INHIBITION OF THE PREGROBBING PHENOMENON IN GOLD ORES

BY

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DECLARATION

I hereby certify that this dissertation is my own original work, except where specifically acknowledged in the text.

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ABSTRACT

In a typical gold-recovery plant, it is estimated that a substantial amount of the gold in residues may be in the form that is recoverable by cyanidation. The gold in residues can be ascribed broadly to (1) the presence of cyanicides, which consume the cyanide radical and thus inhibit dissolution of gold, (2) refractory gold resulting from coatings on some gold particles, (3) large gold particles incompletely dissolved due to inadequate contact time, (4) unliberated gold as a result of too coarse a milled product, and (5) gold dissolved during leaching, then adsorbed by other minerals or by carbonaceous matter in the pulp. This study focuses on the latter, where dissolved gold is pregrobbed during leaching by adsorbent materials in the ore. The term pregrobbing refers to the active adsorption of gold from cyanide pregnant solutions by components of the ore.

It has been suggested that gold already dissolved by cyanide may be adsorbed by other minerals and by carbonaceous matter in the pulp. The presence of carbonaceous matter in gold ores presents a two-fold problem namely, the poor release of gold from the carbonaceous matrix and the uptake of dissolved gold by the carbonaceous leach residues. Studies by several other investigators using ores from various parts of the world have similarly shown that the natural carbonaceous matter associated with refractory gold ores often behaves like activated carbon when in contact with aurocyanide solutions. Some debate also exists over the extent to which gold may be adsorbed onto the surfaces of minerals. Different authors have identified that minerals such as pyrite, copper sulphides, quartz and layered silicates, such as kaolin, phlogopite and illite exhibit gold adsorbing properties.

Activated carbon was first used as a model pregrobber in batch kinetic adsorption experiments in the presence of a gold selective strong base anion-exchange resin. The activated carbon was used to simulate the pregrobbing effect of the carbonaceous material in gold ore. These aspects were investigated focusing both on the kinetic and equilibrium behaviour of the system. Results showed that the pregrobbing phenomenon is a function of the activity and porosity of the pregrobber as well as the gold loading distribution of the resin, the gold concentration of the solution and time.

The gold adsorbing properties of pure minerals pyrite, quartz, kaolin and chalcopyrite were examined. Gold adsorption experiments showed that all the minerals adsorbed gold to some extent, with the copper and sulphide minerals (chalcopyrite and pyrite) showing the strongest pregrobbing effect. It was, however, possible to remove most of the gold from the loaded minerals in the presence of potassium cyanide. The pregrobbing effect of these minerals would therefore, probably not be a problem in most carbon-in-pulp or resin-in-pulp plants.

Tests on several pregrobbing ores indicated that the organic carbon content of ores poses a problem, with ores of high organic carbon content showing lower gold desorption capabilities. Resin in leach studies with a gold selective resin proved to be much more effective than conventional cyanidation, although low gold recoveries are still possible in some cases. The use of organic blinding agents in a resin-in-leach configuration also proved to be an effective combination. Several organic compounds were found to have a blinding effect, reducing the adsorption of gold cyanide by the pregrobbing components in the ore.

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CHAPTER 1

INTRODUCTION

1.1 THE GOLD MINING INDUSTRY

1.1.1 Importance of gold mining

The gold mining industry in South Africa has been the mainstay of the South African economy for over a century. Through gold mining, many cities have come into being and provided employment for millions of people. Much of the infrastructural development of roads, electricity generation, water reticulation, telecommunications, housing and the development of secondary industry to provide the inputs to the gold mining industry have resulted directly from gold mining. Gold has also been South Africa's largest export for a number of years and has accounted for a large portion of total foreign exchange earnings.

South Africa is considered to be the largest gold mining industry in the world with about 40 per cent of the known world gold reserves. It is therefore, safe to say that gold mining will continue to have a vital role in the economic development of the country in terms of contributions to wealth creation, to employment, to infrastructural development and to foreign exchange earnings (Chamber of Mines, http://www.bullion.org.za).

1.1.2 Challenges facing the mining industry

The most fundamental challenge facing the gold mining industry is the productivity of labour and capital and their impact on the cost of mining and extracting gold. Gold mining is both labour and capital intensive and the ever-increasing mining depths, which in some cases, has increased to levels of four kilometres below the surface, technical barriers, steadily declining grades and the fluctuating gold price have put tremendous pressure on profit margins.

These factors have put more emphasis on the development of more effective gold mining processes to improve gold recoveries, minimise possible gold losses during extraction and ultimately to make the gold recovery process more economically viable.

1.2 MINERAL COMPOSITION OF GOLD ORES

Gold is found in nature mainly as native gold. A number of gold alloys, the most important being electrum, a gold-silver alloy, and tellurides constitute the main gold minerals. The other alloys and tellurides have different optical properties and structures than electrum and are rare. To the above three types of gold-bearing minerals, native gold, gold alloys and gold compounds a fourth class must be added namely "invisible" gold which is dispersed in the form of solid solution or submicron inclusions in sulphide minerals and sulfosalts (Yannopoulos, 1991).

Much literature exists that classifies the occurrence of gold in ores under certain headings. McQuiston and Shoemaker (1975) proposed the following classification:

- *Native gold*, which is the most common form of gold found in ores.
- *Gold associated with sulphides*, occurring either as free particles or disseminated in sulphides. Auriferous pyrite with gold finely disseminated in its matrix is rather common.
- *Gold tellurides*, which usually occur along with native gold and sulphides. Calaverite and krennerite are minerals containing about 40 % gold and sylvanetite contains about 25 % gold.
- *Gold in other minerals*, as with arsenic and/or antimony (aurostibnite, $AuSb_2$), with copper porphyries (as selenide and telluride), with lead and zinc minerals, and with carbonaceous materials.

In general, the other minerals associated with the gold conglomerate consists essentially of the following (Stanley, 1987; Adamson, 1972):

- Quartz, primary as well as secondary.
- Muscovite accompanied by variable amounts of chlorite, pyrophyllite, kaolin, illite and chloritoid.
- Pyrite, which is classified into three types, (1) allogenic rounded compact pyrites, (2) allogenic rounded porous synsedimentary pyrites, and (3) authigenic idiomorphic to hypidiomorphic pyrites or pyrite accumulations. Pyrite mainly occurs as allogenic rounded compact pyrites.
- Other sulphides such as chalcopyrite, pyrrhotite, arsenopyrite and pentlandite, which usually occur as small irregular patches; and
- Oval and round grains of primary minerals, which include minerals such as uraninite, zircon, magnetite, chromite, monazite and tourmaline. These minerals are accompanied by alteration products such as hydrated iron oxide and leucoxene, sometimes by secondary minerals such as anatase, and more rarely by calcite.

The mineral distribution varies in different gold conglomerates. Therefore, the mineralogy of the ore and the form in which the gold metal is present, either in a liberated/free form or in association with other minerals, determines the characteristics of the specific ore.

1.3 GOLD BEARING ORES

Gold ores can be categorised into two types namely free milling (non-refractory) and refractory ores. Free milling ores are easy to treat and give recoveries of more that 88 % when subjected to conventional cyanidation (cyanidation is the process used to dissolve gold and will be discussed later on in this chapter). These ores are associated with gold that occurs as nuggets and as large grains that are readily exposed to the cyanide solution.

Refractory gold ores, on the contrary, are difficult to treat and require pre-treatment to make the recovery process economically viable and in some cases possible. A gold ore is termed refractory when poor gold recoveries, usually less than 80 %, are obtained by standard cyanidation processes (Afenya, 1991; Petruk, 1989; La Brooy *et al.*, 1994). The refractory nature of the ore may be due to a variety of causes, chemical or physical in nature, and are summarized below.

- *Products insoluble to cyanidation* – Gold-bearing products that are insoluble in cyanide solutions include gold-bearing minerals such as tellurides, aurostibite and maldonite, and gold-containing compounds. The insoluble gold-bearing minerals and compounds usually occur in small quantities, but they may amount to a significant loss of gold during processing.
- *Encapsulation* – Gold may occur as inclusions in minerals that are insoluble in cyanide solutions. The gold inclusions may be so small that they cannot be liberated or exposed to the cyanide solutions by comminution. Minerals that commonly encapsulate the gold are pyrite, arsenopyrite and quartz.
- *Coatings on gold* – Coatings may form on gold particles during extractive metallurgy, and inhibit dissolution of gold by the cyanide solution. The coatings may be precipitates of iron oxides, and/or lead, antimony and/or arsenic compounds.
- *Decomposition of associated minerals* – Associated minerals, such as pyrrhotite, covellite, chalcocite and native copper may decompose to form cyanide complexes and thereby deplete the activity of the cyanide solution. The oxidation of compounds such as sulphide ions, arsenites and ferrous ions consumes oxygen and inhibit the gold-dissolution process because the process also requires oxygen.
- *Chemically bound "invisible" gold* – Gold can be chemically bound within certain sulphide minerals, particularly pyrite and arsenopyrite. This form of gold is called "invisible" gold and cannot be recovered by cyanidation.
- *Carbonaceous materials and gold adsorbing minerals* – Carbonaceous material in some ores may occur in the form of "active" carbon that adsorbs gold, thus "pregrobbing" the lixiviant. Certain minerals can also adsorb gold during the

cyanidation process. (Bhappu, 1990; Petruk, 1989; Afenya, 1991; Yannopoulos, 1991)

Various procedures have been investigated in an attempt to enhance gold recovery from these difficult ores, including roasting, diesel or kerosene pre-treatment, flotation and chemically oxidation. In the past, where these measures proved unsuccessful, it was common practice to simply stockpile the refractory ores and tailings and in some cases, it was necessary to resort to selective mining (Osseo-Asare *et al.*, 1984).

Today there is a growing interest in these previously rejected and unattractive ores because of the gradual decrease in the grade of the more easily processing ores, the ever-increasing mining depths, the growth in the quantity of the stockpiled material and the new developments in extractive technology.

1.4 THE GOLD RECOVERY PROCESS

There are many different processes for the extraction of gold from the ore body, which includes chemical, physical or surface based processes. Gold may be recovered from the ore by amalgamation with mercury, chlorination, or cyanidation depending on the mineralogy of the ore and the degree of liberation of gold particles. Recovery by amalgamation had declined steadily and attempts to improve recovery using chlorination proved costly and ineffective. The bulk of the world's gold production is, however, recovered by the cyanidation process, which will be discussed in this section.

1.4.1 Cyanidation

JS MacArther and the Forrest brothers of Glasgow introduced the cyanidation process in the 1890's. The process involves the dissolution of the gold in aqueous alkaline cyanide solution and the subsequent separation of the gold bearing solution from the finely ground ore. The process has been used to treat ores, concentrates and calcines on a commercial scale all over the world. The chemistry of cyanidation is based on the fact that under oxidising conditions, gold can be complexed with cyanide and dissolved in alkaline solutions. The cyanidation process consists of the following basic processing steps (Figure 1.1):

1.4.1.1 Comminution

The mineralogy of the gold ore dictates the required fineness of grinding for adequate gold liberation and the economically optimum extraction recovery. Ore hoisted from the mine often has to be first crushed at the mine. The ore is first broken into smaller pieces by a primary crusher and secondary crushers break it down further so that the ore is suitable for milling. Fine grinding of the ore is required to liberate the gold particles and maximise the reaction rate and efficiency of leaching. The grinding takes place in an autogenous or semi-autogenous grinding (SAG) mill, which requires a very high ratio of liquids to solids (Adamson, 1972; Yannopoulos, 1991).

1.4.1.2 Thickening

The reagent economics, size of equipment, and reaction contact time in the subsequent operations, however, require that the liquid content of the pulp must be low. The solids therefore, have to be dewatered. This is done in a thickener by allowing the solids to separate by sedimentation in a virtually still solution. At this point most of the tiny particles of gold contained in the ore have been exposed and liberated from the parent rock.

1.4.1.3 Leaching

Following the dewatering of the milled pulp in a thickening process, the gold is leached to take it into aqueous solution. This is done by contact with a soluble cyanide salt such as sodium or calcium cyanide, which dissolves the gold. In the case of batch and continuous leaching, agitation of the pulp to promote mixing and prevent settling of the solids is commonly performed by compressed air (Stanley, 1987; Fleming and Nicol, 1981; Cornejo and Spottiswood, 1984). The use of air as a means of agitation also provides oxygen, which is necessary to the chemistry of the leaching process. According to Finkelstein (1972), most of the gold dissolves by the reaction:

$$2Au + 4CN^- + O_2 + 2H_2O \leftrightharpoons 2Au(CN)_2^- + 2OH^- + H_2O_2 \qquad \ldots (1.1)$$

and a small but significant proportion dissolves via the Elsner reaction:

$$4Au + 8CN^- + O_2 + 2H_2O \leftrightharpoons 4Au(CN)_2^- + 4OH^- \qquad \ldots (1.2)$$

The other essential for the reaction is calcium hydroxide, which maintains a protective level of alkalinity (pH 10 to 11). The concentration of cyanide ion in the leaching process is normally of the order of 200 ppm at the start of the process and falls to 120 ppm at the end because of side reactions with cyanide-consuming agents contained in the ore, reaction with dissolved carbonic acid and hydrolysis of the cyanide (Yannopoulos, 1991). Depending on the grade of the ore, up to 98% is capable of being extracted in the leaching process.

After leaching the gold ores and concentrates with cyanide a pregnant solution of anionic metal cyanide complexes are obtained from which gold must be recovered. The aurocyanide complexes, which have formed, may be removed by one of the following processes:

- *Zinc cementation*, in which zinc dust and lead nitrate is added to the clarified cyanide solution to precipitate the gold;
- Adsorption onto *activated carbon* in the carbon-in-pulp process or in a number of alterative contacting modes, such as fixed bed, multistage column, fluidised bed and moving bed packed column modes;
- Removal by *ion-exchange resin*; and

- Simultaneous cyanide dissolution and adsorption in the *carbon-in-leach* (CIL) or *resin-in-leach* (RIL) process.

1.4.1.4 Liquid-solid separation

When the dissolution of gold is complete, unless a carbon/resin-in-pulp or similar process is employed, it is necessary to effect a solid/liquid separation between the gold bearing solution and the residue solids, the gold bearing solution being retained for subsequent gold recovery via zinc cementation (Stanley, 1987; McQuiston and Shoemaker, 1975). It is important to perform the separation efficiently in order to ensure the lowest possible loss of dissolved gold and this can be accomplished using continuous vacuum filtration followed by a filtrate clarification stage.

The clarification process employs various types of equipment which includes sand filtration, pressure sand filtration, pre-coat filtration, gravity settling or in some instances two or more of these types used in series or parallel. The clarification stage is necessary before cementation of gold by zinc dust can be started to reduce the relative high suspended solids content of the gold bearing solution from the filter plant. The suspended solids consist of colloidal hydrates of aluminium, iron and magnesium and fine ore particles composed of quartzite and various clay minerals. The removal of the colloidal hydrates is necessary as they can inhibit gold precipitation by coating the zinc dust particles and the siliceous ore particles have to be removed, as they will add to the bulk in the smelt when retained by the precipitation filters (Adamson, 1972; Yannopoulos, 1991; Stanley, 1987).

1.4.2 Zinc cementation

The best known method of recovery from dilute solutions arising from liquid-solid separation is zinc precipitation. The process is based on the electrochemical order of metals in the cyanide solution, which dictates their solubilities in the solvent. The electrochemical order of zinc and gold is such that zinc will displace the gold in the cyanide solution. Barin *et al.* (1980) proposed the following overall chemical reaction for the cementation of gold by zinc.

$$Zn + Au(CN)_2^- + H_2O + 2CN^- \rightleftharpoons Au + Zn(CN)_4^{2-} + OH^- + 0.5H_2 \qquad \ldots (1.3)$$

The early use of zinc shavings was superseded by zinc dust from 1911 (Merrill-Crowe process), which offered a greater surface area per unit mass and required less handling than shavings (Mintek, http://www.mintek.co.za).

The process involves the addition of the pregnant cyanide solution from the clarification process to frame filters. The solution from the filters is sent to vacuum de-aeration tanks where zinc dust and lead nitrate are added. The de-aeration tanks allowed dissolved oxygen in the pregnant solution to be removed just before the addition of the zinc dust. The oxygen is removed because it causes increased zinc consumption by wasteful side reactions oxidising the zinc (Stanley, 1987; Nicol *et al.*, 1987). The solution then flows into a circular tank through precipitation filters, which are precoated with diatomaceous earth and a secondary coating of zinc dust. The pregnant solution has to percolate through the layer of fine zinc particles, which create a very extensive surface for the solid-liquid precipitation reaction (Yannopoulos, 1991).

1.4.3 Adsorption by activated carbon

As mentioned above, there are different ways of recovering gold from the pregnant solution after leaching. Gold can be recovered from these solutions using adsorption onto activated carbon. The discovery of the adsorptive property of charcoal from solutions can be traced back as far as 1785 when J.T. Lowitzs observed that several dissolved organic substances were precipitated on charcoal, but it was not till 1880 when W.N. Davis patented a metallurgical process for the recovery of gold by charcoal from leach liquors (Adamson, 1972). Today activated carbon is used extensively to recover aurocyanide from solution in the gold mining industry.

There are several systems whereby activated carbon is used to recover gold, each of which demands significantly different process designs. The one is the application in which gold is adsorbed from the leached slurry in the adsorption circuit, by contacting the carbon with the leached pulp and separating the two by screening. This process is called the carbon-in-pulp (CIP) process (Figure 1.2).

The leach and adsorption circuits are occasionally combined by adding activated carbon to the leaching tanks to adsorb the gold from solution as cyanidation proceeds. This process is described as the carbon-in-leach (CIL) process.

The process used to treat nominally clear solutions is called the carbon-in-column (CIC) process and involves the use of a packed column of activated carbon through which the clarified leached solution is passed. Of these three processes, carbon-in-pulp is the most commonly employed.

1.4.3.1 The carbon-in-pulp circuit (CIP)

The carbon-in-pulp process, which was developed to its present form in South Africa during the 1970's, is considered to be the most significant advance in gold recovery technology in recent years and has since become the preferred route for gold recovery. The reasons why the CIP route has displaced the zinc precipitation process is because it does not require a liquid-solid separation step, is less labour intensive and it is more cost effective. The CIP process also handles shaley and clayey ore more efficiently than filtration and it produces better gold recoveries (Mintek, http://www.mintek.co.za; Stanley, 1987; Dahya and King, 1983).

The CIP process consists of four essential stages, refer to Figure 1.2:

1. *Adsorption*, in which the dissolved gold in the pulp is loaded onto aerated carbon,

2. *Elution*, in which the gold is removed from the carbon into an alkaline cyanide solution,
3. *Electrowinning*, in which the gold is removed by an electrochemical process from the alkaline cyanide solution and deposited on steel wool electrodes.
4. *Reactivation*, in which the carbon is stripped from impurities, which causes poisoning and loss of activity.

Adsorption

In the adsorption section, the dissolved gold from the cyanidation circuit (with a concentration range of 2 mg/l to 20 mg/l) is adsorbed onto the carbon in a series of stirred tanks arranged in such a way that the flow of the pulp and carbon is counter-current. Hence, the gold value decreases downstream, while the loaded gold value on the carbon increases upstream. The pulp in the adsorption tanks is kept at a pH of between 10 and 11 through the addition of lime (McDougall and Fleming, 1987; Laxen *et al.*, 1994). The carbon and slurry are kept in suspension by air agitation or mechanical mixers. Interstage screening is used to separate the carbon from the pulp. This allows for continuous flow of the pulp downstream while retraining the carbon, which is moved intermittently upstream (Yannopoulos, 1991).

Elution

The loaded carbon from the first adsorption stage is conveyed to a stripping vessel, where the gold is stripped from the carbon into a concentrated pregnant solution. Three methods of stripping have been developed, all of them using a caustic cyanide solution to dissolve the gold as $Au(CN)_2^-$ ions.

- In the Zadra method, a solution containing sodium cyanide and sodium hydroxide is recirculated through a fixed bed of loaded charcoal at atmospheric pressure between 90 ^{0}C and 93 ^{0}C in series with several electrolytic cells that remove the gold by electro-deposition onto a steel wool cathode.

- In the AARL method, the activated carbon is soaked in a solution containing cyanide and caustic for up to several hours in a pressure vessel at 50 to 100 kPa and at a temperature higher than 90 ^{0}C, followed by elution with several bed volumes of hot water.
- In the alcohol stripping method, one of the above techniques are employed, with the addition of water-soluble organic compounds, such as various alcohols (methyl, ethyl, or isopropyl), or ketones, such as acetone or methyl isobutyl ketone. (Yannopoulos, 1991; Adamson, 1972; McDougall, 1991; Fleming and Nicol, 1984, Laxen *et al.*, 1994)

After elution the carbon is discharged from the bottom of the vessel for reactivation, while the pregnant gold-concentrated solution is collected in a tank from where it is fed continuously to electrowinning.

Most CIP plants also have an acid washing step to remove calcium carbonate and other inorganic species, such as base-metal cyanide complexes from the loaded carbon. The acid-washing step can be carried out before or after elution or after regeneration. Most plants use hydrochloric acid at concentrations between 3 and 10 per cent while a few use nitric acid. The strength and temperature of the acid-wash solution vary from plant to plant with the type and the degree of inorganic poisoning that occurs (McDougall, 1991).

Elektrowinning

Gold is recovered from the pregnant stripping solution by electrowinning in specially designed cells (The zinc cementation process, discussed earlier, is also used in some cases). Several different cells have been developed for the treatment of CIP eluates. The Zarda cell was developed by the US Bureau of Mines and was used on all early CIP plants (McDougall, 1991; Fleming and Nicol, 1981). It consists of a cylindrical core of steel wool that acts as the cathode surrounded by an anode of stainless steel mesh. They are contained within a cylindrical polypropyle basket that also acts as a separator from the steel-mesh anode. The eluate is pumped into the cell, where the gold deposited in solid form on the steel wool. Currently, rectangular cells of similar design are used on most CIP plants around the world.

After some three weeks the next step is usually chemical treatment to dissolve the steel wool leaving a sludge, which is filtered, dried, mixed with fluxes and smelted in a furnace at temperatures around 1000 ^{0}C. The molten contents of the furnace are poured into a mould. Being about five times heavier than the other constituents, the gold sinks to the bottom of the mould, and the waste is displaced. The gold bar (bullion) taken from the mould is then sent to refineries for further treatment (Chamber of Mines, http://www.bullion.org.za).

Reactivation

It is necessary to thermally regenerate the carbon in order to remove the inorganic and organic impurities that are adsorbed onto the carbon during the adsorption cycle of the CIP process. These impurities are not removed by elution or acid washing and can result in excessive poisoning and loss of activity of the carbon for gold adsorption. This process involves the heating of the wet carbon to about 650 ^{0}C to 750 ^{0}C in the absence of air for up to 30 minutes. The reactivated carbon is then screened to remove the fines and conditioned with water before being recycled to the adsorption circuit (Stanley, 1987; Yannopoulos, 1991).

1.4.4 Adsorption by ion-exchange resin

The use of a ion-exchange resin for the recovery of gold from cyanide pulp was first proposed in South Africa in 1960 by Davidson and pilot-plant tests were carried out at that time. More recent progress in the development of resin-in-pulp for gold extraction came from the Soviet Union, and a 1978 report indicates that one of the largest gold mines in the Soviet Union is using anion-exchange resin to extract aurocyanide in a RIP process (Yannopoulos, 1991).

Presently the RIP process is being examined as a possible alterative to the CIP process. Ion-exchange resin as an alternative to activated carbon for the recovery of gold is considered to have several advantages (Young, 1987; Johns, 1996):

- Anion-exchange resins are superior to currently available activated carbons with respect to both the rate of loading and equilibrium loading of the gold cyanide ion.
- Resins can be effectively eluted at room temperature, whereas the elution of activated carbon has to be carried out at higher temperatures and pressure.
- Resins can be custom-made to a specific application and has a higher resistance to abrasion.
- Activated carbon requires thermal regeneration for the removal of adsorbed organic materials. Resins do not appear to be poisoned by these organic species, which severely inhibits the loading of gold on activated carbons.

The two major problems with ion-exchange resins, however, are that they are less selective than activated carbon for gold cyanide over the base metal cyanides and the resin particles are smaller, which presents engineering problems associated with the separation, transportation and mixing of the RIP mixture (Johns and Marsh, 1993).

The RIP process (Figure 1.3) is more or less similar to the CIP process and consists of a milling section, followed by classification, whereby the classifier overflow is thickened, and the thickener overflow is leached with cyanide. The leached pulp is then contacted with a strong-base anion-exchange resin, which is the preferred resin for gold extraction, in a counter-current adsorption circuit. After adsorption the loaded resin can be eluted by one of three eluates namely thiourea, thiocyanate and zinc cyanide (Johns and Green, 1996, Fleming and Nicol, 1981).

The first method of elution involves an irreversible chemical reaction in which the gold (I) ion is converted from the anionic cyanide complex (which is strongly bound to an anion-exchange resin) to a cationic thiourea complex (which has no affinity for an anion-exchange resin). The second and third methods of elution involve the reversible displacement of the aurocyanide anion by other anions that also have a high affinity for anion-exchange resins (Nicol *et al.*, 1987). The chemistry involved in the elution of the resin is very complicated and will be discussed briefly in chapter 2.

After elution, the resin that has been eluted with thiourea is in the chloride form, and is suitable for recycling direct to RIP adsorption. In the other two methods, the resin is loaded with strongly bound anions during elution and these anions must be removed and replaced with weakly bound anions in a regeneration step, before the resin is recycled. After elution the gold is precipitated from the eluate, cast into anodes and purified electrolytically (Marcus and Kertes, 1969).

1.5 THE OBJECTIVES OF THIS STUDY

In all the above mentioned gold recovery processes, the most important parts are the leaching and the adsorption sections, since the efficiency of gold leaching and adsorption determines the amount of soluble gold lost in the residues from a plant.

During leaching and in some cases adsorption; where leaching and adsorption are combined (CIL or RIL); dissolved gold is lost due to adsorption by carbonaceous material and by certain minerals in the ore. This adsorption of the gold cyanide complex by components in the ore is called pregrobbing. It is believed that few sites containing primary gold do not exhibit significant and practically irreversible pregrobbing on at least some portions of their ores.

The objectives of this study were to investigate the characteristics of the different pregrobbing materials, the interaction between the pregrobber and adsorbent and ultimately to propose a methodology to recover gold from pregrobbing ores.

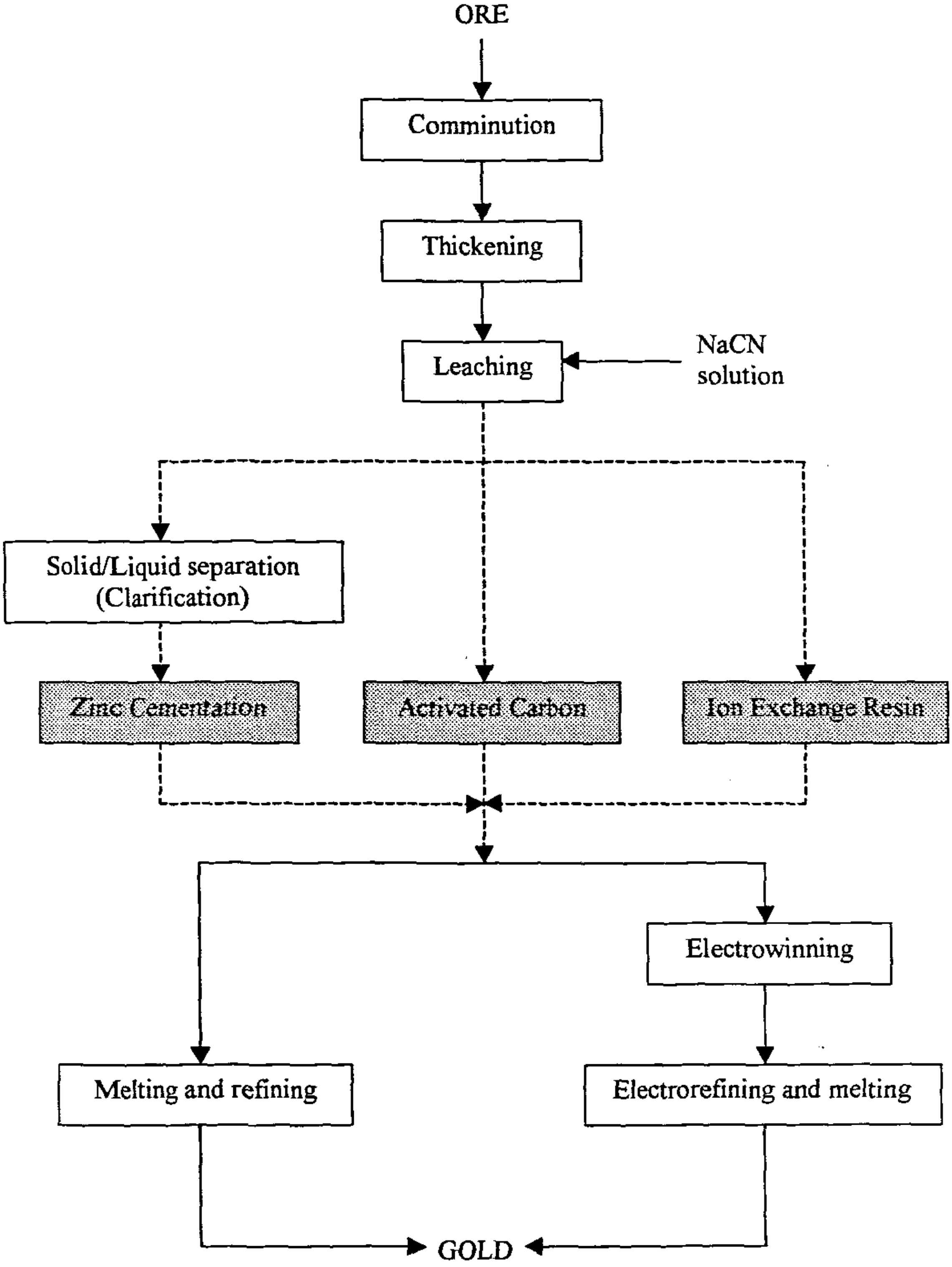

Figure 1.1 - A general flowsheet for the recovery of gold by cyanidation.

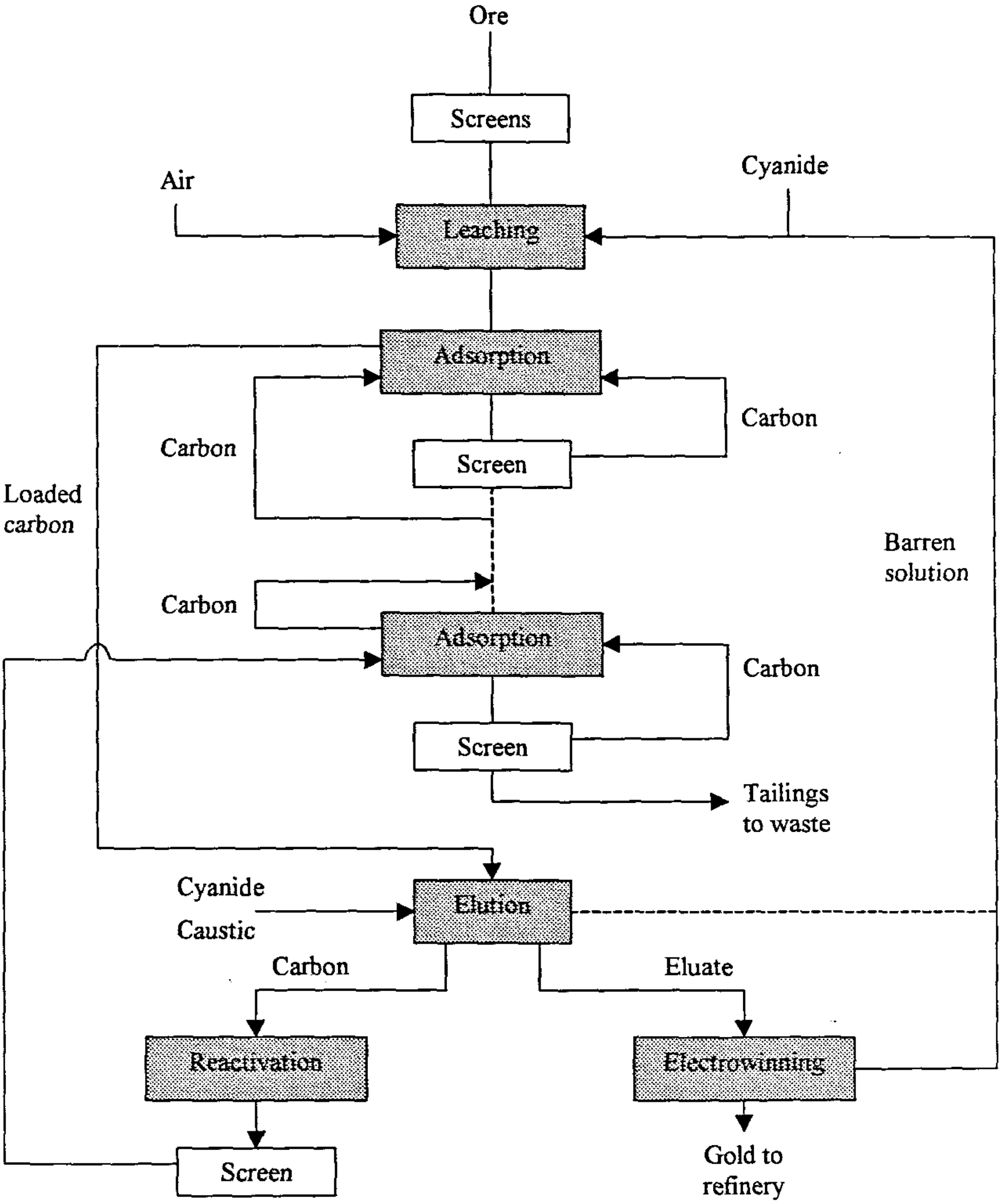

Figure 1.2 - A Typical flowsheet of the carbon-in-pulp (CIP) circuit.

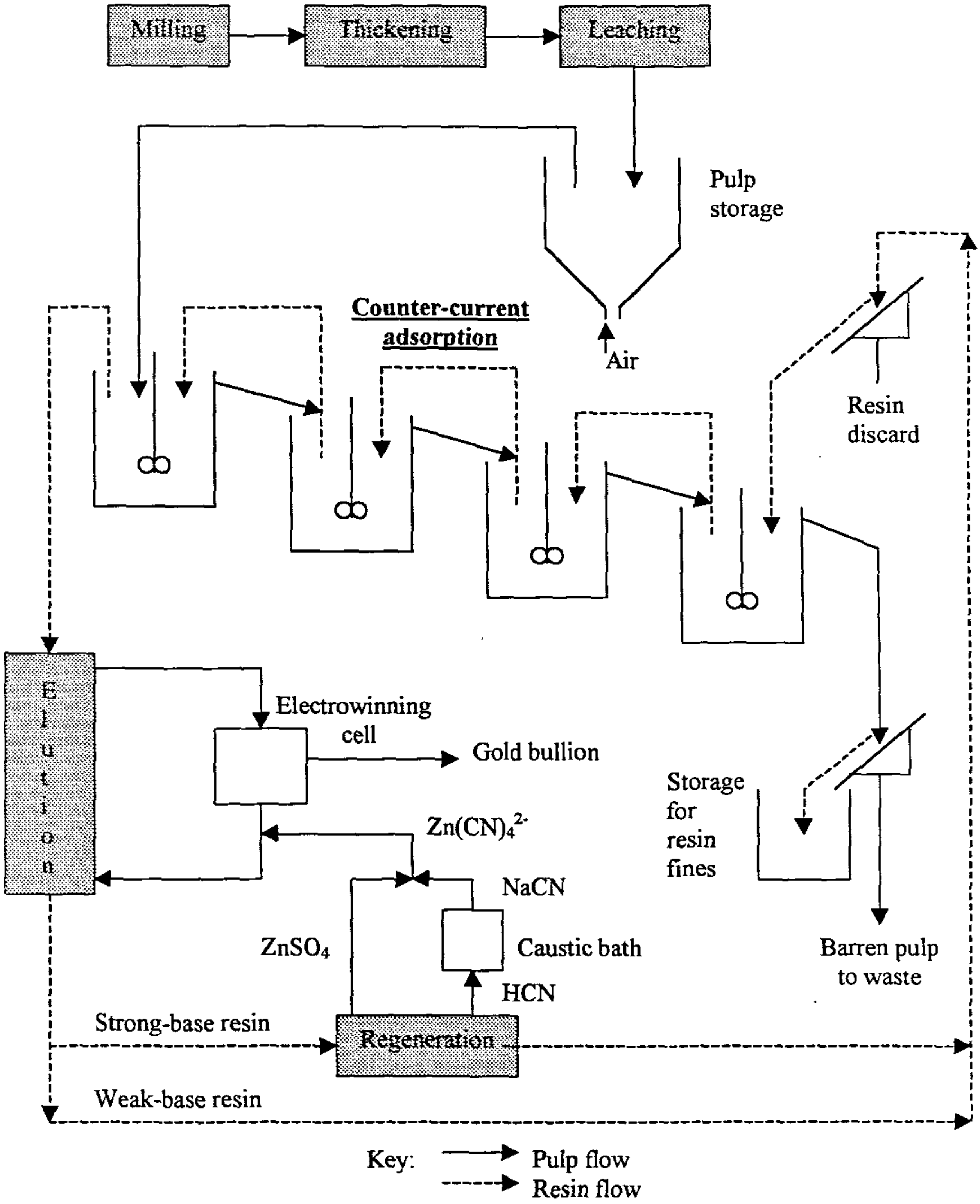

Figure 1.3 - A flow diagram representing the resin-in-pulp (RIP) circuit.

CHAPTER 2

LITERATURE REVIEW

2.1 ACTIVATED CARBON

Activated carbon is a generic name for a broad range of amorphous carbonaceous materials manufactured to exhibit a highly porous internal structure associated with an extensive internal surface area. These substances have neither a definite structural formula nor an identical chemical analysis. In many ways activated carbon is a unique material with properties not possessed by any other class of organic substance (Stanley, 1987). The various products are usually distinguished by their source material, adsorptive properties and hardness. The large internal surface area coupled with high surface activity make activated carbon an effective adsorbent for the removal of a large number of organic and inorganic compounds and complexes from gasses as well as liquids.

2.1.1 Physical manufacture

Activated carbon can theoretically be manufactured from almost any carbonaceous material of animal, plant or mineral origin. In general, raw materials with a dense cellular structure produced a hard brittle product and it is for this reason that carbons made from coconut shell are used almost exclusively in the gold mining industry.

The production of activated carbon from carbonaceous materials is referred to as activation. The manufacturing process involves two principle stages, namely carbonisation and activation.

2.1.1.1 Carbonisation

Carbonisation of activated carbon is the formation of a char from the source material by heating the source material in an inert atmosphere to a temperature not exceeding 600 ^{0}C (McDougall and Fleming, 1987). The raw material is now dehydrated, and oxygen and hydrogen containing groups such as CO, CO_2 and CH_3OH are driven off as decomposed products. Carbonisation consequently results in the formation of a marginally porous char. The size and volumes of the pores may be manipulated by the addition of catalysts or dehydrating additives.

2.1.1.2 Activation

The activation process is necessary so that the carbonised char can develop a porous structure and an extended surface area. This is generally conducted at temperatures between 800 ^{0}C and 1100 ^{0}C in the presence of a suitable oxidising agent to form a highly porous activated carbon. Oxidation with oxygen is an exothermic reaction, which is difficult to control. Consequently oxidants, such as steam and carbon dioxide, which react endothermically with carbon, are preferred. During activation the active oxygen in the activating agent burns away the more reactive portions of the carbon skeleton as carbon monoxide and therefore, as combustion proceeds, preferential etching occurs, which results in the development of a large internal surface area and the creation of a pore structure.

2.1.2 Chemical manufacture

The majority of activated carbon is produced by the physical process discussed above, but a number of chemical alternatives are also available. Chemical activation is mainly applied to uncarbonised vegetable products, primarily wood and peat (McDougall and Fleming, 1987). These materials are first impregnated or mixed with chemicals such as zinc chloride, phosphoric acid or sulphuric acid, which has a dehydrating and oxidising effect. The resulting mixture is dried and then calcined at temperatures in the range of

400 ^{0}C to 700 ^{0}C, which results in the formation of the carbon skeleton and the concomitant creation of a porous structure and extended surface area. As in the physical process, a large number of different types of products can be produced, depending on the characteristics of the raw material, the addition of special additives in the mix and the manner and temperature of the activation process.

2.1.3 Physical and chemical properties

The different types of activated carbon can be distinguished from one another by certain physical properties, e.g. their particle size, the quantity and size distribution of their pores, their bulk density and, from a chemical point of view, their ability to adsorb selected compounds from gasses or from liquids.

Activated carbons are commercially available in granular or in powdered form. Powdered carbons are usually used once on a throwaway basis and are kinetically very active because of their fine particle size. Granular carbons, on the other hand, are generally re-used after regeneration. Activated carbon is not a homogeneous material. The softer a carbon is, the higher its activity. The pore structure and surface area of activated carbon are developed during the carbonisation and activation process. The sizes of the pores are important, because they may exert a screening influence, which prevents molecules from being adsorbed, or else promote adsorption when the pore diameters are of optimal size (Stanley, 1987). The pores, which are not round, but wedge-shaped cavities, are generally classified in terms of their equivalent diameters (McDougall, 1991; Davidson, 1974).

- *macropores* (60 – 10 000 nm), which contribute very little to the total internal surface area of the product and depend mainly on the raw material and manufacturing process.
- *transitional pores or mesopores* (3 – 60 nm), which are situated between graphite-like micro-crystallites, which are also formed by activation and contributes about 5 percent towards the internal surface area.

- *micropores* (less than 3 nm), which are largely the product of the activation process and accounts for about 95 percent of the internal surface area.

The major part of the internal surface area of activated carbon is provided by the planar graphitic surfaces bounding the micropores. The remainder of the surface is constituted by the edges of the planar layers, which bound the mesopores and macropores. Powdered activated carbon has virtually no macropores, but has approximately the same surface area as granular activated carbon. Activated carbon products produced by the wet chemical route contain essentially a macroporous pore-size distribution and have a smaller surface area than thermally activated products. Another important difference between chemically and thermally activated carbons relates to the absence of conducting properties in the former type. Many of the intriguing properties of thermally activated carbons are believed to be related to their conducting properties.

Carbons can be chemically divided into what are called H- and L-carbons (Stanley, 1987). H-carbons are formed at temperatures in excess of 700 ^{0}C and are characterised by taking up acid on immersion in water. L-carbons are activated at around 300 to 400 ^{0}C, and are characterised by taking up base on immersion in water. Oxygen is irreversibly adsorbed by both types of carbon and is only released at high temperatures as CO and CO_2, showing that it is chemically bound to the surface as surface oxides. Although these surface oxides play an important role in the chemical nature of the carbon, their identities are not known with certainty. The temperature and conditions of activation alters the ratio of these functional groups and therefore, plays a key role in determining the overall activity of the carbon.

2.1.4 The mechanism of adsorption

The mechanism of the adsorption of gold cyanides by activated carbon has been subject to disagreement and controversy and despite the commercial importance of the process, no consensus has been reached as yet. Only a brief summary of these mechanisms will be given in this section.

The mechanisms of gold adsorption from cyanide solutions which have been proposed in the literature, can be classified into one of the following categories (McDougall and Fleming, 1987):

1. adsorption of aurocyanide [$Au(CN)_2^-$] accompanied by the reduction of the group to metallic gold [Au(0)].
2. adsorption of the aurocyanide ion group in the form of a metal complex $Ca[Au(CN)_2]_2$.
3. adsorption by an ion-exchange mechanism of the aurocyanide ion group [$Au(CN)_2^-$] without chemical change.
4. AuCN precipitation from the degradation of $Au(CN)_2^-$.

Support for mechanism 1 stems from the obvious deposition of gold metal, which occurs when carbon is added to $AuCl_4^-$ solutions. Gold plating of the outer carbon surface is actually visible when the loading is very high. The same rationale, however, cannot be applied to cyanide solutions where the pH is generally higher than 7. Mechanism 2 gains support from the enhanced loading of gold onto carbon from solutions containing Ca^{2+} and the absence of simple ion-exchange properties. Mechanism 3 is a compromise between all the other postulates. This model was postulated because of the fact that the oxidation state of the adsorbed species was between zero as in the case of metallic gold and one as in the case of $KAu(CN)_2$ powder. Mechanism 4 remains speculative when related to typical plant solutions containing excess free cyanide. The reversibility of the gold adsorption reaction under such conditions together with the irreversible nature of gold adsorption carried out in the absence of free cyanide, suggests that this mechanism will only take place in a system devoid of free cyanide (Stanley, 1987).

From the evidence available at the present time the mechanism can be explained as an easily reversible ion-pair mechanism involving a divalent cation likely to be calcium and the metal cyanide complex. The more specific nature of the functional groups on the carbon surface that are involved in the adsorption process is still unclear and it can therefore, be seen that no adsorption mechanism can be postulated without the carbon being fully characterised (Adams and Fleming, 1989).

2.2 ION-EXCHANGE RESIN

The progressive application of ion-exchange and adsorption technology in the field of hydrometallurgy has been most spectacular in the last few years. This is no doubt partly due to the advent of successful continuous ion-exchange technology and the development of new selective polymeric ion-exchange materials. Ion-exchange can be defined as a reversible exchange of ions between a solid (the resin particle) and a liquid during which there is no substantial change in the structure of the solid. Ion-exchange resins have found widespread use in the recovery, separation and purification of precious metals.

2.2.1 Synthesis and properties

All modern resins are polymeric structures, based on either a styrene or an acrylic matrix, to which functional groups are chemically attached. The polymer matrix is a three-dimensional network that swells in contact with aqueous solutions, adsorbing water and allowing ions present in the aqueous solution to diffuse through the resulting gel to the sites of the active groups. The active groups can be anionic or cationic, and the interactions between these groups and cations or anions in solution are almost invariably coulombic or electrostatic in nature (Helferrich, 1962). The rates of the exchange reactions are therefore high, reversible and generally diffusion-controlled. Their two main characteristics are a given capacity, i.e. the amount of ions that are exchangeable per unit quantity of exchanger, and selectivity, i.e. the restriction that only ions of a certain type, e.g. cations, are thus exchanged. The selectivity of the resins for one ion over another is predominantly a function of the size, charge and polarisability of the ions (Yannopoulos, 1991; Nicol *et al.*, 1987; Marcus and Kertes, 1969).

Amine resins are synthesised by the polymerisation of styrene, using an organic peroxide catalyst, to form linear polystyrene (Streat and Naden, 1987). If divinylbenzene (DVB) is mixed with the styrene, a three-dimensional polymer network is formed. The DVB crosslinks give a structure, which renders the polymer insoluble in most solvents. The characteristic spherical ion-exchange beads are therefore made by suspension polymerisation (Marcus and Kertes, 1969). The catalysed monomer mixture is stirred into water under conditions designed to give the desired droplet size, which after several hours of heating, will yield solid spherical beads. The beads are now hydrophobic, but can adsorb some organic liquids such as toluene, swelling as a result. The beads are converted into an ion-exchange resin by first swelling the polymer with an inert solvent, then introducing the anion-exchange group in two steps. A chloromethyl group is introduced into each benzene ring, after which an amine group can be introduced by a simple addition reaction with chloromethyl ether.

The most commonly used resins in gold recovery processes are strong base and weak base resins (Nicol *et al.*, 1987). Ion-exchange resins of different characteristics can be produced by using different amines. If a tertiary amine such as trimethylamine is used, the product is a strong base quaternary ammonium compound. The use of a secondary amine, such as dimethylamine, gives a tertiary amine product, which is more weakly basic.

2.2.2 Physical structure of resins

Polystyrene resins have an extremely irregular structure, due to the fact that DVB polymerises with itself more rapidly than with styrene. During the progress of polymerisation the product becomes progressively less crosslinked and ultimately some linear polymer is formed, attached to the copolymer matrix. The final resin contains tightly knotted regions and the intermolecular distance is correspondingly reduced. This heterogeneous structure has two results. First, as a relatively small, inorganic ion enters the resin, the process becomes progressively more difficult as the concentration in the resin approaches the total capacity and the less accessible active groups come into use. A second problem occurs with large ions such as the natural humic and fulvic acids (Streat and Naden, 1987). These are large polycarboxylic molecules, which diffuse freely through the loosely crosslinked regions of anion resins but become trapped in the tightly crosslinked regions. As a result, resins can become poisoned, losing capacity, giving higher losses to barrens. To overcome this problem new types of resin, referred to as 'macroporous' or 'macroreticular' resins were developed. These resins are synthesised by making use of solvents in the polymerisation process resulting in a more open but still heterogeneous structure (Yannopoulos, 1991; Nicol *et al.*, 1987). On the molecular scale, these resins have a sintered structure with larger channels. Large molecules travel freely through these channels and they therefore, have a high resistance to organic poisoning.

2.2.3 The chemistry of resin adsorption and elution

According to the ion charge symbol of ion-exchange resins, there are anion-exchange resins and cation-exchange resins. During gold ore cyanidation gold occur as $Au(CN)_2^-$ in the pulp, therefore, in the adsorption process, gold are adsorbed by anion-exchange resin. Consequently, anion-exchange resins are more important than cation-exchange resins in the field of gold metallurgy and will be dealt with in more detail.

Gold is leached by cyanide as the anionic aurocyanide complex, $Au(CN)_2^-$, and the complex is therefore, extracted from solution by an anion-exchange resin. A strong base resin contains quaternary amine functional groups and extracts aurocyanide according to equation (2.1):

$$|-NR_3X^- + Au(CN)_2^- \rightleftharpoons |-NR_3Au(CN)_2^- + X^- \qquad \ldots (2.1)$$

where the symbol $|-$ denotes the matrix of the ion-exchange resin (Fleming and Nicol, 1981; Marcus and Kertes, 1969).

The elution of aurocyanide from the strong base resin is achieved by ion-exchange mass action, i.e. by the reversal of the equilibrium shown in Equation (2.1), or by conversion of the gold to a non-anionic complex. The latter method involves the neutral thiourea ligand. In an acid environment, thiourea reacts with aurocyanide to form a stable gold-thiourea complex. This complex is cationic, and is therefore readily eluted from the anion-exchange resin.

$$|-NR_3Au(CN)_2^- + (NH_2)_2CS + 2HX \rightleftharpoons |-NR_3X^- + [Au(NH_2)_2CS]^+ + 2HCN \quad ...(2.2)$$

Alternatively, the aurocyanide anion can be displaced from the resin by another anion such as the zinc cyanide complex. A number of factors contributed to the choice of this eluent. Firstly, zinc cyanide is relatively cheap and is compatible with existing gold processes. Secondly, it is a very effective eluent, because strong base resins have a higher molar capacity for zinc cyanide than for gold cyanide.

Because zinc cyanide loads strongly onto anion-exchange resins, the resin must be regenerated before being recycled to adsorption. In the case of the zinc cyanide complex, this is achieved effectively and cheaply by the destruction of the complex with acid. The reactions involved are shown in equations (2.3) and (2.4) (Fleming and Nicol, 1981).

$$2|-NR_3Au(CN)_2^- + Zn(CN)_4^{2-} \rightleftharpoons (|-NR_3)_2Zn(CN)_4^{2-} + 2Au(CN)_2^- \quad ...(2.3)$$

$$(|-NR_3)_2Zn(CN)_4^{2-} + 4HX \rightleftharpoons 2|-NR_3X^- + ZnX_2 + 4HCN \quad ...(2.4)$$

2.2.4 Novel selective ion-exchange resins

There is a growing interest in the development of selective polymers for the recovery of precious metals from cyanide solutions. The idea of developing selective ion-exchange resins was to combine the selectivity and specificity of conventional liquid extractants with the advantages of a discrete polymer support material, thus tailor making adsorbents for a specific separation process. Base-metal cyanides are generally present in leach pulps and will therefore, compete for the limited number of sites on a resin. The capacity of a resin for gold thus depends strongly on the relative affinities of the resin for the different anions in the pulp. The affinity of a structure of the resin is a function of the charge on the anion, its polarisability, and its shape (Johns, 1996). Two selective types of resin are at present available to adsorb gold: novel gold selective strong-base resins and novel gold selective weak-base resins. Each type of resin has its own unique chemistry.

2.2.4.1 Gold selective strong-base resins

The attachment of a metal cyanide anion to a gold selective resin is identical to that to a non-selective resin. The elution reaction, however, is different, since a metal cyanide anion that will bond strongly enough to displace the gold cyanide anion, is not readily available. Elution is therefore, achieved by destruction of the metal cyanide complex by an acidic thiourea solution. This method of elution can be used only with gold selective resins since the base metals, particularly cobalt and ion, are poorly eluted and can poison the resin.

2.2.4.2 Gold selective weak-base resins

For weak-base anion-exchangers, the active groups are neutral and must be protonated before they can interact with metal cyanide anions. The elution of weak-base resin is accomplished by reversal of the adsorption reaction. An alkali will cause deprotonation of the resin and metal cyanide anions will leave the reagent. Too high basicity in the resin active group will make the removal of the proton with alkali difficult. Thus, in the selection of an active group for weak-base resin, a trade-off between high loading and good elution may be necessary. The only advantage that a weak-base resin has over a strong-base resin is the ease of elution and regeneration.

2.3 PREGROBBING

During the leaching process, where the gold is dissolved in an aqueous alkaline cyanide solution, gold is lost due to a number of reasons. These gold losses can be ascribed broadly to the following causes (Stanley, 1987):

- Unliberated gold as a result of too coarse a milled product.
- Refractory gold resulting from coatings, generally hydrated oxides of iron, on some gold particles. The coatings occur naturally or as a result of the oxidation of pyrite. Coated gold dissolves very slowly during the leaching process.
- Inadequate aeration resulting in insufficient dissolved oxygen to promote the chemistry of the leaching reaction. Reducing matter contained in the ore frequently causes low oxygen levels.
- The presence of cyanicides, which consume the cyanide radical and thus inhibit dissolution of gold. This is frequently due to the presence of readily oxidised components, metallic copper and copper compounds.
- Too short contact time.
- Adsorption of gold, from solution, by carbonaceous material and by certain shales and clays.

This study focuses on the latter, where dissolved gold is pregrobbed during leaching by adsorbent materials in the ore. The term pregrobbing refers to the active adsorption of gold from cyanide pregnant solutions by components of the ore (Yannopoulos, 1991).

It is believed that few sites containing primary gold do not exhibit significant and practically irreversible pregrobbing on at least some portions of their ores. There is no doubt that gold is adsorbed by carbonaceous material in ore, but some debate exists over the extent to which gold may be adsorbed onto surfaces of mineral ore.

2.3.1 Non-carbonaceous ores

Urban *et al.* (1973) concluded that about 0.1 g/t of the total gold loss in a typical gold plant could be ascribed to the adsorption onto pregrobbers. They suggested that minerals such as pyrite and chalcopyrite and to a lesser extent, clay minerals such as pyrophyllite, kaolin and montmorillonite, were responsible for the adsorption. They also found that other Mg-rich phyllosilicates, or a combination of these with hydrous iron/manganese oxides, have a potential for pregrobbing. Logan (1986), however, found that the phyllosilicate minerals pyrophyllite, kaolinite, phlogopite and illite do not adsorb detectable amounts of gold from cyanide solution and suggested that the finely-divided carbon that is present in the gold-bearing shale is responsible for the adsorption properties of the shale. Hausen and Bucknam (1985) suggested that pyrite is a gold adsorber and showed that small quantities of gold were adsorbed from cyanide solutions onto samples containing approximately 45 % pyrite. Quach *et al.* (1993) showed that gold cyanide, in the absence of oxygen, is adsorbed onto pyrrhotite, with the subsequent release of cyanide ions whereas subsequent workers speculated that chlorite could be responsible for much of the gold adsorption in ores.

More recently, Adams *et al.* (1996) examined the gold-adsorbing properties of a wide variety of minerals, ranging from copper sulphides to clay silicates and quartz and they concluded that copper sulphide minerals yielded the strongest adsorption and that quartz only adsorbed a relatively small quantity of gold, depending on the type of quartz, its surface area and surface characteristics.

2.3.2 Carbonaceous ores

The adverse effects of carbonaceous material in the cyanidation of gold ores have been known for many years. In some areas of the Carlin Mine, Nevada, U.S.A., the carbonaceous ore is so deleterious to cyanidation that a mixture containing five per cent carbonaceous ore and 95 per cent standard cyanidable ore gives an extraction of 76 per cent gold vs. 93 per cent for 100 per cent standard ore (Guay, 1981).

Poor gold extraction by cyanide from these ores is attributed to the pregrobbing characteristic of the carbonaceous matter. The active carbonaceous matter present has the ability of adsorbing dissolved gold from cyanide solutions and so rendering the leach liquor barren. Studies by several investigators using ores from various parts of the world have shown that the natural carbonaceous matter associated with carbonaceous ores behaves like activated carbon when in contact with aurocyanide solutions (Osseo-Asare *et al.*, 1984; Afenya, 1991). They also suggested that the mechanism of gold cyanide adsorption of the carbonaceous matter is similar to that of activated carbon (as discussed in section 2.1.4). Hausen and Bucknam (1985) established through laboratory experiments that the rate of adsorption by certain carbonaceous ores were approximately four times faster than the activated carbon studied. Adams *et al.* (1993) also observed that the carbonaceous material naturally occurring in these ores can be a very potent adsorbent of gold and it prevents gold recovery by conventional cyanidation. As a result, mining of carbonaceous ores in the past was carefully controlled to avoid the carbonaceous matter entering the ores sent for processing. The presence of carbonaceous matter in gold ores therefore, presents a two-fold problem: (1) The poor release of gold from the carbonaceous matrix, and (2) the uptake of dissolved gold by the carbonaceous leach residues.

2.3.2.1 Mineralogy

The term "carbonaceous" has been loosely applied to ore constituents of widely varying characteristics. The mineralogy of carbonaceous gold ores is varied, but for all such ores the most vital constituents are the carbon-containing components, which often interact adversely with dissolved gold.

The carbonaceous material is intimately associated with quartz, sericite, chlorite, carbonates and some amount of sulphide. The frequently encountered sulphide minerals are pyrite, sphalerite, chalcopyrite, arsenopyrite and pyrrhotite. The mineralogy of this type of ore is related to the nature of the carbonaceous material, the gold-bearing medium and the host rock. The carbonaceous material can be classified as follows: (Guay, 1981; Menne, http://www.wantree.com.au/~menne/hgl.htm.; Osseo-Asare *et al.*, 1984):

- an *activated carbon component*, (amorphous, graphitic carbon and carbonate carbon) capable of adsorbing gold complexes from solution, and
- an *organic component,* which consists of (1) a mixture of high molecular weight long chain hydrocarbons usually associated with the activated carbon components, and (2) organic acids similar to humic acids containing functional

groups capable of interacting with gold complexes to form organic gold compounds.

2.3.2.2 The activated carbon component

The activated carbon component is predominantly elemental carbon (C), but may have impurities such as S, Ti and Al. Information available about the structure of the carbon indicates that it could have the following structures: fine grained amorphous, pseudo-graphitic or a well developed graphite structure. It is possible that the carbon may have a combination of amorphous and graphitic structures in the same carbonaceous ore deposit.

The carbon component in the carbonaceous matter is normally very fine and can be as fine as 0.002 μm to 0.005 μm (Afenya, 1991). It is often stated that the carbon component is "similar" to activated carbon. Some of the early work on activated carbon was in fact stimulated by the need to understand the behaviour of carbonaceous ores. It is well known that increase in temperature decreases the uptake of gold by activated carbon in aurocyanide solutions. However, adsorption experiments on carbonaceous ores indicated the opposite effect (Abotsi and Osseo-Asare, 1986). These results suggest that chemical interactions play a much more important role in the case of carbonaceous ores, compared with synthetic activated carbon.

2.3.2.3 The organic component

The organic portion (organic acids and hydrocarbons) contains C, H, O, N and S. Investigators have argued that the great role of chemisorption in the interaction of the carbonaceous ores with aurocyanide complex is a result of the presence of humic acid in the ores. They suggested that the humic acid component of the ore provides surface functional groups, which are capable of forming strong chemical bonds with the aurocyanide complex. Experimentation showed that when five grams of humic acid was added to non-carbonaceous cyanidable ore prior to cyanidation, gold extraction was reduced from 95 per cent to 21 per cent. Similarly, 84 per cent gold uptake was obtained by these investigators when the same amount of humic acid was added to aurocyanide solution in the absence of oxidised ore.

Little is known of the structure of the hydrocarbons, but experimentation involving the removal of a portion of the hydrocarbons from an ore resulted in less gold extraction when the ore was treated by cyanidation, suggesting that the hydrocarbon was adsorbed on the activated carbon.

Organic components have pregrobbing characteristics generally believed to rob gold by chelation. Organic pregrobbing compounds are generally reducing agents, and this reduction could precipitate the gold. However, polymerisation of aurocyanide is also possible. Such polymerisation could be initiated by cyanide abstraction e.g. through the cyanohydrin reaction on reducing end-groups. Organics with reducing end-groups could result from decomposition of roots and other plant residues (Menne, http://www.wantree.com.au/~menne/hgl.htm.).

2.3.3 **Treatment of pregrobbing ores**

Every pregrobbing ore has its peculiar problem, which has to be addressed. Precious gold-bearing ores containing pregrobbing species are poorly amenable to standard cyanidation techniques. A number of processing methods have been developed for treating these ores. The success of any of these methods, or a combination of methods, depends on the mineralogy of the ore (Henly, 1975).

2.3.3.1 Flotation

The simplest method of treating a carbonaceous ore is the method where the carbon is floated off and discarded. The remaining ore is then responsive to cyanidation. This method, however, is only practical where small amounts of gold are associated with the carbonaceous matter and where the gold does not exhibit natural floatability. Where such conditions prevail, flotation has been successfully used to discard the carbonaceous by these investigators when the same amount of humic acid was added to aurocyanide solution in the absence of oxidised ore.

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2.3.3.2 Roasting

Probably the easiest method of destroying carbonaceous matter, and simultaneously oxidising the sulphide minerals, in refractory gold ores is roasting. Roasting drives off carbonaceous materials as CO and CO_2, and decomposes pyrite to iron oxides from which the gold can be leached. The temperatures for roasting many refractory sulphidic ores vary from 550 ^{0}C to 800 ^{0}C (Afenya, *1991*).

The process, however, requires very stringent operating controls. Below 500 ^{0}C or with the use of a slightly reducing atmosphere, roasting is incomplete, resulting in a drastic reduction in gold extraction. The wrong operating conditions can also activate the carbonaceous matter, which will improve its gold adsorbing properties, or convert the pyrite to a refractory form of hematite from which the gold cannot be leached with cyanide.

The process also generates SO_2 and results in the volatilisation of elements such as arsenic (Buckingham and Robles, 1992). Environmental constrains therefore dampened the use of this process. High capital costs and excessive power consumption also restrict its use to ores with a respectable gold content (Wang and Forssberg, 1990).

2.3.3.3 Chemical oxidation

In the chemical oxidation process the ore is subjected to preliminary chemical oxidation techniques to oxidise carbonaceous materials prior to standard cyanidation treatment.

There are currently three oxidising techniques that are of significance: (1) Chlorine oxidation, (2) pressure oxidation, and (3) biochemical oxidation.

Chlorine oxidation

Chlorine (Cl_2) is used as a mildly oxidising agent capable of oxidising the carbonaceous matter and any associated pyrite and dissolving most of the free gold. Mines using chlorine to treat the ores achieved gold recoveries between 83 per cent and 90 per cent after cyanidation (Guay, 1980). As the ore became more refractory, however, chlorine consumption became excessive and a double oxidation process, involving oxidation with air and chlorine, was introduced (Afenya, 1991; Guay, 1980).

In this process air is dispersed in an aqueous slurry of ground ore at 40 to 50 per cent solids at temperatures of 80 to 86 ^{0}C until a considerable portion of the pyrite is oxidised to iron oxides. Some decomposition of the carbonaceous materials also occurs, but it is necessary to follow the air oxidation with chlorination in order to complete the oxidation of the carbonaceous materials and pyrite (Yannopoulos, 1991; Chryssoulis *et al.*, 1992).

The success of this process, however, depends heavily on the mineralogy of the ore and the general high chlorine consumption makes it a costly method, which will not prove economical on low-grade ore.

Pressure oxidation

This technique uses oxygen to oxidise refractory ores at high pressures and temperatures to increase reaction rates. The essential reactions that take place are oxidation of the gold matrix and precipitation of some leach products. The precipitates are decomposed in order to improve gold extraction (Afenya, 1991).

The problem with this process is that it can oxidise sulphidic but not graphitic or carbonaceous materials in the ore, which will act as pregrobbers in the subsequent cyanidation process. In some cases this process can even activate previously non-active impurities (Buckingham and Robles, 1992).

Biochemical oxidation

Bacterial oxidation is a relative new concept for the treatment of carbonaceous ores. The most common bacteria used for leaching carbonaceous ores are *Thiobacillus ferrooxidans*. These bacteria oxidise iron sulphides under acidic condition at temperatures between 30 ^{0}C and 40 ^{0}C. The carbonaceous matter, on the other hand, is only partly oxidised and therefore, not totally rendered inactive (Afenya, 1991).

This microorganism will easily grow on pyritic and arsenopyritic ores. It grows and multiplies at moderate temperatures, but it is inactivated at temperatures above 40 ^{0}C. Hence, bioleaching ore with high sulphur content presents a problem, since the reactions enhanced by the bacteria are exothermic. Therefore, a microbial oxidation system for sulphide ores and concentrates should be equipped with a cooling system, which increases the operating cost. Another disadvantage with this method is that the reaction rate is slow and it takes days rather than hours to treat an ore (Yannopoulos, 1991).

2.3.3.4 Activated carbon or resin-in-leach pulp

Carbon-in-leach (CIL) or resin-in-leach (RIL), discussed in sections 1.4.3 and 1.4.4, are methods in which granular activated carbon or in the case of RIL, an ion-exchange resin, is added to the leaching process to compete with pregrobbing species for the gold cyanide complex. This process works on the principle of using a stronger aurocyanide adsorbent than the carbonaceous matter in the ore (Buckingham and Robles, 1992; Afenya, 1991). This process can improve gold recovery in pregrobbing ores especially when carbons or resins with very high activities are used.

In general ion-exchange resins are superior to currently available activated carbons with respect to both the rate of loading and equilibrium loading of the gold cyanide ion. Ion-exchange resins will therefore be the preferred adsorbent, especially with severely graphitic ore, where the carbonaceous material may outperform the activated carbon.

The carbon or resin-in-pulp process have the advantage of low capital and operating costs, and for ores whose only deleterious constituent is moderate concentrations of carbonaceous material, may be the best way to go.

2.3.3.5 Blinding agents

Certain organic reagents (surfactants), which selectively adsorb on the surfaces of activated carbon and smother the surface, have been used for blinding carbonaceous matter in gold ores prior to cyanidation. Blinding agents are used to passivate the surfaces of the carbonaceous matter in the ore by being adsorbed preferentially to the gold cyanide complex. The ability of surface coatings of organic compounds to modify the gold uptake behaviour of carbonaceous ores has been reported by various investigators.

Abotsi and Osseo-Asare (1987) did experimentation with organic compounds with two possible effects in mind. Firstly, it was expected that these compounds would initially adsorb on the solids as anionic species, thereby imparting a negative charge to the solid/aqueous interface. The electrostatic repulsion between the highly charged negative solid surface and the $Au(CN)_2^-$ anion might then prevent the adsorption of the aurocyanide ion. Secondly, it was expected that these organic additives would coat the surface of the ore and, by limiting the number of available surface sites, inhibit gold uptake.

Traditional plant practice entails the addition of diesel, kerosene or sacresote to the ore when a pregrobber is suspected, but various other surfactants such as sodium lauryl sulphate (SLS), petroleum sulphonate, dodecylsulphate (DDA) and heavy machine oils have been used by investigators and has resulted in varying degrees of success in inhibiting gold adsorption (Osseo-Asare *et al.*, 1984; Adams and Burger, 1998).

It has also been found that the combination of the use of surfactants and a carbon or resin-in-leach process, results in an efficient method for treatment of pregrobbing ores. The RIL process is a better option for this scenario because of the possible poisoning of the carbon by the surfactant in a subsequent CIL process (refer to section 1.4.4). Experimentation where surfactants were combined with the RIL process showed that surfactants can substantially decrease the activity of the pregrobbing species and may enhance leaching kinetics by affecting pulp viscosity and surface tension.

2.4 SIGNIFICANCE OF LITERATURE REVIEW

From the literature review it is clear that pregrobbing ores poses a definite problem to the gold mining industry. Various investigators have identified different mineral species and other components, which exhibit gold adsorbing properties. There is also a wide range of different treatment processes that were practiced or that are currently in use, with varying degrees of success.

Presently the resin-in-pulp process is being examined as a possible alterative to the carbon-in-pulp process. It is evident that ion-exchange resins are a good alternative to activated carbon for the recovery of gold. A gold selective ion-exchange resin used in a resin-in-leach system will provide good competition for the pregrobbing components and can therefore be an effective way of treating pregrobbing ores.

The significance of the literature review is summarised as follows:

- To identify possible pregrobbing minerals, conduct gold adsorption tests and determine their leachabality in a cyanide environment.
- To quantify the interaction between a gold selective resin and a pregrobber through surface, kinetic and equilibrium studies.
- To investigate the mechanism of pregrobbing.
- To perform preliminary tests on the use of organic compounds to blind the pregrobber.
- To propose a methodology to recover gold from pregrobbing ores.

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 EXPERIMENTAL MATERIALS

The gold used in the experimental work was in the form of potassium dicyanoaurate, $KAu(CN)_2$, a pure crystalline salt. The leaching experiments were conducted with potassium cyanide (KCN). Experimental solutions of 1000 ppm were prepared by weighing off 1.463 g $KAu(CN)_2$ and 2.503 g KCN respectively and making it up in a 1 litre volumetric flask using distilled water. Sodium hydroxide (10M NaOH) was used to adjust and maintain the pH at the required level. All reagents used in experimental work were of analytical grade, and distilled water was used throughout.

The three adsorbents used in this study include a gold selective strong base anion-exchange resin, a strong base anion-exchange resin (Duolite A161) and a medium base anion-exchange resin (Duolite A378). No pre-treatment of the resins were required. All the resins were stored under deionised distilled water in sealed containers. The respective resin properties can be seen in Table 3.1.

A coconut shell activated carbon, ANK 11/8, was used as a synthetic pregrobber in competitive adsorption experiments. Before any experiments were conducted the virgin carbon was dry sieved into the 1.0 to 2.0 mm sieve size fraction. After sieving, the activated carbon was washed with distilled water for removal of fines, dried for several days at 40 ^{0}C and stored in a dessicated sealed container to avoid adsorption of moisture from the atmosphere.

Samples of relative pure minerals, pyrite, chalcopyrite, quartz and kaolin were obtained from various sources. Pyrite is known as iron sulphide (FeS_2) and chalcopyrite ($CuFeS_2$) is a combination of copper and iron sulphide, but mainly copper sulphide. The chemical analyses of the kaolin and quartz samples are shown in Table 3.2. These minerals were thoroughly washed with distilled water, dried at 40 ^{0}C and then milled and screened to obtain the required particle size distribution of 80 % under 75 μm and 20 % between 106 and 75 μm. The minerals were then stored in sealed containers.

Five different pregrobbing gold ores, from various gold mines, were used in this study. The ores, supplied by Mintek, were already milled to 80 % < 75 μm. The ores were analysed for gold loading, organic carbon and pyritic sulphur content (Table 3.3).

Tests with a variety of organic compounds or surface-active agents (surfactants) were conducted. The effects that diesel, kerosene, sodium lauryl sulphate (SLS), tricaprylylmethylammonium chloride (Aliquat 336) and dodecylamine (DDA) have on inhibiting gold adsorption by pregrobbing ores were investigated with the aid of resin-in-leach experiments. The organic compounds were chosen to cover a range of properties, such as ionicity, emulsification effects and water solubility. The structures and properties of the compounds tested are presented in Table 3.4.

3.2 BATCH KINETIC EXPERIMENTS

All batch kinetic adsorption experiments were conducted in 1 litre perspex batch reactors of height 150 mm, internal diameter 110 mm, and with four evenly spaced baffles of width 10 mm. The reactors were fitted with perspex lids to prevent spillage or evaporation of the solution. The solution were mechanically stirred with a flat blade impeller of width 60 mm and height 50 mm at a stirring speed of 300 rpm. Before any experiments were conducted it was determined that no gold cyanide was adsorbed onto the perspex vessel or the stirrer. All the experiments were carried out at room temperature and at a pH of 11.

The kinetic experiments were performed by contacting carefully determined amounts of carbon and resin with a synthetic gold cyanide solution for a duration of 24 hours. In the kinetic experiments were pre-loaded activated carbon was used, tests were also conducted to determine that none of the pre-loaded gold on the carbon came off and adsorbed onto the resin during experimentation. This was done by contacting the resin with the loaded carbon in distilled water for 24 hours. The solution and resin particles were then analysed and no gold was detected.

The activated carbon was weighed in the dry state for determination of specific amounts used in the experiments. The weighted amounts of carbon were wetted with distilled water just before addition in order to remove entrapped air from the pores. This was done because entrapped air bubbles could shield the carbon surface from the solution, resulting in erroneous film transfer coefficient values. The resins were stored under water, and a special procedure had to be followed to accurately prepare specific dosages. Although it is common practice to use "wet- settled" volumes (Van Vliet *et al.*, 1981), it can also be inaccurate due to vibrations, which may influence the final volume. A more accurate way of measuring small volumes of resin is to use "tapped" volumes. This is done by placing the resin in a measuring cylinder, which is filled to the top with water, (to prevent disturbances of the resin bed), and tapping it until the volume stays constant.

During the first thirty minutes samples were taken at 5 minute intervals for calculation of film transfer coefficient values. Subsequent samples were taken at ever increasing intervals until the end of the experiment. Liquid samples were filtered as it was taken, using a syringe filter, and stored in glass vials. Sample portions were approximately 5 ml each, representing 0.5 % of the reactor volume. The cumulative volume change during the course of the experiment therefore, was considered sufficiently small not to be taken into account during data analysis.

3.3 GOLD ADSORPTION EXPERIMENTS

Milled pure mineral and ore samples were loaded with gold in a synthetic aurocyanide solution at a pH of 11. The same equipment was used as described in Section 3.2. About 50 g of ore, and due to a lack of samples, 30 g of pure mineral were used for each experiment. After 24 hours the solutions were filtered under vacuum using a Buchner flask and funnel. The loaded solids were washed with distilled water to ensure the removal of any entrained gold present on the mineral or ore. The washed mineral and ore samples were then dried overnight in an oven at 40 ^{0}C and analysed for gold.

3.4 CYANIDATION EXPERIMENTS

The pure mineral and ore samples were leached in a solution containing approximately 200 mg/l potassium cyanide. The same quantities of mineral and ore samples were used as in the loading experiments. The slurry was mechanically stirred for 24 hours, after which it was filtered. The mineral and ore samples were then washed, dried and analysed for gold. As the pH may affect the leaching efficiency, it was maintained at 11 by the addition of small quantities of sodium hydroxide.

The ores used in the resin-in-leach experiments in the presence of an organic additive were pre-conditioned for 1 hour in a solution containing 1 per cent reagent, prior to the addition of potassium cyanide and resin. This pre-conditioning step allows the surfactant to adsorb onto the carbonaceous particles before the dissolution of gold.

3.5 ANALYTICAL METHODS

The pH of all the solutions was monitored by using a Piccolo ATC pH-meter with a HI 1290 amplified electrode.

The gold concentration in solution was determined with a Perklin Elmer 3300 atomic absorption spectrophotometer (AAS). Five to six calibration standards, at least one with higher and one with lower concentration than that of the test sample, were used. Gold concentrations were measured at a wavelength of 242.8 nm and a slit width of 1.0 nm. Calibration standards were prepared from a Merck Titrisol gold standard solution containing 1000 mg gold as tetrachloroauric (III) acid in a 12.7 per cent hydrochloric acid solution. Samples with expected concentrations of gold higher than 50 mg/l were first accurately diluted prior to analysis.

Two methods were used to determine the gold loading on the minerals and ores, namely a gravimetric method (fire assay) and a spectrophotometric method (acid leaching). The fire assay analyses were performed by Mintek and is the traditional method employed for determination of gold in ores. In the fire assay analysis one part of the finely ground ore is mixed with three parts of a flux containing litharge and carbon. The mixture is fused, at 900 – 1100 ^{0}C, for at least an hour. After cooling, a button of lead, which has collected all the gold and other precious and base metals, is separated from the slag. The button is placed in a cupel. Cuppelation, consisting of heating the cupel to 950 – 1000 ^{0}C, is then carried out, and the lead oxides are absorbed by the cupel. The remaining bead is treated with nitric acid to dissolve silver, leaving the gold metal to be weighed.

The spectrophotometric method employed involves the conversion of the gold to $AuCl_4^-$ by dissolving it in an acid and measuring the absorbance due to these ions. The acid used for this purpose is called *aqua regia* and is generally used for the dissolution of gold for analytical purposes and consists of 82 % hydrochloric acid (HCl) and 18 % nitric acid (HNO_3) (Bratzel *et al.*, 1972). Hydrochloric acid in the presence of oxidants such as nitric acid dissolves gold as follows:

$$Au + 4HCl + HNO_3 \rightarrow H[AuCl_4] + 2H_2O + NO \qquad \ldots (3.1)$$

The acid leaching procedure followed to determine the gold loading of the minerals and ores via acid attack was as follows:

The sample (5 to 10 g) is leached twice with 10 ml freshly prepared *aqua regia* while stirring constantly. The sample is boiled to dryness after adding each aliquot. A third aliquot of *aqua regia* is added and the temperature of the mixture is raised to near boiling, then cooled slowly to room temperature. The mixture is then filtered and washed with a 5% (v/v) HCl solution into a 100 ml volumetric flask. The gold is extracted as a chloro complex and the HCl therefore, prevent the dissolved gold of precipitating out.

The contents of each volumetric flask were then analysed for gold on an Inductively Coupled Plasma (ICP), which allows the direct analysis of the acid solution. The ICP was used because it is more accurate that the AAS when analysing low gold concentrations.

The same procedure as mentioned above was used to determine the gold loadings on the carbon and resin particles. It was, however, necessary to "ash" the carbon and resin before it could be leached with *aqua regia* and this was accomplished by placing the carbon or resin in a porcelain crucible and burn it in a muffle furnace at 800 ^{0}C for about 8 hours. The crucible containing the ash was then allowed to cool, after which it was leached with *aqua regia* and analysed on the ICP.

Table 3.1 - Product specifications of the ion-exchange resins.

Resin	Particle size (mm)	Density (kg/l)	Theoretical capacity (mmol/g)	Moisture retention capacity (%)
Gold selective resin	0.6 – 1.2	0.32	0.7 – 0.9	50 – 55
Duolite A161	0.3 – 1.2	0.70	1.1	51 – 56
Duolite A378	0.3 – 1.2	0.70	1.3	55 - 61

Table 3.2 - Typical chemical analysis of the quartz and kaolin sample.

Quartz		Kaolin	
	%		%
SiO_2	99.65	SiO_2	67.6
Al_2O_3	0.09	Al_2O_3	22.5
Fe_2O_3	0.025	Fe_2O_3	0.32
TiO_2	0.037	CaO	0.13
ZrO_2	0.006	K_2O	2.62
CaO	0.018	Na_2O	0.4
MgO	0.004	TiO_2	0.72
L.O.I	0.17	L.O.I	6.97
		P_2O_5	0.19

Kaolin is hydrated aluminium silicate (Al_2O_3. 2 SiO_2. 2 H_2O) and fine grained silica and muscovite mica are important accessory minerals in the clay.

Table 3.3 - The mineralogical analysis of the pregrobbing gold ores.

Ore no.	Au (g/t)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	7.02	0.90	1.30
No. 2	5.73	0.50	1.70
No. 3	5.20	0.59	5.20
No. 4	10.00	0.70	0.40
No. 5	1.25	0.90	0.75

Note that the organic carbon content is not the same as the total carbon content. Pyritic sulphur is an indication of the pyrite content (FeS_2) in the ore.

Table 3.4 - The structures and properties of organic compounds tested.

Reagent	Structure	Molecular weight	Solubility in water
1. Diesel	Hydrocarbons C_{16}-C_{35}	≈ 250	Insoluble
2. Kerosene	Hydrocarbons C_{20}-C_{30}	≈ 250	Insoluble
3. Sodium lauryl sulphate (SLS)	$CH_3(CH_2)_{11}.O.SO_3Na$	288.38	Soluble
4. Tricaprylylmethyl-ammonium chloride (Aliquat 336)	Mixture of C_8-C_{10} C_8 is dominant	442	Insoluble
5. Dodecylamine (DDA)	$C_{12}H_{27}N$	185.36	Soluble

CHAPTER 4

MECHANISM OF PREGROBBING

4.1 THEORY

This section describes a dual resistance model for the adsorption of gold cyanide onto activated carbon and ion-exchange resins, which incorporates both external film diffusion and intraparticle diffusion. This type of model is not novel and has been used by numerous authors in the predictive modelling of adsorption processes (Nieuwoudt, 1989; Petersen, 1991; Van Vliet *et al.*, 1980; Van Deventer, 1984).

4.1.1 Diffusion model assumptions

The assumptions made in developing the model are summarised as follows:

- The carbon and resin particles are treated as perfect spheres for modelling purposes.
- Metal cyanide concentrations are sufficiently low so that interference among them in mass transfer can be ignored.
- Isothermal conditions are assumed during adsorption
- The adsorption reaction on the surface of the carbon and the ion-exchange reaction on the resin occur instantaneously, so that equilibrium exists at the solid-liquid interface.
- Accumulation of metal cyanides in the liquid phase within the pores of the carbon or resin is negligible.

- The radial transport of metal cyanide into the pores of the adsorbents can be described by a surface diffusion mechanism.
- Pore diffusion is assumed to be negligible.
- The diffusivity of metal cyanide remains constant during a run, and is independent of the position inside the carbon or resin particle.
- Adsorption of metal cyanides is assumed to be reversible, especially when free cyanide ions are present in the solution.

4.1.2 Equilibrium expressions

Adsorption isotherms or equilibrium data are the basic design requirements of any adsorption system. The capacity of an adsorbent is usually described by an appropriate equilibrium isotherm model. The term equilibrium isotherm describes the relationship between the concentration of the adsorbate in the liquid phase and the concentration on the surface of the adsorbent. The isotherm permits the determination of the maximum amount of adsorbate the adsorbent can remove from the bulk liquid and it is generally described mathematically by fitting the experimental data to empirical or semi-empirical functions. An isotherm can describe the equilibrium relationship for a single adsorbate or for a multicomponent system. Since multi-solute isotherms are not applicable to this study the focus will be on single solute isotherms (Weber and Smith, 1987).

There are three commonly used single-solute isotherms for aqueous systems, namely, the Linear, Langmuir and Freundlich isotherms (Coulson and Richardson, 1991).

4.1.2.1 Linear isotherm

$$q_e = AC_e^n \qquad \ldots (4.1)$$

The linear isotherm is the simplest isotherm model and describes a linear relation between the equilibrium concentrations in the liquid and solid phases. This isotherm is motivated by visualising that at low concentrations no interaction takes place between neighbouring adsorbed species and solid loading is therefore, proportional to liquid concentrations. The linear isotherm is, however, only applicable at very low liquid adsorbate concentrations.

4.1.2.2 Langmuir isotherm

The Langmuir isotherm is one of the oldest adsorption isotherm models to describe single component adsorption from aqueous solutions. This model has been derived from statistical thermodynamics, as well as from simple kinetic considerations. It is based on the assumption of monolayer adsorption on a fixed number of equivalent adsorption sites and no interaction between adsorbed molecules. The model has the following form:

$$q_e = \frac{AC_e}{B + C_e} \qquad \ldots (4.2)$$

The Langmuir isotherm has been successfully applied to adsorption from aqueous solutions over limited concentration ranges for a number of adsorbate-adsorbent systems. At low adsorbate concentrations however, the Langmuir isotherm is reduced to a linear form.

4.1.2.3 Freundlich isotherm

$$q_e = AC_e^n \qquad \ldots (4.3)$$

The Freundlich isotherm equation was found to provide the best description of the data patterns encountered for all the adsorbents used in this study. This isotherm has been widely used to describe single solute adsorption from aqueous aurocyanide solutions onto many different adsorbents. The isotherm may be derived theoretically under the assumption that the adsorption energy obeys an exponential distribution. The disadvantage of the Freundlich isotherm is that it does not approach true linearity at low equilibrium concentrations.

4.1.3 Adsorption kinetics

The kinetics of an adsorption process is characterised by external and intraparticle mass transport dynamics. Transport of adsorbate molecules from the solution to adsorption sites on the adsorbents takes place according to the mechanism of film transport through the external boundary layer coupled with intraparticle surface diffusion. The dynamics of the external and intraparticle transfer mechanisms are characterised by a film transfer coefficient, k_f, and an effective surface diffusion coefficient, D_s, respectively. These coefficients can be derived from unsteady-state batch reactor adsorption rate studies.

4.1.3.1 Material balance equations

Although this model accounts for accumulation in two types of pores, (macro- and micropores) Petersen (1991) showed that it was possible to model the adsorption of metal cyanides onto activated carbon and ion-exchange resins successfully, without considering diffusion into the micropores. The diffusion into the micopores will, therefore, not be included in the mass balance equations.

The Freundlich isotherm has been used in this study to describe the equilibrium loading of gold cyanide on the adsorbents.

$$q_s = AC_s^n \qquad \ldots (4.4)$$

If the adsorption rate is determined by film transfer, diffusion through the liquid film surrounding the carbon and resin particles can be described by Fick's law:

$$n_L = k_f(C - C_s) \qquad \ldots (4.5)$$

A mass balance over the batch stirred reactor yields:

$$-V\frac{dC}{dt}=n_L a \quad \ldots (4.6)$$

It was assumed that the carbon and resin particles could be treated as equivalent spheres, therefore:

$$a=\frac{6M}{d_p\rho} \quad \ldots (4.7)$$

Substituting equations 4.5 and 4.7 into 4.6 leads to:

$$-V\frac{dC}{dt}=\frac{n_L 6M}{d_p\rho}=\frac{k_f(C-C_s)6M}{d_p\rho} \quad \ldots (4.8)$$

Simplifying and substituting equation 4.4 yields:

$$\frac{dC}{dt}=\frac{6k_fM}{d_pV\rho}\left[\left(\frac{q_s}{A}\right)^{\frac{1}{n}}-C\right] \quad \ldots (4.9)$$

From a mass balance over the reactor:

$$q_s=\frac{(C_i-C)V}{M} \quad \ldots (4.10)$$

Substituting equation 4.10 into equation 4.9 leads to:

$$\frac{dC}{dt}=\frac{6k_fM}{d_pVB\rho}\left(\frac{(C_i-C)V}{M}\right)^{\frac{1}{n}}-\frac{6k_fMC}{d_pV\rho} \quad \ldots (4.11)$$

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

The diffusion of solute into macropores can be described by the following equation:

$$\frac{dq_{macro}}{dt} = \frac{60D_{macro}}{d_p^{\,2}}\left(\frac{q_s^{\,2} - q_{macro}^{\,2}}{2q_{macro}}\right) \qquad \text{... (4.12)}$$

4.1.4 Parameter estimation

4.1.4.1 External mass transfer coefficient

Film transfer can be assumed to determine adsorption rate in the early stages of a batch adsorption experiment and the film theory postulates a linear concentration gradient from the bulk liquid to the adsorbent particle surface. The linear film transfer model is the simplest model for film transfer controlled kinetics and assumes that the adsorbate concentration at the particle surface (C_s) is negligible small compared to the adsorbate concentration in the bulk liquid. It is also only applicable over the initial portion of the kinetic curve.

The linear driving force expression for the flux of solute through the external boundary layer is:

$$\frac{dC}{dt} = \frac{6k_f M}{d_p V\rho}(C_s - C) \qquad \text{... (4.13)}$$

During the initial stages of an adsorption experiment, C >> C_s, hence equation 4.13 can be simplified to:

$$\frac{dC}{dt}=\frac{6k_fM}{d_pV\rho}C \qquad \ldots (4.14)$$

Integrating equation 4.14 yields:

$$\ln\left(\frac{C_i}{C}\right)=\frac{6k_fM}{d_pV\rho}t \qquad t\rightarrow 0 \qquad \ldots (4.15)$$

An expression for k_f is then found:

$$k_f=\frac{\ln\left(\frac{C_i}{C}\right)}{t}\frac{d_pV\rho}{6M} \qquad \ldots (4.16)$$

Experimentally, k_f is determined from the initial slope of a plot of ln (C_i/C) versus time for a given particle diameter.

4.1.4.2 Intraparticle diffusivity

The surface diffusion phenomenon can be explained as the adsorption and resulting accumulation of adsorbate on the outer pore surfaces so as to induce a surface concentration gradient, which leads to diffusion along the pore wall.

The surface diffusion coefficient, D, in the homogeneous surface diffusion model is actually a lumped intraparticle diffusion coefficient and can be estimated by using the Runga-Kutta solution for the batch kinetics of a single solute in a Powell least squares optimisation routine (Van Deventer, 1984).

4.1.5 Mechanism of pregrobbing

The adsorption performance of an adsorbent-adsorbate system is typically characterised by the rate at which adsorption occurs and by the ultimate capacity of the adsorbent in the particular system. The extent of pregrobbing in an adsorption system can, therefore, be characterised by its influence on the equilibrium or isotherm behaviour and the adsorption kinetics of the adsorbent. The adsorption profile of an ion-exchange resin in an aqueous aurocyanide solution can be described with a simple film diffusion model (Petersen, 1991). Such a model also incorporates an equilibrium expression, and as mentioned in section 4.1.2.3, in most cases, the Freundlich isotherm could be used to present the equilibrium expression in the form of equation 4.4.

The presence of a pregrobber in an aurocyanide solution containing a resin, when measuring the overall solution phase, will result in an increase in both the kinetics and the equilibrium capacity. The mass transfer parameter, k_f, which presents the rate of aurocyanide adsorption onto the resin, together with equilibrium parameters A and n, will be used to comment on the pregrobbing characteristics and mechanism.

4.1.5.1 Equilibrium capacity

The extent of pregrobbing on an adsorption system can be determined by differences in the mass transfer (k_f) and equilibrium parameters (A), where for example A_1 is the equilibrium value for the adsorption profile of the resin in a gold cyanide solution and A_2 is the equilibrium value for the adsorption profile of the resin and a pregrobber in a gold cyanide solution. In Figure 4.1, the ultimate adsorption capacities of the two profiles are represent by parameters A_1 and A_2, respectively.

Therefore: $\frac{A_1}{A_2}$ = final extent of pregrobbing (EP) on the system. ... (4.17)

where $0 < EP < 1$

4.1.5.2 Rate of adsorption

The rate of pregrobbing in an adsorption system can be determined by calculating k_f values for the different adsorption profiles. The k_f values for the resin and pregrobber in profile 3 (refer to Figure 4.1) can be calculated individually by subtracting profile 1 from 3 and by subtracting profile 2 from 3, respectively.

The influence of the pregrobber on the resin can therefore, be determined by comparing the k_f value of the resin profile in the presence of the pregrobber to the k_f value of the resin profile where no pregrobber was present. The same scenario applies for the k_f values for the two pregrobbing profiles. These profiles can be compared directly since the same amount of resin and pregrobber was used in the different experiments.

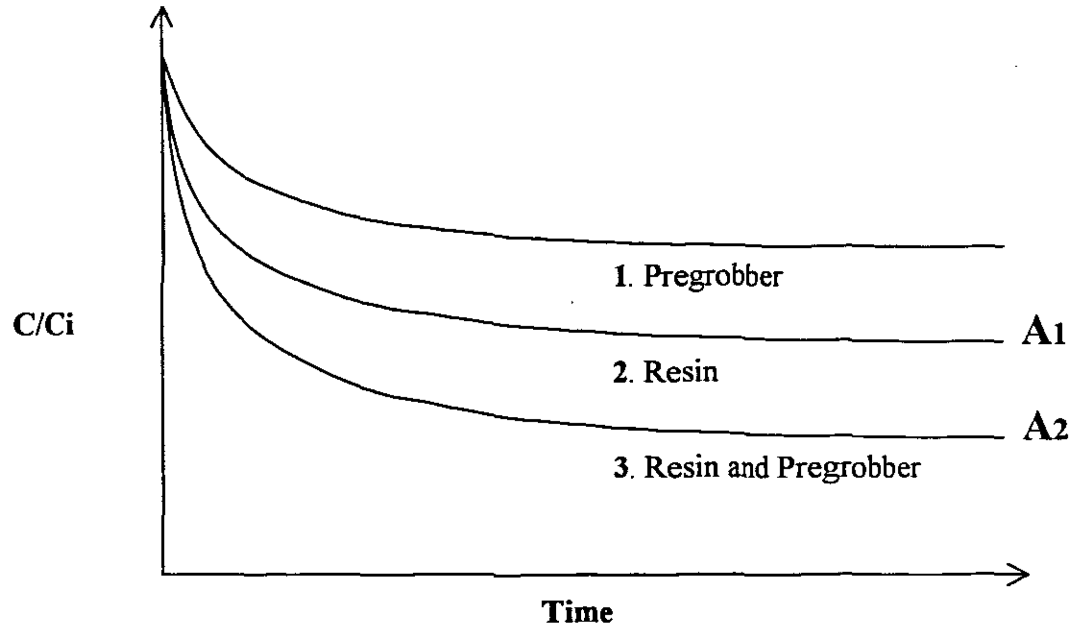

Figure 4.1 - Graphical representation of the different adsorption profiles

4.1.5.3 Mechanism

The total pregrobbing on a system can be defined by the extent of pregrobbing and by the rate of adsorption. To incorporate the influence of pregrobbing on the rate of adsorption and on the equilibrium capacity of a system, equations 4.4 and 4.11 can be modified as follows:

$$\text{Loading of gold on the resin} = (PR)\,AC^{n} \quad \ldots (4.18)$$

where: $$\text{Pregrobbing (PR)} = f\,(\text{EP, Rate}) \quad \ldots (4.19)$$

$$\frac{dC}{dt} = \left\{ \frac{6k_f M}{d_p V B \rho} \left(\frac{\left(C_i - C_{(t)}\right)V}{M} \right)^{\frac{1}{n}} - \frac{6k_f M C_{(t)}}{d_p V \rho} \right\} - \left\{ \frac{6k_{f,\,pregrobber} M_{ore} C_{(t)}}{d_{p,\,ore} V \rho_{ore}} \right\} \qquad \ldots (4.20)$$

When evaluating the model pregrobber, adsorption of gold on the pregrobber takes place uniformly over time according to a first-order decay. The kinetics and equilibrium values of this first order decay were dependent on the activity and porosity of the pregrobber, the gold concentration of the solution, the gold loading distribution of the adsorbent and time. Pregrobbing can therefore, be defined as follows:

Pregrobbing = *f* (activity and porosity of the pregrobber, solution concentration,
loading of the adsorbent, and time) ... (4.21)

It was not the focus of this study to develop a mathematical model for the system, but rather to present experimental trends for these parameters, hence qualifying the above relationship.

4.2 PREGROBBER ACTIVITY

Since the activity of the pregrobbing carbonaceous material in ores will vary, it was necessary to investigate the effect of different pregrobber activities on gold adsorption through batch kinetic adsorption experiments involving a resin with a pregrobber in a synthetic gold cyanide solution. Activated carbon was used as a synthetic pregrobber to simulate the pregrobbing effect of carbonaceous material in gold ores. Different pregrobber activities were obtained by pre-loading the carbon samples with gold cyanide to 25 %, 50 % and 75 % of its equilibrium loading capacity. Tests were also conducted to determine that none of the pre-loaded gold on the carbon came off and adsorbed onto the resin during experimentation (Section 3.2).

Comparative adsorption experiments performed on the different types of ion-exchange resins used in this study (Section 3.1) showed that a gold selective resin was the most effective resin for gold adsorption, especially in solutions containing other base metal cyanide complexes that compete with gold for resin sites. A gold selective resin was therefore, used for all the batch kinetic experiments. The raw experimental data for the experiments performed in this chapter are tabulated in Appendix A.

Figures 4.2 to 4.5 present batch kinetic results for the adsorption of gold cyanide on the gold selective resin, the loaded carbon and on the combined adsorption where the resin was in solution with the loaded carbon. The same quantities of resin and carbon were used throughout the experimentation. As expected, when measuring the solution phase, the presence of a pregrobber resulted in an increase in both the kinetic as well as the equilibrium loading capacity. As explained in Section 4.1.3.2, the influence of the pregrobber activity on the adsorption characteristics of the adsorbent can be determined by subtracting the combined resin/pregrobber profile from the pregrobber profile. The pregrobbing profile can be determined by subtracting the combined resin/pregrobber profile from that of the resin profile. Figures 4.6 and 4.7 show the adsorption profiles of the pregrobber and the resin at the different pregrobber activities, respectively. The figures clearly illustrate that if the pregrobber activity is increased, the adsorption profiles of the pregrobber and the resin shifted.

Table 4.1 and Figures 4.8, 4.9 and 4.10 show film transfer coefficients estimated from the initial rate data for the resin and the carbon profiles individually at each pregrobber activity. The value of k_f for the pregrobber profiles at the different activities increased from 2.77 x 10^{-4} to 4.93 x 10^{-4} m/s while the k_f values for the resin profiles decreased from 9.43 x 10^{-4} to 9.14 x 10^{-4} m/s. From these results the influence of the pregrobber on the adsorption characteristics of the resin is evident, since the film transfer coefficient for the standard resin adsorption profile is 1.34 x 10^{-3} m/s.

Equilibrium loading values for the resin and the pregrobber calculated in Table 4.2 shows a decrease in the loading capacity of the resin with an increase in pregrobber activity. The value of A for the resin profile decreased from 18.23 to 15.78 mg/l in the presence of the pregrobber with the highest activity. This decrease in the loading capacity of the resin is partially due to the low gold concentration in the solution after 24 hours, which effectively means a decrease in the diffusion gradient between the solution and the resin/pregrobber. The equilibrium capacity of the resin should, however, be more or less the same given enough residence time and sufficient gold concentrations.

In general the results indicate a decrease in the rate of adsorption of the adsorbent for an increase in the pregrobber activity and also an increase in the extent of pregrobbing for an increase in pregrobber activity. The activity of the carbonaceous material in gold ores will therefore, have a significant impact on the total extent of pregrobbing that will take place in any particular system.

4.3 GOLD LOADING DISTRIBUTION OF ADSORBENT

Similar batch adsorption experiments as mentioned in the previous section were conducted to investigate what effect different gold loadings on the adsorbent will have on the extent of pregrobbing. The resin samples were therefore, pre-loaded with gold cyanide to 50 % of its equilibrium loading capacity and then contacted with a pregrobber (50 % loaded activated carbon) in a synthetic gold cyanide solution.

Figure 4.11 show batch kinetic results for the adsorption of gold cyanide on the 50 % loaded resin, the 50 % loaded carbon, the combined adsorption of the 50 % loaded resin plus the 50 % loaded carbon and the combined adsorption of the resin plus the 50 % loaded carbon. Again, the same quantities of resin and carbon were used throughout the experimentation. The adsorption profile of the loaded resin shows a clear lack in performance compared to that of the virgin resin.

Figure 4.12 shows the adsorption profiles of the pregrobber the resin and the loaded resin respectively. If the gold loading of the resin increases form 0 % to 50 %, the adsorption profile of the pregrobber shifted, which effectively means an increase in the loading distribution of the resin will result in an increase in the overall extent of pregrobbing. Table 4.3 show A values and film transfer coefficients (Figure 4.13) estimated for the adsorption profiles. The value of A for the 50 % loaded resin was 8.13 mg/l, whereas the value of A for the 50 % loaded resin in the presence of the pregrobber was 5.56 mg/l. The equilibrium loading value of the pregrobber increased from 4.59 mg/l in the presence of the virgin resin to 6.64 mg/l in the presence of the loaded resin and the film transfer coefficients increased from 3.48 x 10^{-4} to 4.83 x 10^{-4} m/s, respectively. The k_f values of the resin decreased form 9.40 x 10^{-4} to 2.08 x 10^{-4} m/s, which confirms that the overall extent of pregrobbing increases with an increase in the gold loading distribution of the adsorbent.

4.4 POROSITY OF PREGROBBER

The aim of the work in this section was to investigate the effect of carbon porosity on gold adsorption as the pore structure of pregrobbing carbonaceous material in gold ores may vary widely from one carbon to another. To be able to compare the effect of different carbon porosities of the same type of carbon on gold adsorption, it was necessary to modify the pore structure of the carbon. Thermal regeneration was seen as the ideal method to change the pore structure of the carbon.

Van Vliet and Venter (1985) have conducted research studies on the various intraparticle structural changes that occur during progressive thermal treatment of an activated carbon. They concluded that above 850 ^{0}C and during the residence-time interval from 10 to 30 minutes, an almost stoichiometric conversion of the micropores to mesopores took place resulting in an increase in total pore volume. This increase in pore volume during this period was probably due to erosion of the matrix between the micropores. After 30 minutes, further conversion of the micropores to larger pore types occurred, as well as progressive destruction of the activated carbon matrix with a net result in the extensive loss of micropore volume and an increase in mesopore and macropore volume.

The virgin carbon used in this study was therefore, thermally treated at a temperature of 850 ^{0}C for a period of 20 minutes. Immediately after thermal treatment the carbon was stored in sealed Schutt-bottles under nitrogen to prevent the formation of additional oxygen-containing functional groups on the carbon surface (Voges, 1996).

Batch kinetic adsorption tests in a clear gold cyanide solution were performed on the treated carbon and on untreated carbon to compare their gold adsorption properties. Porosity tests have indicated that the treated carbon had a larger total pore volume than that of the untreated carbon. Furthermore, the equilibrium loading capacity of the untreated and treated carbon was 14.46 mg/l and 17.93 mg/l, respectively. Figure 4.14 shows the adsorption profiles of the two batches of carbon tested and the profiles where the resin was present. The profiles indicate clear differences in the kinetics, as well as the equilibrium loading capacity, of the carbon batches.

Figure 4.15 shows the adsorption profiles of the carbon and the treated carbon when in contact with the resin and the profiles of the resin when in contact with the pregrobbers. From the figure it can be seen that the adsorption profile of the treated carbon is below that of the untreated carbon when in contact with the resin, which indicates that the increase in porosity resulted in an increase in the overall extent of pregrobbing. Equilibrium loading values and film transfer coefficients (Figure 4.16) calculated in Table 4.4 shows that the rate of adsorption of gold on the pregrobber increased from 4.93 x10^{-4} to 8.86 x 10^{-4} m/s and the A value increased from 6.96 to 9.98 mg/l with the increase in porosity. The k_f values of the resin decreased from 9.14 x 10^{-4} to 9.08 x 10^{-4} m/s and the A value decreased from 12.28 to 11.83 mg/l with the increase in porosity, which ultimately means that the gold adsorption onto the resin was affected negatively and that the extent of pregrobbing increases with an increase in pregrobber porosity.

4.5 SOLUTION CONCENTRATION

The effect of solution concentration on pregrobbing was investigated since an increase in gold concentration in solution has a positive effect on adsorption rate due to the increased diffusion gradient between the solution and the surface of the adsorbent/pregrobber. Likewise, equilibrium experiments by several investigators using different initial gold solution concentrations showed a considerable difference in adsorption capacities (Davidson *et al.*, 1982).

To determine the effect that solution concentration has on pregrobbing, batch adsorption experiments were carried out with the resin and a pregrobber (50 % loaded carbon) in solutions with high initial gold concentrations and in solutions with low initial gold concentrations. Figures 4.17 and 4.18 give the batch kinetic results for the adsorption of gold cyanide on the adsorbents for the different gold solution concentrations. The extent of pregrobbing was determined by subtracting the combined resin/pregrobber profile from that of the resin profile for the different solution concentrations. Figure 4.19 illustrates the pregrobbing profiles for the high and low solution concentrations and it can be seen that solution concentration has a definite impact on the total extent of pregrobbing. In the solution with the low initial gold concentration, pregrobbing takes place initially and then decreases with a decrease in gold concentration and in the solution with a high initial gold concentration, the effect of pregrobbing increases with a decrease in solution concentration.

Table 4.5 shows equilibrium loading values and film transfer coefficients (Figure 4.20) estimated from the profiles for the different solution concentrations. The equilibrium loading capacity of the resin could not be determined in the solution with the low gold concentration, since the initial gold concentration was not high enough for the resin to reach its equilibrium loading capacity. The value of A for the pregrobber, however, decreased from 9.38 mg/l in the solution with the high gold concentration to 7.85 mg/l in the solution with the low gold concentration. The k_f values for the adsorption profile of the resin decreased from 9.40 x 10^{-4} m/s in the solution with the high gold concentration to 9.31 x 10^{-4} m/s in the solution with the low gold concentration. The extent of pregrobbing also decreased significantly with the k_f values for the pregrobber in the low gold concentration being 2.89 x 10^{-4} m/s and that in the high gold concentration 3.48 x 10^{-4} m/s. The increased reaction kinetics observed with an increase in solution concentration therefore, indicates that pregrobbing will take place to a lesser extent in solutions with a low gold concentration than in solutions with a high gold concentration.

Table 4.1 - Film transfer coefficients estimated to determine the effect of different pregrobber activities on the extent of pregrobbing.

Pregrobber activity	Resin k_f *(m/s)*	Carbon k_f *(m/s)*
Resin	1.34×10^{-3}	-
Carbon	-	9.61×10^{-4}
25 % loaded carbon	-	8.59×10^{-4}
50 % loaded carbon	-	7.76×10^{-4}
75 % loaded carbon	-	6.97×10^{-4}
Resin + carbon	9.14×10^{-4}	4.93×10^{-4}
Resin + 25 % loaded carbon	9.27×10^{-4}	4.24×10^{-4}
Resin + 50 % loaded carbon	9.40×10^{-4}	3.48×10^{-4}
Resin + 75 % loaded carbon	9.43×10^{-4}	2.77×10^{-4}

Table 4.2 - **The equilibrium loading values of the adsorbent and pregrobber as determined for the different pregrobber activities.**

Experiment	Initial solution concentration *(mg/l)*	Equilibrium concentration *(mg/l)*	Gold adsorbed from solution *(mg/l)*	Initial loading on carbon *(mg/l)*	Loading on solids *(mg/l)*	
					Carbon	Resin
1. Resin	29.36	9.58	19.78	-	-	19.78
2. Carbon	29.24	14.78	14.46	0	14.46	-
3. 25 % loaded carbon	29.82	18.04	11.78	3.33	15.11	-
4. 50 % loaded carbon	29.35	19.97	9.38	5.66	15.04	-
5. 75 % loaded carbon	29.77	21.77	8.00	7.20	15.20	-
6. Resin + carbon	29.01	2.27	26.74	0	10.46	15.78
7. Resin + 25 % loaded carbon	29.65	3.40	26.25	3.33	12.31	16.97
8. Resin + 50 % loaded carbon	29.06	4.69	24.37	5.66	12.75	17.49
9. Resin + 75 % loaded carbon	29.18	5.96	23.22	7.20	13.65	18.23

Table 4.3 - Equilibrium loading values and film transfer coefficients estimated to determine the effect of the gold loading distribution of the resin on the extent of pregrobbing.

Experiment	k_f *(m/s)*		A *(mg/l)*	
	Resin	Carbon	Resin	Carbon
1. Resin	1.34×10^{-3}	-	19.78	-
2. Carbon	-	9.61×10^{-4}	-	14.46
3. 50 % loaded resin	4.36×10^{-4}	-	8.13	-
4. 50 % loaded carbon	-	7.76×10^{-4}	-	9.38
5. Resin + 50 % loaded carbon	9.40×10^{-4}	3.48×10^{-4}	14.99	4.59
6. 50 % loaded resin + 50 % loaded carbon	2.08×10^{-4}	4.83×10^{-4}	5.56	6.64

Table 4.4 - Equilibrium loading values and film transfer coefficients estimated *to determine the effect of pregrobber porosity on the extent of* pregrobbing.

Experiment	k_f *(m/s)*		A *(mg/l)*	
	Resin	**Carbon**	**Resin**	**Carbon**
1. Resin	1.34×10^{-3}	-	19.78	-
2. Untreated carbon	-	9.61×10^{-4}	-	14.46
3. Treated carbon	-	1.00×10^{-3}	-	17.93
5. Resin + untreated carbon	9.14×10^{-4}	4.93×10^{-4}	12.28	6.96
6. Resin + treated carbon	9.08×10^{-4}	8.86×10^{-4}	11.83	9.98

Table 4.5 - Equilibrium loading values and film transfer coefficients estimated to determine the effect of solution concentration on the extent of pregrobbing.

Experiment	k_f *(m/s)*		A *(mg/l)*	
	Resin	**Carbon**	**Resin**	**Carbon**
High concentration				
1. Resin	1.34×10^{-3}	-	19.78	-
2. 50 % loaded carbon	-	7.76×10^{-4}	-	9.38
3. Resin + 50 % loaded carbon	9.40×10^{-4}	3.48×10^{-4}	14.99	4.59
Low concentration				
4. Resin	1.16×10^{-3}	-	*	-
5. 50 % loaded carbon	-	6.00×10^{-4}	-	7.85
6. Resin + 50 % loaded carbon	9.31×10^{-4}	2.89×10^{-4}	*	*

* Did not reach equilibrium loading capacity

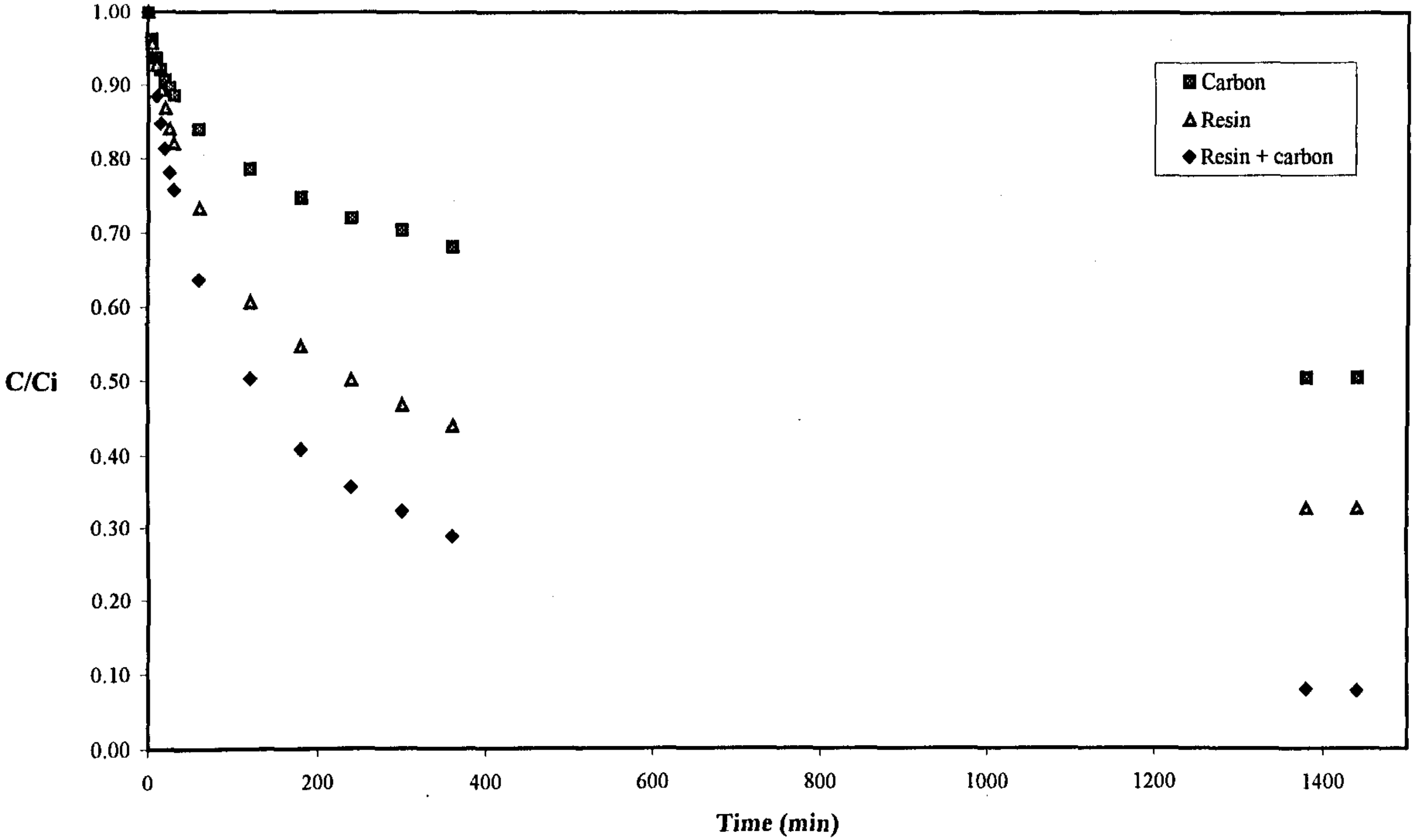

Figure 4.2 - Batch kinetic results for the adsorption of gold cyanide on the resin and carbon to determine the effect of pregrobber activity on the extent of pregrobbing.

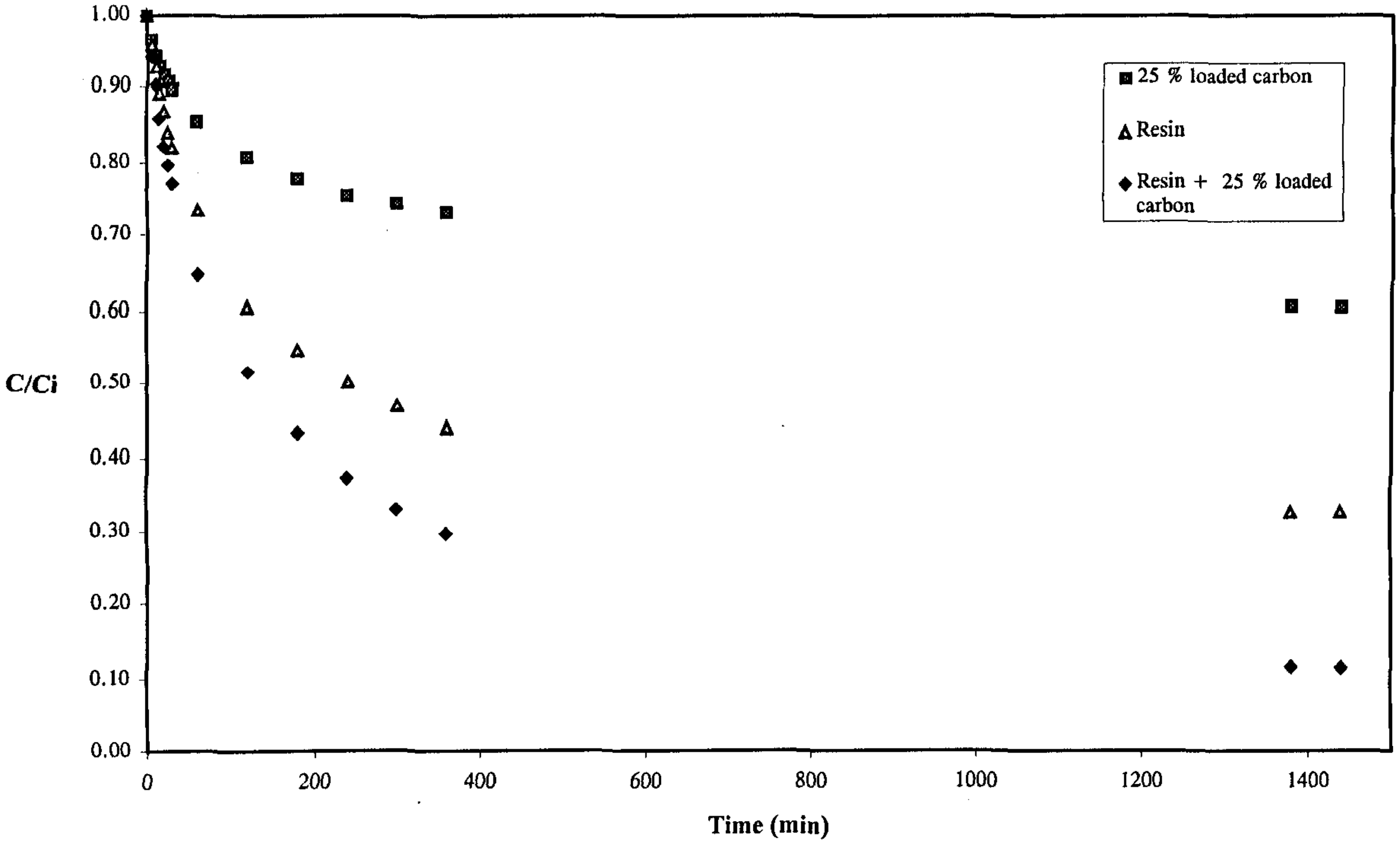

Figure 4.3 - Batch kinetic results for the adsorption of gold cyanide on the resin and 25 % loaded carbon to determine the effect of pregrobber activity on the extent of pregrobbing.

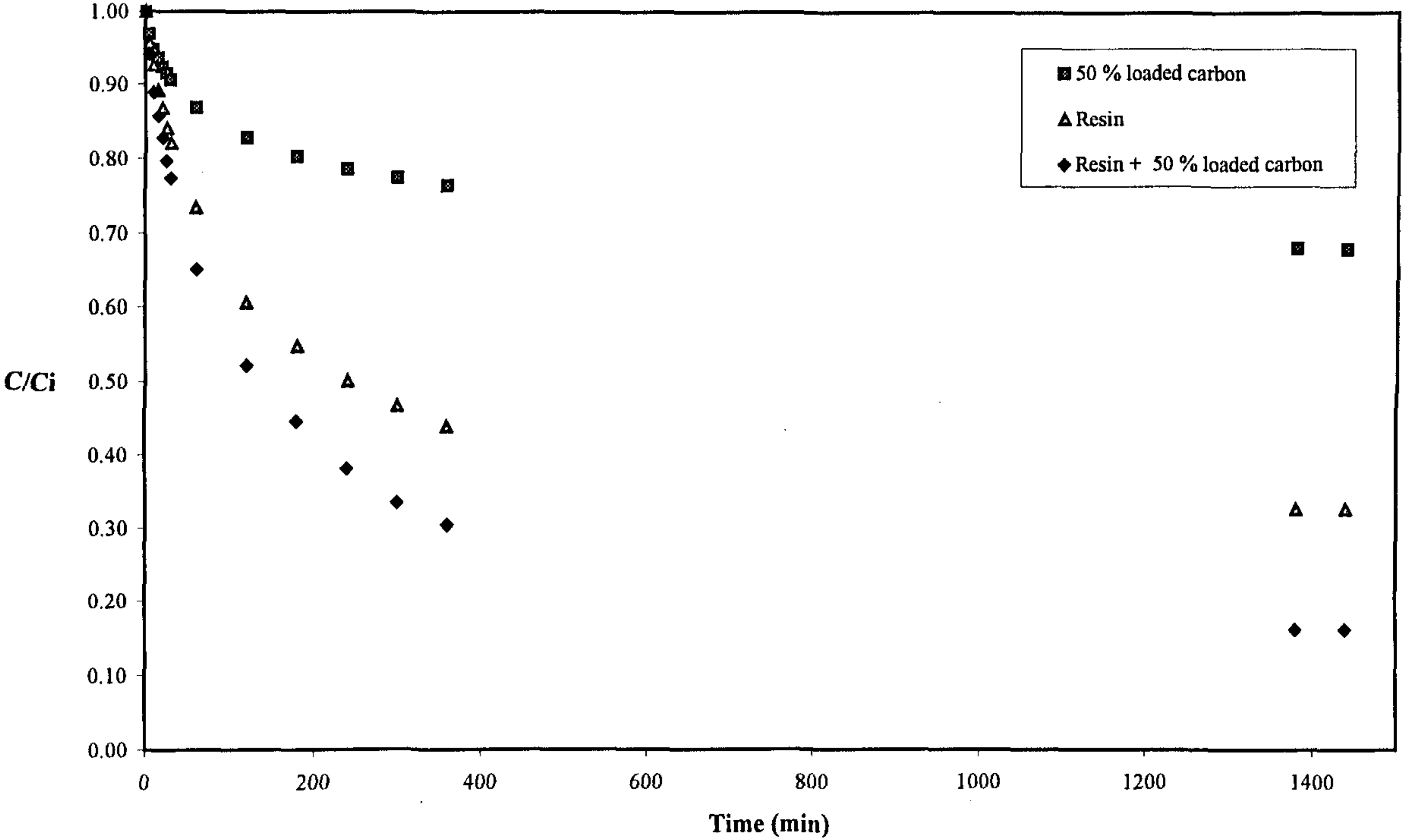

Figure 4.4 - Batch kinetic results for the adsorption of gold cyanide on the resin and 50 % loaded carbon to determine the effect of pregrobber activity on the extent of pregrobbing.

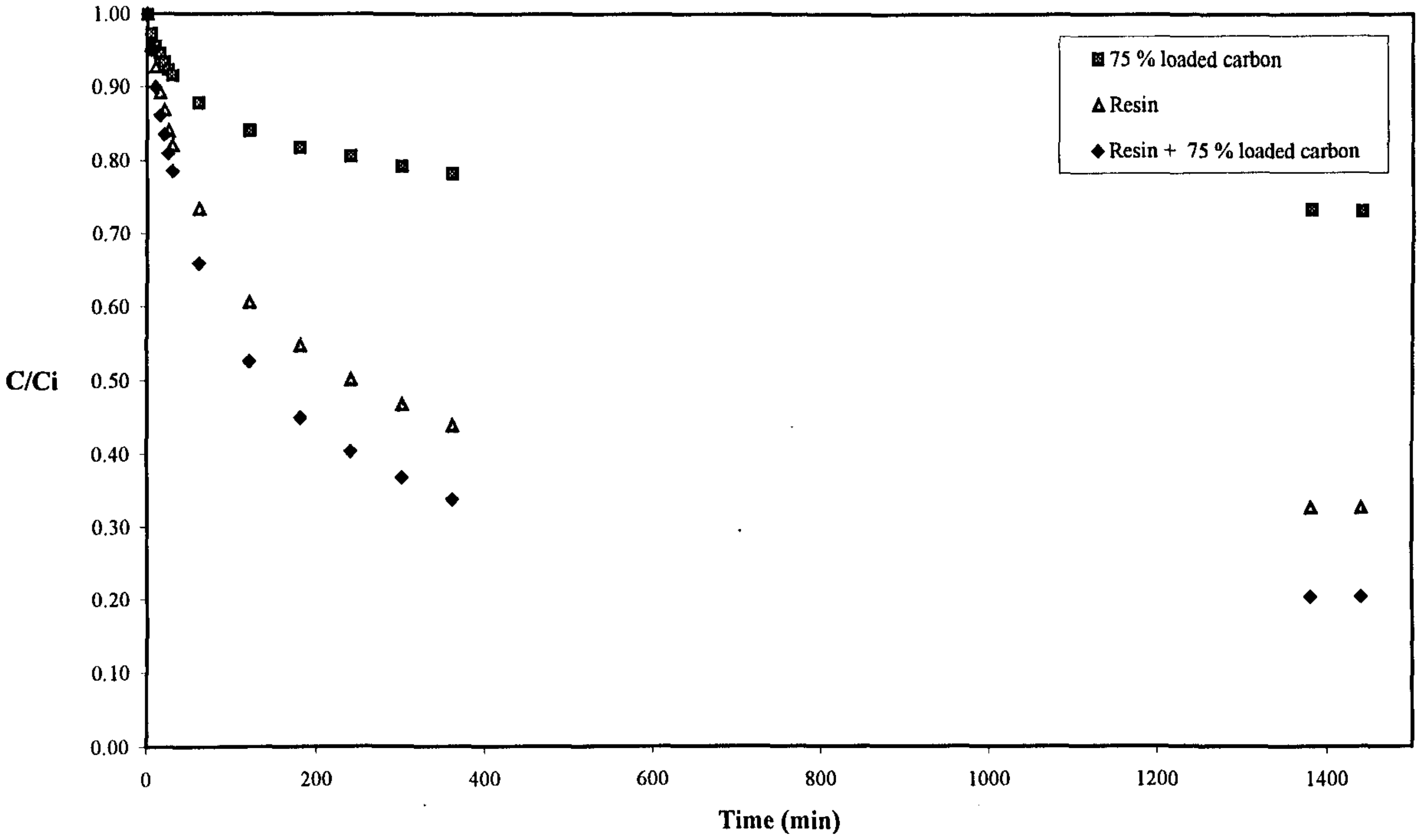

Figure 4.5 - Batch kinetic results for the adsorption of gold cyanide on the resin and 75 % loaded carbon to determine the effect of pregrobber activity on the extent of pregrobbing.

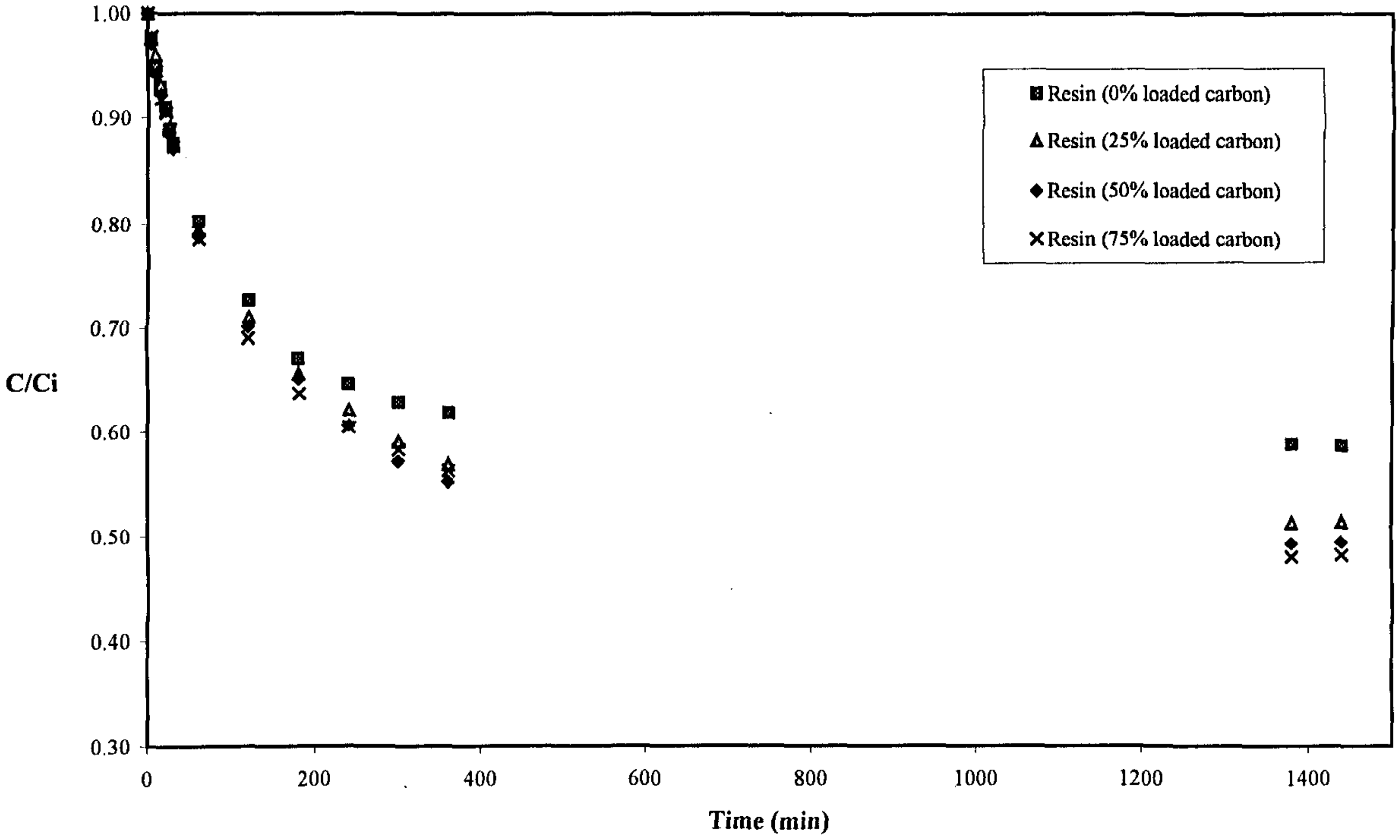

Figure 4.6 - Batch kinetic results for the adsorption of gold cyanide on the resin at the different pregrobber activities.

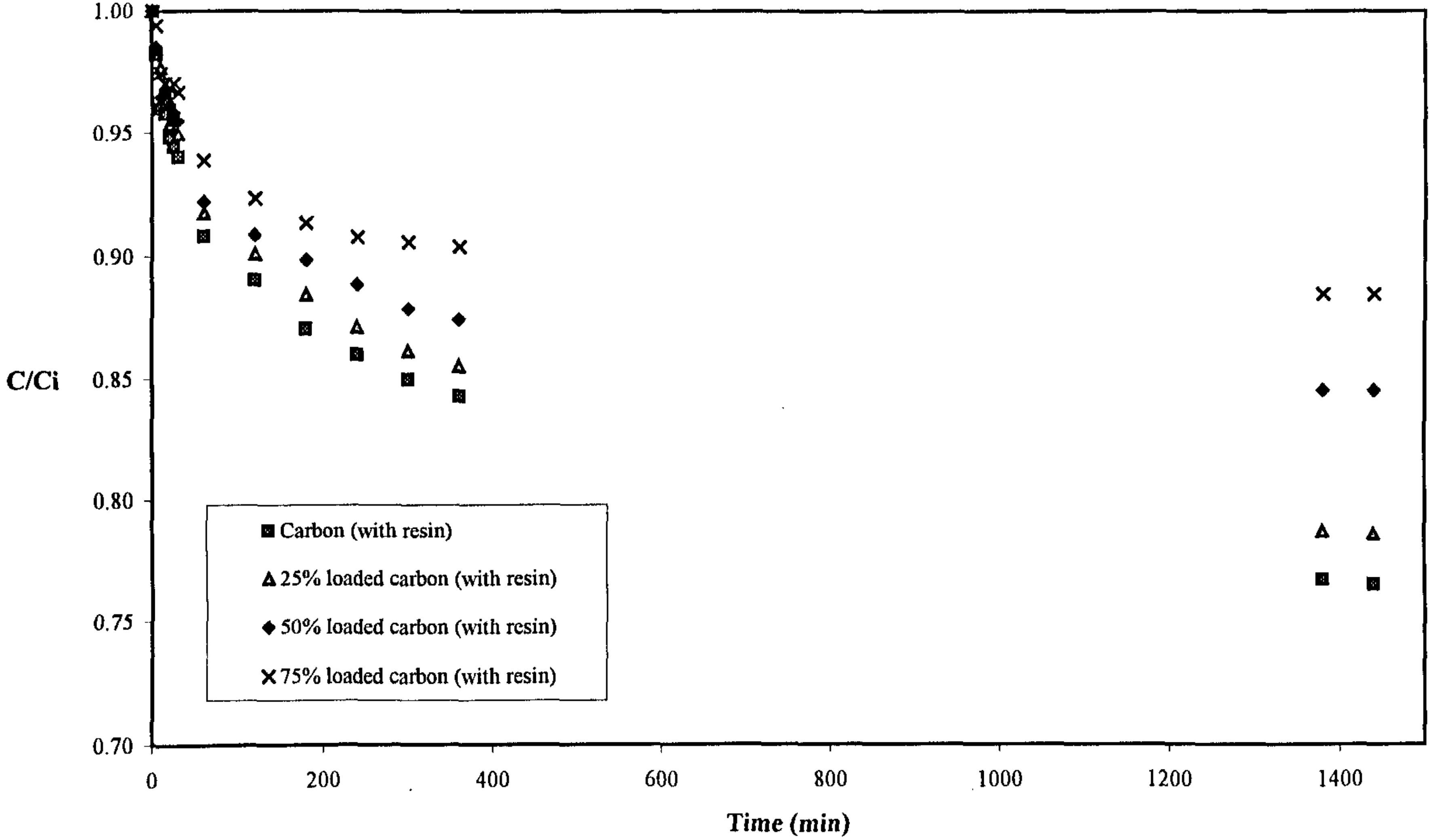

Figure 4.7 - **Batch kinetic results for the adsorption of gold cyanide on the carbon at the different pregrobber activities.**

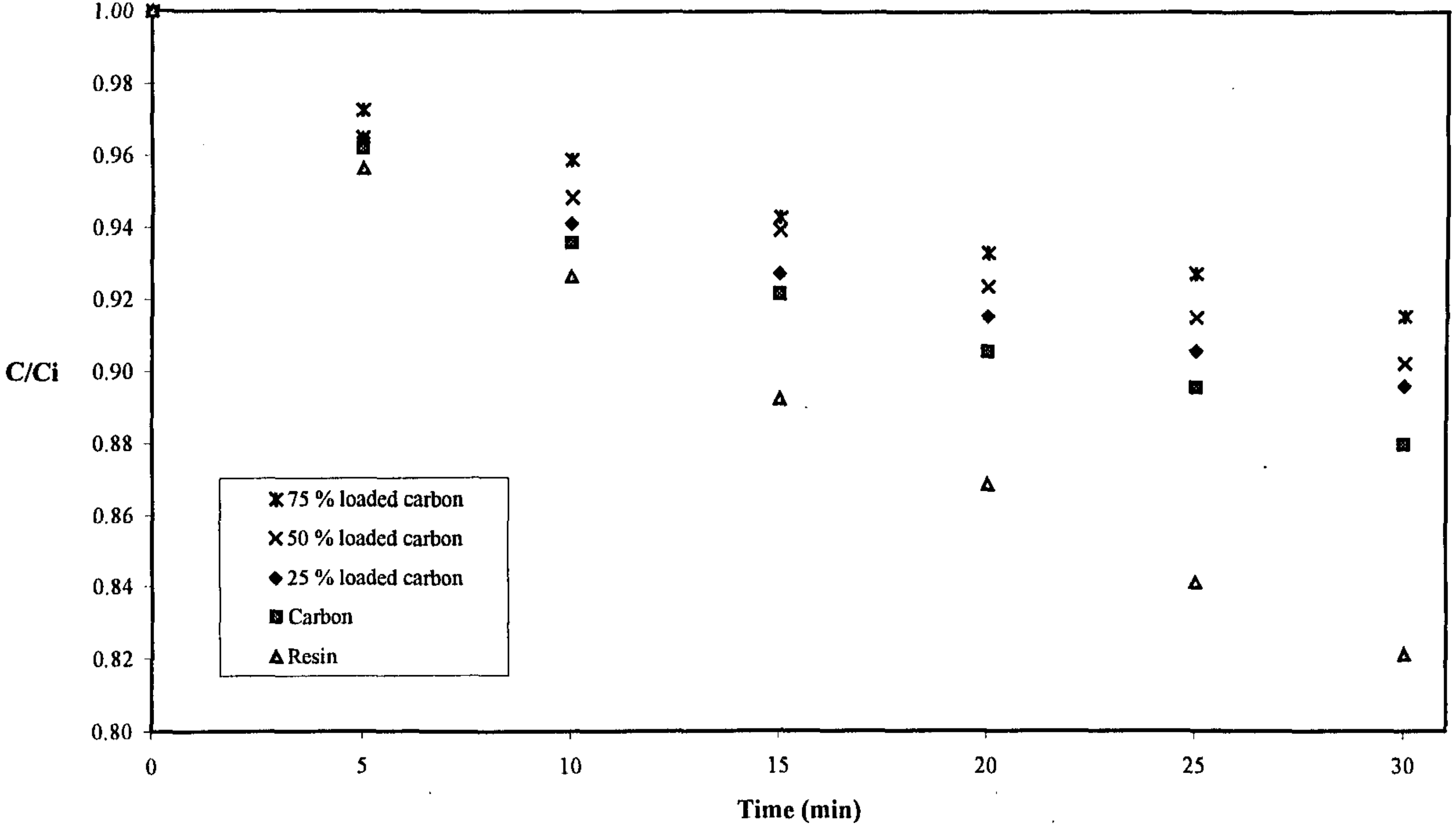

Figure 4.8 - The initial rate data for the determination of film transfer coefficients of the adsorbent and the different pregrobber activities.

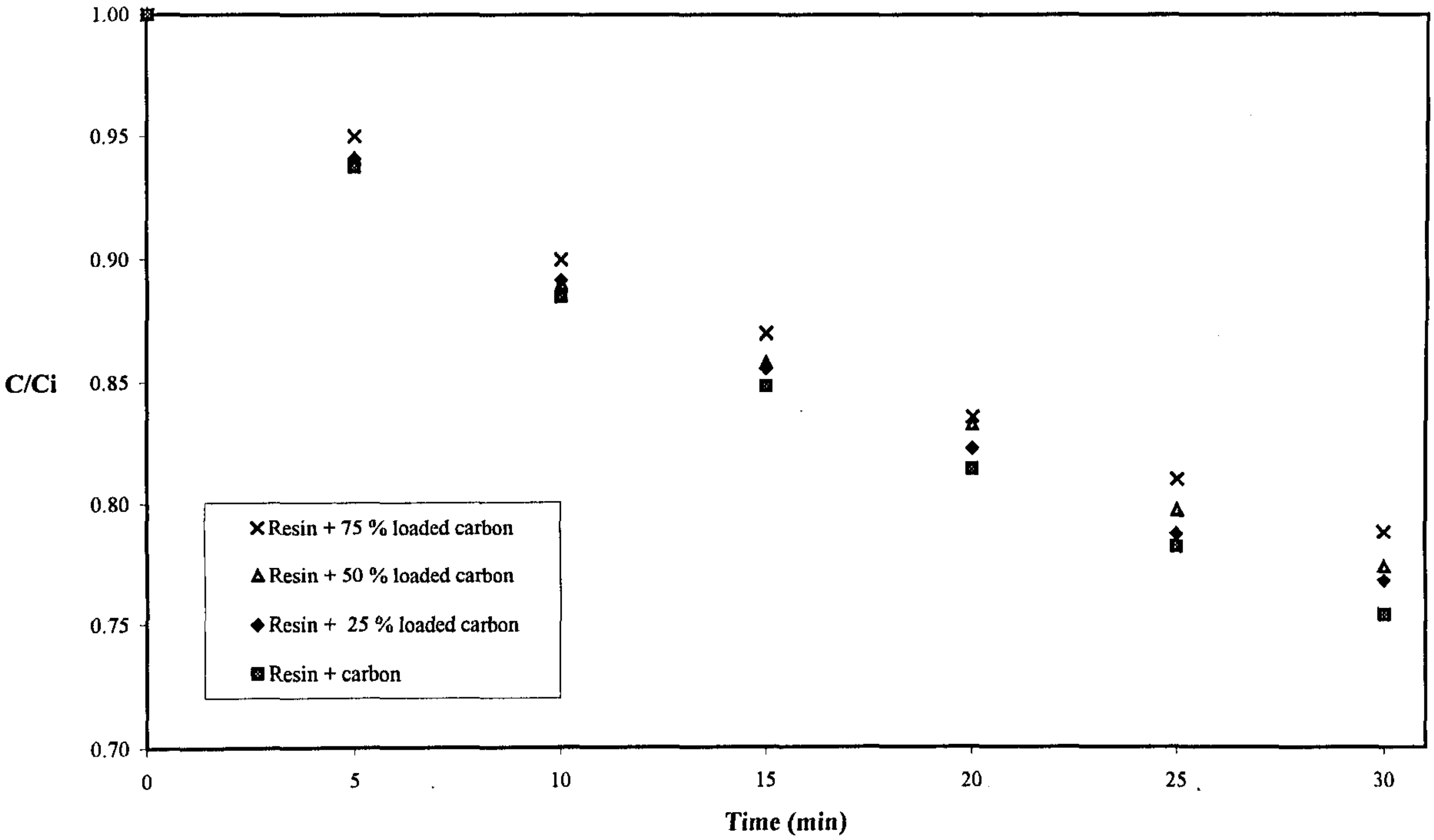

Figure 4.9 - The initial rate data for the determination of film transfer coefficients for the combined profiles of the resin in the presence of the pregrobber.

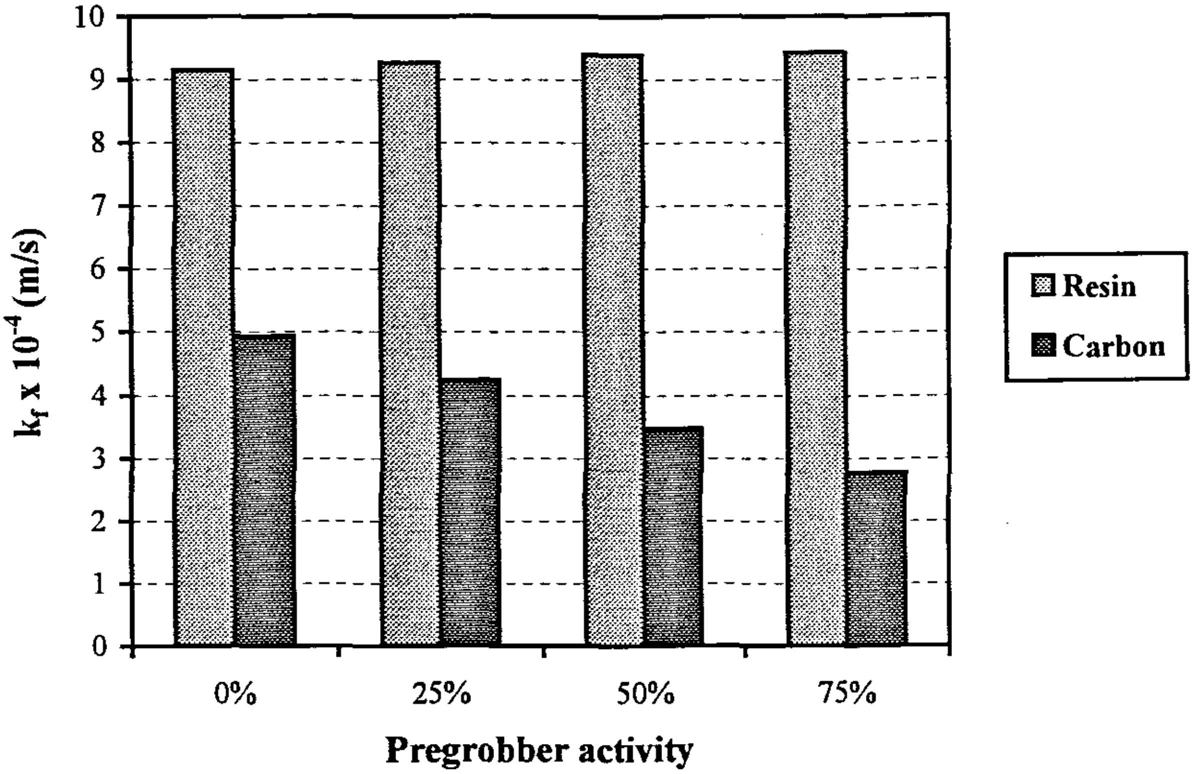

Figure 4.10 - Graphical representation of the film transfer coefficients estimated when evaluating the resin and the carbon separately at the different pregrobber activities.

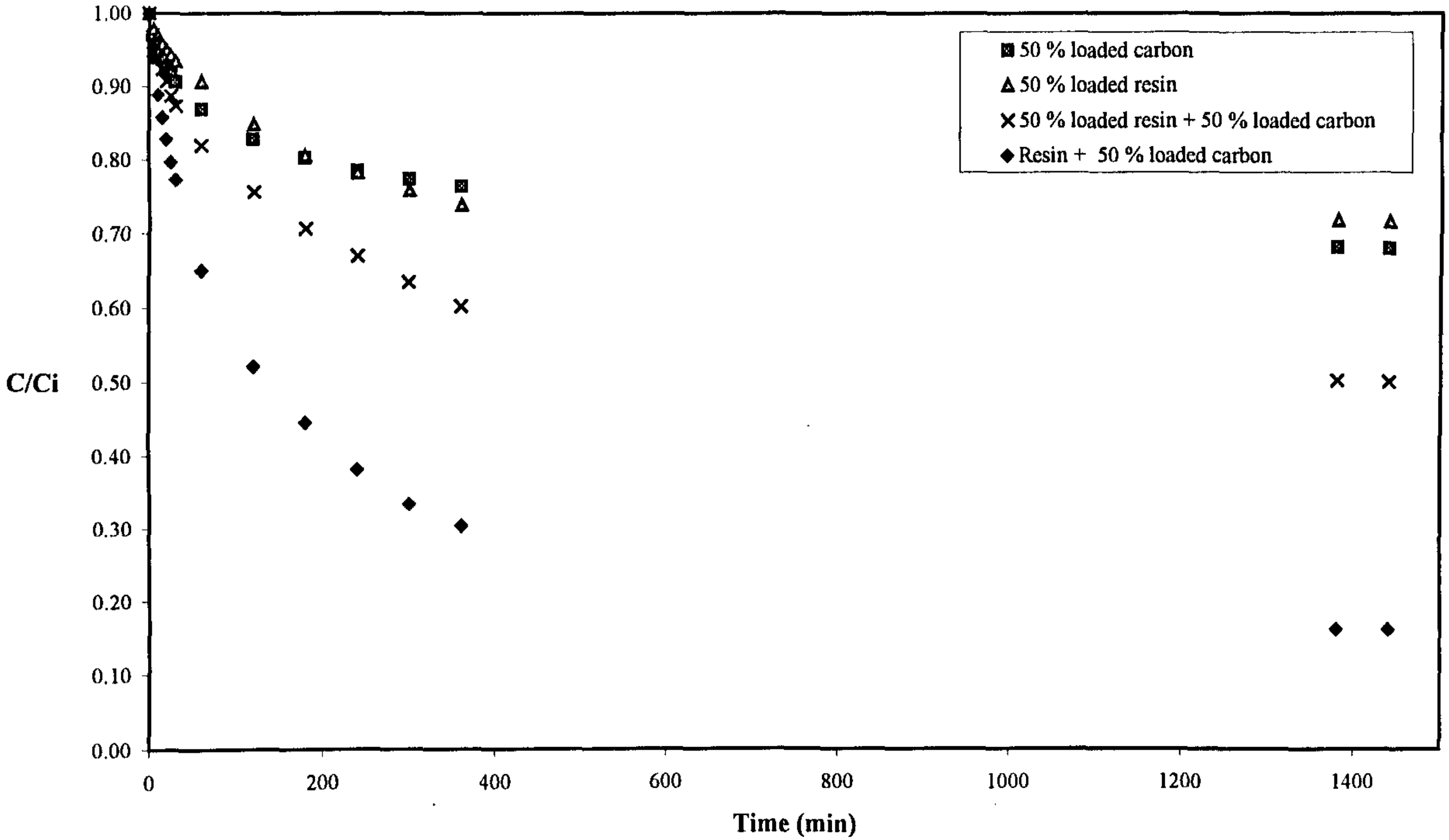

Figure 4.11 - Batch kinetic results for the adsorption of gold cyanide on 50 % loaded resin and 50 % loaded carbon to determine the effect of the loading distribution of the resin on the extent of pregrobbing.

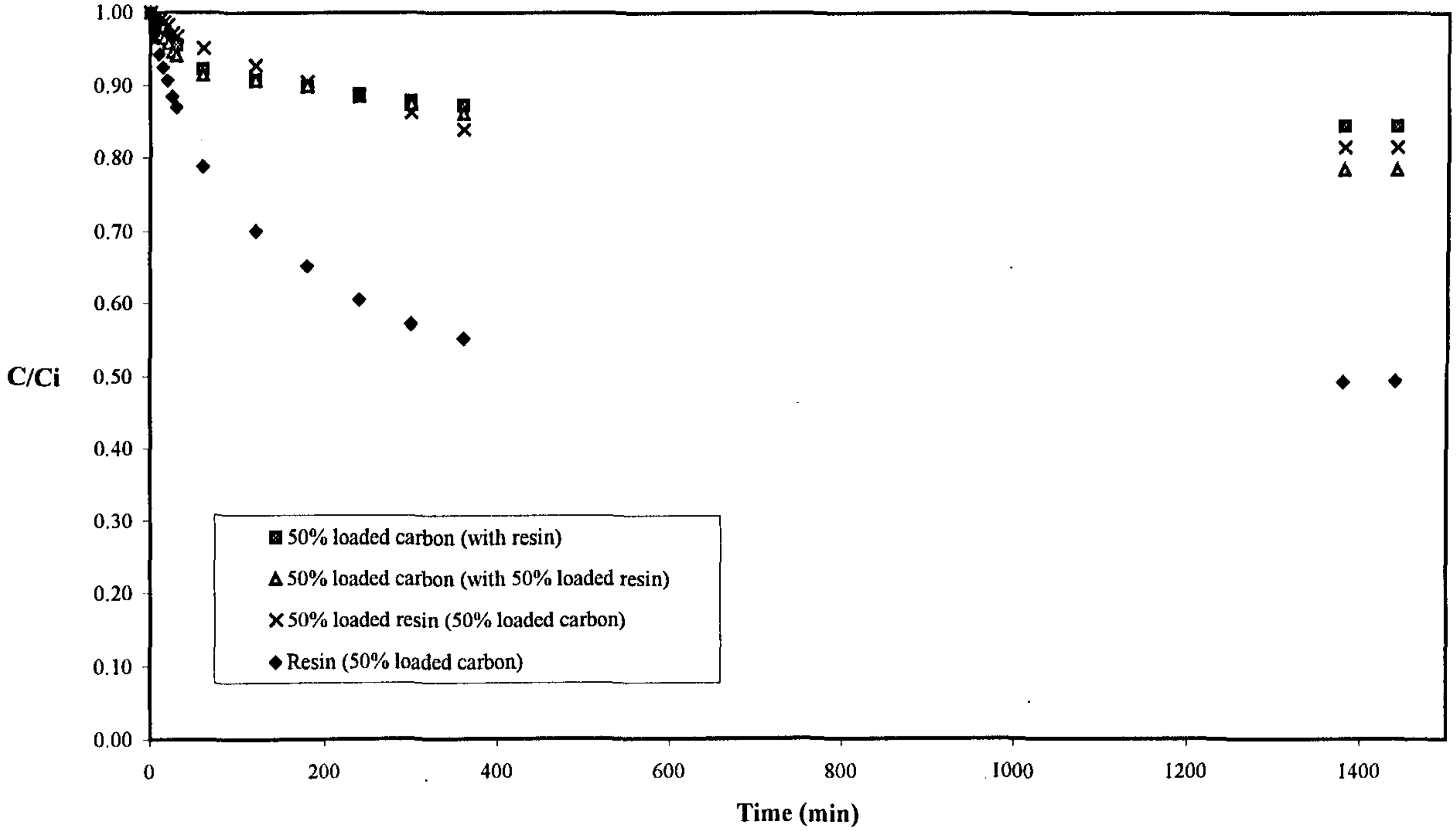

Figure 4.12 - **Batch kinetic results for the adsorption of gold cyanide on the resin and pregrobber at different resin gold loadings.**

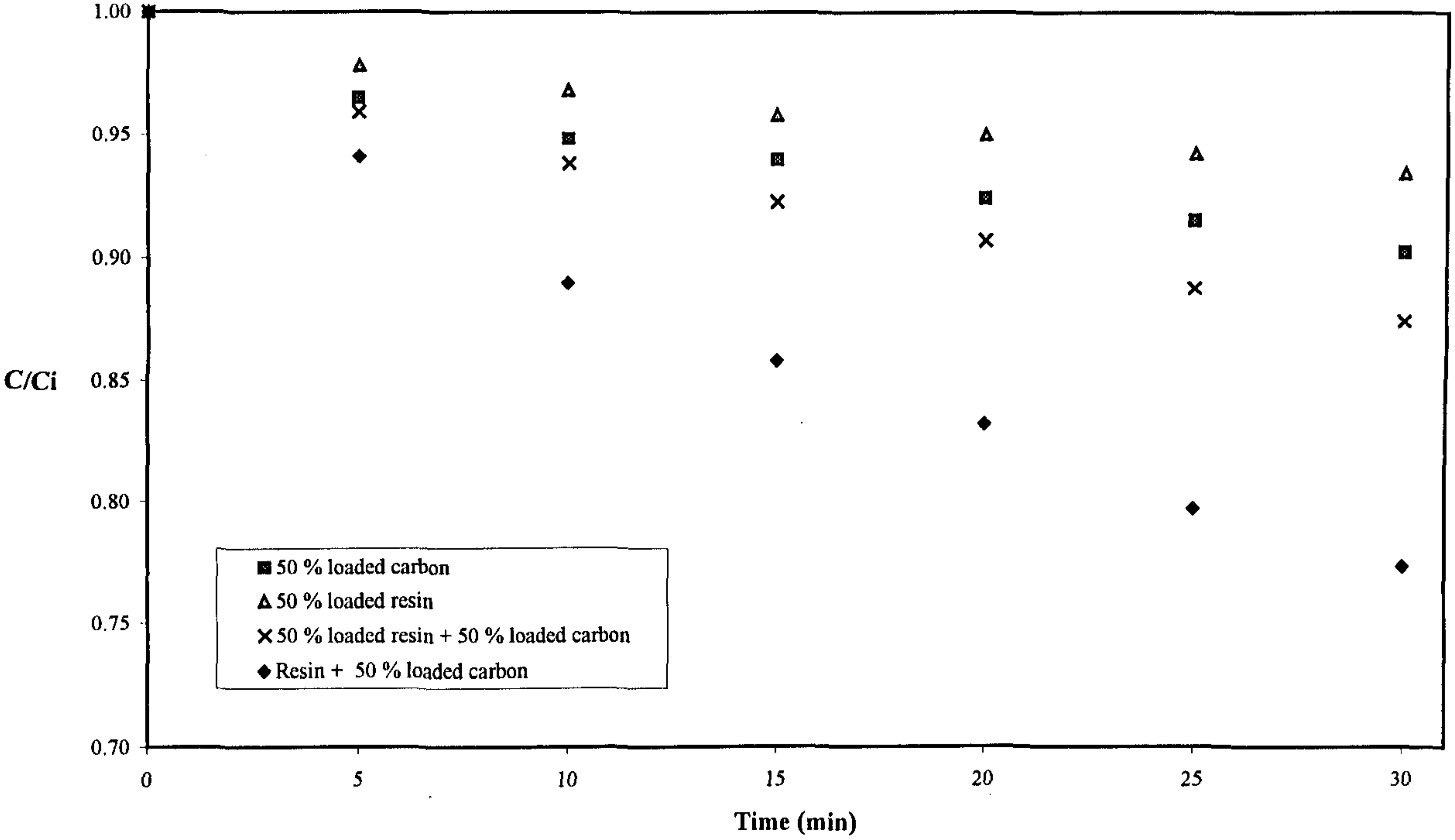

Figure 4.13 - The initial rate data for the determination of film transfer coefficients for the resin and loaded resin in the presence of the pregrobber.

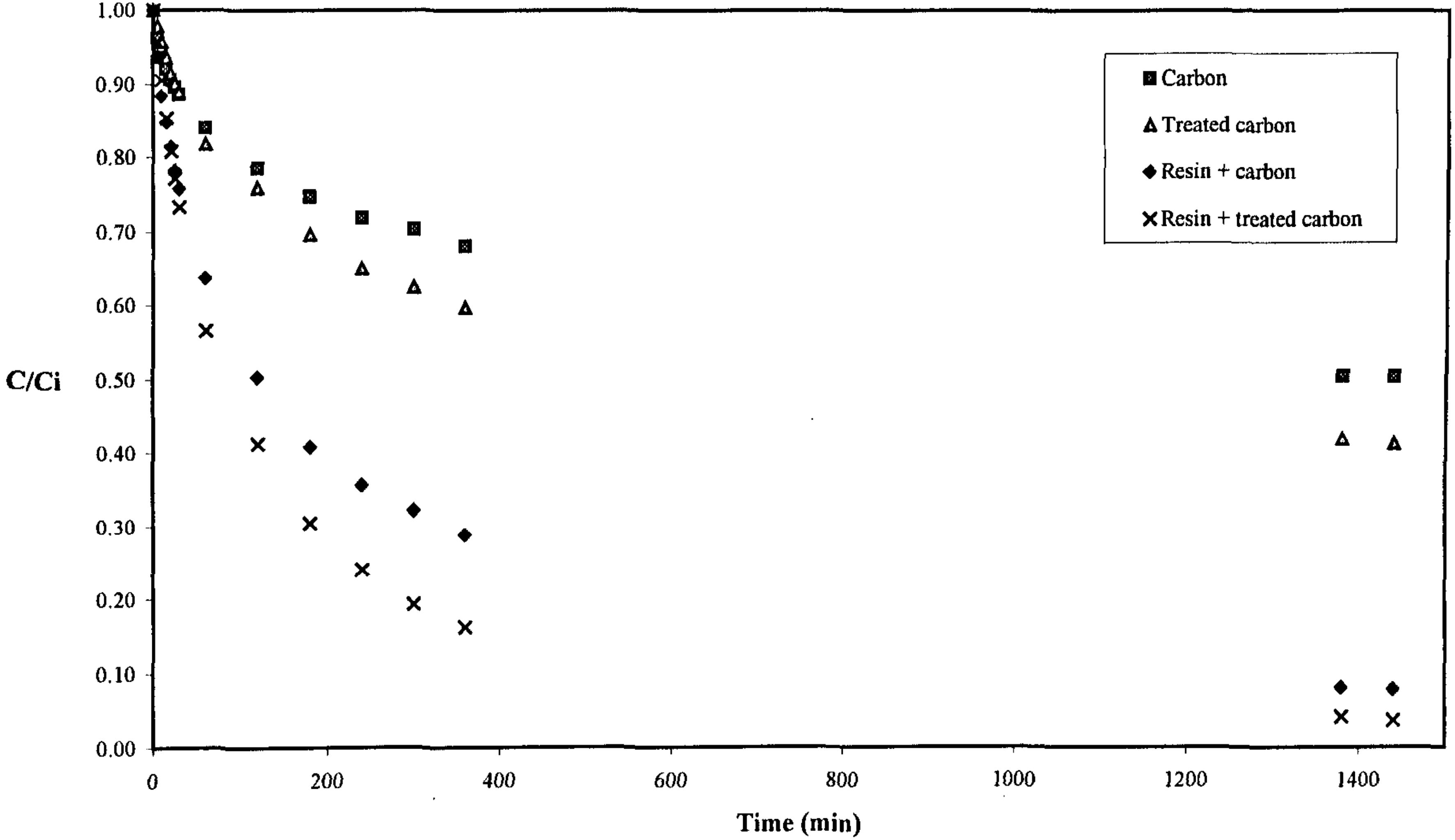

Figure 4.14 - Batch kinetic results for the adsorption of gold cyanide on the resin and treated carbon to determine the effect of pregrobber porosity on the extent of pregrobbing.

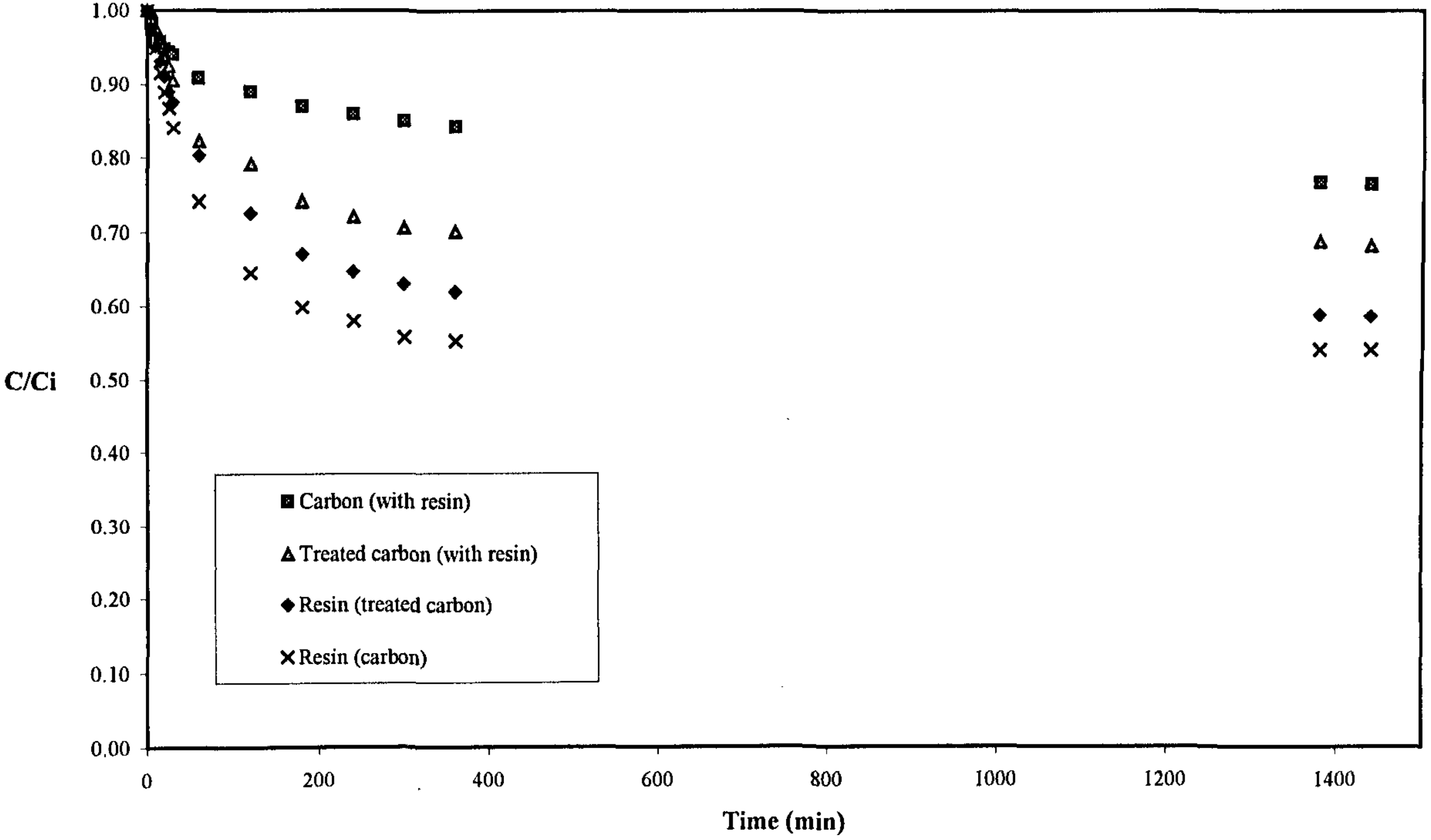

Figure 4.15 - **Batch kinetic results for the adsorption of gold cyanide on the resin, carbon and the treated carbon when evaluated separately.**

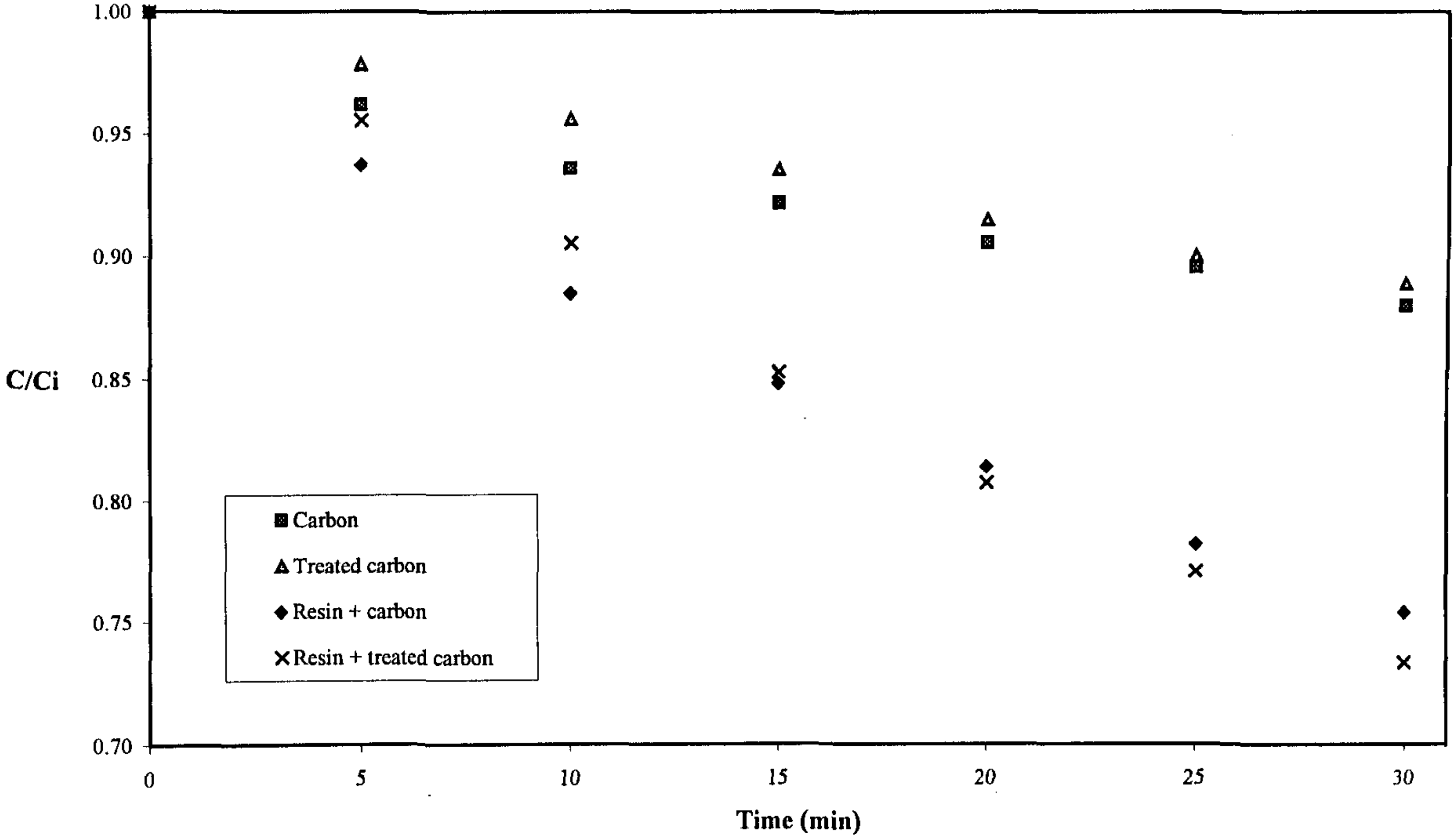

Figure 4.16 - The initial rate data for the determination of film transfer coefficients for the combined profiles of the resin when in contact with the treated carbon and untreated carbon.

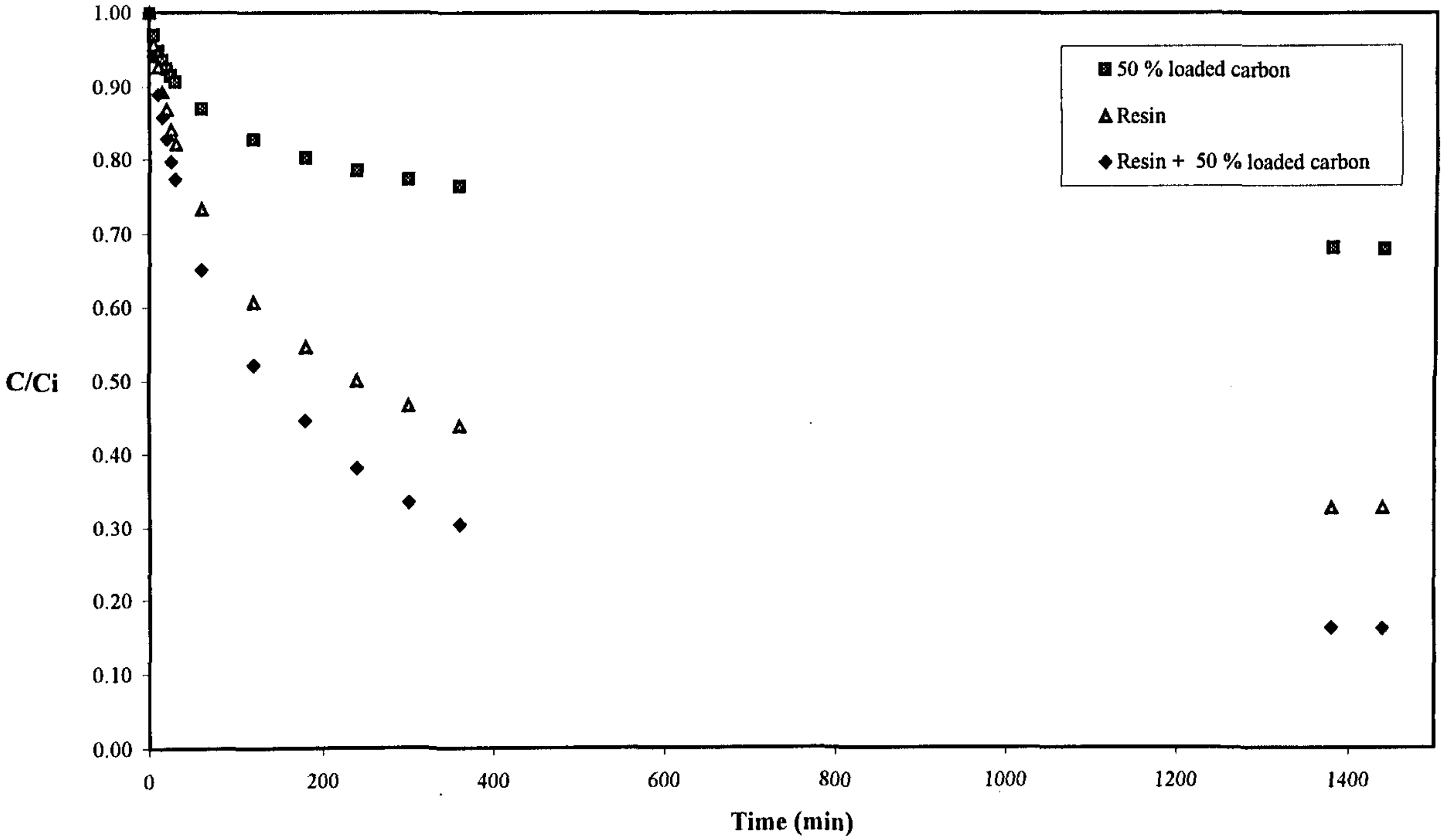

Figure 4.17 - Batch kinetic results for the adsorption of gold cyanide on the resin and 50 % loaded carbon in a solution with a high initial gold cyanide concentration.

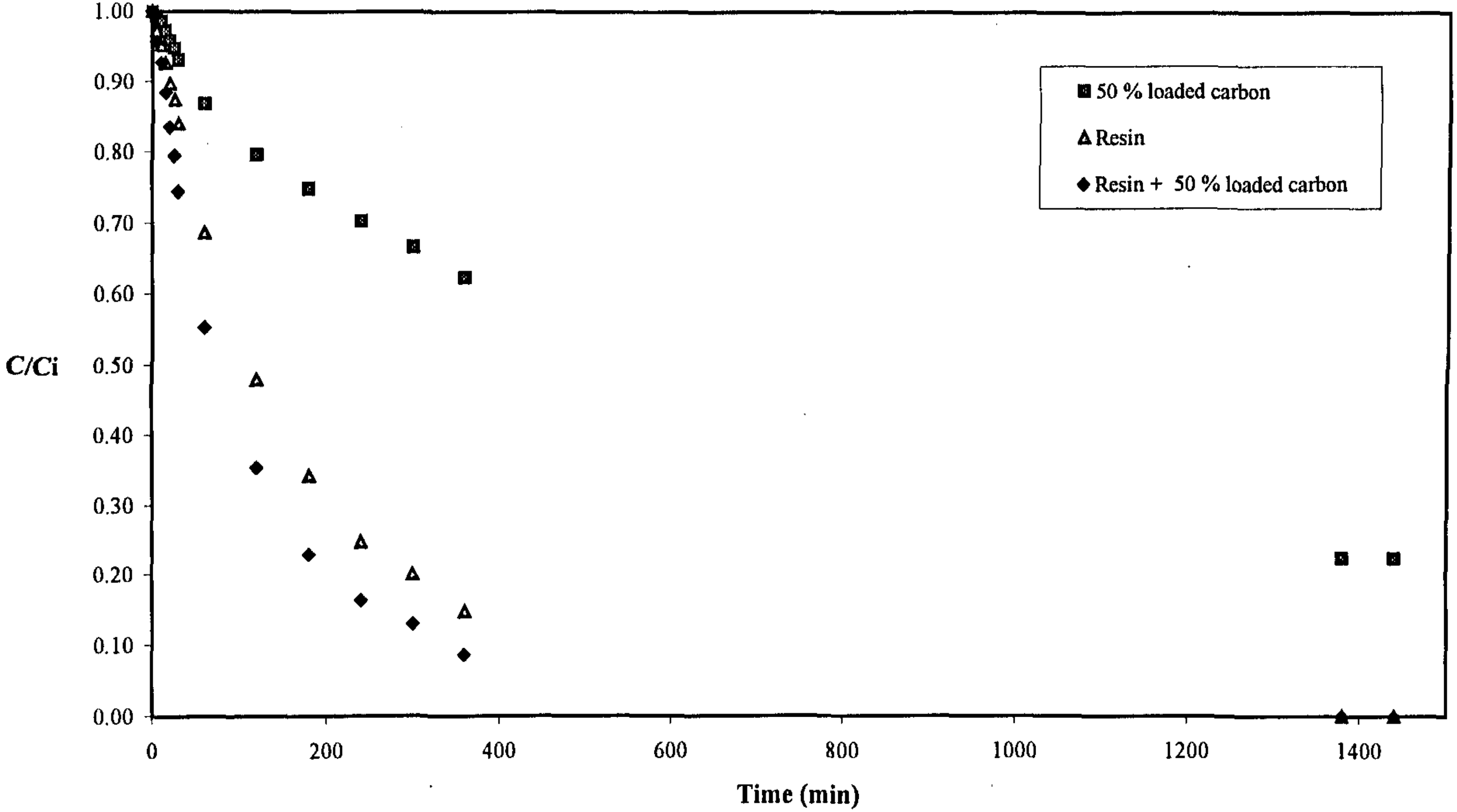

Figure 4.18 - **Batch kinetic results for the adsorption of gold cyanide on the resin and 50 % loaded carbon in a solution with a low initial gold cyanide concentration.**

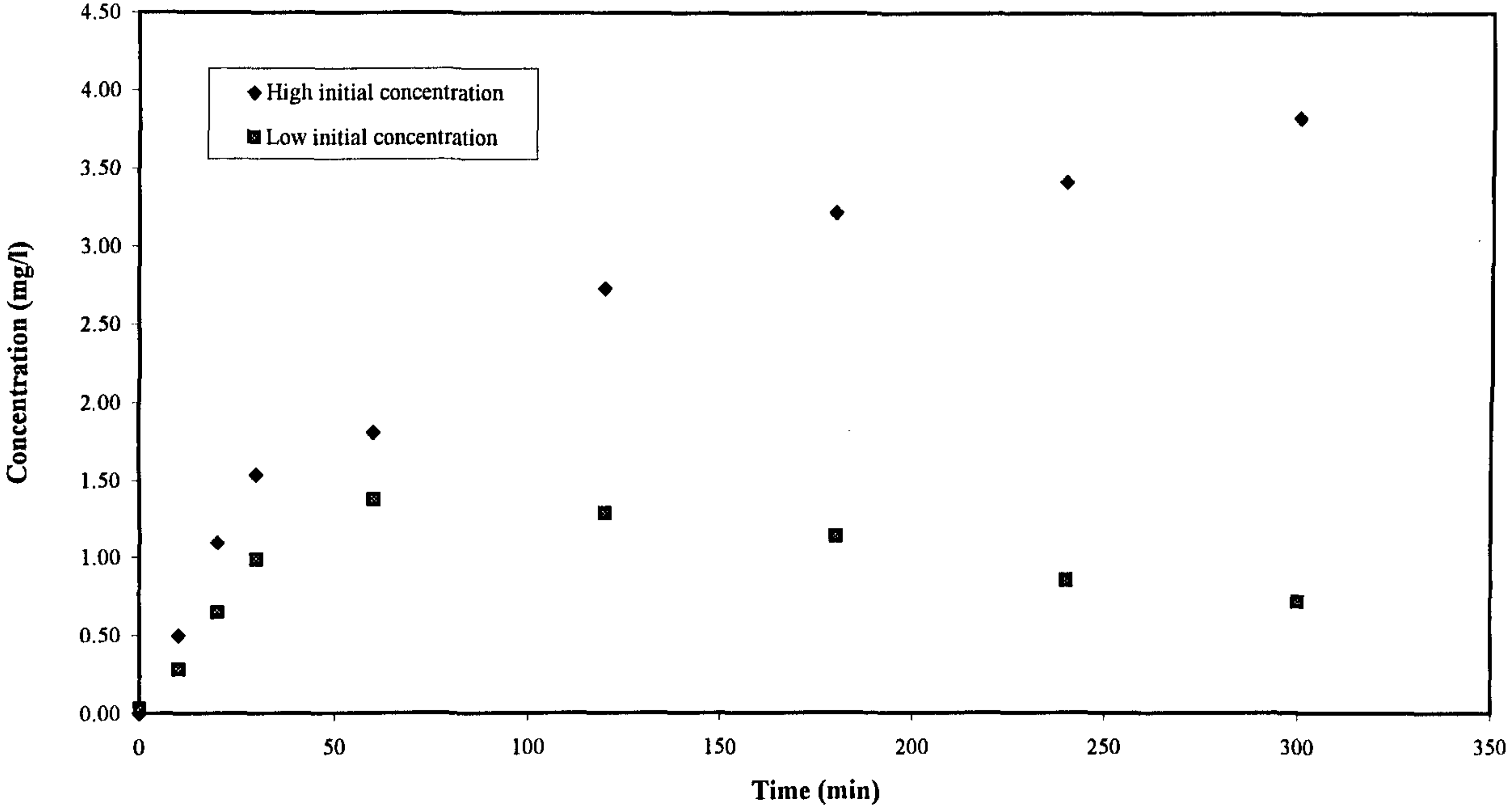

Figure 4.19 - Batch kinetic results for the adsorption of gold cyanide on the pregrobber in a solution with a high initial gold concentration and in a solution with a low initial gold concentration

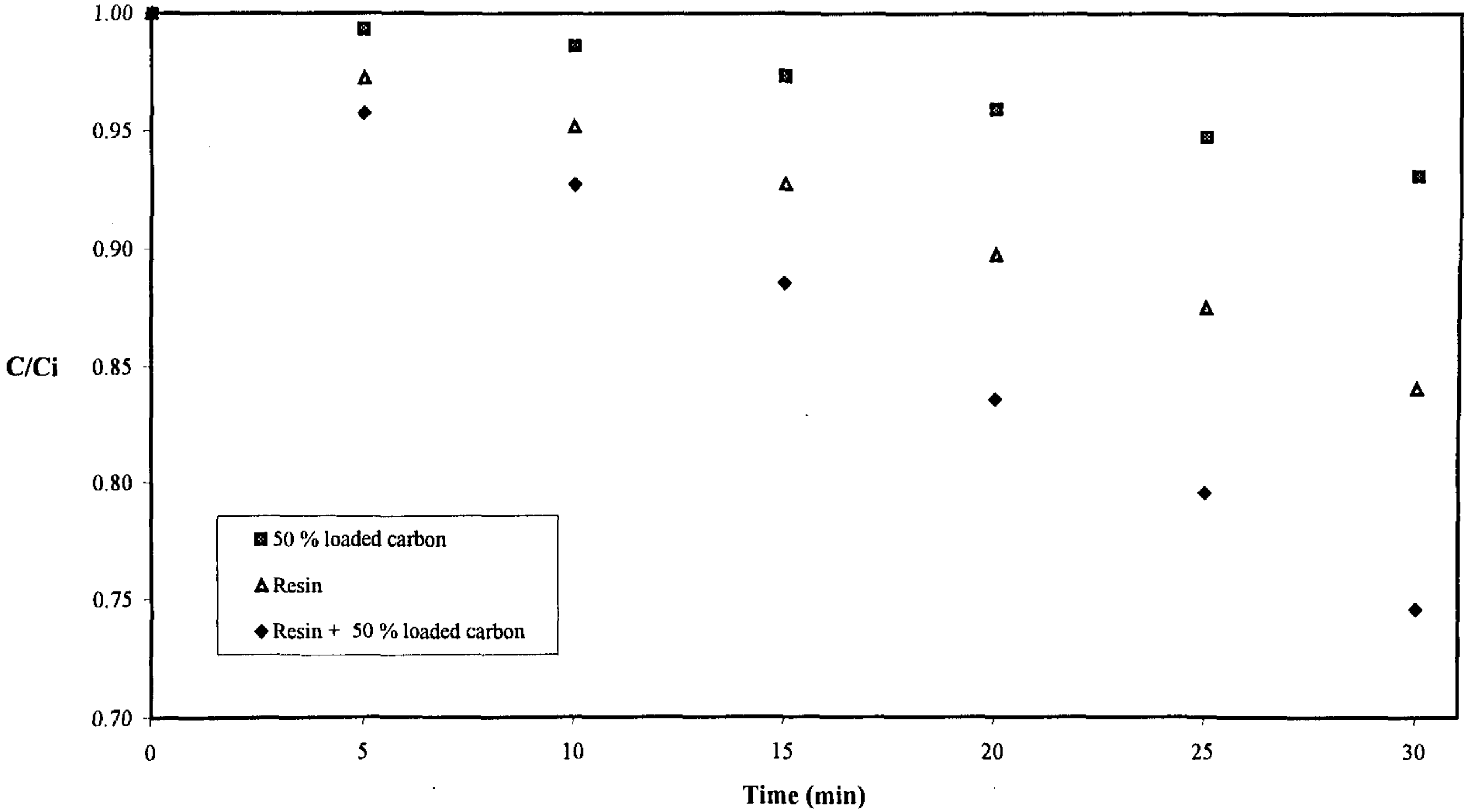

Figure 4.20 - The initial rate data for the determination of film transfer coefficients for the resin and pregrobber in a solution with a low initial gold concentration.

CHAPTER 5

PREGROBBING MINERALS IN GOLD ORES

5.1 GOLD ADSORPTION ONTO PURE MINERALS

The aim of the work in this section was to establish the presence and extent of pregrobbing by minerals in gold ores. Several pure minerals, pyrite, chalcopyrite, quartz and kaolin that are commonly found in gold ores were used to investigate the adsorption of gold onto the surfaces of minerals. The milled mineral samples were each contacted with a synthetic aurocyanide solution and then analysed for gold. The experimental procedure is described in Chapter 3, sections 3.1 and 3.2. The solution analyses were considered to be more prone to error that the analyses of the solids and therefore, all the results are based on the actual gold loading on the solids. The results and experimental conditions are in Table 5.1.

Gold was adsorbed onto all the minerals studied, but to varying extents. Chalcopyrite and pyrite were found to be relatively strong adsorbers of gold. Quartz and kaolin also adsorbed significant amounts of gold, but not nearly to the same extent as the sulphide minerals. The mineral samples were also loaded with gold in solutions containing high gold concentrations to provide samples for scanning electron microscopy (SEM) to give more information on the speciation and distribution of the loaded gold on the mineral surfaces. No visible gold, however, was found on the any of the loaded minerals because the gold loadings for the minerals were below the detection limit of the instrument.

Adams *et al.* (1996), however, investigated the strong gold adsorption properties of chalcopyrite and pyrite through Mössbauer spectroscopy and scanning electron microscopy and concluded that gold adsorbed onto these minerals as metallic gold, with no evidence that the Au(I) complex is present. This result is consistent with ion-chromatographic analysis that showed that residual free cyanide is present after adsorption. Scanning electron micrographs of gold loaded chalcopyrite showed that the metallic gold accumulates on the edges and at dislocations, i.e. defect sites on the surface of the mineral. The fact that visible metallic gold was only found on defect sites suggests that gold cyanide reacts with the oxidised copper phase that is present at these sites. Adams *et al.* (1996) could not detect any visible gold on pyrite by SEM, because of the same reasons as given above. They, however, ascribes the gold adsorbing properties of pyrite to the semiconductor properties of sulphide minerals and suggested that the mechanism of adsorption of aurocyanide onto pyrite involves an electrochemical reduction, with the formation of metallic gold on the surface.

Habashi (1978), who investigated the chemistry and metallurgy of chalcopyrite, suggested that chalcopyrite undergoes aqueous oxidation in neutral and alkaline solutions with the slow formation of cupric hydroxide. He also showed that when both copper and gold are present in a cyanide solution the polymeric AuCNCuCN compound is formed. The insoluble AuCN tends to become reduced in alkaline solution, with the formation of metallic gold (Au^0) and $Cu(CN)_2^-$.

The small amounts of gold adsorbed by quartz and kaolin can be related to surface-charging effects and the surface area of the minerals. According to Adams *et al.* (1996) the amount of gold adsorbed by silicate minerals, such as quartz and kaolin, is mainly dictated by the available surface area. They observed different gold loadings on quartz samples with different surface areas. Mössbauer spectroscopy showed that no metallic gold was present on the quartz, suggesting that the silicate minerals contain only chemically bound gold in the form of $Au(CN)_2^-$. Petersen (1997) found that gold adsorbed onto quartz, and did not merely attach physically to the surface and showed through infra-red tests that $Au(CN)_2^-$ was present on the mineral surface. He also found that at a pH of 12 the loading of gold on quartz was approximately one third of the gold loading at a pH of 10, which indicates that the adsorption phenomenon is probably electrostatic in nature.

Other investigators suggested that the edges of clay minerals, such as kaolin, exhibits surface-charging effects owing to the hydroxylation and ionisation of broken Al-O and Si-O bonds, and their activation by cationic species. They also stated that ion-exchange is possible between the free hydroxyl groups at the edges of the layer planes of clay minerals and anions in solution.

5.2 CYANIDATION OF PURE MINERALS

Gold adsorption experiments showed that gold was adsorbed onto all the minerals studied. To determine the effect that pregrobbing by these minerals will have on a CIP or RIP plant, it was necessary to investigate whether the pregrobbed gold could be recovered by cyanidation. The loaded minerals were leached in a potassium cyanide solution and then analysed for gold. The results and experimental conditions are shown in Table 5.2.

It was possible to obtain over 90 % desorption of adsorbed gold from all the minerals. In the presence of potassium cyanide, chalcopyrite and pyrite showed relatively complete desorption of gold. Although the percentage desorption of adsorbed gold for chalcopyrite and pyrite were more or less the same as that of quartz and kaolin, the leaching of these minerals were not as effective as that off the silicate minerals. Small amounts of gold could not be removed from the sulphide minerals by cyanidation, possibly because of chemical reactions and electrochemical reduction between the gold and the mineral surface. It is also possible that some of the desorbed gold could have readsorbed on the minerals during cyanidation. This is not a problem and can be overcome by using an ion-exchange resin or activated carbon in the leaching solution. It must, however, be stated that the chalcopyrite and pyrite samples used in this study was not exposed to oxidation. Severe oxidation of these minerals was not investigated but it is possible that the oxidation state of these minerals can influence its adsorption and leaching behaviour.

The desorption of adsorbed gold of the silicate minerals, quartz and kaolin, were close to 100 %. Urban *et al.* (1973) showed that the adsorption of gold onto some silicate minerals is a slow, reversible phenomenon that is reduced by an increase in cyanide levels. Taking in account that no activated carbon or ion-exchange resin was used during leaching, only very small amounts of gold were not removed by cyanidation. The remaining gold can possibly be explained by the presence of small cracks on the particles, which can potentially trap aurocyanide ions.

In general, gold could successfully be removed from the minerals investigated in the presence of potassium cyanide. The adsorption phenomenon can possibly be totally reversible if activated carbon or an ion-exchange resin is present in the leaching solution. The pregrobbing effect of these minerals would therefore, probably not be a problem in most CIP or RIP plants.

5.3 ADSORPTION VERSUS PHYSICAL ATTACHMENT

Although the results in Table 5.1 clearly shows that gold is adsorbed onto the minerals, further tests were conducted to confirm the physical adsorption of gold, and that it was not merely an attachment onto the surface of the minerals particles.

In the tests the mineral samples were loaded in a synthetic aurocyanide solution under the same conditions as the adsorption studies in section 5.1. The loaded minerals were then removed from the solution and a portion of each mineral sample were analysed for gold. The remaining loaded mineral samples were thoroughly washed with water and then analysed for gold.

The results (Table 5.3) show the presence of gold with a loading equivalent of 25 and 35 per cent of the initial gold concentration for the kaolin and quartz samples respectively. Only a small percentage of gold was removed from the sulphide minerals by washing, with pyrite and chalcopyrite showing a 30 and 19 per cent gold loss, respectively. The small gold losses by these minerals confirms that the gold adsorption onto these minerals is more chemical and electrochemical in nature and not so much a surface area effect.

5.4 GOLD ADSORPTION ONTO PREGROBBING ORES

The gold adsorbing properties of several pregrobbing gold ores were investigated by contacting the ores with a synthetic aurocyanide solution. The ores were analysed for gold loading, organic carbon and pyritic sulphur content prior to contact with the aurocyanide solution. The organic carbon content was found to vary between 0.5 and 0.9 per cent, which is relatively high for gold ores and probably responsible for the pregrobbing characteristics of the ores.

Table 5.4 shows the results and conditions of the gold adsorption experiments. The ores all showed some adsorption of gold. The ores containing the highest levels of organic carbon content had in general the higher gold loadings. Figure 5.1 shows that there is an approximate linear correlation between the amount of gold adsorbed by the ore and the total content of organic carbon in the ore. However, according to Osseo-Asare *et al.* (1984), this is not always the case, because of the different activities associated with the organic carbon in the ores as well as varying amounts of hydrocarbons and organic acids that are present and to a smaller extent the varying pyritic sulphur contents of the ores.

Table 5.1 and 5.4 show that the gold uptake by the silicon minerals was considerably less than that of the carbonaceous ores. This suggests that there is a greater degree of chemical interaction between the $Au(CN)_2^-$ complex and the carbon containing surface functional groups on the carbonaceous ores than with the silicon containing functional groups on the silicon minerals.

5.5 CYANIDATION OF PREGROBBING ORES

After adsorption the loaded ores were leached in a potassium cyanide solution without the presence of activated carbon or an ion-exchange resin. The purpose of the experiments in this section were to determine the gold recovery from the loaded ores by conventional cyanidation. The use of an ion-exchange resin during cyanidation of the pregrobbing gold ores (resin-in-leach) will be discussed in Chapter 6. The results of the desorption experiments are shown in Table 5.5.

The desorption efficiencies were low for all the ores, especially those with a high organic carbon content. The low desorption efficiencies can be ascribed to the relative high initial gold contents of the ores and because there was no activated carbon or ion-exchange resin present to adsorbed the gold as it goes into dissolution. It is therefore, possible that the dissolved gold could have been pregrobbed by the carbonaceous material in the ore.

To obtain more information on the gold adsorption properties of the ores, washing experiments similar to those described above were carried out (Table 5.6). The percentage gold loss on the ores due to washing was low for all the ores. The correlation between the efficiency of gold desorption and the total organic carbon content of the ore, and the fact that only small amounts of gold were removed by washing, illustrates that the presence of carbonaceous material in gold ores probably has a greater effect than that of the mineral phase.

Table 5.1 - The adsorption of gold onto pure minerals.

Conditions

pH: 11
Time: 24 hours
Stirring speed: 300 rpm
Mass of mineral: 30 g
Volume of solution: 500 ml

Mineral	Initial gold on mineral (g/t)	Gold addition (mg/l)	Final gold on mineral (g/t)
Kaolin	0.00	150	15.37
Quartz	0.00	150	16.04
Pyrite	0.00	150	55.90
Chalcopyrite	0.00	150	97.20

Table 5.2 - The desorption of gold from pure minerals.

Conditions

pH: 11
Time: 24 hours
Stirring speed: 300 rpm
Mass of mineral: 30 g
Volume of solution: 500 ml

Mineral	Gold on mineral after adsorption (g/t)	KCN addition (mg/l)	Gold on mineral after desorption (g/t)	Desorption (%)
Kaolin	15.37	200	0.45	97.07
Quartz	16.04	200	0.62	96.13
Pyrite	55.90	200	3.74	93.31
Chalcopyrite	97.20	200	3.90	95.99

Table 5.3 - The loss in gold content on pure minerals due to washing.

Conditions

pH: 11
Time: 24 hours
Stirring speed: 300 rpm
Mass of mineral: 30 g
Volume of solution: 500 ml
Gold addition: 150 mg/l

Mineral	Gold on mineral after adsorption (g/t)	Gold on mineral after washing (g/t)	Loss due to washing (%)
Kaolin	9.22	2.27	75
Quartz	15.87	5.70	64
Pyrite	47.78	33.30	30
Chalcopyrite	83.48	67.54	19

Table 5.4 - The adsorption of gold onto pregrobbing ores.

Conditions

pH: 11

Time: 24 hours

Stirring speed: 300 rpm

Mass of mineral: 50 g

Volume of solution: 500 ml

Gold addition: 50 mg/l

Ore	Initial gold on ore (g/t)	Final gold on ore (g/t)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	7.02	37.20	0.90	1.30
No. 2	5.73	9.67	0.50	1.70
No. 3	5.20	18.32	0.59	5.20
No. 4	10.00	24.30	0.70	0.40
No. 5	1.25	32.21	0.90	0.75

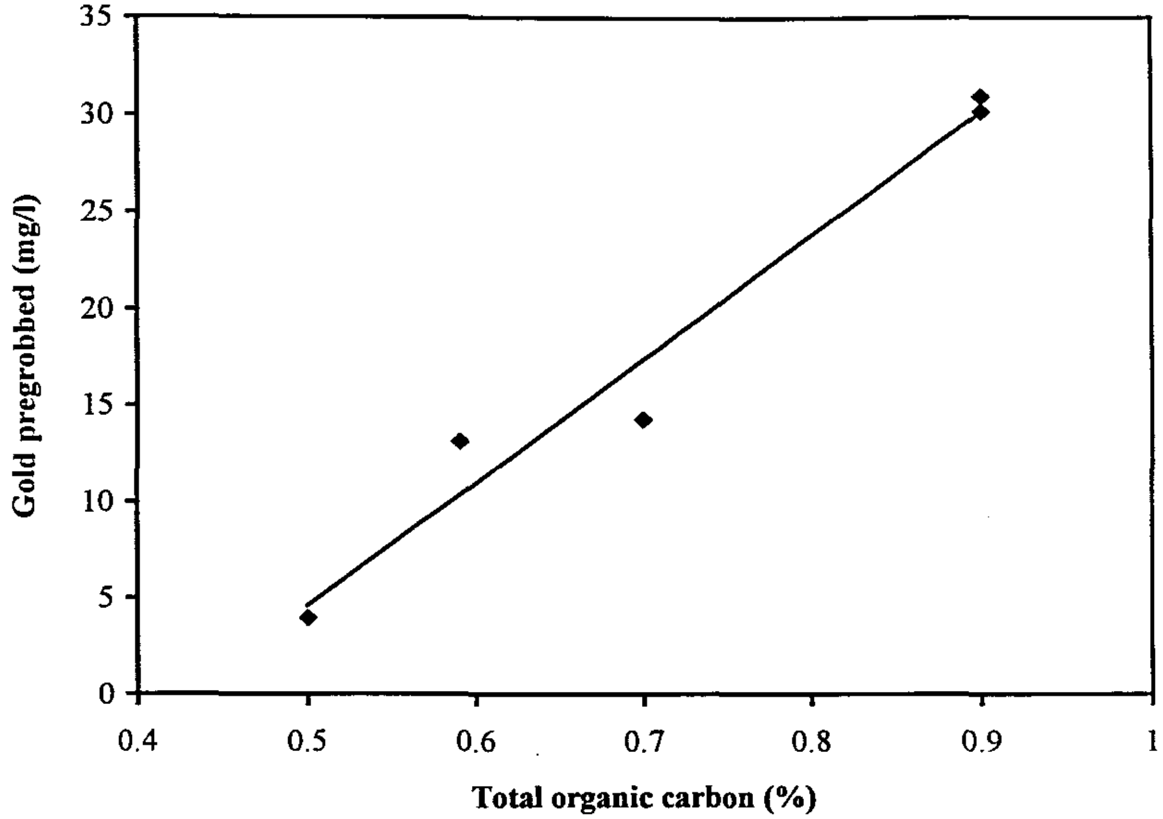

Figure 5.1 - **Effect of the total content of organic carbon on the quantity of gold adsorbed by the pregrobbing ores.**

Table 5.5 - The desorption of gold from loaded pregrobbing ores.

Conditions

pH: 11

Time: 24 hours

Stirring speed: 300 rpm

Mass of mineral: 50 g

Volume of solution: 500 ml

KCN addition: 200 mg/l

Ore	**Gold on ore after adsorption (g/t)**	**Gold on ore after desorption (g/t)**	**Desorption (%)**	**Organic carbon (%)**	**Pyritic sulphur (%)**
No. 1	37.20	21.54	42	0.90	1.30
No. 2	9.67	6.03	38	0.50	1.70
No. 3	18.32	6.88	62	0.59	5.20
No. 4	24.30	11.59	52	0.70	0.40
No. 5	32.21	17.33	46	0.90	0.75

Table 5.6 - **The loss in gold content on pregrobbing ores due to washing.**

Ore	Gold on ore after adsorption (g/t)	Gold on ore after washing (g/t)	Loss due to washing (%)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	37.20	32.56	12	0.90	1.30
No. 2	9.67	9.40	3	0.50	1.70
No. 3	18.32	13.44	27	0.59	5.20
No. 4	24.30	16.52	32	0.70	0.40
No. 5	32.21	25.63	20	0.90	0.75

CHAPTER 6

RECOVERY OF GOLD FROM PREGROBBING ORES

In the previous chapter it was established that the gold adsorbing properties and the poor leaching behaviour of pregrobbing ores are generally attributable to the presence of carbonaceous matter and, to a lesser extent, sulphide minerals. These pregrobbing components have the ability of adsorbing dissolved gold from cyanide solutions. Also, gold may be associated with these components in the ore and not be leached by the cyanide complexing agents used in conventional cyanidation techniques. The pregrobbing ores used for experimentation in this chapter were therefore, analysed for pyritic sulphur and organic carbon content and it was assumed that these components are responsible for the pregrobbing characteristics of the ores. The extent of pregrobbing by these ores was therefore, explained in terms of the organic carbon and pyritic sulphur contents of the ore. A possible correlation between the efficiency of gold extraction and total organic carbon and pyritic sulphur content were also investigated.

As discussed in Section 2.3.3, several techniques have been employed to counteract the detrimental effect of these ores during the recovery of gold and that the success of these processing methods, or a combination of methods, depends mainly on the m 1 mineralogy of the ore. Off these processes, resin-in-leach and the use of surfactants are some of the more promising methods. The work in this chapter therefore, focuses on the use of an ion-exchange resin in the leaching solution and preliminary tests on the influence of certain organic compounds or surfactants on the leaching efficiency of pregrobbing ores.

Three scenarios for the recovery of gold from the different pregrobbing ores were investigated namely, (1) the conventional cyanidation of the ores in a potassium cyanide solution, (2) cyanidation in the presence of a gold selective resin (RIL) and, (3) cyanidation in the presence of a resin and an organic blinding agent.

6.1 CONVENTIONAL CYANIDATION OF PREGROBBING ORES

When a carbonaceous gold ore is leached the aurocyanide produced is readily adsorbed by the carbonaceous matter and the solution robbed of its gold. It was mentioned in section 2.3.2 that several investigators have shown that the natural carbonaceous matter associated with pregrobbing gold ores often behaves like activated carbon when in contact with aurocyanide solutions. Dissolution of gold proceeds until chemical equilibrium is attained between the cyanide complex adsorbed by the ore and the cyanide complex in solution. The remaining gold on the ore at equilibrium therefore, either dissolved gold that was readsorbed by the ore or gold that was associated with the pregrobbing components that could not be leached, is gold that was pregrobbed by the ore. To determine the pregrobbing effect of the carbonaceous matter in the ores investigated, leaching experiments with potassium cyanide were conducted. The results and experimental conditions are shown in Table 6.1.

All the ores pregrobbed gold to a certain degree. Very low recoveries were especially obtained from ores 1, 2, 3 and 5. The low recoveries of ores 1 and 5 are attributed to their high organic carbon content. Although ore no. 3 contains only 0.59 % organic carbon, it is possible that the high pyritic sulphur content can be responsible for its poor leachability. Ore no. 2 showed a very low gold recovery and it is obviously a highly pregrobbing ore. It is difficult to conclude why such a low recovery was obtained, because in comparison with the other ores it has a relative low organic carbon and pyritic sulphur content. It is possible that the natural carbon in the ore has a very high activity for gold adsorption or that the organic carbon in the ore is associated with high levels of organic acids (refer to Section 2.3.2.3), such as humic acid, which contain surface functional groups that are capable of forming strong chemical bonds with aurocyanide complexes to form organic gold compounds which cannot be dissolved by cyanide.

6.2 CYANIDATION IN THE PRESENCE OF AN ION-EXCHANGE RESIN

In the resin-in-leach (RIL) process an ion-exchange resin is added to the leaching solution to compete with pregrobbing species for the gold cyanide complex. This process works on the principle of using an adsorbent with a higher activity than the carbonaceous matter in the ore. During leaching the gold in the ore is dissolved by the cyanide and the majority of the forming gold cyanide complex is adsorbed by the more strongly adsorbent, the ion-exchange resin, until the concentration of gold on the resin is in chemical equilibrium with the concentration of gold on the carbonaceous material. Therefore, if pregrobbing materials exhibit cycles of gold adsorption and desorption, a shifting in equilibrium conditions by adding a resin to the leaching process, could result in lowering the contribution of the pregrobbing characteristic of the ore.

The different types of ion-exchange resins used in this study (Section 3.1) were compared in clear gold cyanide solutions and in solutions containing other base metal cyanide complexes to determine the most effective resin to use with the pregrobbing ores. The gold selective resin had a higher gold loading capacity than the other commercial resins in the solution containing other base metal cyanides that compete with gold for resin sites. Since the pregrobbing gold ores also contain other base metals, it was decided that the gold selective resin will have the biggest impact on the pregrobbing characteristics of the ore and is therefore, used for all the resin-in-leach experiments in this chapter.

The results and conditions of the second-stage tests, i.e. the contacting of the pregrobbing ores with a gold selective resin in the presence of potassium cyanide are shown in Table 6.2. All the ores showed an increase in gold recovery. Although ores 1 and 5 showed the largest increase in gold recovery, they still had the lowest overall recovery. The high organic carbon contents of these ores are probably responsible for this. Acceptable gold recoveries were obtained from ore 4 with an 89 per cent recovery. Very low gold recoveries were obtained from ore no. 2. Except for the reasons given in the previous section, it is not possible to explain the poor leaching behaviour of this ore with the information available. A complete mineralogical analysis of this ore (which was not performed in this study) is necessary to identify and characterise the possible pregrobbing components.

In general the increases of between 11 to 33 per cent obtained (Figure 6.1), illustrates that aurocyanide is adsorbed by the carbonaceous matter in the ore and that the presence of a resin that competes with the pregrobbing components for the gold cyanide complex can be an effective method of treating these ores.

6.3 CYANIDATION IN THE PRESENCE OF A RESIN AND AN ORGANIC COMPOUND

The aim of the work in this section was to investigate the effects of organic additives and surfactants on aurocyanide uptake by pregrobbing ores. Organic compounds or surface-active agents (surfactants) are described as blinding agents because they are capable of passivating the surfaces of the carbonaceous matter in the ore by being adsorbed preferentially to the gold cyanide complex (refer to section 2.3.3.5).

The literature reviewed was not consistent in its explanation on the exact mechanisms by which these organic compounds inhibit gold adsorption by carbonaceous ores. It was postulated that these compounds would adsorbed on the solid as anionic species, thereby imparting a negative charge to the solid/aqueous interface. The electrostatic repulsion between the highly charged negative solid surface and the $Au(CN)_2^-$ anion might then prevent the adsorption of the aurocyanide ion. A second explanation was that these organic additives would coat the surface of the ore and, by limiting the number of available surface sites, inhibit gold uptake.

According to Abotsi and Osseo-Asare (1987) both the hydrophobic and electrostatic interactions are important. They concluded through electrophoretic mobility experiments that above a pH of 3, the surfaces of the various solids in the ore investigated were negatively charged, which results in a repulsion between the negatively charged solids and the aurocyanide anion. They also observed an increase in gold adsorption by the ore with a decrease in pH and explained this due to a decrease in the electrostatic repulsion since the electrophoretic mobility results indicated that the surfaces of the solids were less negative with a decrease in pH. It is a well known fact, however, that activated carbon adsorbs organic compounds and it is therefore, possible that the adsorption of the organic additives can limit the available surface sites on the carbon for the adsorption of the gold cyanide complex. These two mechanisms were found to be adequate to explain the effectiveness of organic compounds to decrease the activity of the pregrobbing carbonaceous matter in the ore.

The combination of the use of surfactants with an adsorbent-in-leach system for treatment of pregrobbing gold ores is not a new concept. The only adsorbent used with surfactants up to now, however, is activated carbon. Activated carbon is not the best choice, because if the surfactant is capable of blinding the carbonaceous matter in the ore it will also blind the activated carbon to some extent, especially at high dosages. Ion-exchange resins not only have potentially higher loading capacities and loading rates than activated carbon, but are also less likely to be poisoned by organic matter such as surfactants. The combination of the gold selective resin used in this study and a surfactant should therefore, be more effective in minimising the adsorptive properties of the carbonaceous material in the ores.

The organic blinding agents used in this study were diesel, kerosene, sodium lauryl sulphate (SLS), tricaprylylmethylammonium chloride (Aliquat 336) and dodecylamine (DDA). The organic compounds were chosen to cover a range of properties, such as ionicity, emulsification effects and water solubility and on the basis of their possible interactions with the carbonaceous ore and/or the aurocyanide complex. Relative high dosages (up to 1%) of these blinding agents were used to investigate its effect on the pregrobbing characteristics of ores 1, 2 and 3. These ores were chosen on the basis of their varying organic carbon and pyritic sulphur content and because very low gold recoveries were obtained from these ores in the resin-in-leach experiments. The results and conditions of the experiments are shown in Table 6.3 to Table 6.7.

Since traditional plant practice entails the addition of diesel or kerosene to the pregrobbing ore, it was decided to use these compounds as a reference to evaluate the performance of the other compounds tested. Although increases in gold recoveries of up to 34 % were obtained, none of the compounds sufficiently inhibit the adsorption of gold by the pregrobbing material to provide acceptable overall gold recoveries, with some off the compounds even having a negative impact on the gold recoveries. Figures 6.2 to 6.4 illustrate the gold recoveries obtained in the presence of the organic compounds. The addition of diesel had a positive effect on the leaching behaviour of all the ores, but for ores 1 and 2 the overall recoveries of 60 % and 47 % respectively, are still low and would probably not be acceptable to any gold plant. Kerosene was less effective than diesel in the case of ore 3 which had a 63 % recovery, but gave more or less the same recoveries than diesel for the other two ores.

SLS was overall the most effective reagent, which resulted in a 34 % increase in the recovery obtained for ore 2. SLS form anionic species in solution and according to Abotsi and Osseo-Asare (1987) who investigated similar anionic reagents, the anionic species adsorb onto the negatively charged carbonaceous particles resulting in an increase in the negative charge of the carbonaceous solid/water interface. The anionic surfactant therefore, depresses gold loading onto the carbonaceous ore as a result of the repulsion between the highly negatively charged ore particles and the $Au(CN)_2^-$ anion.

DDA, and to a lesser extent Aliquat 336, both had a negative effect on gold recovery. Significant decreases in gold recoveries of up to 25 % were obtained for ores 1 and 3 in both cases and only slight increases were observed for ore 2. These results are more or less in agreement with that observed by Abotsi and Osseo-Asare (1987) using the same surfactants. Aliquat 336, which is completely cationic and DDA, which forms cationic and neutral species, enhances gold uptake by the carbonaceous ore, presumably by acting as an activator linking the negatively charged aurocyanide complex to the negatively charged solid surface.

From Figure 6.5, which compare the gold recoveries obtained from ores 1, 2 and 3 when applying the different organic additives, it appears if no correlation exists between the organic carbon and pyritic sulphur content and the gold recoveries obtained. On average the lowest gold recoveries were obtained for ore 2, which has the lowest organic carbon content. Moreover, certain ores reacted positively to a specific organic compound whereas other ores reacted negatively to that same compound. Since there is such a vast difference in the mineralogy of pregrobbing ores and the fact that different pregrobbing ores have different gold activities, as well as varying amounts of hydrocarbons and humic acids present, it may prove best to optimise the blinding conditions for each specific ore by treating each type of ore with a specific organic compound.

Table 6.1 - Conventional cyanidation of pregrobbing ores.

Conditions

pH: 11

Time: 24 hours

Stirring speed: 300 rpm

Mass of mineral: 50 g

Volume of solution: 500 ml

KCN addition: 200 mg/l

Ore	Initial gold on ore (g/t)	Gold on ore after leaching (g/t)	Recovery (%)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	7.02	4.92	30	0.90	1.30
No. 2	5.73	4.80	16	0.50	1.70
No. 3	5.20	2.36	55	0.59	5.20
No. 4	10.00	2.18	78	0.70	0.40
No. 5	1.25	0.89	29	0.90	0.75

Table 6.2 - **Cyanidation of pregrobbing ores in the presence of a gold selective resin (RIL).**

Conditions

pH: 11
Time: 24 hours
Stirring speed: 300 rpm
Mass of mineral: 50 g
Volume of solution: 500 ml
KCN addition: 200 mg/l
Resin volume: 5 ml

Ore	**Initial gold on ore (g/t)**	**Gold on ore after RIL (g/t)**	**Recovery (%)**	**Organic carbon (%)**	**Pyritic sulphur (%)**
No. 1	7.02	3.06	56	0.90	1.30
No. 2	5.73	4.02	30	0.50	1.70
No. 3	5.20	1.75	66	0.59	5.20
No. 4	10.00	1.10	89	0.70	0.40
No. 5	1.25	0.47	62	0.90	0.75

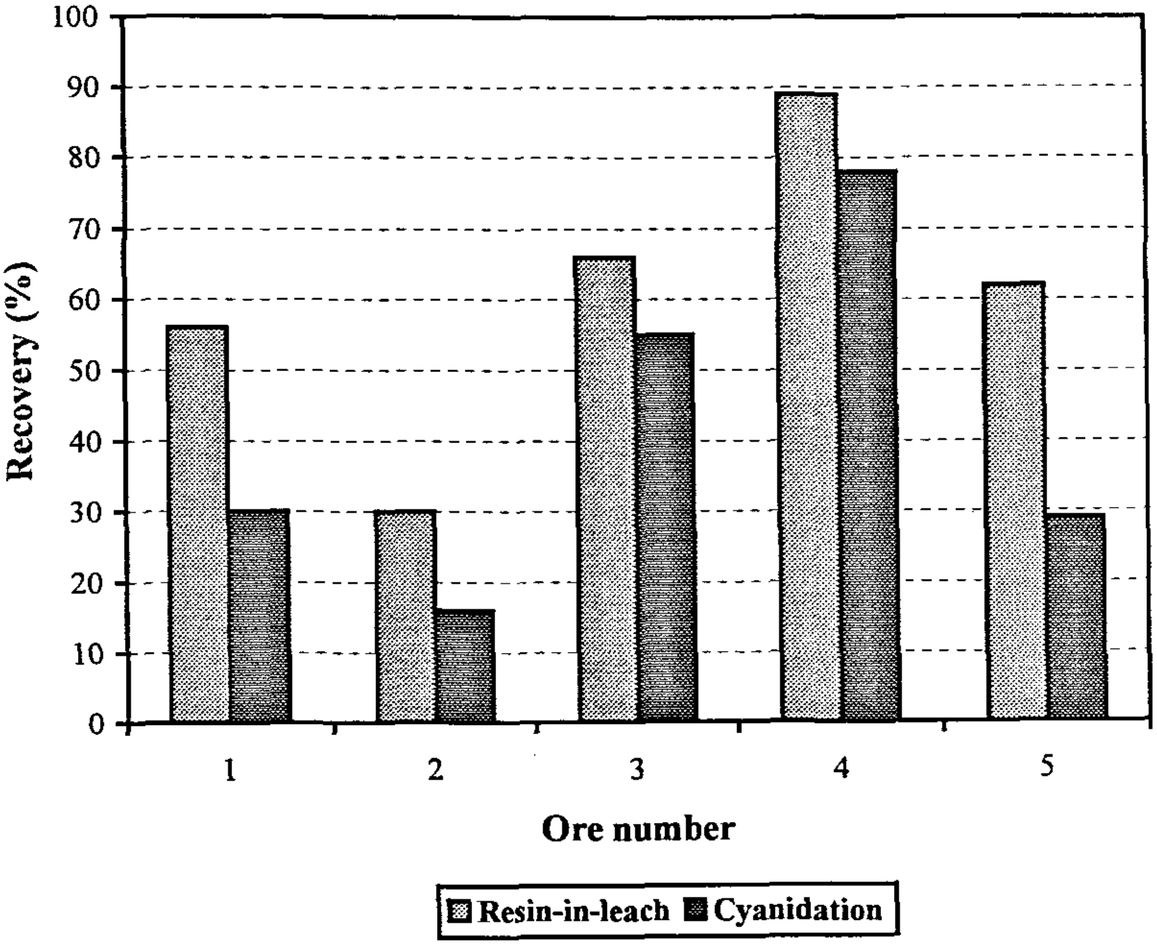

Figure 6.1 - **Percentage increase in gold recovery by making use of an ion-exchange resin in the leaching solution.**

Table 6.3 - **Cyanidation of pregrobbing ores in the presence of a gold selective resin and diesel.**

Conditions

pH: 11
Time: 24 hours
Stirring speed: 300 rpm
Mass of mineral: 50 g
Volume of solution: 500 ml
KCN addition: 200 mg/l
Resin volume: 5 ml
Diesel addition: 1 %

Ore	Initial gold on ore (g/t)	Gold on ore after RIL (g/t)	Recovery (%)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	7.02	2.78	60	0.90	1.30
No. 2	5.73	3.02	47	0.50	1.70
No. 3	5.20	1.16	78	0.59	5.20

Table 6.4 - Cyanidation of pregrobbing ores in the presence of a gold selective resin and kerosene.

Conditions

pH: 11

Time: 24 hours

Stirring speed: 300 rpm

Mass of mineral: 50 g

Volume of solution: 500 ml

KCN addition: 200 mg/l

Resin volume: 5 ml

Kerosene addition: 1 %

Ore	Initial gold on ore (g/t)	Gold on ore after RIL (g/t)	Recovery (%)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	7.02	2.66	62	0.90	1.30
No. 2	5.73	2.92	49	0.50	1.70
No. 3	5.20	1.94	63	0.59	5.20

Table 6.5 - Cyanidation of pregrobbing ores in the presence of a gold selective resin and sodium lauryl sulphate (SLS).

Conditions

pH: 11
Time: 24 hours
Stirring speed: 300 rpm
Mass of mineral: 50 g
Volume of solution: 500 ml
KCN addition: 200 mg/l
Resin volume: 5 ml
SLS addition: 1 %

Ore	Initial gold on ore (g/t)	Gold on ore after RIL (g/t)	Recovery (%)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	7.02	2.44	65	0.90	1.30
No. 2	5.73	2.06	64	0.50	1.70
No. 3	5.20	1.34	74	0.59	5.20

Table 6.6 - **Cyanidation of pregrobbing ores in the presence of a gold selective resin and tricaprylymethyl-ammonium chloride (Aliquat 336).**

Conditions

pH: 11
Time: 24 hours
Stirring speed: 300 rpm
Mass of mineral: 50 g
Volume of solution: 500 ml
KCN addition: 200 mg/l
Resin volume: 5 ml
Aliquat 336 addition: 1 %

Ore	Initial gold on ore (g/t)	Gold on ore after RIL (g/t)	Recovery (%)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	7.02	3.48	50	0.90	1.30
No. 2	5.73	3.22	44	0.50	1.70
No. 3	5.20	2.08	60	0.59	5.20

Table 6.7 - **Cyanidation of pregrobbing ores in the presence of a gold selective resin and dodecylamine (DDA).**

Conditions

pH: 11
Time: 24 hours
Stirring speed: 300 rpm
Mass of mineral: 50 g
Volume of solution: 500 ml
KCN addition: 200 mg/l
Resin volume: 5 ml
DDA addition: 1 %

Ore	Initial gold on ore (g/t)	Gold on ore after RIL (g/t)	Recovery (%)	Organic carbon (%)	Pyritic sulphur (%)
No. 1	7.02	4.50	36	0.90	1.30
No. 2	5.73	3.48	39	0.50	1.70
No. 3	5.20	3.08	41	0.59	5.20

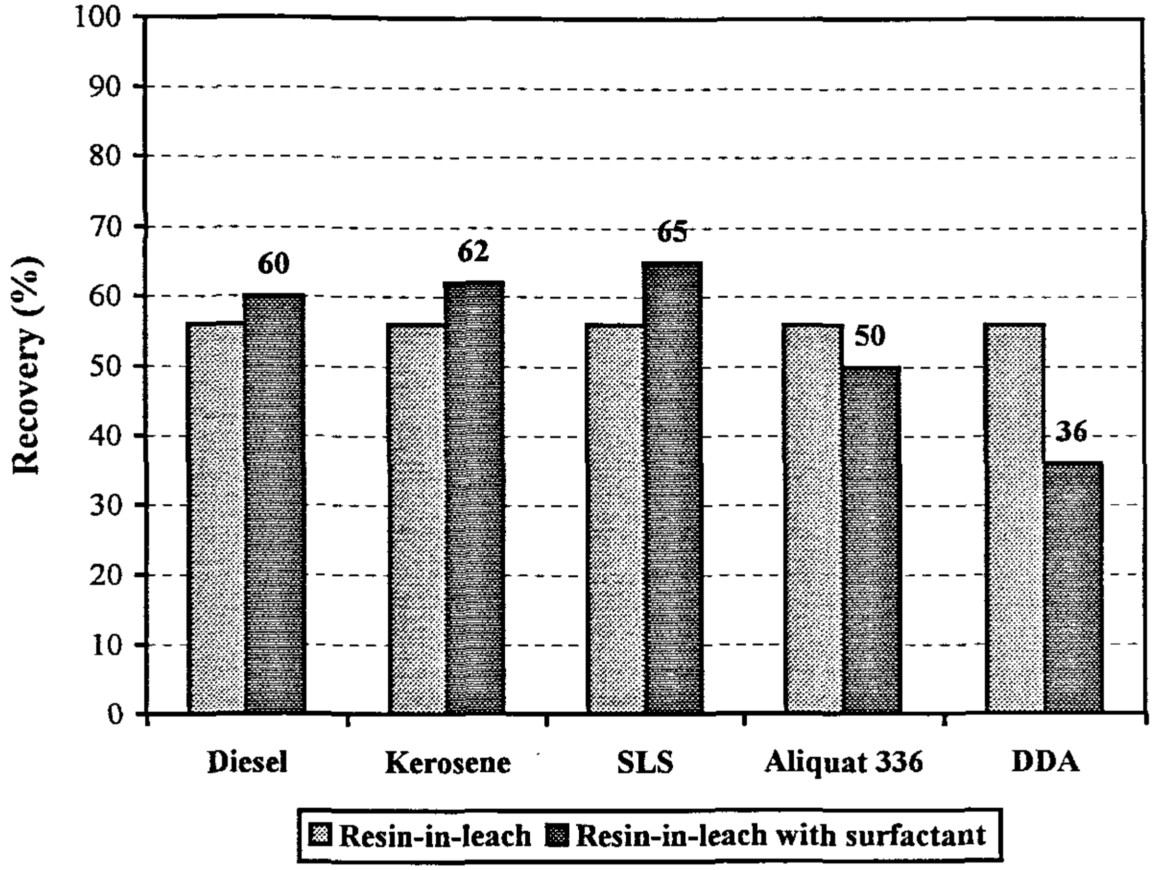

Figure 6.2 - The gold recoveries obtained from ore no. 1 in the presence of the organic compounds.

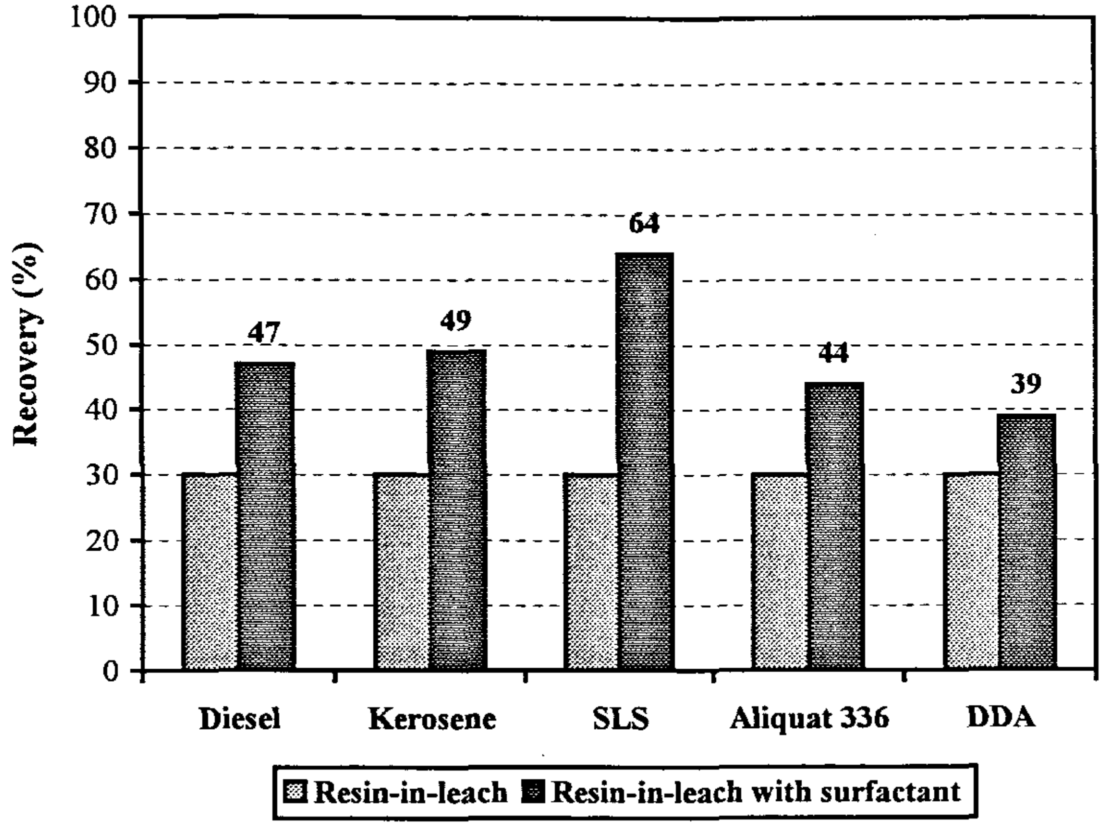

Figure 6.3 - The gold recoveries obtained from ore no. 2 in the presence of the organic compounds.

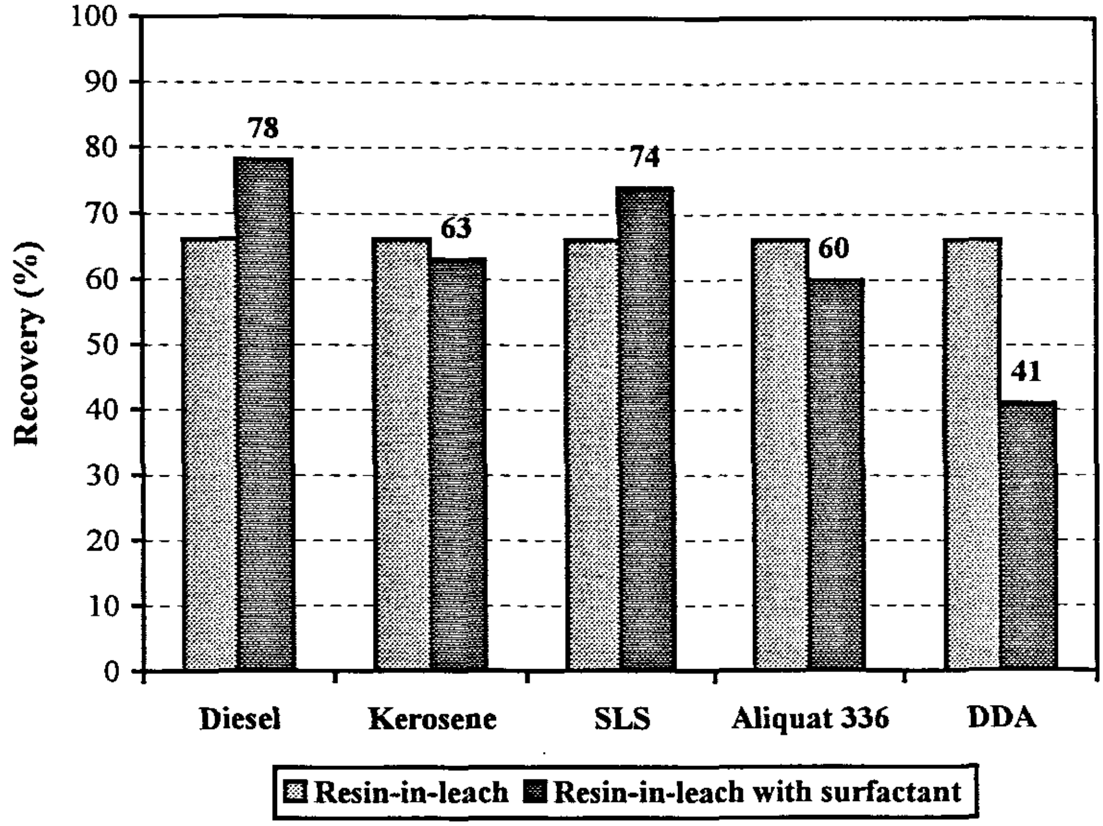

Figure 6.4 - The gold recoveries obtained from ore no. 3 in the presence of the organic compounds.

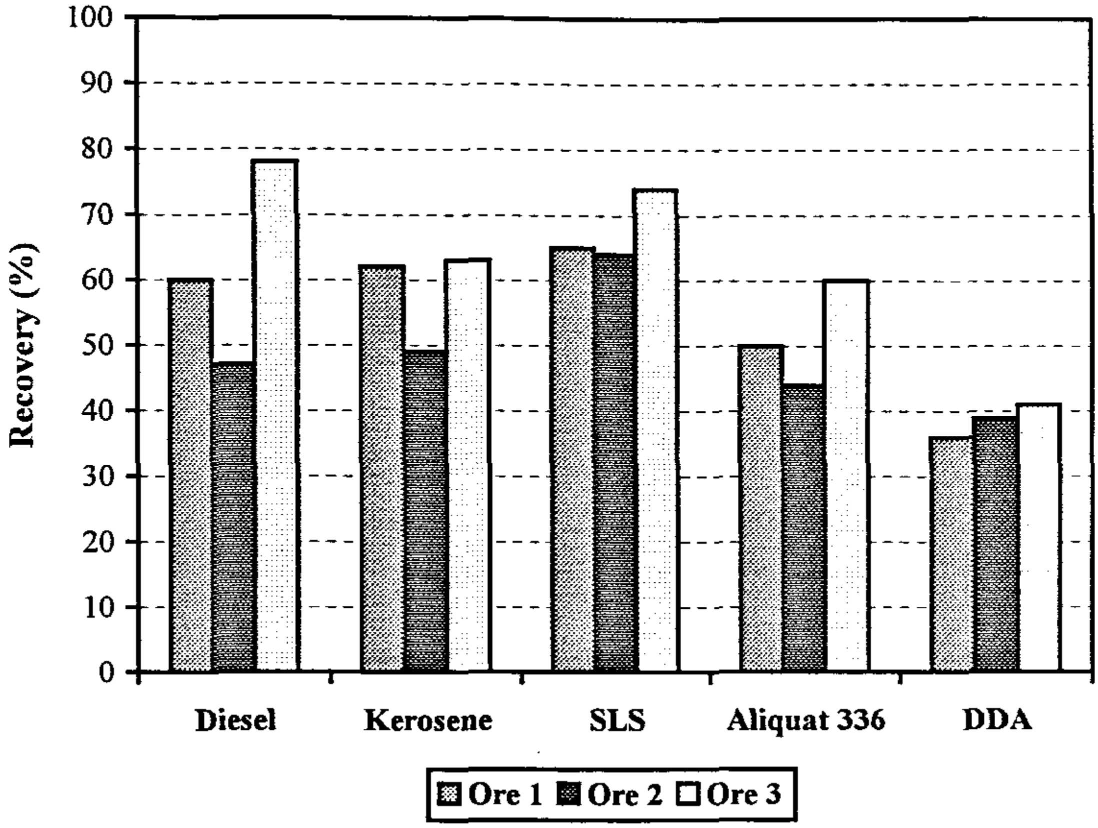

Figure 6.5 - A comparison of the gold recoveries obtained when applying the different organic compounds.

CHAPTER 7

CONCLUSIONS AND SIGNIFICANCE

A literature survey revealed that pregrobbing ores poses a definite problem to the gold mining industry and it is believed that few sites containing primary gold do not exhibit significant and practically irreversible pregrobbing on at least some portions of their ores. There is also a wide range of different treatment processes that were practiced or currently used, with varying degrees of success.

The primary objectives of this study were to investigate the mechanism of pregrobbing by carbonaceous matter in gold ores and to suggest a methodology to minimise the effect of pregrobbing on gold adsorption.

- It was found that pregrobbing is a function of the activity and porosity of the pregrobber, the concentration of gold in the pregnant solution, the gold loading distribution of the adsorbent, and time.

- All the pure minerals investigated adsorbed gold to some extent. The copper and iron sulphide minerals, chalcopyrite and pyrite, were relative strong adsorbers of gold. The silicate minerals, quartz and kaolin, displayed the smallest effect but still adsorbed significant amounts of gold.

- It was postulated that gold adsorbs onto chalcopyrite and pyrite due to chemical reaction and electrochemical reduction, with the formation of metallic gold on the surface of the mineral. Gold adsorption onto the silicate minerals seemed to be related to surface charging effects and the surface area of the minerals.

- Only small amounts of adsorbed gold could be removed from chalcopyrite and pyrite by washing, whereas 64 and 75 per cent of the loaded gold was removed from quartz and kaolin, respectively. This also indicates that the gold adsorption onto sulphide minerals is more chemical in nature and that the adsorption onto the silicate minerals is mainly due to its surface characteristics.

- It was possible to remove most of the gold from the loaded minerals in the presence of cyanide. The adsorption phenomenon is therefore, reversible and the pregrobbing effect of these minerals will probably be minimal in CIP or RIP plants.

- The gold adsorption onto ores containing high organic carbon content were in general the highest. The total organic carbon content can, however, not always be used as a guideline for the pregrobbing potential of an ore, because carbons have different gold activities, as well as varying amounts of hydrocarbons and organic acids present.

- Conventional cyanidation of the pregrobbing ores proved to be ineffective. The poor leaching behaviour of these ores is generally attributable to the presence of carbonaceous matter, which has the ability of adsorbing dissolved gold from cyanide solutions. Dissolution of gold proceeds until chemical equilibrium is attained between the cyanide complex adsorbed by the ore and the cyanide complex in solution.

- The presence of a gold selective resin in the leaching solution that competes with the pregrobbing species for the gold cyanide complex resulted in increased gold recoveries. Increases of between 11 to 33 per cent were obtained. RIL can therefore, be an effective method of treating ores whose only deleterious constituent is moderate concentrations of carbonaceous material.

- The blinding of the carbonaceous material in the ore with organic compounds in a resin-in-leach configuration proved to be an effective combination. Several compounds, of which diesel and SLS were the most effective, were found to have a blinding effect on the ore, reducing the adsorption of gold cyanide.

- For the organic compounds tested, results showed that each type of pregrobbing ore requires a specific blinding agent, since the blinding effect by the reagent may be positive on some ores and negative on others. Optimisation of conditions for blinding would therefore, probably be required for each pregrobbing ore.

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APPENDIX A

TABULATION OF EXPERIMENTAL DATA

CHAPTER 4

EXPERIMENT 1

Batch kinetic results for the adsorption of gold cyanide on a gold selective resin.

Conditions

Initial gold concentration: 30 mg/l

Volume of wet-settled resin: 0.4 ml

Volume of solution: 1.0 L

Stirring speed: 300 rpm

Time: 24 hours

pH: 11

Time (minutes)	Resin	
	C (mg/l)	C/Ci
0	29.36	1.00
5	28.07	0.96
10	27.20	0.93
15	26.21	0.89
20	25.51	0.87
25	24.69	0.84
30	24.11	0.82
60	21.54	0.73
120	17.81	0.61
180	16.06	0.55
240	14.71	0.50
300	13.72	0.47
360	12.91	0.44
1380	9.58	0.33
1440	9.58	0.33

EXPERIMENT 2

Batch kinetic results for the adsorption of gold cyanide on coconut shell activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	Carbon	
	C (mg/l)	C/Ci
0	29.24	1.00
5	28.13	0.96
10	27.37	0.94
15	26.90	0.92
20	26.49	0.91
25	26.20	0.90
30	25.91	0.89
60	24.56	0.84
120	22.98	0.79
180	21.87	0.75
240	21.05	0.72
300	20.58	0.70
360	19.94	0.68
1380	14.79	0.51
1440	14.78	0.51

EXPERIMENT 3

Batch kinetic results for the simultaneous adsorption of gold cyanide on the resin and activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Volume of wet-settled resin: 0.4 ml
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	**Resin + Carbon**	
	C (mg/l)	**C/Ci**
0	29.01	1.00
5	27.19	0.94
10	25.67	0.89
15	24.62	0.85
20	23.62	0.81
25	22.69	0.78
30	21.99	0.76
60	18.48	0.64
120	14.61	0.50
180	11.86	0.41
240	10.34	0.36
300	9.35	0.32
360	8.41	0.29
1380	2.33	0.08
1440	2.27	0.08

EXPERIMENT 4

Batch kinetic results for the adsorption of gold cyanide on 25 % loaded activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	25% loaded carbon	
	C (mg/l)	C/Ci
0	29.82	1.00
5	28.77	0.96
10	28.07	0.94
15	27.67	0.93
20	27.32	0.92
25	27.02	0.91
30	26.73	0.90
60	25.51	0.86
120	24.11	0.81
180	23.23	0.78
240	22.53	0.76
300	22.18	0.74
360	21.83	0.73
1380	18.10	0.61
1440	18.04	0.60

EXPERIMENT 5

Batch kinetic results for the simultaneous adsorption of gold cyanide on the resin and 25% loaded activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Volume of wet-settled resin: 0.4 ml
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	Resin + 25% loaded carbon	
	C (mg/l)	C/Ci
0	29.65	1.00
5	27.90	0.94
10	26.79	0.90
15	25.51	0.86
20	24.40	0.82
25	23.64	0.80
30	22.88	0.77
60	19.21	0.65
120	15.30	0.52
180	12.85	0.43
240	11.10	0.37
300	9.81	0.33
360	8.82	0.30
1380	3.42	0.12
1440	3.40	0.11

EXPERIMENT 6

Batch kinetic results for the adsorption of gold cyanide on 50 % loaded activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	50% loaded carbon	
	C (mg/l)	C/Ci
0	29.35	1.00
5	28.43	0.97
10	27.83	0.95
15	27.46	0.94
20	27.12	0.92
25	26.86	0.92
30	26.60	0.91
60	25.51	0.87
120	24.31	0.83
180	23.57	0.80
240	23.06	0.79
300	22.71	0.77
360	22.43	0.76
1380	20.02	0.68
1440	19.97	0.68

EXPERIMENT 7

Batch kinetic results for the simultaneous adsorption of gold cyanide on the resin and 50% loaded activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Volume of wet-settled resin: 0.4 ml
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	**Resin + 50% loaded carbon**	
	C (mg/l)	**C/Ci**
0	29.06	1.00
5	27.34	0.94
10	25.86	0.89
15	24.94	0.86
20	24.08	0.83
25	23.17	0.80
30	22.48	0.77
60	18.94	0.65
120	15.16	0.52
180	12.99	0.45
240	11.10	0.38
300	9.73	0.33
360	8.87	0.31
1380	4.70	0.16
1440	4.69	0.16

EXPERIMENT 8

Batch kinetic results for the adsorption of gold cyanide on 75 % loaded activated carbon.

Conditions

Initial gold concentration: 30 mg/l

Mass of carbon: 0.5 g

Volume of solution: 1.0 L

Stirring speed: 300 rpm

Time: 24 hours

pH: 11

Time (minutes)	**75% loaded carbon**	
	C (mg/l)	**C/Ci**
0	29.77	1.00
5	28.95	0.97
10	28.42	0.95
15	28.13	0.95
20	27.78	0.93
25	27.49	0.92
30	27.26	0.92
60	26.15	0.88
120	25.04	0.84
180	24.34	0.82
240	23.99	0.81
300	23.58	0.79
360	23.29	0.78
1380	21.83	0.73
1440	21.77	0.73

EXPERIMENT 9

Batch kinetic results for the simultaneous adsorption of gold cyanide on the resin and 75% loaded activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Volume of wet-settled resin: 0.4 ml
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	**Resin + 75% loaded carbon**	
	C (mg/l)	**C/Ci**
0	29.18	1.00
5	27.72	0.95
10	26.27	0.90
15	25.16	0.86
20	24.40	0.84
25	23.64	0.81
30	22.94	0.79
60	19.26	0.66
120	15.36	0.53
180	13.14	0.45
240	11.80	0.40
300	10.75	0.37
360	9.87	0.34
1380	5.96	0.20
1440	5.96	0.20

EXPERIMENT 10

Batch kinetic results for the adsorption of gold cyanide on 50% loaded resin.

Conditions

Initial gold concentration: 30 mg/l

Volume of wet-settled resin: 0.4 ml

Volume of solution: 1.0 L

Stirring speed: 300 rpm

Time: 24 hours

pH: 11

Time (minutes)	50% loaded resin	
	C (mg/l)	C/Ci
0	28.69	1.00
5	28.07	0.98
10	27.78	0.97
15	27.49	0.96
20	27.26	0.95
25	27.03	0.94
30	26.81	0.93
60	26.00	0.91
120	24.35	0.85
180	23.14	0.81
240	22.46	0.78
300	21.77	0.76
360	21.20	0.74
1380	20.62	0.72
1440	20.57	0.72

EXPERIMENT 11

Batch kinetic results for the simultaneous adsorption of gold cyanide on 50% loaded resin and 50% loaded activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Volume of wet-settled resin: 0.4 ml
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	**50% loaded resin + 50% loaded carbon**	
	C (mg/l)	**C/Ci**
0	29.55	1.00
5	28.35	0.96
10	27.72	0.94
15	27.26	0.92
20	26.81	0.91
25	26.23	0.89
30	25.83	0.87
60	24.23	0.82
120	22.34	0.76
180	20.91	0.71
240	19.82	0.67
300	18.79	0.64
360	17.82	0.60
1380	14.84	0.50
1440	14.79	0.50

EXPERIMENT 12

Batch kinetic results for the adsorption of gold cyanide on the treated (increased porosity) activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	Treated carbon	
	C (mg/l)	C/Ci
0	30.56	1.00
5	29.90	0.98
10	29.22	0.96
15	28.59	0.94
20	27.98	0.92
25	27.52	0.90
30	27.17	0.89
60	24.98	0.82
120	23.21	0.76
180	21.29	0.70
240	19.89	0.65
300	19.09	0.62
360	18.27	0.60
1380	12.83	0.42
1440	12.63	0.41

EXPERIMENT 13

Batch kinetic results for the simultaneous adsorption of gold cyanide on the resin and the treated activated carbon.

Conditions

Initial gold concentration: 30 mg/l
Volume of wet-settled resin: 0.4 ml
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	**Resin + Treated carbon**	
	C (mg/l)	**C/Ci**
0	30.85	1.00
5	29.48	0.96
10	27.94	0.91
15	26.32	0.85
20	24.91	0.81
25	23.78	0.77
30	22.62	0.73
60	17.44	0.57
120	12.74	0.41
180	9.42	0.31
240	7.44	0.24
300	5.98	0.19
360	5.01	0.16
1380	1.26	0.04
1440	1.09	0.04

EXPERIMENT 14

Batch kinetic results for the adsorption of gold cyanide on the 50% loaded activated carbon.

Conditions

Initial gold concentration: 10 mg/l
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	50% loaded carbon	
	C (mg/l)	C/Ci
0	10.12	1.00
5	10.05	0.99
10	9.98	0.99
15	9.85	0.97
20	9.71	0.96
25	9.59	0.95
30	9.42	0.93
60	8.80	0.87
120	8.07	0.80
180	7.59	0.75
240	7.13	0.70
300	6.76	0.67
360	6.32	0.62
1380	2.27	0.22
1440	2.27	0.22

EXPERIMENT 15

Batch kinetic results for the adsorption of gold cyanide on the resin.

Conditions

Initial gold concentration: 10 mg/l
Volume of wet-settled resin: 0.4 ml
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	Resin	
	C (mg/l)	C/Ci
0	10.18	1.00
5	9.90	0.97
10	9.69	0.95
15	9.44	0.93
20	9.14	0.90
25	8.91	0.88
30	8.56	0.84
60	7.00	0.69
120	4.89	0.48
180	3.49	0.34
240	2.53	0.25
300	2.05	0.20
360	1.51	0.15
1380	0.00	0.00
1440	0.00	0.00

EXPERIMENT 16

Batch kinetic results for the simultaneous adsorption of gold cyanide on the resin and 50% loaded activated carbon.

Conditions

Initial gold concentration: 10 mg/l
Volume of wet-settled resin: 0.4 ml
Mass of carbon: 0.5 g
Volume of solution: 1.0 L
Stirring speed: 300 rpm
Time: 24 hours
pH: 11

Time (minutes)	Resin + 50% loaded carbon	
	C (mg/l)	C/Ci
0	10.15	1.00
5	9.72	0.96
10	9.41	0.93
15	8.99	0.89
20	8.49	0.84
25	8.08	0.80
30	7.57	0.75
60	5.62	0.55
120	3.60	0.35
180	2.34	0.23
240	1.67	0.16
300	1.33	0.13
360	0.89	0.09
1380	0.00	0.00
1440	0.00	0.00

APPENDIX B

PUBLISHED PAPER

ENVIRONMENTAL IMPROVEMENTS IN MINERAL PROCESING AND EXTRACTIVE METALLURGY (M.A. Sánchez, F. Vergara and S.H. Castro, Eds.) University of Concepción.

INHIBITION OF PREGROBBING BEHAVIOUR DURING GOLD EXTRACTION

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ABSTRACT

The gold adsorbing properties of pure pregrobbing minerals pyrite, quartz, kaolin and chalcopyrite were examined. These pregrobbing minerals showed a very slight pregrobbing effect, which was not significant enough to detect gold losses from a synthetic aurocyanide solution. Gold could be detected on the minerals by the direct analysis of gold on the mineral phase by making use of acid leaching. Pregrobbing ores are mineralogically quantified to identify and characterise the pregrobbing components.

Activated carbon was first used as a model pregrobber in batch kinetic adsorption experiments. Known masses of carbon were pre-loaded in a synthetic gold cyanide solution. The carbon was then added with a gold-selective resin to a clean gold cyanide solution. Preliminary results showed that the effect of pregrobbing is greatly affected by the gold concentration of the solution and that the pregrobbing phenomenon is a function of the gold loading distribution of the resin.

INTRODUCTION

The optimisation of gold recovery in the gold mining industry is an important aspect, which led to various research and development to improve gold extraction in the cyanide process. Only a relative small amount of gold is not extracted by the cyanidation process and the main reasons for this is [Stanley, 1987]:

a) gold enclosed by other minerals, or coated gold, thus shielded from contact with the cyanide solution;
b) gold dissolved during leaching then adsorbed by other minerals or by extraneous matter in the milled pulp;

c) large gold particles incompletely dissolved if the residence time in the cyanide solution was inadequate;
d) incomplete dissolution of gold grains due to galvanic interaction between gold in contact with certain minerals, causing decrease in dissolution rates.

This paper focuses on gold that is pregrobbed by other minerals during the leaching process, where the term pregrobbing refers to the active adsorption of gold from cyanide pregnant solutions by components of the ore. It has been suggested that gold already dissolved by cyanide may be adsorbed by other minerals and by extraneous matter in the pulp. There is no doubt that gold is adsorbed by carbonaceous matter in ore in the form of graphite, amorphous carbon and other minerals. Some debate however, exists over the extent to which gold may be adsorbed onto the surfaces of minerals. Adams and Burger, (1998) identified several pregrobbing minerals, ranging from pyrite, amorphous carbon, copper sulphides, chalcopyrite, quartz and layered silicates, such as kaolin, phlogopite and illite and showed that when a active carbonaceous material is present, the pregrobbing effect is greatly enhanced in the presence of activated carbon.

It has been speculated that pregrobbing is an exchange adsorption phenomenon where gold cyanide complex anions are adsorbed onto surfaces of the adsorbent and other mineral phases. If this is true, the differential gold loading on the adsorbent will therefore affect the extent to which the gold is pregrobbed. In view of the fact that the rate of adsorption of gold cyanide for resin is very much faster compared to activated carbon, one would expect that a gold selective resin could yield good competition for potential pregrobbers. Many studies were done to explain the interaction between gold cyanide and the pregrobbing mineral ore. All of these, however, used activated carbon in solution, whereas the use of a gold selective ion-exchange resin has not been investigated as yet. The aim of this paper is therefore to minimise the effect of pregrobbing by investigating the interaction between a gold-selective ion-exchange resin and a pregrobbing ore.

EXPERIMENTAL PROCEDURE

Materials

Batch kinetic adsorption tests were conducted with a variety of commercial strong and medium base resins, coconut shell activated carbon and a gold selective strong base resin. These adsorbents were added to a clear gold cyanide solution ($KAu(CN)_2$) at room temperature. To ensure an excess of cyanide ions KCN was added to each experiment. The pH was adjusted by adding small amounts of 10 M NaOH to the solution. Only the 1.0 to 2.0 mm sieve size fraction of the carbon was used. All reagents were of analytical grade and distilled water was used throughout.

Samples of milled (80% < 75μm) pure pregrobbing minerals kaolin, pyrite, quartz and chalcopyrite and two different pregrobbing ores were used to investigate their gold adsorption properties.

ENVIRONMENTAL IMPROVEMENTS IN MINERAL PROCESING AND EXTRACTIVE METALLURGY (M.A. Sánchez, F. Vergara and S.H. Castro, Eds.) University of Concepción.

Adsorption Experiments

The adsorption experiments were carried out under the same conditions. A 1-liter Perspex vessel with three evenly spaced baffles was used. All the experiments were conducted at a pH of 11 and were mechanically stirred at a speed of 300 rpm.

Analytical method

The final solutions were analysed for gold using a Perklin Elmer 3300 atomic absorption spectrometer (AA) with an air-acetylene flame and an absorbance peak of 242.8 nm.

The pregrobbing minerals and ores were tested for gold by making use of an acid leaching method [Brazil, 1972]. The rock sample is leached twice with constant stirring with aliquots of freshly prepared aqua regia. The sample is boiled to dryness after adding each aliquot. A third aliquot of aqua regia is added and the temperature of the mixture is raised to near boiling, then cooled slowly to room temperature. The mixture is then filtered and washed with a 5% HCL solution. The final solutions were analysed on a Graphite Tube Atomizer.

RESULTS AND DISCUSSION

Pregrobbing components in gold ores

Pregrobbing is defined as the adsorption of gold cyanide onto minerals in ore. In order to investigate the adsorption of gold cyanide onto minerals, four pure minerals, which were identified by various authors as pregrobbing minerals, were obtained. Milled samples (80% < 75µm) of kaolin, pyrite, quartz and chalcopyrite were each individually added to a clear gold cyanide solution and stirred for 24 hours. The samples were all pretreated and dried prior to analysis. The final solutions were then analysed for gold.

Although different quantities of the minerals were used, no significant gold losses from the solution could be detected. This makes it difficult to quantify the minerals affinity for gold by testing the final solution. To get a more accurate reading, the actual gold loading on the solid was determined by making use of an acid leaching method. Small amounts of gold were detected on the pure minerals, but shown to have a negligible pregrobbing effect in comparison with the carbonaceous phases. The pregrobbing ores adsorbed significant amounts of gold cyanide. The pregrobbing components in the ore are characterised by performing a mineralogical analysis on the ore. Carbonaceous matter in the form of graphite, amorphous carbon (including kerogen) and other minerals were identified.

Another more general way of defining pregrobbing is by viewing it as the inhibition of the leachability of gold from the ore and not the physical adsorption of gold onto the minerals during the leaching process. The experimentation, using this approach, can be divided into three stages to ultimately increase the final gold recovery. The first experiment involves the leaching of the ore sample with a gold recovery of between 50% and 60%.The remaining gold in the ore, therefore the non-leachable gold, is seen as gold that is pregrobbed.

In the second experiment the gold recovery is increased by adding a gold selective resin to the leaching process (resin in leach). A possible explanation for this may be that the resin adsorbs most of the gold as it goes into dissolution, preventing the pregrobbing components from adsorbing it. This supports the scenario that if pregrobbing materials exhibit cycles of gold adsorption and desorption, a shifting in equilibrium conditions associated with the resin, could result in lowering the contribution of the pregrobbing characteristic of the ore.

Finally, surfactants such as diesel or kerosene were added to the leaching process. The surfactants act as organic blinding agents by covering the surfaces of the carbonaceous material and therefore preventing it from adsorbing gold cyanide.

Several attempts have been made in the past to separate the various carbonaceous components from pregrobbing ores, or to blind then. Abotsi and Osseo-Asare, (1986) sequentially treated the ore with hot caustic, acetone, benzene, HF, H_2SO_4 and HNO_3 for periods of 7 to 21 days each, in an attempt to separate various carbon components. Adams and Burger, (1998) reported that surfactants such as NP10, sodium lauryl sulphate and petroleum sulphonate were the best potential blinding agents, but also showed that there are some indications that these reagents also blind the gold surface to some extent, thereby decreasing the leaching efficiency. It is therefore necessary to use a specific surfactant for a specific pregrobbing ore, mainly because of the different mineralogical compositions and gold activities of the ores.

The mechanism of pregrobbing

The mechanism of pregrobbing can be explained by investigating factors such as adsorbent and pregrobber activity, solution concentration, kinetic and equilibrium conditions and the porosity of the pregrobber. In order to investigate the effect of pregrobber activity, batch kinetic adsorption experiments with a gold selective resin and a pregrobber in solution were carried out. Activated carbon was first used as a synthetic pregrobber to simulate the pregrobbing effect of carbonaceous material in ore. The pregrobbing activity of the carbonaceous material in the ore will vary and therefore different degrees of pregrobbing were investigated by pre-loading carbon with gold cyanide.

Carbon samples (0.5g) were loaded at 25%, 50%, and 75% off its equilibrium loading capacity and individually added with the resin to a clear gold cyanide solution. Tests were also done to show that none of the pre-loaded gold on the carbon came off and adsorbed onto the resin during experimentation. The experimental results are shown in Table I and Figure 1 respectively.

The experiments were done over a 24-hour period, where after the carbon and resin particles were separated and analysed to determine their individual gold loading. To compare the rate of the different reactions the film transfer coefficients (k_f) for each experiment were also calculated. The results are given in Table II.

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Table I. Adsorption of gold cyanide (ppm) onto adsorbent and pregrobber

Time (min)	Carbon	Resin	Resin + 100% loaded carbon	Resin + 75% loaded carbon	Resin + 50% Loaded carbon	Resin + 25% Loaded carbon	Resin + 0% loaded carbon
0	30.00	30.00	30.00	30.00	30.00	30.00	30.00
10	29.18	27.92	29.45	28.62	26.89	27.59	26.18
20	27.92	26.18	27.90	26.97	24.98	25.53	24.05
30	27.34	22.89	26.25	25.84	23.16	23.88	22.31
60	26.18	22.40	23.26	23.16	20.28	20.78	18.72
120	24.63	19.01	20.27	19.75	16.74	16.66	14.66
180	23.47	17.17	18.31	17.79	14.34	14.39	12.24
240	22.70	15.82	16.76	16.35	12.72	12.43	10.40
300	22.11	14.85	15.73	15.11	11.57	10.99	9.04
1380	16.98	12.04	12.74	10.27	6.59	3.15	1.78
1440	16.79	11.95	12.64	10.16	6.49	3.36	1.58

The competitive adsorption between adsorbent and pregrobber can clearly be seen from the results. As expected the stronger the activity of the pregrobber the more gold was adsorbed from the solution. The film transfer coefficients increase with an increase in activity, which means that the overall reaction kinetics is also faster. The adsorption profiles of the different experiments

Figure 1. Different degrees of pregrobbing on the adsorption characteristics of the resin (Ci = 30 ppm ; M_{resin} = 0.4ml ; M_{carbon} = 0.5g)

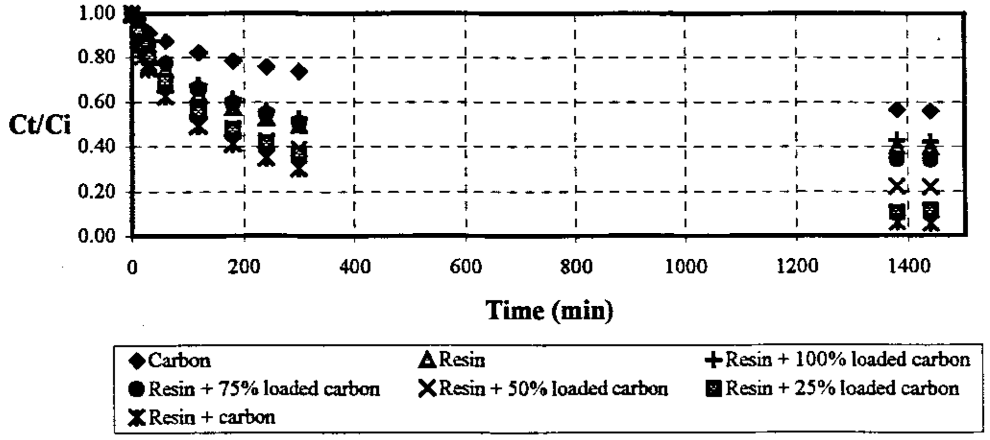

Table II. Gold concentrations in solution and on solids.

	Initial conc.	Equilibrium values	ppm Adsorbed from solution	Initial conc. on carbon	Loading on Solids		K_f
					Carbon	Resin	
Carbon	30	16.79	13.21	0	13.21		8.68E-05
Resin	30	11.95	18.05			18.05	0.000237
Resin + 0% Loaded carbon	30	1.58	28.42	0	10.93	16.37	0.000334
Resin + 25% Loaded carbon	30	3.36	26.64	3.85	12.41	16.99	0.000256
Resin + 50% loaded carbon	30	6.49	23.51	6.46	12.82	17.08	0.000161
Resin + 75% loaded carbon	30	10.16	19.84	10.54	12.95	17.36	0.000116
Resin + 100% loaded carbon	30	12.64	17.36	13.34	13.04	17.65	8.98E-05

however, are the same except for the difference in the kinetic and equilibrium values, therefore given enough residence time and sufficient gold concentrations both the resin and the carbon will reach there equilibrium capacity. It can therefore be assumed, focussing at the different activities of activated carbon, that this adsorption trend will be the more or less the same for all carbonaceous material in ore.

Concentration dependent experiments

The gold cyanide concentration of the solution is an important factor which will effect the kinetic and equilibrium conditions and possibly determine the extent to which pregrobbing will take place. The experiments discussed above were done using high enough gold concentrations so that both the adsorbent and pregrobber can reach their respective equilibrium loading capacity. If the initial gold concentration of the solution is too low for both the adsorbents to reach equilibrium, the effect of the pregrobber on the resin can be different.

Experiments were done with the resin in a clear gold cyanide solution, followed by similar experiments with the resin and a pregrobber (50% loaded carbon) in solution. A 10 ppm gold cyanide solution was used for the first experiment and a 30 ppm gold cyanide solution for the second. The results are shown in Table III. By subtracting the values of A (resin in solution) from B (resin and 50% loaded carbon) in the table, the effect that the pregrobber had on the system can be obtained.

Table III. The effect of pregrobbing on the resin at different gold concentrations

Time (min)	Ci = 10 ppm			Ci = 30 ppm		
	A. Resin	B. Resin + 50% loaded carbon	Effect of pregrobbing	A. Resin	B. Resin + 50% Loaded carbon	Effect of pregrobbing
0	10.00	10.00	0.00	30.00	30.00	0.00
10	9.69	9.41	0.28	28.36	28.33	0.03
20	9.14	8.42	0.72	26.18	26.05	0.13
30	8.56	7.57	0.99	26.01	24.39	1.62
60	7.00	5.62	1.38	22.40	20.59	1.81
120	4.89	3.60	1.29	19.01	16.28	2.73
180	3.49	2.34	1.15	17.17	13.95	3.22
240	2.53	1.67	0.86	15.82	12.40	3.42
300	2.05	1.33	0.72	14.85	11.02	3.83
1380	0.00	0.00	0.00	12.04	4.55	7.49
1440	0.00	0.00	0.00	11.95	4.46	7.48

From the results it is clear that the effect of pregrobbing is much lower at lower gold concentrations. The column in the table named 'effect of pregrobbing', shows the amount of gold cyanide that was adsorbed by the pregrobber from the one time interval to the next.

In the case of the 10 ppm solution, pregrobbing takes place at the beginning of the experiment and decreases as the gold in the solution decreases. In the 30 ppm solution the effect of pregrobbing increases as the gold concentration decreases. The gold concentration of the solution is therefore an important factor concerning to what extent the pregrobbing effect will be on the system and will subsequently determine the resin and pregrobbing activities.

CONCLUSION

Two types of pregrobbing were identified. The one phenomenon is where the gold cyanide is adsorbed by minerals in the gold ore during the leaching process and the second is gold that is hold by the ore and therefore non-leachable.

Pregrobbing minerals were identified and tested for their gold adsorbing properties. Small amounts of gold were detected on pure minerals pyrite, quartz, kaolin and chalcopyrite by analysing the mineral phase, but shown to have a negligible pregrobbing effect in comparison with the carbonaceous phases found in gold ores.

Surfactants were used as organic blinding agents by covering the mineral particles. The carbonaceous material in ores have different activities and it is therefore necessary to use a specific surfactant for a certain pregrobbing ore, but there is also a possibility that it can have a detrimental effect on gold leaching.

Batch kinetic adsorption experiments with a synthetic pregrobber (activated carbon) showed that the effect of pregrobbing is greatly affected by the gold concentration of the solution. The pregrobbing effect was found to be lower at lower gold concentrations.

Preliminary results showed that the pregrobbing phenomenon is a function of the gold loading distribution of the resin and that a shifting in the equilibrium conditions of the resin could result in lowering the effect of pregrobbing.

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APPENDIX C

SUBMITED PAPER

INHIBITION OF THE PREGROBBING PHENOMENON IN GOLD ORES

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Abstract

Activated carbon was used as a synthetic pregrobber in batch kinetic adsorption experiments to simulate the pregrobbing effect of carbonaceous material in gold ores. Results showed that the pregrobbing phenomenon is a function of the activity and porosity of the pregrobber as well as the gold loading distribution of the resin and the gold concentration of the solution.

The gold adsorbing properties of pure minerals pyrite, quartz, kaolin and chalcopyrite were examined. Gold adsorption experiments showed that all the minerals adsorbed gold to some extent, with the copper and sulphide minerals (chalcopyrite and pyrite), having the strongest affinity for gold. It was however, possible to remove most of the gold from the loaded minerals in the presence of potassium cyanide.

Tests on several pregrobbing ores indicated that the organic carbon content of ores poses a problem, with ores of high organic carbon content showing lower gold desorption capabilities. Resin-in-leach studies proved to be much more effective than conventional cyanidation, although low gold recoveries are still possible in some cases. The use of organic blinding agents in a resin-in-leach configuration also proved to be an effective combination of reducing the pregrobbing phenomenon.

1. Introduction

Cyanidation is the most effective and widely used process for the recovery of gold. During the leaching process, where the gold is dissolved in an aqueous alkaline cyanide solution, gold is lost due to a number of reasons. The gold in residues can be ascribed broadly to the following causes [1]:

- Large gold particles incompletely dissolved due to inadequate contact time.
- Refractory gold resulting from coatings on some gold particles. The coatings occur naturally or as a result of the oxidation of pyrite.

- The presence of cyanicides, which consume the cyanide radical and thus inhibit dissolution of gold. This is frequently due to the presence of readily oxidised components, metallic copper and copper compounds.
- Unliberated gold as a result of too coarse a milled product.
- Gold dissolved during leaching, then adsorbed by other minerals or by carbonaceous matter in the pulp.

This study focuses on the latter, where dissolved gold is pregrobbed during leaching by adsorbent materials in the ore. The term pregrobbing refers to the active adsorption of gold from cyanide pregnant solutions by components of the ore [2].

There is no doubt that gold is adsorbed by carbonaceous material in ore, but some debate exists over the extent to which gold may be adsorbed onto surfaces of mineral ore. Urban *et al.* [3] suggested that minerals such as pyrophyllite, pyrite and chalcopyrite are responsible for gold losses. Logan [4], however, found that pyrophyllite, kaolinite, phlogopite and illite do not adsorb detectable amounts of gold from cyanide solution, but that pyrite exhibits some gold adsorbing properties. Hausen and Bucknam [5] also suggested that pyrite is a gold adsorber and showed that small quantities of gold were adsorbed from cyanide solutions onto samples containing approximately 45 % pyrite. Adams *et al.* [6] examined the gold adsorbing properties of a wide variety of minerals, ranging from copper sulphides to clay silicates and quartz, and concluded that copper sulphide minerals yielded the strongest adsorption and that quartz only adsorbed a relatively small quantity of gold, depending on the type of quartz, its surface area, and its surface characteristics. More recently, Rees and van Deventer [7] showed that chalcopyrite and pyrite were very strong pregrobbers and found that silicate and clay minerals were not pregrobbing.

The poor gold extraction by cyanide from carbonaceous ores has been known for many years and is attributed to the pregrobbing characteristic of the carbonaceous matter. The well documented carbonaceous ores from the Carlin Mine, Nevada, was found to be so deleterious to cyanidation that a mixture containing five per cent carbonaceous ore and 95 per cent standard cyanidable ore gives an extraction of 76 per cent gold versus 93 per cent for 100 per cent standard ore [8]. The carbonaceous material associated with these ores have been classified by several investigators [8, 9, 10] into two main components namely: an activated carbon component, (amorphous, graphitic carbon and carbonate carbon) capable of adsorbing gold complexes, and an organic component, which consists of (a) a mixture of high molecular weight long chain hydrocarbons, and (b) organic acids similar to humic acids containing functional groups which form complexes with aurocyanide.

Several techniques have been developed for treating these ores, which include: (a) flotation where the carbon is floated off and discarded; (b) roasting or chemical oxidation to destroy carbonaceous matter, and simultaneously oxidising the sulphide minerals; (c) activated carbon or resin-in-leach pulp where activated carbon or an ion-exchange resin is added to the leaching process to compete with pregrobbing species for the gold cyanide complex; and (d) the use of organic blinding agents which adsorb on the surfaces of the carbonaceous matter.

It will be attempted in this study to elucidate on the mechanism of pregrobbing and to suggest a methodology to minimise the effect of pregrobbing on gold adsorption.

2. Experimental procedures

2.1. Materials

The gold used in the experimental work was in the form of potassium dicyanoaurate, $KAu(CN)_2$, a pure crystalline salt. The leaching experiments were conducted with potassium cyanide (KCN). Sodium hydroxide (10M NaOH) was used to adjust and maintain the pH at the required level. All reagents used in experimental work were of analytical grade, and distilled water was used throughout.

A gold selective strong base anion-exchange resin was used as adsorbent and a coconut shell activated carbon, ANK 11, was used as a synthetic pregrobber in competitive adsorption experiments.

Samples of relative pure minerals, pyrite, chalcopyrite, quartz and kaolin were obtained from various sources. These minerals were thoroughly washed with distilled water, dried at 40 ^{0}C and then ground and screened to obtain the required particle size distribution of 80 % under 75 μm and 20 % between 106 and 75 μm. Six pregrobbing gold ores, from various gold mines, were used in this study. These ores were milled to 80 % < 75 μm and analysed for gold loading, organic carbon and pyritic sulphur content.

Tests with a variety of organic compounds and surface-active agents (surfactants) were conducted. The effects that diesel, kerosene, sodium lauryl sulphate (SLS), tricaprylylmethylammonium chloride (Aliquat 336) and dodecylamine (DDA) have on inhibiting gold adsorption by pregrobbing ores were investigated with the aid of resin-in-leach experiments. The organic compounds were chosen to cover a range of properties, such as ionicity, emulsification effects and water solubility.

2.2. Batch kinetic experiments

All batch kinetic adsorption experiments were conducted in 1 litre perspex batch reactors with four evenly spaced baffles. The reactors were fitted with perspex lids to prevent spillage or evaporation of the solution. The solution was mechanically stirred with a flat blade impeller at a stirring speed of 300 rpm. Before any experiments were conducted, it was determined that no gold cyanide was adsorbed onto the perspex vessel or the stirrer. All the experiments were carried out at room temperature and at a pH of 11.

2.3. Gold adsorption experiments

Milled pure mineral samples were loaded with gold in a synthetic aurocyanide solution at a pH of 11. After 24 hours the solutions were filtered under vacuum using a Buchner flask and funnel. The loaded solids were washed with distilled water to ensure the removal of any entrained gold present on the mineral or ore. The washed mineral and ore samples were then dried overnight in an oven at 40 ^{0}C and analysed for gold.

2.4. Cyanidation experiments

The pure mineral and ore samples were leached in a solution containing approximately 200 mg/l potassium cyanide. The slurry was mechanically stirred for 24 hours, after which it was filtered. The mineral and ore samples were then washed, dried and analysed for gold. As the pH may affect the leaching efficiency, it was maintained at 11 by the addition of small quantities of sodium hydroxide.

The ores used in the resin-in-leach experiments in the presence of an organic additive were pre-conditioned for 1 hour in a solution containing 1 per cent reagent, prior to the addition of potassium cyanide and resin. This pre-conditioning step allows the organic reagent to adsorb onto the carbonaceous particles before the dissolution of gold.

2.5. Analytical methods

The gold concentration in solution was determined with a Perklin Elmer 3300 atomic absorption spectrophotometer (AAS). Calibration standards were prepared from a Merck Titrisol gold standard solution containing 1000 mg gold as tetrachloroauric (III) acid in a 12.7 per cent hydrochloric acid solution.

Two methods were used to determine the gold loading on the activated carbon, the resin and the ores and mineral samples, namely a gravimetric method (fire assay) and a spectrophotometric method (acid leaching). The fire assay analysis was performed by Mintek in South Africa. The spectrophotometric method employed involves the conversion of the gold to $AuCl_4^-$ by dissolving it in an acid and measuring the absorbance due to these ions. The acid used for this purpose is called aqua regia and is generally used for the dissolution of gold for analytical purposes and consists of 82 % hydrochloric acid (HCl) and 18 % nitric acid (HNO_3). The acid leaching procedure followed was as described by Bratzel *et al.* [11].

To determine the gold loading on the carbon and resin particles it was necessary to "ash" the carbon and resin before it could be leached with aqua regia. This was accomplished by placing the carbon or resin in a porcelain crucible and burnt it in a muffle furnace at 800 ^{0}C for about 8 hours. The crucible containing the ash was then allowed to cool, after which it was leached with aqua regia, filtered and washed with a 10% HCl solution and analysed by Inductively Coupled Plasma (ICP), which allows the direct analysis of the acid solution.

3. Results and discussion

3.1. Adsorption model

The adsorption performance of an adsorbent-adsorbate system is typically characterised by the rate at which adsorption occurs and by the ultimate capacity of the adsorbent in the particular system. The extent of pregrobbing in an adsorption system can therefore be characterised by its influence on the equilibrium or isotherm behaviour and the adsorption kinetics of the adsorbent.

The film diffusion/intraparticle diffusion model has been described by various authors [12, 13, 14] for the adsorption of metal cyanides on activated carbon or ion-exchange resin, and will therefore not be presented here. Using this model, the film transfer coefficient, k_f was determined from the initial plot of ln C_i/C versus time data, whereas the intraparticle diffusion parameter, D_s was obtained by using the batch adsorption data in a Powell regression routine.

Mechanism of pregrobbing

The presence of a pregrobber in an aurocyanide solution containing a resin, when measuring the overall solution phase, will result in an increase in both the kinetics and the equilibrium capacity. The mass transfer parameter, k_f, which presents the rate of aurocyanide adsorption onto the resin, together with equilibrium parameter A, which presents the equilibrium loading capacity of the adsorbents, will be used to comment on the pregrobbing characteristics and mechanism.

When evaluating the model pregrobber, adsorption of gold on the pregrobber takes place uniformly over time according to a first-order decay. The kinetics and equilibrium values of this first order decay were dependent on the activity and porosity of the pregrobber, the gold concentration of the solution, the gold loading distribution of the adsorbent and time. Pregrobbing can therefore be defined as follows:

Pregrobbing = f (activity and porosity of the pregrobber, solution concentration, loading of the adsorbent, and time) ... (12)

It would not be the focus of this paper to develop a mathematical model for the system, but rather to present experimental trends for these parameters, hence qualifying the above relationship.

Pregrobber activity

Since the activity of the pregrobbing carbonaceous material in ores will vary, it was necessary to investigate the effect of different pregrobber activities on gold adsorption through batch kinetic adsorption experiments involving a resin with a pregrobber in a synthetic gold cyanide solution. Activated carbon was used as a synthetic pregrobber to simulate the pregrobbing effect of carbonaceous material in gold ores. Different pregrobber activities were obtained by pre-loading the carbon samples with gold cyanide to 25 %, 50 % and 75 % of its equilibrium loading capacity. Tests were also conducted to determine that none of the pre-loaded gold on the carbon came off and adsorbed onto the resin during experimentation.

Figure 1 represents batch kinetic results for the adsorption of gold cyanide on the resin, the loaded carbon and on the combined adsorption where the resin was in solution with the loaded carbon. The same quantities of resin and carbon were used throughout the experimentation. As expected, when measuring the solution phase, the presence of a pregrobber resulted in an increase in both the kinetic as well as the equilibrium loading capacity. When evaluating the equilibrium loading capacity of the resin at the different pregrobber activities, a decrease in the loading capacity of the resin is obtained with an increase in pregrobber activity. The value of A for the resin profile decreased from 18.23 to 15.78 mg/l in the presence of the pregrobber with the highest activity.

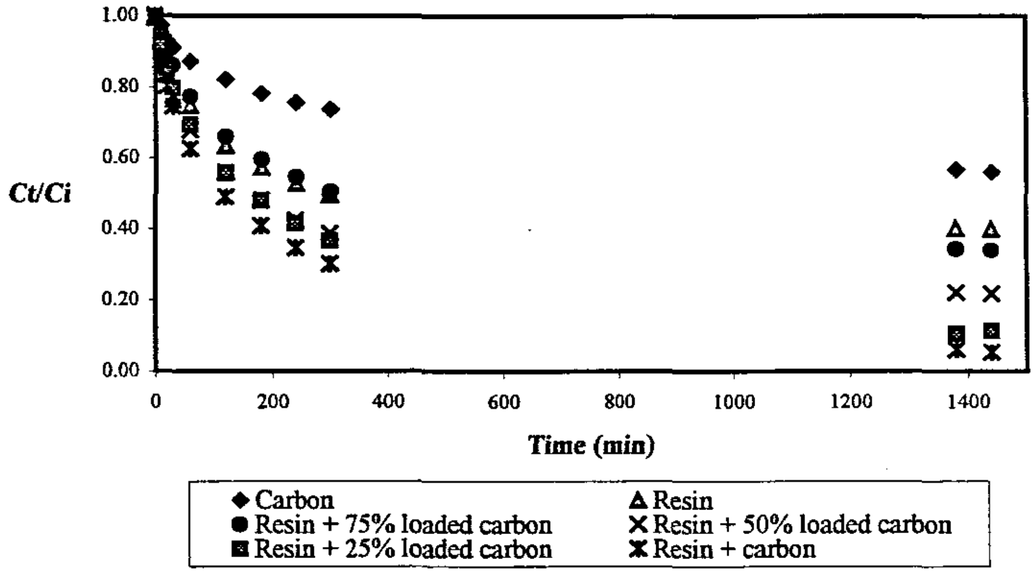

Figure 1. Different degrees of pregrobbing on the adsorption characteristics of the resin ($C_i = 30$ ppm ; $M_{resin} = 0.4$ml ; $M_{carbon} = 0.5$g).

Table 1 shows film transfer coefficients estimated from the initial rate data for the resin and the carbon profiles individually, at each pregrobber activity. The value of k_f for the pregrobber profiles at the different activities increased from 2.77 x 10^{-4} to 4.93 x 10^{-4} m/s while the k_f values for the resin profiles decreased from 9.43 x 10^{-4} to 9.14 x 10^{-4} m/s. From these results the influence of the pregrobber on the adsorption characteristics of the resin is evident, since the film transfer coefficient for the standard resin adsorption profile is 1.34 x 10^{-3} m/s.

In general the results indicate a decrease in the rate of adsorption of the adsorbent for an increase in the pregrobber activity and also an increase in the extent of pregrobbing for an increase in pregrobber activity. The activity of the carbonaceous material in gold ores will therefore have a significant impact on the total extent of pregrobbing that will take place in any particular system.

Table 1. Film transfer coefficients estimated to determine the effect of different pregrobber activities on the extent of pregrobbing.

Pregrobber Activity	**Resin** k_f *(m/s)*	**Carbon** k_f *(m/s)*
Resin	1.34×10^{-3}	-
Carbon	-	9.61×10^{-4}
25 % loaded carbon	-	8.59×10^{-4}
50 % loaded carbon	-	7.76×10^{-4}
75 % loaded carbon	-	6.97×10^{-4}
Resin + carbon	9.14×10^{-4}	4.93×10^{-4}
Resin + 25 % loaded carbon	9.27×10^{-4}	4.24×10^{-4}
Resin + 50 % loaded carbon	9.40×10^{-4}	3.48×10^{-4}
Resin + 75 % loaded carbon	9.43×10^{-4}	2.77×10^{-4}

Gold loading distribution of adsorbent

Similar batch adsorption experiments as mentioned in the previous section were conducted to investigate the effect of different gold loadings on the adsorbent on the extent of pregrobbing. The resin samples were pre-loaded with gold cyanide to 50 % of its equilibrium loading capacity and then contacted with a pregrobber (50 % loaded activated carbon) in a synthetic gold cyanide solution.

Table 2 shows A values and film transfer coefficients estimated for the adsorption profiles. The value of A for the 50 % loaded resin was 8.13 mg/l, whereas the value of A for the 50 % loaded resin in the presence of the pregrobber was 5.56 mg/l. The equilibrium loading value of the pregrobber increased from 4.59 mg/l in the presence of the virgin resin to 6.64 mg/l in the presence of the loaded resin and the film transfer coefficients increased from 3.48×10^{-4} to 4.83×10^{-4} m/s respectively. The k_f values of the resin decreased form 9.40×10^{-4} to 2.08×10^{-4} m/s, which confirms that the overall extent of pregrobbing increases with an increase in the gold loading distribution of the adsorbent.

Porosity of pregrobber

The aim of the work in this section was to investigate the effect of carbon porosity on gold adsorption as the pore structure of pregrobbing carbonaceous material in gold ores may vary widely from one carbon to another. To be able to compare the effect of different carbon porosities of the same type of carbon on gold adsorption, it was necessary to thermally treat the carbon to modify its pore structure.

Table 2. Equilibrium loading values and film transfer coefficients estimated to determine the effect of the gold loading distribution of the resin on the extent of pregrobbing.

Experiment	k_f *(m/s)*		A *(mg/l)*	
	Resin	Carbon	Resin	Carbon
1. Resin	1.34×10^{-3}	-	19.78	-
2. Carbon	-	9.61×10^{-4}	-	14.46
3. 50 % loaded resin	4.36×10^{-4}	-	8.13	-
4. 50 % loaded carbon	-	7.76×10^{-4}	-	9.38
5. Resin + 50 % loaded carbon	9.40×10^{-4}	3.48×10^{-4}	14.99	4.59
6. 50 % loaded resin + 50 % loaded carbon	2.08×10^{-4}	4.83×10^{-4}	5.56	6.64

Batch kinetic adsorption tests in a clear gold cyanide solution were performed on the treated carbon and on untreated carbon to compare their gold adsorption properties. Porosity tests have indicated that the treated carbon had a larger total pore volume than that of the untreated carbon. Furthermore, the equilibrium loading capacity of the untreated and treated carbon was 14.46 mg/l and 17.93 mg/l respectively.

Equilibrium loading values and film transfer coefficients calculated in Table 3 show that the rate of adsorption of gold on the pregrobber increased from 4.93×10^{-4} to 8.86×10^{-4} m/s and the A value increased from 6.96 to 9.98 mg/l with the increase in porosity. The k_f values of the resin decreased from 9.14×10^{-4} to 9.08×10^{-4} m/s and the A value decreased from 12.28 to 11.83 mg/l with the increase in porosity, which ultimately means that the gold adsorption onto the resin was affected negatively, and that the extent of pregrobbing increases with an increase in pregrobber porosity.

Table 3. Equilibrium loading values and film transfer coefficients estimated to determine the effect of pregrobber porosity on the extent of pregrobbing.

Experiment	k_f *(m/s)*		A *(mg/l)*	
	Resin	Carbon	Resin	Carbon
1. Resin	1.34×10^{-3}	-	19.78	-
2. Untreated carbon	-	9.61×10^{-4}	-	14.46
3. Treated carbon	-	1.00×10^{-3}	-	17.93
5. Resin + untreated carbon	9.14×10^{-4}	4.93×10^{-4}	12.28	6.96
6. Resin + treated carbon	9.08×10^{-4}	8.86×10^{-4}	11.83	9.98

Solution concentration

The effect of solution concentration on pregrobbing was investigated since an increase in gold concentration in solution has a positive effect on adsorption rate due to the increased diffusion gradient between the solution and the surface of the adsorbent/pregrobber. Likewise, equilibrium experiments by several investigators using different initial gold solution concentrations showed a considerable difference in adsorption capacities [15].

To determine the effect of solution concentration on pregrobbing, batch adsorption experiments were carried out with the resin and a pregrobber (50 % loaded carbon) in solutions with high initial gold concentrations and in solutions with low initial gold concentrations. The extent of pregrobbing was determined by subtracting the combined resin/pregrobber profile from that of the resin profile for the different solution concentrations. Figure 2 illustrates the pregrobbing profiles for the high and low solution concentrations and it can be seen that solution concentration has a definite impact on the total extent of pregrobbing.

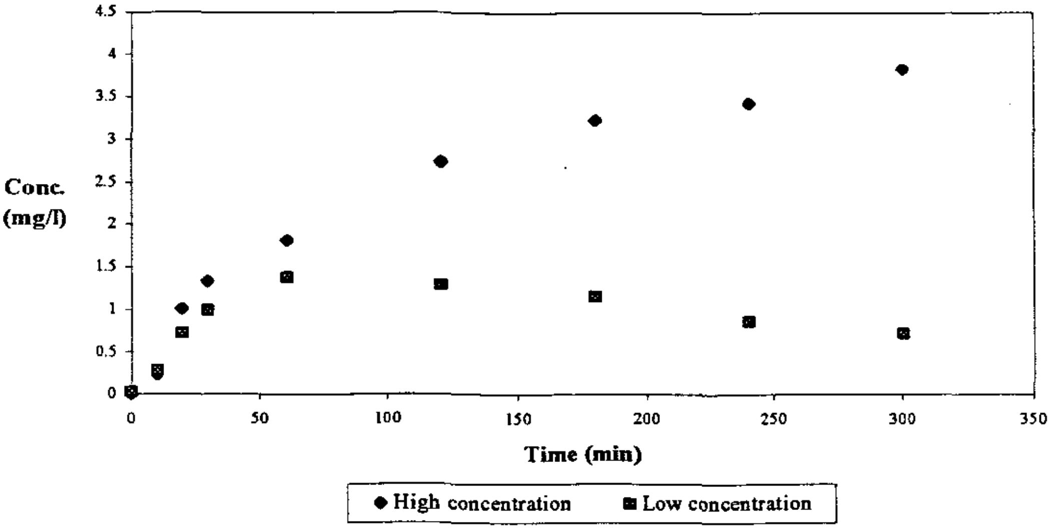

Figure 2. The effect of pregrobbing at different gold concentrations (Ci = 30 ppm ; Ci = 10 ppm ; M_{resin} = 0.4ml ; M_{carbon} = 0.5g)

Table 4 shows equilibrium loading values and film transfer coefficients estimated from the profiles for the different solution concentrations. The equilibrium loading capacity of the resin could not be determined in the solution with the low gold concentration, since the initial gold concentration was not high enough for the resin to reach its equilibrium loading capacity. The value of A for the pregrobber however, decreased form 9.38 mg/l in the solution with the high gold concentration to 7.85 mg/l in the solution with the low gold concentration. The k_f values for the adsorption profile of the resin decreased from 9.40 x 10^{-4} m/s in the solution with the high gold concentration to 9.31 x 10^{-4} m/s in the solution with the low gold concentration. The extent of pregrobbing also decreased significantly with the k_f values for the pregrobber in the low gold concentration being

2.89 x 10^{-4} m/s and that in the high gold concentration 3.48 x 10^{-4} m/s. The increased reaction kinetics observed with an increase in solution concentration therefore indicates that pregrobbing will take place to a lesser extent in solutions with a low gold concentration than in solutions with a high gold concentration.

Table 4. Equilibrium loading values and film transfer coefficients estimated to determine the effect of solution concentration on the extent of pregrobbing.

Experiment	k_f *(m/s)*		A *(mg/l)*	
	Resin	**Carbon**	**Resin**	**Carbon**
High concentration				
1. Resin	1.34 x 10^{-3}	-	19.78	-
2. 50 % loaded carbon	-	7.76 x 10^{-4}	-	9.38
3. Resin + 50 % loaded carbon	9.40 x 10^{-4}	3.48 x 10^{-4}	14.99	4.59
Low concentration				
4. Resin	1.16 x 10^{-3}	-	*	-
5. 50 % loaded carbon	-	6.00 x 10^{-4}	-	7.85
6. Resin + 50 % loaded carbon	9.31 x 10^{-4}	2.89 x 10^{-4}	*	*

* Did not reach equilibrium loading capacity

3.2. Pregrobbing minerals in gold ores

It was important to establish the presence and extent of pregrobbing by minerals in gold ores and to determine whether the pregrobbed gold could be recovered by cyanidation. Several pure minerals, pyrite, chalcopyrite, quartz and kaolin, which are commonly found in gold ores, were used to investigate the adsorption of gold onto the surfaces of minerals. The milled mineral samples were each contacted with a synthetic aurocyanide solution and analysed for gold. The loaded minerals were then leached in a potassium cyanide solution and again analysed for gold. The results and experimental conditions are presented in Table 5.

Gold was adsorbed onto all the minerals studied, but to varying extents. Chalcopyrite and pyrite were found to be very strong adsorbers of gold. Quartz and kaolin also adsorbed significant amounts of gold. Adams *et al.* [6] investigated the strong gold adsorption properties of chalcopyrite and pyrite through Mössbauer spectroscopy and scanning electron microscopy (SEM) and concluded that gold adsorbed onto these minerals as metallic gold. They suggested that in the case of chalcopyrite the gold cyanide reacts with the oxidised copper phase and that the gold adsorbing properties of pyrite can be attributed to the semiconductor properties of sulphide minerals. They suggested that the mechanism of adsorption of aurocyanide onto pyrite involves an electrochemical reduction, with the formation of metallic gold on the surface. This mechanism agrees with the work done by Rees and van Deventer [7] who also explained the adsorption of gold onto chalcopyrite to the reduction of gold at the mineral surface.

Habashi [16], who investigated the chemistry and metallurgy of chalcopyrite, suggested that chalcopyrite undergoes aqueous oxidation in neutral and alkaline solutions with the slow formation of cupric hydroxide. He also showed that when both copper and gold are present in a cyanide solution the polymeric AuCNCuCN compound is formed. The insoluble AuCN tends to become reduced in alkaline solution, with the formation of metallic gold (Au^0) and $Cu(CN)_2^-$.

The small amounts of gold adsorbed by quartz and kaolin can be related to surface-charging effects and the surface area of the minerals. According to Adams *et al.* [6] the amount of gold adsorbed by silicate minerals, such as quartz and kaolin, is mainly dictated by the available surface area. They observed different gold loadings on quartz samples with different surface areas. Mössbauer spectroscopy showed that no metallic gold was present on the quartz, suggesting that the silicate minerals contain only chemically bound gold in the form of $Au(CN)_2^-$. Petersen [17] found that gold adsorbed onto quartz and did not merely attach physically to the surface and showed through infrared tests that $Au(CN)_2^-$ was present on the mineral surface. He also found that at a pH of 12 the loading of gold on quartz was approximately one third of the gold loading at a pH of 10, which indicates that the adsorption phenomenon is probably electrostatic in nature.

Table 5. Adsorption and cyanidation of pure minerals.

Mineral	Gold Addition *Ppm*	Au on minerals after adsorption *g/t*	KCN addition *ppm*	Au on mineral after cyanidation *g/t*	Desorption %
Kaolin	150	15.37	200	0.45	97.07
Quartz	150	16.04	200	0.62	96.13
Pyrite	150	55.90	200	3.74	93.31
Chalcopyrite	150	97.20	200	3.90	95.99

Conditions: Volume: 500ml pH: 11 Time: 24 hours Stirring speed: 300 rpm

It was however, possible to obtain over 90 % desorption of adsorbed gold from all the minerals. In the presence of potassium cyanide, chalcopyrite and pyrite showed relatively complete desorption of gold. Small amounts of gold could not be removed from the sulphide minerals by cyanidation, possibly because of chemical reactions and electrochemical reduction between the gold and the mineral surface.

The desorption of adsorbed gold of the silicate minerals, quartz and kaolin, were close to 100 %. The remaining gold can possibly be explained by the presence of small cracks on the particles, which can potentially trap aurocyanide ions. Urban *et al.* [3] showed that the adsorption of gold onto some clay minerals is a slow, reversible phenomenon that is reduced by an increase in cyanide levels. Rees and van Deventer [7] also indicated that pregrobbing onto minerals could be dramatically decreased by increasing the initial free cyanide concentration and they found that the reduction of gold at the mineral surface could almost be completely inhibited when cyanide and activated carbon were present.

In general, gold could successfully be removed from the minerals investigated in the presence of potassium cyanide. The adsorption phenomenon can possibly be totally reversible if activated carbon or an ion-exchange resin is present in the leaching solution. The pregrobbing effect of these minerals would therefore probably not be a problem in most CIP or RIP plants operating at sufficient cyanide levels.

3.3. Gold adsorption onto carbonaceous gold ores

The gold adsorbing properties of several pregrobbing gold ores were investigated by contacting the ores with a synthetic aurocyanide solution. The ores were analysed for gold loading, organic carbon and pyritic sulphur content prior to contact with the aurocyanide solution.

Table 6 shows the results and conditions of the gold adsorption experiments. The ores all showed some adsorption of gold. The ores containing the highest levels of organic carbon content had in general the higher gold loadings.

Table 6. Adsorption of gold cyanide onto carbonaceous gold ores.

Ore	Initial Au on ore *g/t*	Au on ore after adsorption *g/t*	Organic carbon *%*	Pyritic sulphur *%*
No. 1	7.02	37.20	0.90	1.30
No. 2	5.73	9.67	0.50	1.70
No. 3	5.20	18.32	0.59	5.20
No. 4	10.00	24.30	0.70	0.40
No. 5	1.25	32.21	0.90	0.75

Conditions: Volume: 500ml pH: 11 Stirring speed: 300 rpm
Au addition: 50 mg/l Time: 24 hours

Figure 3 shows that there is an approximate linear correlation between the amount of gold adsorbed by the ore and the total content of organic carbon in the ore used in this study. However, this is not always the case, because of the different activities associated with the organic carbon in the ores as well as varying amounts of hydrocarbons and organic acids that is present and to a smaller extent the varying pyritic sulphur contents of the ores.

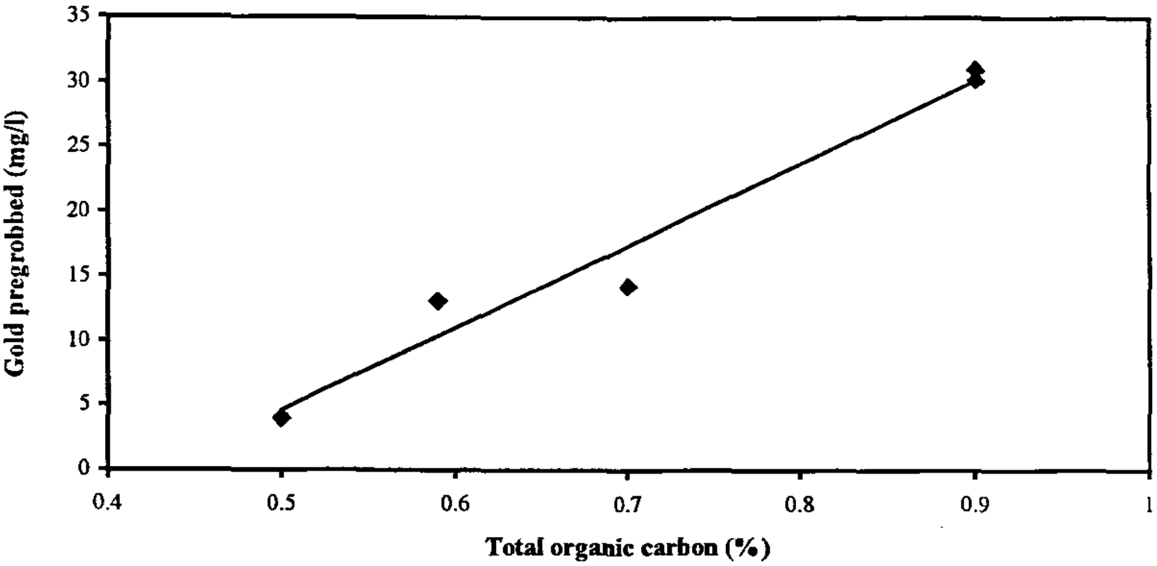

Figure 3. Effect of the total content of organic carbon on the quantity of gold adsorbed by the pregrobbing ores.

3.4. The recovery of gold from pregrobbing ores

The gold adsorbing properties and the poor leaching behaviour of pregrobbing ores is generally attributable to the presence of carbonaceous matter and, to a lesser extent, sulphide minerals. Several techniques exist to suppress the detrimental effect of these ores during the recovery of gold. The work in this section focuses on the use of an ion-exchange resin in the leaching solution, which compete with pregrobbing species for the gold cyanide complex and tests on the influence of certain organic blinding compounds on the leaching efficiency of pregrobbing ores.

Three scenarios for the recovery of gold from the different pregrobbing ores were investigated namely, (1) the conventional cyanidation of the ores in a potassium cyanide solution, (2) cyanidation in the presence of a gold selective resin (RIL) and, (3) cyanidation in the presence a resin and an organic blinding agent.

Cyanidation and resin-in-leach of pregrobbing ores

When a carbonaceous gold ore is leached the carbonaceous matter readily adsorbs the gold cyanide complex as it goes into dissolution. To determine the pregrobbing effect of the carbonaceous matter in the ores investigated, leaching and resin-in-leach experiments were conducted. The results and experimental conditions are shown in Table 7.

All the ores pregrobbed gold to a certain extent. Very low recoveries were obtained, especially from ores 1, 2, 3 and 5. The low recoveries of ores 1 and 5 are probably attributed to their high organic carbon content. Although ore no. 3 contains only 0.59 %

organic carbon it is possible that the high pyritic sulphur content can be responsible for its poor leachability.

Ore no. 2 showed a very low gold recovery of only 16 per cent and it is obviously a highly pregrobbing ore. It is possible that the natural carbon in the ore has a very high activity for gold adsorption or that the organic carbon in the ore is associated with high levels of organic acids such as humic acid, which are capable of bonding with aurocyanide complexes to form organic gold compounds which can not be dissolved by cyanide.

Table 7. Leaching and resin-in-leach of the pregrobbing ores.

Ore	Initial Au on ore g/t	Au on ore after leaching g/t	Recovery %	Au on ore after RIL g/t	Recovery %	Organic carbon %	Pyritic sulphur %
No. 1	7.02	4.92	30	3.06	56	0.90	1.30
No. 2	5.73	4.80	16	4.02	30	0.50	1.70
No. 3	5.20	2.36	55	1.75	66	0.59	5.20
No. 4	10.00	2.18	78	1.10	89	0.70	0.40
No. 5	1.25	0.89	29	0.47	62	0.90	0.75

Conditions: Volume: 500ml KCN: 200 ppm pH: 11 Stirring speed: 300 rpm
Resin volume: 5 ml Time: 24 hours

The second-stage tests, i.e. the contacting of the pregrobbing ores with a gold selective resin in the presence of potassium cyanide resulted in an overall increase in gold recovery. Although ores 1 and 5 showed the largest increase in gold recovery, they still had the lowest overall recovery. The high organic carbon contents of these ores are probably responsible for this. Acceptable gold recoveries were obtained from ores 4 with an 89 per cent recovery. Very low gold recoveries were obtained from ore no. 2. Except for the reasons given above, it is not possible to explain the poor leaching behaviour of this ore with the information available. A complete mineralogical analysis will have to be done on the ore to identify and characterised possible pregrobbing components.

In general the increases of between 11 to 33 per cent obtained, illustrates that aurocyanide is adsorbed by the carbonaceous matter in the ore and that the presence of a resin that competes with the pregrobbing components for the gold cyanide complex can be an effective method of treating certain pregrobbing ores.

Resin-in-leach with an organic blinding agent

The organic blinding agents used in this study were diesel, kerosene, sodium lauryl sulphate (SLS), tricaprylylmethylammonium chloride (Aliquat 336) and dodecylamine (DDA). The organic compounds were chosen to cover a range of properties, such as ionicity, emulsification effects and water solubility. Relative high dosages (up to 1%) of these blinding agents were used to investigate its effect on the pregrobbing characteristics. The results and conditions of the experiments are shown in Table 8.

Table 8. The effect of the blinding agents on the pregrobbing ores.

Blinding agent	Ore	Initial Au on ore g/t	Au on ore after RIL g/t	Recovery %	Organic carbon %	Pyritic sulphur %
Diesel	No. 1	7.02	2.78	60	0.90	1.30
	No. 2	5.73	3.02	47	0.50	1.70
	No. 3	5.20	1.16	78	0.59	5.20
Kerosene	No. 1	7.02	2.66	62	0.90	1.30
	No. 2	5.73	2.92	49	0.50	1.70
	No. 3	5.20	1.94	63	0.59	5.20
SLS	No. 1	7.02	2.44	65	0.90	1.30
	No. 2	5.73	2.06	64	0.50	1.70
	No. 3	5.20	1.34	74	0.59	5.20
Aliquat 336	No. 1	7.02	3.48	50	0.90	1.30
	No. 2	5.73	3.22	44	0.50	1.70
	No. 3	5.20	2.08	60	0.59	5.20
DDA	No. 1	7.02	4.50	36	0.90	1.30
	No. 2	5.73	3.48	39	0.50	1.70
	No. 3	5.20	3.08	41	0.59	5.20

Conditions: Volume: 500ml KCN: 200 ppm pH: 11 Stirring speed: 300 rpm
Resin volume: 5 ml Time: 24 hours

Although increases in gold recoveries of up to 34 % were obtained, none of the compounds sufficiently inhibit the adsorption of gold by the pregrobbing material to provide acceptable overall gold recoveries, with some off the compounds even having a negative impact on the gold recoveries. The addition of diesel had a positive effect on the leaching behaviour of all the ores, but for ores 1 and 2 the overall recoveries of 60 % and 47 % respectively, are still low and would probably not be acceptable to any gold plant. Kerosene was less effective than diesel in the case of ore 3 which had a 63 % recovery, but gave more or less the same recoveries than diesel for the other two ores.

SLS was overall the most effective reagent, which resulted in a 34 % increase in the recovery obtained for ore 2. SLS form anionic species in solution and according to Abotsi and Osseo-Asare [18] who investigated similar anionic reagents, the anionic species adsorb onto the negatively charged carbonaceous particles resulting in an increase in the negative charge of the carbonaceous solid/water interface. The anionic surfactant therefore depresses gold loading onto the carbonaceous ore as a result of the repulsion between the highly negatively charged ore particles and the $Au(CN)_2^-$ anion. A second possibility is that the surfactant could coat the surface of the ore and, by limiting the number of available surface sites, inhibit gold uptake.

DDA, and to a lesser extent Aliquat 336, both had a negative effect on gold recovery. Significant decreases in gold recoveries of up to 25 % were obtained for ores 1 and 3 and only slight increases were observed for ore 2. These results are more or less in agreement with that observed by Abotsi and Osseo-Asare [18] using the same surfactants. Aliquat 336, which is completely cationic and DDA, which forms cationic and neutral species, enhances gold uptake by the carbonaceous ore, presumably by acting as an activator linking the negatively charged aurocyanide complex to the negatively charged solid surface.

From Figure 4, it seems as if there does not exist a correlation between the organic carbon or pyritic sulphur content and the gold recoveries obtained. On average the lowest gold recoveries were obtained for ore 2, which has the lowest organic carbon content. Moreover, certain ores reacted positively to a specific organic compound whereas other ores reacted negatively to that same compound. Since there is such a vast difference in the mineralogy of pregrobbing ores and the fact that different pregrobbing ores have different gold activities, as well as varying amounts of hydrocarbons and humic acids present, it may prove best to optimise the blinding conditions for each specific ore by treating each type of ore with a specific organic compound.

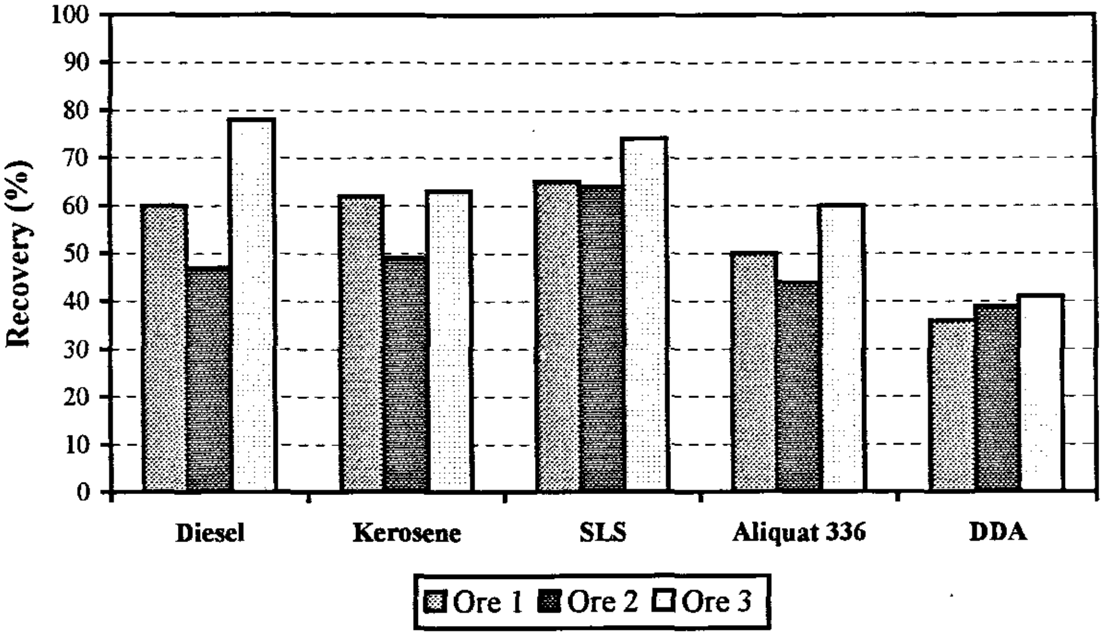

Figure 4. **A comparison of the gold recoveries obtained when applying the different organic compounds.**

4. Conclusions

It was found that pregrobbing is a function of the activity and porosity of the pregrobber, the concentration of gold in the pregnant solution, the gold loading distribution of the adsorbent, and time.

All the pure minerals investigated adsorbed gold to some extent. The copper and iron sulphide minerals, chalcopyrite and pyrite, were strong adsorbers of gold. It was possible to remove most of the gold from the loaded minerals in the presence of cyanide. The adsorption phenomenon is therefore reversible at relative high cyanide levels and the pregrobbing effect of these minerals will probably be minimal in CIP or RIP plants.

The gold adsorption onto ores containing high organic carbon content was in general the highest. The total organic carbon content can however not always be used as a guideline for the pregrobbing potential of an ore, because carbons have different gold activities, as well as varying amounts of hydrocarbons and organic acids present.

Conventional cyanidation of the pregrobbing ores proved to be ineffective. The presence of a gold selective resin in the leaching solution resulted in increased gold recoveries. RIL can therefore be an effective method of treating ores whose only deleterious constituent is moderate concentrations of carbonaceous material.

The blinding of the carbonaceous material in the ore with organic compounds in a resin-in-leach configuration proved to be an effective combination. Several compounds, of which diesel and SLS were the most effective, were found to have a blinding effect on the ore, reducing the adsorption of gold cyanide.

Acknowledgements

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Nomenclature

a - External surface area of carbon and resin (m^2)
A - Parameter in Freundlich isotherm
C - Solute concentration (mass fraction) ($mg.l^{-1}$)
C_e - Equilibrium solution concentration ($mg.l^{-1}$)
C_i - Initial solution concentration ($mg.l^{-1}$)
C_s - Solution concentration at liquid-adsorbent interface ($mg.l^{-1}$)
d_p - Diameter of adsorbent particles (m)
k_f - External film transfer coefficient ($m.s^{-1}$)
M - Mass of adsorbent (kg)
n - Exponent in Freundlich isotherm
n_L - Rate of diffusion through liquid film ($mg.m^{-2}.s^{-1}$)
q_s - Solute loading at solution-adsorbent interface ($mg.g^{-1}$)
q_e - Solid phase adsorbate concentration ($mg.g^{-1}$)
t - Time variable (s)
V - Volume of solution in reactor (L)
ρ - Density ($kg.m^{-3}$)

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NOMENCLATURE

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a - External surface area of carbon and resin (m^2)

A - Parameter in Freundlich isotherm

A_{macro} - Total macro pore area (m^2)

B - Parameter in Langmuir isotherm

C - Solute concentration (mass fraction) ($mg.l^{-1}$)

C_e - Equilibrium solution concentration ($mg.l^{-1}$)

C_i - Initial solution concentration ($mg.l^{-1}$)

C_s - Solution concentration at liquid-adsorbent interface ($mg.l^{-1}$)

d_p - Diameter of adsorbent particles (m)

D - Diffusion coefficient ($m^2.s^{-1}$)

D_{macro} - Diameter of macropores (m)

k_f - External film transfer coefficient ($m.s^{-1}$)

M - Mass of adsorbent (kg)

n - Exponent in Freundlich isotherm

n_L - Rate of diffusion through liquid film ($mg.m^{-2}.s^{-1}$)

q_{macro} - Solute loading into macropores ($mg.g^{-1}$)

q_s - Solute loading at solution-adsorbent interface ($mg.g^{-1}$)

q_e - Solid phase adsorbate concentration ($mg.g^{-1}$)

t - Time variable (s)

V - Volume of solution in reactor (L)

Greek letters

μ - Viscosity of permeate (s^{-1})

ρ - Density ($kg.m^{-3}$)