
M	mass of adsorbent [g]
n	exponent in Freundlich isotherm
n_L	rate of diffusion through liquid film [mg/m^2 s]
q	metal loading on adsorbent [mg/g]
t	time variable [s]
V	volume of solution in reactor [l]

GREEK LETTERS

ρ	density of ACB [kg/m^3]

SUBSCRIPTS

e	equilibrium
o	concentration at time = 0
s	liquid-adsorbent interface

APPENDIX A

BASIC PROGRAMME FOR PARAMETER ESTIMATION

```
REM BASIC PROGRAMME FOR EVALUATING FILM MASS TRANSFER COEFICIENT
REM INPUTS [LINE 80] IN THE FOLLOWING ORDER.....
REM ESTIMATE OF Kf (m/s) ; CONCENTRATION,t=0 (ppm) ; TIME INTERVALS (sec) ;
REM LENGTH OF RUN (s) ; MASS OF ADSORBENT (g) ; DENSITY OF ADSORBENT (g/l)
REM DIAMETER OF ADSORBENT PARTICLES (m) ; VOLUME OF REACTOR (l) ;
REM A AND n (FREUNDLICH ISOTHERM PARAMETERS)

READ K, C1, T, E, M, R, D, V, A, n
DATA 6E-9,15,120,1800,15,75,3E-6,0.8,0.67,0.131
PRINT "EVALUATION OF Kf"
PRINT "================"
PRINT "TIME", "CONCENTRATION", "C/Co"
PRINT 0, C1, 1

REM EXECUTION
LET Z = 1 / n
LET B = A ^ Z
LET Q = C1
FOR J = T TO E STEP T
FOR I = C1 TO 0 STEP -.05
LET Y = Q - I
LET X = (((6 * K * M) / (R * D * V * B)) * ((((C1 - I) * V) / M) ^ Z) - ((
IF ABS(Y - X) < .05 THEN 220
NEXT I
LET W = I / C1
PRINT J, I, W
LET Q = I
NEXT J
END
```

APPENDIX B

TEST METHOD FOR ION-EXCHANGE

Weigh out 1.000 ± 0.005 g of carbon black into each of seven 150 ml short neck, flat bottomed, glass stoppered flasks with B34 sockets. Add 25 ml of N/10 (approx), N/100 (approx), N/1000 (approx) hydrochloric acid respectively to three flasks, 25 ml of water to a fourth flask and 25 ml of N/10 (approx), N/100 (approx), N/1000 (approx) potassium hydroxide respectively to the remaining three flasks. Prepare blanks by adding the same amounts of acid, water and alkali to seven further flasks. Finally add 25 ml of patassium chloride solution (2N) to each of the fourteen flasks. Stopper the flasks and shake them vigorously for 17 hours, i.e. overnight.

Filter the carbon black mixtures and blanks on Whatman No 540 filter papers and collect at least 20 ml of each filtrate in 25 ml measuring cylinders. Measure the pH of the filtrates from the carbon black mixtures using a combined glass/reference electrode, e.g. Pye Ingold, Type 401 and a reliable pH meter, e.g. Pye Dynacap.

Transfer two 5 ml aliquots of each of the fourteen solutions to 100 ml. Erlenmeyer flasks. To the aliquots of the blank and filtrate prepared from 25 ml hydrochloric aced (N/10 approx) and 25 ml potassium chloride solution (2N) add 30 ml of potassium hydroxide (N/100 approx). To each of the aliquots of the other blanks and filtrates add 5 ml of potassium hydroxide (N/100 approx) using B D H 4460 indicator. At the end point the colour change is from yellow/green to pink and should occur on the addition of 1 - 2 drops of acid.

CALCULATION:

Calculate the average titration for each pair of aliquots.

$$\text{Exchange capacity } (\mu \text{ eg/g}) = 104 \times (A-B)\, N$$

A = blank titration

B = titration of carbon black filtrate

N = true normality of the hydrochloric acid (N/100 approx)

Positive values indicate cation exchange and negative values indicate anion exchange.

Plot exchange capacity against pH. From the curve read off exchange capacities at pH 2 and pH 12.

APPENDIX C

TEST METHOD FOR ABSORPTION STIFFNESS

Weigh out five 0.05 g carbon black samples into five 500 ml Erlenmeyer flasks. Add 10 ml of a 10 % (V/V) acetone in water solution to the flask from a 50 ml burette and shake well with a swirling motion for 20 seconds. Add 5 ml and swirl for 10 seconds, then continue the 5 ml addition with 10 second swirling until small pellets up to 5 mm in diameter are formed. At this point reduce the additions to 2 ml but continue the 10 second swirling until pellets of about 1 cm in diameter are formed. Reduce the additions to 1 ml, again with 10 second swirling, until damp pellets of approximately 1.5 cm are formed. From this point onwards use 0.5 ml additions until one fragile sphere is formed. Add acetone solution in increments of 0.2 ml until the sphere withstands vigorous swirling without breaking up. This is the end-point and at this stage the sphere will cause slight smearing of the flask. The addition of a few drops of acetone solution will noticeably increase the smearing.

APPENDIX D

TABULATION OF EXPERIMENTAL RESULTS

EXPERIMENT NO. 1

Determination of the ion-exchange capacity of ACB by acid/base titrations.

pH	Blank Titration (ml)	Sample Titration (ml)
1.4	0.20	0.20
2.4	0.30	0.25
3.6	0.55	0.52
4.8	0.53	0.55
11.1	0.85	0.50
12.4	2.60	1.25
6.9	0.55	0.55

EXPERIMENT NO. 2

Ion-exchange with potassium chloride in a batch stirred reactor.

Conditions:

C_o (K^+) = 500 mg/l
pH = 7
[ACB] = 30 g/l

Time (minutes)	C/C_o
0	1.00
2	0.99
4	0.98
6	0.98
8	0.98
10	0.98
30	0.98

EXPERIMENT NO. 3

The adsorption of gold, as potassium gold cyanide, onto ACB.

Conditions:

C_o (Au) = 15 mg/l
[ACB] = 10 g/l
pH = 7

Time (minutes)	C/C_o
0	1.00
2	0.73
4	0.52
6	0.46
8	0.43
15	0.42
30	0.42

EXPERIMENT NO. 4

The adsorption of iron, as sodium ferro cyanide, onto ACB.

Conditions:

C_o (Fe) = 15 mg/l
[ACB] = 10 g/l
pH = 7

Time (minutes)	C/C_o
0	1.00
2	0.73
4	0.55
6	0.49
8	0.47
15	0.47
30	0.47

EXPERIMENT NO. 5

The adsorption of gold, as gold iodide, onto ACB.

Conditions:

C_o (Au) = 15 mg/l
[ACB] = 10 g/l
pH = 7

Time (minutes)	C/C_o
0	1.00
2	0.70
4	0.50
6	0.42
8	0.40
15	0.38
30	0.38

EXPERIMENT NO. 6

Equilibrium gold loading, as potassium gold cyanide, on ACB at pH 7 at a constant stirring rate of 400 rpm.

ACB (g)	C_o (mg/l)	C_e (mg/l)	q_e (g/kg)
10.01	7.8	1.1	0.67
10.00	8.5	1.7	0.68
10.03	10.1	2.7	0.74
9.99	11.7	4.3	0.74
10.01	12.8	4.5	0.83
10.00	14.4	6.0	0.84
10.03	16.2	7.4	0.88
10.01	21.4	11.9	0.95
10.02	30.3	20.7	0.96
10.02	35.2	24.8	1.04
10.00	40.2	30.3	0.99

* q_e was calculated by mass balance

EXPERIMENT NO. 7

The effect of oxygen addition on the adsorption of gold cyanide onto ACB in a batch stirred reactor.

Conditions:

C_o (Au) = 15 mg/l
[ACB] = 15 g/l

Time [minutes]	C/C_o (No O_2)	C/C_o (O_2)
0	1.00	1.00
2	0.64	0.64
4	0.40	0.39
6	0.30	0.28
8	0.24	0.23
10	0.22	0.22
20	0.22	0.22
30	0.22	0.22

EXPERIMENT NO. 8

The adsorption of gold cyanide onto ACB with the addition of MnO_2 in a batch stirred reactor.

Conditions

C_o (Au) = 15 mg/l
[ACB] = 15 g/l
pH = 7

Time [minutes]	C/C_o (NO MnO_2)	C/C_o (MnO_2)
0	1.00	1.00
2	0.60	0.52
4	0.41	0.26
6	0.27	0.13
8	0.22	0.09
10	0.22	0.09
20	0.22	0.09
30	0.22	0.09

EXPERIMENT NO.9

The effect on gold cyanide adsorption on ACB with the addition of H_2O_2 in a batch *stirred reactor.*

Conditions:

C_o (Au) = 20 mg/l
[ACB] = 10 g/l
pH = 7

Time [minutes]	C/C_o (No H_2O_2)	C/C_o (H_2O_2)
0	1.00	1.00
2	0.71	0.61
4	0.60	0.46
6	0.54	0.42
8	0.53	0.41
10	0.53	0.40
20	0.50	0.40
30	0.50	0.40

EXPERIMENT NO. 10

The effect on gold cyanide adsorption onto ACB with a lowering in pH in a batch stirred reactor.

Conditions:

C_o [Au] = 15 mg/l
[ACB] = 10 g/l
pH = 2

Time [minutes]	C/C_o : pH = 2	C/C_o : pH = 7
0	1.00	1.00
2	0.65	0.71
4	0.43	0.51
6	0.38	0.43
8	0.36	0.41
10	0.35	0.41
20	0.35	0.41
30	0.35	0.41

EXPERIMENT NO. 11

The effect of temperature on the adsorption of gold cyanide onto ACB in a batch stirred reactor.

Conditions:

C_o (Au) = 15 mg/l
[ACB] = 10 g/l
Temp. = 60 °C

Time [minutes]	C/C_o (25 °C)	C/C_o (60 °C)
0	1.00	1.00
2	0.72	0.65
4	0.53	0.45
6	0.41	0.41
8	0.40	0.39
10	0.40	0.38
20	0.40	0.38
30	0.40	0.38

EXPERIMENT NO. 12

The effect of ageing on the adsorptive behaviour of ACB.

Conditions:

C_o (Au) = 15 mg/l
[ACB] = 10 g/l
Age : Exposed to atmospheric conditions for 6 months

Time [minutes]	C/C_o (Normal)	C/C_o (6 months)
0	1.00	1.00
2	0.69	0.73
4	0.51	0.58
6	0.43	0.51
8	0.42	0.50
10	0.42	0.50
20	0.42	0.50
30	0.42	0.50

EXPERIMENT NO. 13

The effect of acetone addition on gold cyanide adsorption onto ACB.

Conditions:

C_o (Au) = 15 mg/l
[ACB] = 10 g/l

Time [minutes]	C/C_o [no acetone]	C/C_o [acetone]
0	1.00	1.00
2	0.71	0.73
4	0.55	0.54
6	0.48	0.46
8	0.41	0.42
10	0.40	0.41
20	0.40	0.41
30	0.40	0.41

EXPERIMENT NO. 14

The effect of methanol addition on gold cyanide adsorption onto ACB.

Conditions:

C_o (Au) = 15 mg/l
[ACB] = 10 g/l

Time [minutes]	C/C_o [no methanol]	C/C_o [methanol]
0	1.00	1.00
2	0.70	0.72
4	0.52	0.53
6	0.46	0.45
8	0.44	0.43
10	0.43	0.43
20	0.43	0.42
30	0.43	0.42

EXPERIMENT NO. 15

Equilibrium gold loading, as potassium gold cyanide, on ACB in a batch stirred reactor with oxygen addition at a constant stirring rate of 400 rpm.

ACB [g/l]	C_o [mg/l]	C_e [mg/l]	q_e [g/kg]
9.97	8.6	1.7	0.69
10.01	11.9	3.8	0.81
10.03	15.0	6.1	0.89
10.00	18.9	9.7	0.92
9.98	22.5	13.4	0.91
10.02	26.7	17.4	0.93
10.00	30.4	20.2	1.02
9.99	34.4	24.1	1.03
10.04	36.8	26.9	0.99

* q_e was calculated by mass balance

EXPERIMENT NO. 16

Equilibrium gold loading, as potassium gold cyanide, on ACB in a batch stirred reactor with the addition of H_2O_2 at a constant stirring rate of 400 rpm.

ACB [g/l]	C_o [mg/l]	C_e [mg/l]	q_e [g/kg]
10.03	10.0	1.1	0.89
10.01	13.3	2.4	1.09
10.06	16.1	5.5	1.06
10.05	18.3	6.5	1.18
9.96	21.3	9.2	1.21
10.01	23.5	12.0	1.15
9.98	27.7	15.0	1.27
10.00	29.9	17.3	1.26

* q_e was calculated by mass balance

EXPERIMENT NO. 17

Equilibrium gold loading, as potassium gold cyanide, on ACB in a batch stirred reactor at pH 2 at a constant stirring rate of 400 rpm.

ACB [g/l]	C_o [mg/l]	C_e [mg/l]	q_e [g/kg]
10.01	10.2	1.8	0.84
10.02	11.8	2.9	0.89
10.01	13.7	4.1	0.96
10.05	18.0	7.5	1.05
9.97	20.8	9.8	1.18
10.02	25.2	13.6	1.16
10.01	28.8	17.1	1.17
9.98	33.3	21.3	1.14
10.03	36.6	24.8	1.18

* q_e was calculated by mass balance

EXPERIMENT NO. 18

The elution of gold from ACB in a batch stirred reactor at various temperatures using a NaOH solution.

Conditions:

[NaOH] = 2% (m/m)
Au on ACB = 0.87 g/kg
Volume = 800 ml
ACB mass = 15 g

TEMPERATURE (°C)	Au concentration in solution (mg/l)
25	2.3
35	3.7
45	4.6
60	6.4
80	7.9
95	8.4

EXPERIMENT NO. 19

The elution of gold from ACB using a NaOH solution.

Conditions:

[NaOH] = 2%
Au on ACB = 0.76 g/kg
Volume = 800 ml
ACB mass = 10 g
Temperature = 25 °C

Time [minutes]	Concentration in liquid [mg/l]
0	0.0
5	0.8
10	1.3
20	1.3
30	1.5
60	1.5

EXPERIMENT NO. 20

The elution of gold from ACB using a NaOH solution.

Conditions:

[NaOH] = 2%
Au on ACB = 0.81 g/kg
Volume = 800 ml
ACB mass = 10 g
Temperature = 80 °C

Time [minutes]	Concentration in liquid [mg/l]
0	0
5	3.1
10	4.0
20	4.5
30	4.8
60	4.9

EXPERIMENT NO. 21

The effect of operating temperature and acetylene feed rate on the AS value.

Retort No.	Temperature (°C)	Flow rate [rotameter]	AS value [ml/5 g ACB]
5	860	140	64.2
	900	140	75.2
	940	140	69.6
	860	160	62.8
	900	160	59.2
	940	160	54.2
	860	180	42.6
	900	180	59.6
	940	180	62.0
8	860	140	73.0
	900	140	72.0
	860	160	66.8
	900	160	62.4
	940	160	66.0
	860	180	65.4
	900	180	63.8
	940	180	53.0
17	860	140	80.0
	900	140	72.0
	940	140	65.0
	860	180	63.4
	900	180	66.0
	940	180	58.0