RECOVERY POTENTIAL OF GOLD AND SILVER FROM ANODE SLIMES BY

CYANIDATION AND ADSORPTION PROCESS

BY

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A dissertation submitted to the University of Zambia in
partial fulfillment of the requirements for the degree of
Master of Mineral Sciences in Metallurgy and Mineral
Processing.

THE UNIVERSITY OF ZAMBIA LUSAKA

1990

DECLARATION

I declare that this dissertation was written in accordance with the rules and regulations governing the award of Master of Mineral Sciences Degree of the University of Zambia. I further declare that the dissertation has neither in part nor in whole been presented as substance for award of any degree either to this or any other University.

Where other peoples' work has been drawn upon, acknowledgement has been made.

Signature of author ....

Date: ..... 27/08/1990 ......

APPROVAL

This dissertation of **DELAX TENTHANI CHILUMBU** is approved as fulfilling part of the requirements for the award of the degree of Master of Mineral Sciences in Metallurgy and Mineral Processing by the University of Zambia.

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....   20 Feb 1991

....   09th August 1991

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To My Mother and Father for their unflinching support.

ABSTRACT

The cyanidation process for extracting precious metals(gold and silver) from the gold-slimes was investigated. The recovery of these metals from cyanidation solution by adsorption on activated carbon has been studied. This was to assess the cyanidation and adsorption process as a potential alternative recovery process to the conventional metallurgical *Process* presented in the report.

From the cyanidation tests, the recovery of silver was found to increase with an increase in cyanide concentration. Recoveries of 80% and 77% of silver and gold respectively were achieved

Adsorption isotherms of gold, silver and copper have been generated. From these isotherms, an approximation of the loading capacity of gold and silver on activated carbon has been obtained. The typical results of loading capacity on the activated carbon show that the amount of gold and silver adsorbed per unit weight of carbon depends upon the amount of activated carbon, the retention time and the concentration of these metals in solution.

And a desorption system was used to desorb the loaded activated carbon. From the foregoing studies a flowsheet has been proposed. Information on the nature of adsorbed species (gold and silver) on the activated carbon was obtained by XRF and XRD studies. The loaded and free regions of the activated carbon viewed under SEM, show that the adsorbate appears to adsorb selectively on specific features.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS AND ABBREVIATIONS

C	Aqueous/gas concentration
P_{O_2}	Oxygen partical pressure
ξ	Boundary thickness
N	Number of moles
RAM	relative atomic or molecular mass
p	gas pressure
V_{AIR}	Volume of air
N_{O_2}	number of moles of oxygen
N_{AG}	number of moles of
R	universal gas constant
T	Temperature
Q	Air flow rate
V_{O_2}	Volume of oxygen
V	Volume
N_{AU}	Number of moles of gold
t	time
m	mass
ß	Constant
	surface concentration
k	rate constant
Vm	Volume of unimolecular adsorbed layer
Fc	Flow rate of carbon
Fs	Flow rate of solution
r	rate

A_c	Area of carbon
ρ_s	Density of solution
K_t	Transfer coefficient
C_o	Initial concentration
M_c	Mass of carbon
a_{equal}	amount adsorbed at equalibrium
a_t	amount of the adsorbed substance at time t
P_o	equilibrium pressure of gas at STP
a_{max}	amount adsorbed per unit mass
x	amount of the adsorbed substance
N_{KCN}	number of moles of potassium cyanide

CHAPTER 1

GENERAL INTRODUCTION

1.1 USES OF PRECIOUS METALS (GOLD AND SILVER)

There is hardly a facet of daily life that is not influenced by the precious metals (gold and silver) or their alloys. For instance, gold serves as a store of wealth and is widely used for investments owing to its high negotiability and every government has gold reserves to hedge against trade fluctuations. This is perhaps one of the strategic importance of gold in international finance [28].

In modern medicine radiology is expanding and almost every medical speciality has become dependent on x-ray diagnosis and silver is used to manufacture these medical x-ray films for accurate diagnosis and minimizes radiation exposure [28].

The major modern therapeutics, use gold in the treatment of rheumatoid arthritis. The radiation or x-ray treatment require internal barriers of solid gold. Gold and silver is most favoured in dentistry because it is more bio-compatible. Silver and gold have many medical uses.

Precious metals and their alloys play a very important role in many segments of the electronics and communications industries. Precious metals alloys cladded to common base metal alloys are widely used in jewelry and the electrical industries. They are used in the area of electronics known as microelectronics, where miniturization of circuitry and

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components are maximized [28, 33].

These are among the many uses of precious metals in the world. As a result gold and silver is in demand for these and other uses.

1.2 MODE OF OCCURRENCE OF PRECIOUS METALS (GOLD AND SILVER)

The world demand for precious metals has resulted in intense exploration activies world for many years, owing to relatively high stable prices for the metals [1, 3]. Precious metals(gold and silver), are distributed in minute quantities throughout the world, mostly associated with quartz veins, placer or the alluvial deposits and deposits of base metals from which the precious metals are by-products [2, 29, 42].

1.3 EXTRACTION METHODS OF PRECIOUS METALS.

Precious metals have been extracted from there ores by various methods. Chlorination, amalgamation, gravity concentration, and direct smelting, are amongst the early methods used to extract precious metals.

The following factors; high cost, low recoveries, health hazards, depletion of high grade ores, insecurity and the eventual discovery of the low grade deposits, fuelled the development of extraction techniques. This led to the development of the cyanidation process by Macarthur and the Forrests and the continuous precipitation of gold using zinc dust in the absence of air by Merrill and

perfected by Crowe suitable for low grade ores [27, 29, 42, 43]. The cyanide leach and zinc cementation recovery method has been in use until very recent times, when zinc cementation has been falling out of favour in preferance to the activated carbon adsorption-desorption method developed by Zadra [20, 10] in the early 1950s at the US Bureau of Mines. The advantages of activated carbon extraction of precious metals over other methods are cheapness, efficiency and easiness of operation. It is also a relatively clean operation [8, 9, 10].

The extraction of precious metals technology has now been developed to a stage where the recovery of these metals is dependent, largely on the ore mineralogy and the application of the possible unit operations and processes [43].

1.4 EXTRACTION OF PRECIOUS METALS FROM ANODE SLIMES

Direct smelting of anode slimes is no longer a favoured method of extracting precious metals due to excessive matte and slag formation causing a high recirculating load of precious metals. A more favoured approach is that of separating the components of the slimes one by one. Various attempts have been made to recover precious metals from anode slimes by other methods. Smelting in a slag resistance electric furnace has not proved to be practical due to the products, copper-lead-silver-gold alloy and a

copper selenide-copper telluride matte which cannot be easily parted.

The aeration of slimes in aqueous cyanide is feasible. The problem of separating a number of metals contained in cyanidation solution and the cost of reagents made the process impracticable. Chlorination method has been tried, but owing to the highly corrosive nature of the chlorine/chloride gases this process [7] is not used. However research studies are still continuing [4, 6, 17] into possible alternatives of extracting precious metals from its deposits.

1.5 DEFINITION OF THE PROBLEM AND SCOPE OF WORK

Zambia extracts considerable amounts of gold and silver metals from copper anode slimes, a by-product of copper refining [13]. The general plan practiced by most refineries, including the Ndola precious metals plant, is to separate the slime components one by one [7, 11], as indicated in fig. 1. in the thesis. The process currently in use, at the Ndola precious metals plant is highly corrosive and requires acid resistant plant components, and equipment. There is a general frequent equipment failure that could be partly attributed to this corrosive environment. The operating atmosphere is also toxic from the spillage of various acid fumes eminating from the leaching and roasting processes, posing serious healthy

Figure 1. NDOLA ANODE SLIMES PROCESS FLOWSHEET.

hazards. The high rate of equipment breakdown necessitates shutdowns to facilitate repairs and this makes the process a maintenance intensive operation which in turn increases operating costs.

The siliceous material (gangue) obtained in the Copperbelt anode slimes is unaffected by most leaching agents. The slimes are eventually smelted in a dore furnace to obtain dore bullion (gold and silver alloy) prior to subsequent refining to pure products.

The siliceous and other unwanted materials (gangue) make up an average of 80% of the smelting charge, which means the major part of smelting economics is used to separate this gangue as slag.

If the bulk of this 80% gangue could be eliminated prior to smelting then it would reduce flux consumption, energy cost, operation time, loss of precious metals to discard slag, slag handling costs, the deterioration of refractory lining in dore' furnaces necessitating less periodic shutdown and replacement of refractory bricks. This would also increase smelting capacity and the production of gold and silver metals.

There is currently a general downward variation of silver and gold content in the Zambia Consolidated Copper Mines Limited (ZCCM) anode slimes and this may further have adverse effects in the economics of the conventional metallurgical process [11]. Therefore it is necessary to

re-examine the viability of the current process flowsheet,
with a view of changing to a more economical process.
The important factors in metallurgical process consideration
are the balance between operation cost, high overall
metallurgical recoveries, ease of plant operation and
maintenance, and process plant flexibility within capital
constraints [34]. Hence process innovation is an important
step in cost containment when it seeks to maximize
throughput per unit volume of the reactor thus reducing
capital cost.

An attempt has been made in this work to assess the
possibility of recovering precious metals from copper anode
slimes by cyanide leaching followed by adsorption
process, using activated carbon.

The carbon adsorption methods is comparatively a low cost
proposition. Carbon is widely used in extracting gold and
much research continues on different carbons, synthetic
resins, and carbon adsorption methods. Activated carbon
processes could provide flexibility in adapting changes in
technology i.e. the replacement of activated carbon with
synthetic resin. The use of activated carbon has greatly
improved the efficiency of precious metals recovery
operation due to its high affinity of adsorbing gold and
silver [4, 6, 8, 10].

The aim of the work was to determine the recovery
potential of precious metals from copper anode slimes by

cyanide leaching and adsorption on activated carbon.
Copper anode slimes comprise different elements which could
enhance or passivate either the cyanidation or the
adsorption of the desired values. Therefore rational
understanding of the chemistry of these processes required
mineralogical evaluation of the anode slimes. Thus the
preliminary stage in this work involved mineralogical study,
size analysis and cyanidation chemistry. Adsorption-
desorption was studied as the last stage. The
characterization of the adsorbed species was also attempted.
The results of the above investigations are presented in
this report. The work is divided into seven chapters. The
first chapter is the introduction, chapter two deals with
the literarature review on the mineralogical studies of the
anode slimes, while chapter three deals with size, and
chemical analysis of the copper anode slimes. The theory of
cyanidation is presented in chapter four, while chapter five
deals with cyanidation experiments of the anode slimes.
Chapter six deals with the adsorption, theories and studies,
of gold and silver on the activated carbon. Finally the
investigations on the adsorption of gold and silver from the
cyanidation of the anode slimes, desorption, the
characterization of the adsorbed species and the proposed
flowsheet are all presented in chapter seven. This is
followed by discussions and conclusions.

Chapter 2

LITERATURE REVIEW

2.1 ANODE SLIMES COMPOSITION

Copper anode slimes are made up of those components of the
copper anodes which are not soluble in the electrolyte or
insoluble products formed by the copper anode reaction. They
contain varying quantities of copper, silver, gold, sulphur,
selenium, tellerium, lead, arsenic, antimony, nickel, iron,
and silica, as outlined in Table 1 [7, 16, 24, 36].
The colour of raw slimes is grayish black and the average
particle size is -200 mesh.

TABLE 1 COMPONENTS OF COPPER ANODES AND COMPOSITION OF
ANODE SLIMES

Element	% Proportion into anode slimes	% Proportion in electrolyte	Mineral Compound
Gold	99	1	Au, $AgAuTe_2$
Silver	98	2	Ag_2Te, CuAgSe
Platinum metals	98	2	Pt, Pd
Copper	–	–	Cu_2Cl_2, Cu, Cu_2S
			Cu_2Te, Cu_2O
Selenium	98	2	Se;
Tellurium	98	2	Te,

cont. table 1

Arsenic	25	75	$Al_2O_3.B_2ASO_4$
			$SbASO_4$
Antimony	60	40	Sb_2O_3
Silica	99	1	SiO_2
Iron	0	100	Fe_2O_3, FeS
Lead	98	2	$PbSO_4$, $Pb_2Sb_2O_6$
Zinc	–	–	ZnO
Bismuth	0	100	–

2.2 MINERALOGY OF COPPERBELT ANODE SLIMES (earlier studies).

The mineralogical composition of Zambia Consolidated Copper

Mines (ZCCM) copper refinery slimes were examined by

the Mining Industry Technical Services Unit (MITS).

Mineralogical examinations were undertaken at different

times between 1973-1982 on Mufulira, Nkana and Ndola

copper refinery slimes.

The findings in general of Vink & Wheeler [12] were that

copper was present, occurring as cuprites (Cu_2O) in small

grains generally between 20μm – 150μm, and as metallic

copper with grains mostly about 100 μm. Antlerite $Cu_3(SO_4)$

$(OH)_4$ could be positively identified by x-ray diffraction

analysis. The most probable nature of occurrences of silver

and selenium is eucairite (CuAgSe). A mineral phase

$2Al_2O_3.9SiO_2.7H_2O$ was tentatively identified.

The presence of mullite ($3Al_2O_3 . 2SiO_2$) could be shown with certainity using XRD. Kostie and Voermans [13] say that native copper is present in almost every siliceous particle (gangue- unwanted material mostly siliceous minerals). The bigger gangue particles always contain disseminated native copper grains 10 μm in size. Maximum grain size is about 200 μm. About 90% of the native copper is locked to gangue minerals. No copper sulphides were observed. ·

Glassy bluish material has been observed, which XRD and Debye Scherrer photograph showed as mainly composed of copper sulphate-selenates such as chalcanthite ($CuSO_4.5H_2O$) and its isomorph chalcomenite ($CuSeO_4.5H_2O$ and $CuSeO_3.2H_2O$). The gangue particles are almost exclusively composed of quartz.

Vink, Wheeler and Rappard [14] on their mineralogical examination of Nkana slimes by XRD reported positive identification of antlerite $Cu_3(SO_4)$ $(OH)_4$, but klockmanite (CuSe) and eucairite (CuAgSe) were also thought to be present.

The identification of berzeliamite (Cu_2-xSe) and aluminium sulphate were tentative.

Kostie and Voermans [13] noted very small amount of native silver, chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4) and pyrite (FeS_2). Their work indicated the presence of hydrated copper-sulphate-selenides. According to these mineralogical reports, fine grained material which makes up the bulk of

the sample has been x-rayed indicating chalcanthite

($Cu.SO_4.5H_2O$), eucairite (CuAgSe), klockmanmite (CuSe), and

quartz (SiO_2) .

A bright mineral with a high reflectivity identified as

metallic silver has been described. This metallic silver did

not exceed 10 m. The presence of metallic silver was

positively identified by XRD analysis and the presence of

mullite ($3Al_2O_3. 2SiO_2$) could be demonstrated with

certainty. Vink and Co-wokers [12, 14] also positively

identified the compound copper aluminate $CuAlO_2$ (an

isostructural aluminium equivalent of $CuFeO_2$). Tentatively

identified were alpha copper selenide Cu_2Se and aluminium

sulphate $Al_2(SO_4)_3$.

The presence of venzelianite (Cu_2Se_x) has been indicated by

x-ray diffractograms.

2.3 ACID WASHED SLIMES

The anode slimes from which the sulphuric acid contained in it

from the copper electrorefining cells was washed off is

termed 'acid washed slimes'.

The report on mineralogical examination of one sample of

this 'acid washed' Ndola Copper Refinery anode slimes

concluded that: the bulk of the material consists

predominantly of chalcanthite ($CuSO_4.5H_2O$) with lesser

quartz and minor amounts of Cu-Ag.Se bearing minerals. The

report [13] says that these minerals are found in trace to

minor amounts and include naumannite (Ag_2Se) and metallic

silver. The results of the various examinations indicating

positively identified mineral phase of anode slimes are

given in Table 2.

According to MITS mineralogical reports, the quartz is by

far the most abundant gangue mineral. The presence of gold

was not precisely known, but it was suspected to be present

mainly as native gold with minor amounts as gold tellurides

($AgAuTe_2$). Nicol. M. J et al in their report [43], say

that the only gold compounds that occur in natural state are

the telluride ($AuTe_2$) and stibnite species ($AuSb_2$).

2.4 DECOPPERIZED SLIMES

The term decopperized slimes refers to the copper anode

slimes in which the copper has been leached out by digesting

in the concentrated sulphuric acid at 200 °c for 8 hours

and then filtering and washing the leached pulp.

Sulphuric acid digested anode slimes mineralogical

examinations indicated the presence of, native selenium

which occurs mainly free and with grain sizes up to 600 m,

naumannite (Ag_2Se) eucarite ($AgCuSe$), and anglesite

($PbSO_4$). Again quartz was found to be the major portion of

the gangue material [13].

2.5 DESELENISED SLIMES

A similar definition applies to the deselenised slimes

implying the removal of selenium. This was done by roasting

the slimes at 700°c temperature until no reddish fumes were

observed. X-ray-diffractograms of deselenised slime indicated large amounts of native silver, mainly occurring as tiny disseminations of 5-10 μm in size, in siliceous particles [13].

CHAPTER 3

EXPERIMENTAL WORK

MINERALOGICAL AND CHEMICAL ANALYSIS

SOURCE OF THE SAMPLE USED IN THE INVESTIGATIONS

The sample of anode slimes used in the investigations was obtained from a composite of all the samples obtained for each batch of the slimes received for processing at Ndola precious metals plant, for the financial year 1987/88. Each anode slimes batch received for processing at the precious metals plant is sampled and assayed to determine the contained metal values for purposes of Plant control, financial accounting and metallurgical reports. At the end of every financial year the batch samples are made into a composite sample and assayed to determine the average input into the plant, as total contained metal values received during the financial year.

SIZE CLASSIFICATION OF THE ANODE SLIMES.

The aim of sizing was to check the size distribution of the anode slimes and help in the setting up of the leaching conditions. It also served the purpose of assisting in evaluating the MITS mineralogical data on the specific distribution of various minerals constituents in various size fraction as outlined in table 2.

Many techniques are employed in laboratory sizing, including screening (wet or dry), infrasizing, elutriation,

cyclosizing and sedimentation .

A representative anode slime sample obtained by riffle

sampling was subjected to dry screening. The size

distribution data is summarized in the histogram of figure 2.
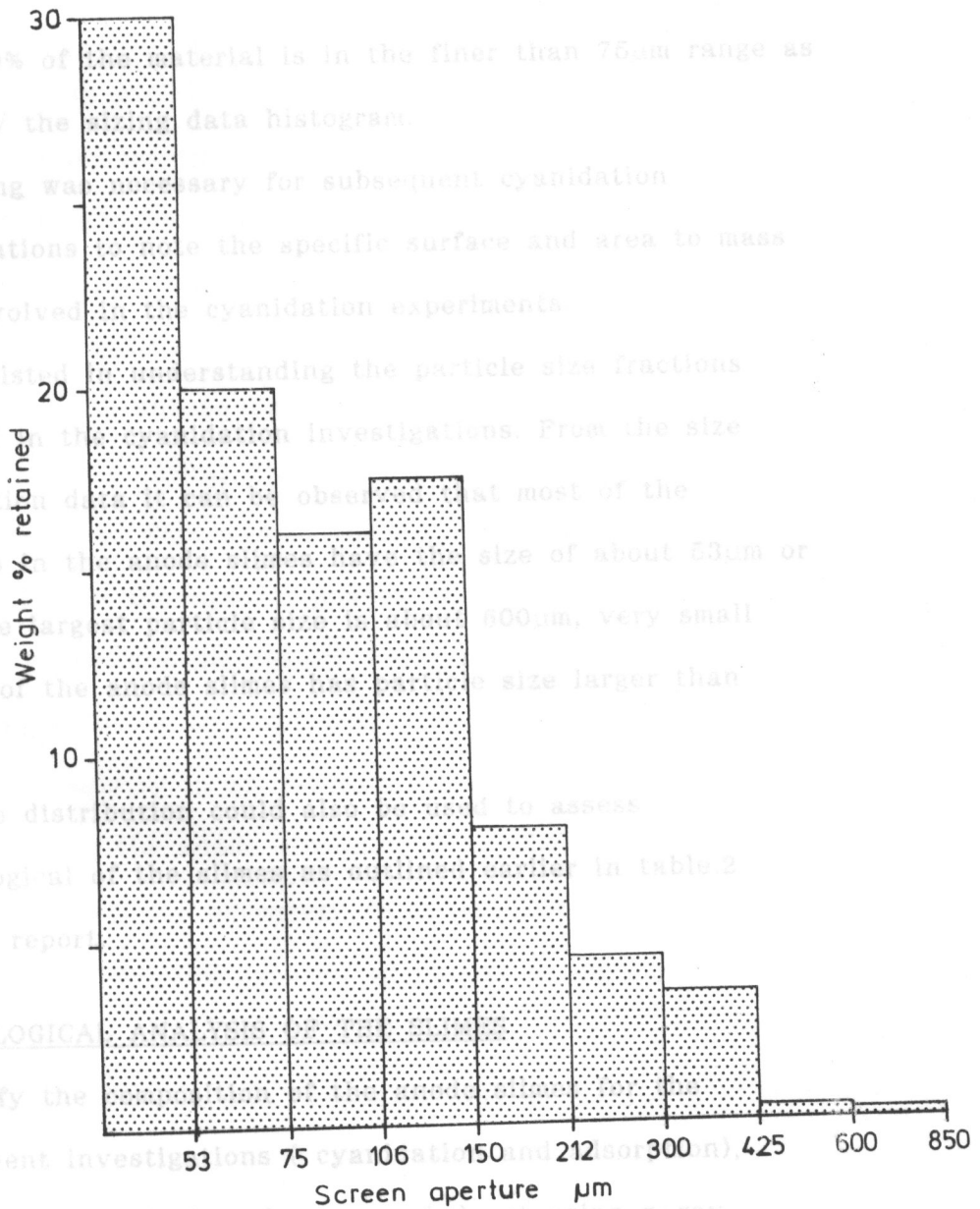
Fig. 2   Size distribution of copper anode slimes

About 50% of the material is in the finer than 75μm range as shown by the sizing data histogram.

The sizing was necessary for subsequent cyanidation investigations to note the specific surface and area to mass ratio involved in the cyanidation experiments.

This assisted in understanding the particle size fractions involved in the cyanidation investigations. From the size distribution data it can be observed that most of the particles in the anode slimes have the size of about 53μm or less. The largest particle size is about 600μm, very small portion of the anode slimes has particle size larger than 212μm.

The size distribution could also be used to assess mineralogical of the slimes as outlined earlier in table.2 of MITS report.

3.3 MINERALOGICAL ANALYSIS OF THE SLIMES

To verify the composition of the anode slimes for the subsequent investigations (cyanidation and adsorption), further mineralogical work was carried out using x-ray fluorescence spectrometry and x ray diffractometry.

The mineralogy can also be studied using the optical properties of the minerals in the anode slimes i.e petrology and ore microscopy.

The mineralogical investigations by MITS on the copper anode slimes highlight the fact that, there are variations as to which of the mineral phases identified, could be

predominant in a given sample. This is presumably due to the

inherent variations in the ore geology.

In their reports Kostie, Vink and their co-workers

[12, 13, 14] did mention the use of x-ray fluorescence

spectrometric qualitative element analysis in their work.

To assist in the subsequent minerological studies of the anode

slimes the use of x-ray fluorescence in the present work was

found necessary. This was in order to make comparisons with

the elements in the mineral phases identified by XRD method,

and to substantiate the results obtained. Therefore the

work was conducted by both x-ray fluorescence spectrometry

and diffractometry in an attempt to verify mineral phases

predominant in the anode slimes used in the investigations.

This information was necessary to subsequent investigations

of the cyanidation and adsorption process as earlier on

outlined.

The chemical analysis was restricted only to metals of

interest (copper, silver, gold, selenium)

3.3.1 ANODE SLIMES X RAY SPECTROMETRIC FLUORESCENCE (XRF) ANALYSIS

The aim of x-ray fluorescence analysis was the qualitative

detection of the elements in the sample. The XRF

spectrometry is a qualitative/quantitative method of

analysis for chemical elements either in solid or liquid

form. It operates on the basis of (quantum theory) electron

transitions within the atoms, of the wavelength

characteristic of the emitting elements. The x-ray line

spectrum of an element arises when electrons are expelled

from inner orbits (k, l, m,) of its shells, and electrons from

orbits further out fall into the vacancies. Weak spectral

lines or absorption edge are seldom observed in XRF

spectrometry [22](high resolution electron probe

microanalysis [15] may be used to detect trace elements in

the anode slimes e.g. platinum, palladium). The wavelength of

the radiation in XRF lies somewhere between 0.5 and 2.5 A°.

The phenomena used in the photoelectric absorption whereby

atoms of the sample become excited and send out their

characteristic radiation is termed fluorescence [22].

Copper anode slimes samples were presented for XRF analysis

both in raw and in roasted form to obtain clarity on some of

the elements peaks suspected to have been obscured by

the predominant elements whose peaks may have been

coinciding and therefore difficult to detect.

3.3.2 Sample preparation and analytical procedure for XRF

The samples were made into disc pellets prior to XRF

analysis. The method used to prepare pellets is as

outlined:

(1) A homogeneous and ground sample was first prepared.

(2) A sample was weighed of approximately 8 grams from the

bulk of the sample obtained by spinning riffler.

(3) One gram of powder wax was mixed with the homogenized

sample. This mixture was then put into the die for

forming pellets. The die was pressed applying 15

tons/cm² pressure for one minute. The formed pellet was

then removed from the die for analysis.

The samples were fitted in the XRF sample holder for

qualitative element scan analysis. The XRF parameters are as

indicated on the scan given in figure 3 in the appendix.

3.3.3 RESULTS OF THE XRF ANALYSIS.

The X-ray fluorescence scan of the copper anode slimes is

indicated in fig.3. The peaks of different elements are

labelled as identified. The overlapping of peaks of

different elements complicated the positive determination of

some elements as marked on fig.3. in the appendix.

The elements identified in this scan were compared to those

reported in MITS mineralogical reports, and literature

review. The notable elements in this scan and absent from the

reports are tellerium and magnesium. The following minor

amounts of chlorine, cobalt, calcium, bismuth, antimony,

nickel and iron, were also identified.

The peaks of suspected trace elements of platinum and

palladium were not identified.

The peaks of gold element were also identified, but as

to which of these peaks resulted from sample could not be

ascertained, since a gold x-ray tube was used. Therefore

gold peaks from the tube inherently occurred on the graph.

However most of the elements on the XRF scan agree with

those reported in the mineralogical investigations by MITS.
Major peaks recorded by the scan are those of silver
selenium, copper, silicon, lead and sulphur. The Gold peaks
may have been a result of gold in the sample or those of the
gold tube used in XRF analysis or both.

3.3.4 X RAY DIFFRACTOMETRY ANALYSIS

An attempt was made to determine the mineral phases that
comprise the copper anode slimes used in the investigations.
This was necessary to gain an insight into the subsequent
chemical reactions in the cyanidation process and the
complex cyanide compounds formation. This mineralogical
study was to assist in the evaluation of cyanidation
chemistry of the anode slimes. Knowledge of the cyanide
complexes formed was necessary in the assessment of adsorption
of the precious metals on activated carbon.

X-ray diffractograms were recorded for raw slimes and the
roasted slimes.

The copper anodes slimes were roasted at temperatures of
650°C – 700°C until there were no reddish fumes of selenium
dioxide being observed. The aim was to drive off as much,
selenium and other volatile compounds such as sulphides, as
possible and to assess the dominating compounds in the roasted
slimes after decomposing sulphide and selenide compounds.

X-ray powder diffractometry was mainly used for qualitative
identification of the compounds by their diffraction patterns
based on the principles of Bragg's Law [39].

3.3.5 SAMPLE PREPARATION FOR XRD ANALYSIS

The sample for x-ray powder diffractometry was obtained by the same method employed in XRF analysis. A homogeneous sample with particle size of between 1μm and 50μm is recommended for x-ray powder diffraction analysis [39] . The x-ray diffractograms of copper anodes slimes used in the experiments are shown in figures 4 and 5 in the appendix.

3.3.6 RESULTS OF THE XRD ANALYSIS

The following mineral phases were identified,(see figs. 4 and 5 in the appendix):

Chlorargyrite (AgCl), Naumannite (Ag_2Se), quartz (SiO_2), and selenium (Se) which was recorded as a metal. Chlorargyrite is the only mineral phase not reported in the MITS mineralogical investigation.

Berzelianite ($Cu_{2-x}Se$) and cuprite (Cu_2O) minerals could also be identified. The mineral phases bellidoite (Cu_2Se), chalcocite ($Cu_{1.96}S$) and some phase close to umangite (Cu_3Se_2) could be inferred from the diffractograms. The krennerite or cavarite (Au,Ag)Te_2 and eucarite (CuAgSe) minerals were suspected.

The siliceous mineral identified positively was quartz. The mineral phases of gismondine ($CaAl_2SiO_2.4H_2O$), and bredigite ($Ca_{1.7}Mg_{0.3}SiO_4$) were also suspected. Other peaks on the diffractograms could not be identified, though these were largely thought to be peaks of the copper compounds.

According to The x-ray diffractogram of the roasted slimes

sample, figure 5, this material is largely composed of

native copper, copper oxide (cuprite), native silver and

gold, and siliceous material mainly quartz.

Comparison of the x-ray diffractograms for roasted and

unroasted anode slimes samples shows that the selenide

compound peaks are absent from the roasted slimes

diffractogram probably due to the volatization of the

selenium. This indicates that most of the metal compounds

that had selenium in their mineral phase were decomposed.

The presence of Cu-Ag mineral phases for example Ag, CuAg,

and Cu could be assumed to be present in the roasted sample.

Quartz was the major proportion of gangue mineral reported by

MITS investigations, and confirmed in the present work.

3.4 CHEMICAL ANALYSIS

The copper anode slimes were analysed by atomic absorption

spectrophotometry (AAS). The fire assay method was also used

in the determination of gold and silver. The amount of

insoluble (gangue) material and analytical moisture were

determined by gravimetric methods. Further analysis of

copper and selenium were done by short-iodide and gravimetric

methods, respectively. The results are presented in Table 3.

3.4.1 ATOMIC ABSORPTION ANALYSIS LIMITATIONS

The chemical composition of major minerals of interest,

copper, selenium, silver, and gold were determined by AA6

Varian Techtron atomic absorption spectroscopy. Atomic absorption analysis relies on the absorption of energy by valence electrons of ground state atoms. The measurements can be subjected to the following interferences:

(a) Matrix effects, which influence the amount of sample reaching the flame.

(b) Chemical interference affect the number of atoms formed in the flame [47, 46].

Interferences in the AAS analysis of the elements: gold, silver, selenium and copper.

GOLD

In the analysis of gold excess amounts of iron or copper supress the results. Nitric and sulphuric acids are reported to give a severe depression.

SILVER

Flame interference in the analysis of silver results from use of hydrochloric acid or chlorides in sample solution.

SELENIUM

In selenium analysis, the air/acetylene flame absorbs a substantial amount of light at its normal wavelength. The argon/hydrogen flame may be used instead but its low temperature causes serious interference effects. The nitrous oxide/ acetylene flame gives slightly lower sensitivity.

COPPER

Large excesses of transition elements in the presence of mineral acids depress the response in copper analysis. These interferences may have been encountered in the analysis of anode slimes.

The analysis of the anode slimes by atomic absorption has inherent difficulties as outlined above. Therefore further analysis was done using other methods as outlined ealier.

3.4.2 <u>AAS ANALYTICAL PROCEDURE</u>

The sample weight ranged from 0.1g to 1.0 grams of the anode slimes, the main reason for this weight limitation was to maintain the concentration of elements to be analysed within the recommended AAS concentration range for accuracy [45, 46, 47]. The analysis for each element was done in triplicate.

COPPER

The sample to be analysed for copper was digested in analytical grade, nitric acid, 60%-62% perchloric acid and a few drops of sulphuric acid, mixed thoroughly, heated on low heat to dryness,and redissolved the residue in nitric acid,then filtered and made up the volume with distilled water prior to analysis on AAS.

SELENIUM

For selenium analysis, the same procedure as for copper was maintained, except in this case, instead of heating to

complete dryness, the sample was heated only for 15 minutes to enhance digestion but avoiding losing selenium as SeO_2 fumes.

GOLD AND SILVER

For gold and silver the same procedure was adhered to, the difference was that in case of gold, after heating to dryness the sample was redissolved in aqua regia 1:1 ratio of nitric:hydrochloric acids, whereas the sample for silver analysis was redissolved in analytical grade nitric acid.

3.4.3 INSOLUBLE MATERIAL DETERMINATION IN THE ANODE SLIMES

Determination of insoluble material was done gravimetrically. The sample was digested in nitric, perchloric and sulphuric acid, and heated to dryness. The residue redissolved in nitric acid, was filtered, and then ignited in the muffle furnace for 30 minutes. The fraction of the insoluble was the final weight divided by initial weight [49].

3.4.4 GOLD AND SILVER FIRE ASSAY LIMITATIONS

Fire assaying involves separating the metal from the other constituents of the ores by fusion, cupellation and parting, and weighing it in a state of purity [25]. Although fire assaying gold and silver is widely used and recommended method it is not entirely free of error. Fire assaying

accuracy is subject to careful analysis in all the stages of analysis. The impurities like tellurium, selenium, bismuth, manganese, copper, vanadium, zinc, arsenic, antimony, iron, and tin all induce extra losses of precious metals in cupellation and ought to be removed prior to this stage, as slag, after fusion or in leaching the sample, at a preliminary stage.

There is an inevitable loss of silver in cupellation. The amount of silver loss, results from many factors: temperature, proportion of Lead to silver, the amount and nature of impurities. Other losses may be due to spurting, absorption of bullion by the cupel and volatilization of silver either alone or accompanied by other metals.

There is always some loss of gold in cupelling albeit negligible. The loss of gold in cupelling is greater with pure gold and alloys poor in silver than in alloys rich in silver. The nitric acid for parting must be free from hydrochloric acid and chlorine in order to have no solvent action on the gold and also because any chlorides present would precipitate insoluble silver chloride on the gold (see equations below).

a) Cl^- + HNO_3 forms aqua regia which may dissolve some of the gold.

b) Cl^- + Ag^- forms a precipitate $AgCl$, which could cause erroneous weight. The nitric acid must be hot before dropping the bead as the bead tends to break-up into

extremely fine particles. When gold disintergrates in
parting, some of it may be lost to decantation. This
decanted gold would be so finely divided as to be invisible.
There are errors that may result from rare metals which may
be retained and weighed as gold. In addition to this there
is always a small amount of silver which persistently resist
solution and this is dependent on number of factors like
ratio of silver to gold in the original bead, the strength
of acid used and the time of acid treatment [25].
Therefore for fire assay to be accurate necessary precaution
must be taken.

3.4.5 FIRE ASSAY PROCEDURE AND ANALYSIS

In view of the foregoing, extreme care was exercised in the
fire assay analysis of copper anode slimes. The following
procedure was used in the fire assaying of the slimes:
5 grams samples in triplicate obtained by cone and
quartering, were initially leached with sulphuric acid in
the presence of mercuric nitrates to decompose base metals
and other soluble elements. The silver in solution was
precipitated as silver chloride. The filtered residue of
gold and silver was subjected to fire assay.
Preheating of the sample was found necessary prior to fusion
in order to drive off free and combined water, organic
matter, carbon dioxide and other volatile constituents that
would otherwise rise through the lead during fusion and

cause spurting (the ejection of particles), which could be a source of loss to the assay. The flux ratio used was as follows: 73 parts litharge, (PbO), 12 parts sodium carbonate (NaCO$_3$), 10 parts Borax (Na$_2$B$_4$O$_7$.10H$_2$O), 5 parts silica (SiO$_2$). A 20 kW - 300 V three phase cupellation furnace equipped with a gas extraction system was used in the analysis. Fusion temperature was maintained uniformly during 15 minutes of fusion at 1000°C. Cupellation temperature range of 910°c to 940°c was maintained until completion of cupellation.

The silver/gold bead thus obtained was hammered to about 1mm thick and weighed prior to parting. The remaining bead of gold was weighed and per cent gold and silver determined. The weighing was done on an electronic balance.

3.4.6 COPPER ANALYSIS BY SHORT-IODIDE METHOD.

PROCEDURE

A sample weight of 0.5 grams was digested with nitric, hydrochloric, and sulphuric acid analytical grade, evaporating the latter to strong fumes. Adding ammonium hydroxide slightly in excess to form a copper-ammonium complex and acidifying the mixture with acetic acid. To this was added potassium iodide and titrated with standard sodium thiosulphate until the dark brown colours turned to a straw yellow. Starch of 0.5 % was added to the solution and the titration was continued until the colour changed from purple/blue to yellowish marking the end point.

3.4.7 SELENIUM ANALYSIS BY GRAVIMETRY.

PROCEDURE

The method used was by the decomposition of the anode slimes sample in the mixture of nitric, hydrofluoric, and perchloric acids and then addition of hydrochloric acid. Subsequently, the dissolved constituents were precipitated with sulphur dioxide. The precipitate was finally volatilized and the weight loss of the precipitate noted.

The analysis was done in triplicate, the average sample weight used was 1.0 grams. The sample was heated in the decomposition acid mixture above, evaporating gently to copious fumes of perchloric acid. After which the sample was cooled and hydrochloric acid added, This was warmed gently to dissolve the salts, then the mixture was filtered. To the filtrate was added again hydrochloric acid and subsequently precipitated with sulphur dioxde. This was allowed to stand for two hours. The precipitate was then filtered through a porcelain crucible. The filter cake(precipitate) was weighed before and after igniting in the muffle furnace.
The % selenium was determined by the weight loss of the precipitate which represented the volatilized selenium.

YTICAL RESULTS

3.4.8 RESULTS OF THE CHEMICAL ANALYSIS

The results obtained by various methods were compared as indicated in table 3.

The gold content by fire assay was higher than that recorded by atomic absorption analysis. Careful consideration of inherent limitations highlighted in both methods, indicates that fire assay analysis was more reliable than AAS.

The difference of the arithmetic mean of the fire assay and AAS analysis is given in table 3. The arithmetic mean differences are shown, to indicate the variation in the methods used. It was observed that the differences were larger for the metals with higher percentages.

The silver was higher for AAS and low for fire assay. The observations show that both the methods are reliable considering the inherent limitations of the methods.

However these results give the average chemical composition of the anode slimes used in the investigations.

CHAPTER 4

LITERATURE REVIEW

CYANIDATION OF SILVER AND GOLD ORES

4.1 PRECIOUS METALS CYANIDATION.

Various forms of reactions have been given for the dissolution of gold in cyanide solutions and analogous equations have been given for silver .

$$4Au + 8NaCN + O_2 + 2H_2O = 4NaAu(CN)_2 + 4NaOH.....(1)$$
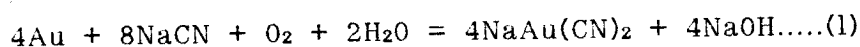
This is known as Elsner's equation, it fits with the free energies for the reaction work done by Barsky, Swanson and Hedley.

$$Au + 4NaCN + O_2 + 2H_2O = 2NaAu(CN)_2 + 2NaOH + H_2.... (2)$$
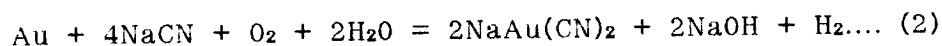
The reaction equation (2) was suggested by Janin and then Ramsay.
The reactions in equations (3) and (4) were suggested by Bodlaender [31, 35].

$$2Au + 4NaCN + O_2 + 2H_2O = 2NaAu(CN)_2 + 2NaOH + H_2O_2..(3)$$
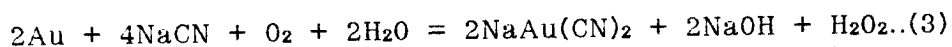
The hydrogen peroxide formed in equation (3) is used in the reaction as shown (4) below.

$$2Au + 4NaCN + H_2O_2 = 2NaAu(CN) + 2NaOH ....(4)$$
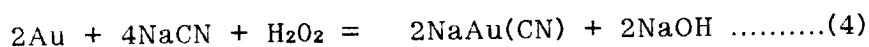
The overall equation, however, is the same as Elsner's although as pointed out by other workers, Elsner's equation

is considered not strictly correct, as it does not show the intermediate formation of hydrogen peroxide. Elsner's equation ignores galvanic action and subsidiary chemical changes that may have an important influence on commercial extraction.

Christ and then Julian and Smarts suggested that the dissolution of gold and other metals in cyanide depends primarily on electromotive force exerted during the cyanidation action [42]. Bodlaender's equations only represent the partial state of affairs. Evidence has been shown that unknown substance is formed which reacts like H_2O_2, and the reaction represented by the equation given by Bodlaender is limited to an insignificant part of the whole mass.

The formation of hydrogen peroxide (H_2O_2) during the reaction indicates equation (2) may not represent the reaction occurring, as it assumes that the oxygen is reduced completely to hydroxyl ions. The first stage however is the reduction to hydrogen peroxide, so that the reaction could be written as in Bodlaender's equation [31, 35, 42]. Addition of hydrogen peroxide to the cyanide solution increases the rate of solution of silver while small amounts have little effect on the rate of solution of gold and large amounts decrease the rate [26]. The ratio of the amount of metal dissolved should permit a distinction to be made between the dissolution reaction of gold and silver. From

the foregoing Burkin [26], proposed that silver dissolves

in cyanide solutions in the presence of oxygen in accordance

with Bodlaender's equation, whereas with gold, Elsner's

equation represents the predominant reaction.

Boonstra was in favour of Bodlaender's equation, which

was in agreement with corrosion theory, pointed out that

Bodlaender's equation should be further divided into the

following steps [34]:

Cathodic reaction

$$O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$$

$$H_2O_2 + 2e = 2OH^-$$

Anodic reaction.

$$Au = Au^+ + e$$

$$Au^+ + CN^- = AuCN^-$$

$$AuCN + CN^- = Au(CN)^-_2$$
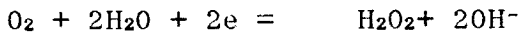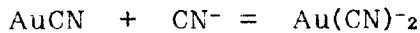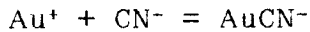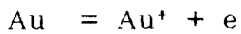
More recently Habashi showed that the dissolution process

was elecrochemical in nature and follows mainly the overall

equation as in equation (3) [34].

4.1.1 SELECTION OF LEACHING CONDITIONS

The gold complexes in aqueous solutions of hydrometallurgical

interest exist in one of two oxidation state, the aurous

(+1) or the auric (+3). The thermodynamics predict that

neither aurous nor auric cations will be stable in aqueous

solution, in order to stabilize these ions in aqeuous

solution it is necessary to introduce a complexing ligand and to employ a suitable oxidizing agent, since no reaction occurs unless both are present in the solution. Both gold (+1) and gold (+3) are B-type metal ions, which means that the stability of their complexes tends to decrease as the electronegativity of the ligand donor atom increases. This accounts for stability orders such as $SeCN^- > SCN > OCN$ or $CN > NH_3 > H_2O$. Gold (+1) forms an extremely stable aurocyanide complex with cyanide ion, the stability constant is of the order of $2 \cdot 10^{38}$. Because of the strong stabilizing effect of cyanide ion, [47] metallic gold will be readily oxidized to aurocyanide ions by dissolved oxygen.

The relative stabilities of metals and metal complexes in aqueous solutions are conveniently represented in the potential-pH diagram, indicating the predominant species which are present at equilibrium at given reduction potentials and hydrogen ion concentrations. The E_h-pH diagram for the system Au-H_2O-CN^-, in figure 6 is a classic example used to identify soluble gold complexes to aid leaching. The oxidation potential is so low that O_2 gas may be used to drive the reaction as shown below.

$2Au_{(s)} + 4(CN)^-_{(aq)} + 2H^+_{(aq)} + \quad O_{2(g)} = 2Au(CN)^-_{2(aq)} + H_2O..(5)$
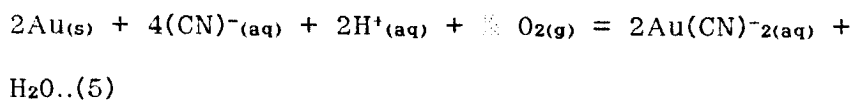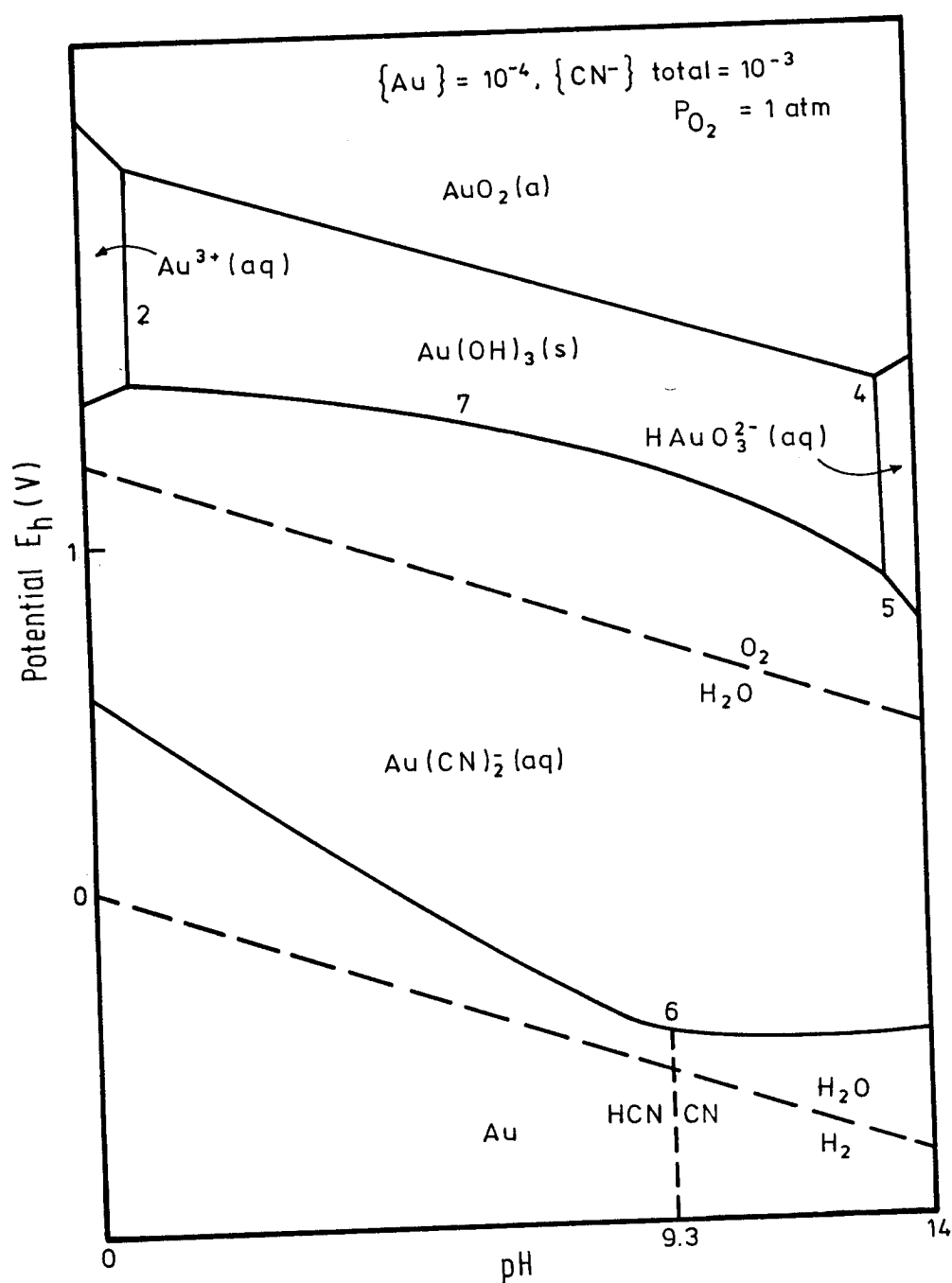
FIG. 6 E_h-pH diagram for Au–CN–H_2O system at 25°C

As can be noted in figure 6, the maximum chemical driving

force for the reaction occurs at pH ~ 9.5 which corresponds

broadly to the conditions used in industrial practice of pH

~ 11. The E_h- pH diagram while useful in selecting leaching

conditions do not take into account the rate at which the

various reactions may occur, they represent thermodynamic

equilibria. The kinetics of various reactions have a more

profound effect on the phase and species present in any

system. The rates of leaching reactions are generally

limited by diffusional processes and therefore tend to be

slow [37].

The kinetics of the dissolution of gold are electrochemical

in nature and involve an oxidative or anodic reaction on

the gold surface. The electrochemical nature of the

dissolution of gold in aerated cyanide solution was

recently reviewed by Nicol [43]. Using current-potential

curves, passivating oxide films during anodic dissolution of

gold were noted. On the basis of measurements of current at

various potentials, it was generally accepted that the

dissolution of gold occurred by way of the following

mechanism:

$$Au + CN^-_{(aq)} = AuCN_{Ads} + e,$$

$$AuCN_{Ads} + CN^-_{(aq)} = Au(CN)_2^-_{(aq)}$$
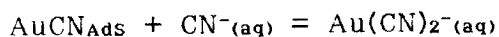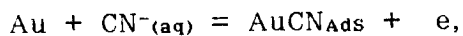
where $_{Ads}$ represents adsorption.

Passivation was therefore associated with an adsorbed layer

of AuCN. The presence of foreign heavy-metal atoms on the surface would likely disrupt the formation of such a layer, thus reducing the extent of passivation [43].

These observations were made with pure gold, however the situation may be different with actual gold ores.

4.1.2 EFFECT OF CYANIDE CONCENTRATION ON DISSOLUTION OF PRECIOUS METALS

The effect of cyanide concentration on the rate of dissoluton has been widely reported by various investigators. The variations, as to when maximum rate of precious metals dissolution is obtained, may probably be due to a variety of techniques employed in determining these figures. Factors such as pulp density, speed of agitation, rate of aeration etc, must have influcenced the results [26, 35, 42, 44]. Cyanide reacts with water (H_2O), according to the equation 6 below, to give HCN (hydrocyanic acid) which is has no dissolution effect.

$$NaCN + H_2O = NaOH + HCN ....(6)$$
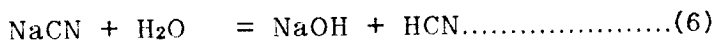
Hydrocyanic acid has no dissolution action on gold, it is a weak acid with the dissociation constant for the reaction given as $4.93 . 10^{-10}$ for equation 7

$$HCN = H^+ + CN^- ....(7)$$
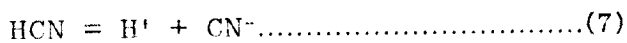
Sodium cyanide is stabilised by maintaining the pH range between 11-13 with sodium hydroxide (NaOH). The amount of

NaOH should be enough to give the required pH without reversing the dissolution reaction. If there is too much hydrogen peroxide it reacts with cyanide to give cyanate, as given in the equation 8. below..

$$H_2O_2 + NaCN = NaCNO + H_2O \dots\dots\dots(8)$$
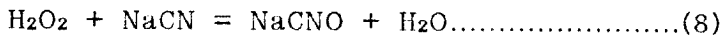
This reaction [32] inhibits dissolution of gold and silver due to oxidation of cyanide ion to cyanate ion which has no dissolution action on the metal. Crosse [42] showed that gold is attacked in hydrocyanic acid HCN or acidulated cyanide solution in the presence of oxygen, in which case insoluble auricyanide is formed instead of the usual aurocyanide as indicated in equation 9.

$$2Au + 2HCN + O_2 = 2AuCN + H_2O_2 \dots\dots\dots(9)$$

The dissolution of precious metals increases linearly with increasing cyanide concentration until a maximum is reached, further increase does not increase the amount of gold (silver) dissolved but has a slight retarding effect.
This decrease in the rate of dissolution at high cyanide concentration is due to the increase in pH of the solution, which inhibits the forward reaction. The cyanide ion undergoes hydrolysis according to the following equation.

$$CN^- + H_2O = HCN + OH^- \dots\dots\dots(10)$$
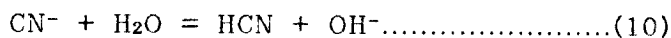
The major cause of the cyanide consumption is not the

combination of the cyanide with gold or silver but side

reaction with cyanide consuming agents contained in the ore,

reaction with dissolved carbonic acid, [32, 42] and

hydrolysis of the cyanide.

4.1.3 EFFECT OF PARTICLE SIZE

Barsky, et al. found the maximum rate of dissolution of

gold to be 3.25 mg per cm^2 per hour. Metallic silver of

the same thickness would take twice as long to dissolve. In

most cases under plant conditions the rate of dissolution is

affected by such factors as the association of the gold and

silver.

The particle size of the solids has a significant effect on

the rate of leaching, the smaller the particle the greater

the ratio of the area to mass, hence the increased rate of

transfer of reactants and products [35].

4.1.4 OXIDIZING AGENTS

Potassium permanganate, sodium dioxide, and bromine have

been mainly employed to assist in the dissolution of the

gold and silver. When bromine is used, little or no oxygen

is required, it reacts as shown in the equations 11 and 12.

$$2 KBr + KBrO_3 + 3KCN + 3 H_2SO_4 = 3 BrCN + 3K_2SO_4 + 3H_2O \ldots (11)$$

$$Br CN + 3KCN + 2Au = 2 K Au (CN)_2 + KBr \ldots (12)$$
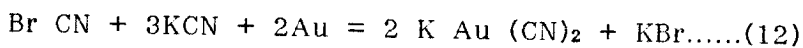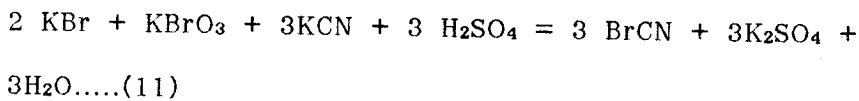
Julian and Smart consider that the activity of

bromocyanogen, (BrCN), is not due to the liberation of

cyanogen, though that probably occurs, but due to the

liberation of oxygen, [35, 45]. as in equation 13, below

$$2 \; Br \; CN \; + \; KCN \; + \; 4KOH \; = \; 2KBr \; + \; 2KCN \; + \; KCNO \; + \; 2H_2O \; + \; O..(13)$$
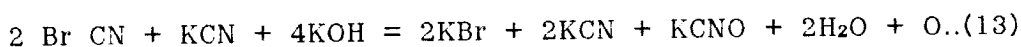
4.1.5 EFFECT OF OXYGEN ON CYANIDATION

Oxygen appears to be an indispensable factor, either directly

or indirectly in the dissolution of gold and silver by

cyanide solution [32]. The oxygen content of cyanide

solution at saturation is about 8 mg/l dependant on the

altitude(above sea level). In air-agitated leach vessels, air

consumption, at STP is approximately 300 l/s per 1000 m^3 of

agitated volume, and in mechanical draft tube agitators the

air requirement is only about 20 l/s of the same agitated

volume. The rate of dissolution of gold and silver in

cyanide solution was found to be directly proportional to

the partial pressure of oxygen. The importance of oxygen is

highlighted in the work done by Kudryk and Kellogg,

represented by a schematical diagram, illustrating the

mixed-potential electrochemical dissolution model [44]. In

the absence of external EMF the rate of gold dissolution is

governed by the requirement that the rate of the anodic

process is equal to the rate of the cathodic reduction of

oxygen [44].

4.2 KINETICS OF CYANIDATION

The kinetics of cyanidation reaction were determined by various workers using the rotating disc method [26, 35]. It was found that reaction rate was controlled by three reaction mechanism and these were: diffusion of reactants across liquid film, diffusion of reactants across some solid film on surface, and chemical reaction rate. It was observed that varying concentration of cyanide, the rate of reaction became constant after sometime, but with an increase in oxygen partial pressure (P_{o2}) the rate of reaction is increased. As such in this case we can say that P_{o2} is the rate controlling parameter [31] as shown in diag.(a). overleaf.

The most noticeable effect of extra aeration of solution is a substantial reduction in cyanide consumption.

Habashi considers that most reactions in gold and silver cyanidation are electrochemical, according to the cathodic and anodic equations given in the schematic diagram (b), Assuming from the chemical reactions at the metal interface in diagram b, that [CN^-] and [O_2] concentrations at the surface both are equal to zero (as they are consumed at the surface by the dissolution reaction of gold)the concentration gradients across the film would be:

[CN^-]   and   [O^-]

where [CN^-] and [O_2] = concentration of CN^- and O_2 in the bulk of the solution in mole/l and = the thickness of the
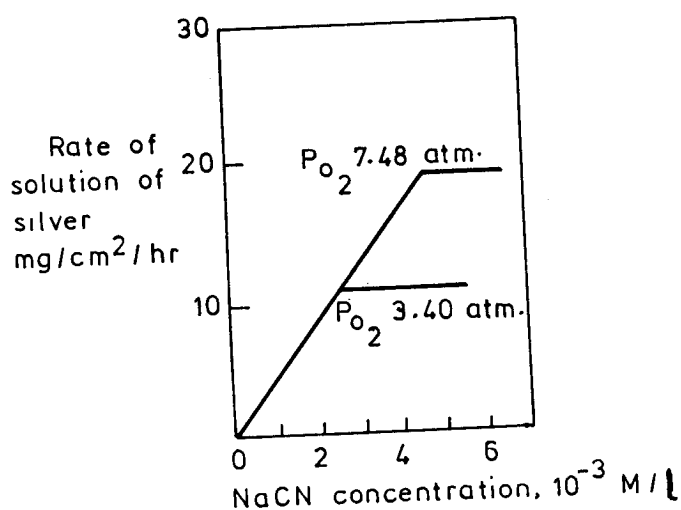
Diagram a. Rate of solution of silver at different O_2 pressures and different NaCN conc. at 24°C
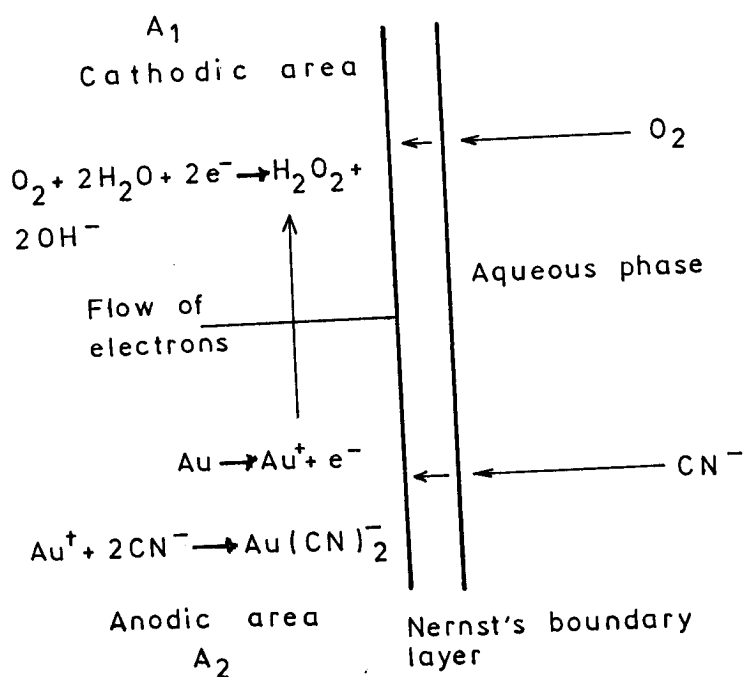
Diagram b. Schematic representation of the dissolution of gold in cyanide solution

boundary layer in centimeters (cm).

The diffusion rate of oxygen across boundary of thickness δ could be represented by Fick's law.

$$\frac{d(O_2)}{dt} = \frac{D_{O2}}{\delta} \ A_1[O_2]............(a)$$

Where $\frac{d(O_2)}{dt}$ = the rate of diffusion of O_2 in moles/sec.

D_{O2} = the diffusion coeffficient of dissolved oxygen in cm^2/sec.

A_1 = surface area at which the cathodic reactions take place

$[O]$ = dissolved oxygen concentration in mole/litre

δ = thickness of the boundary layer in centimeters

The diffusion rate of CN^- across boundary film is given by

$$\frac{d}{dt}(CN^-) = \frac{D_{CN^-}}{\delta} \ A_2[CN^-].......(b)$$

Where $\frac{d(CN—)}{dt}$ = the rate of diffussion of CN^- ion (mol/s)

D_{CN^-} = the diffussion coefficient of cyanide ion

A_2 = the surface area at which the anodic reaction takes place

According to precious metals dissolution equation 1, the rate of diffusion of species will equal to:

$$2\frac{d(O_2)}{dt} = 2\frac{D_{O2}}{\delta} \ A_1[O_2].........(c)$$

$$\frac{d(CN^-)}{dt} = \frac{D_{CN^-}}{\delta} \ A_2 \ [CN^-].......(d)$$

At steady state conditions the rate equation is given as below:

The rate of metal dissolution = r

$$r = \frac{2A \; D_{CN^-}.D_{O_2} \; [CN^-] \; [O_2]}{\delta \{ D_{CN^-} \; [CN^-] + 4D_{O_2}[O_2]\}} \quad ......(e)$$

at low CN^- concentration, the first term in the denominator may be neglected and this equation simplifies to:

$$Rate = \frac{A \; D_{CN^-} \; [CN^-]}{\delta} = K_1 \; [CN^-].....(f)$$

At high CN^- concentration and Low O_2 concentration the second term in the denominator may be neglected and this simplifies the equation to:

$$Rate = 2 \; A \; \frac{D_{O_2} \; [O_2]}{\delta} = K_2 \; [O_2]..........(g)$$

Where   A = surface area at which the reaction is taking

   place

   K_2 = the reaction rate constant.

These equations indicate that, at high CN^- the rate of reaction of dissolution is controlled by the oxygen concentration. At optimum condition neither CN^- or O_2 will control the other and this may be represented as follows:

$$D_{CN^-} \; [CN^-] = 4 \; D_{O_2} \; [O_2]$$

$$\frac{[CN^-]}{[O_2]} = \frac{4D_{O_2}}{D_{CN^-}}..........(h)$$

Therefore at optimum condition we should have the following ratio of concentration of the reactive consumption:

$$\frac{[CN-]}{[O_2]} = 6\ldots\ldots\ldots(i)$$

Burkin [26] showed by rotating disc method experiments, that at high revolution per minute, the rate of reaction was very fast because the reactants are delivered to the surface much faster, suggesting chemical reaction as rate controlling. The following equation was derived:

Rate of dissolution $= \dfrac{Q}{t} = KACn$ moles/sec......(i)

Where, Q = the quantity of metal dissolved, $moles$, t = the time of reaction,sec; K = the reaction rate constant, litre cm^{-2} $sec^{-1/2}$; A = the area of the disc surface reacting, cm^2; C = the concetration of cyanide in the solution, mole per litre; n = the number of revolution per second.

The reaction rate constant can be calculated from Levich's boundary layer theory [26].

$$K = \frac{6.18 \times 10^{-4}D^{2/3}}{mV^{1/6}}\ldots\ldots\ldots(k)$$

Where m = the stoichiometric coefficient of the reaction is the number of solute ions reacting with one metal atom; V = the rate of dissolution of the metal.

The diffusion coefficient D for potassium cyanide is unknown, but an approximation equal to 1.85×10^{-5} cm^2 sec^{-1} for $7 - 10 \times 10^{-3}m$ solutions may be used.

The experimentally determined values of reaction rate

constant were found to differ significantly from one another

and from the theoretically calculated values.

In general, actual rates are lower than theoretical values

due to the influence of various factors obtained in actual

processes.

The most striking feature of the leaching reaction is the

relative speed with which some 80 to 90% of the gold

dissolves in 2 to 4 hours and the subsequent deceleration of

the reaction, so that up to 40 hours is required to leach

the more refractory 10% of gold in the ore. Depending on

the ore up to 98% is capable of being extracted in the

cyanidation process [44].

2.1 EFFECT OF FOREIGN ELEMENTS

The presence of foreign elements   in   , the metal to be

leached affect the leaching process. The low values found

for the reaction rate constants of copper, silver and gold,

dissolving in cyanide solutions, when the rate controlling

process was the rate of transport of cyanide ions to the

metal surface, are explained as being due to the formation

of an insoluble film of a product on the surface.

In the case of copper, $CuCN^-$ is insoluble in the aqueous

phase and forms on the gold surface and acts as a barrier to

dissolution of precious metals.

The formation of an insoluble material during the reaction

may be represented as in equations (ia) and (iib). The metal

more likely reacts into two steps to give the soluble cyanide ion.

$$M + CN^- = M\,(CN) + e \quad \text{.............................} \quad (ia)$$

$$M\,(CN) + CN^- = M(CN)_2{}^- + e \text{........................} \quad (iib)$$
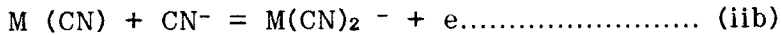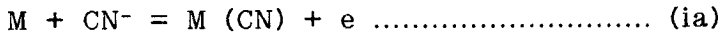
Equation (iib) is the rate controlling step, that is the rate of reaction between the insoluble cyanide and more cyanide ions to give the soluble double cyanide. The rate of attack on the metal depends on the rate of transport of the reactant through the film to the metal surface [26]. Some impurities like Pb, Bi, Ti, catalyse the reaction rate whereas Fe, Zn, S, retard the reaction rate, due to the reaction with dissolution reagents as given below.

$$2FeS + 20H^- = Fe(OH) + S_2{}^{2-} \text{.................}(14)$$

$$Fe(OH) + O_2 + H_2O = Fe(OH)_3 \text{...................}(15)$$
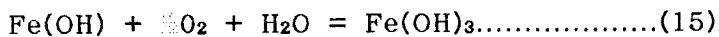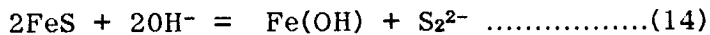
These reactions use up oxygen in the aqueous solution and thus depleting the oxygen desired for cyanidation of the preferred metal values.

$$ZnS + 4CN = \{Zn[CN]_4\}^{2-} + S^{2-} \text{...............}(16)$$

$$S^{2-} + [CN^-] + O_2 + H_2O = CN\,S^- + 2OH^- \text{.....}(17)$$
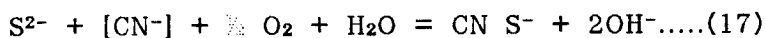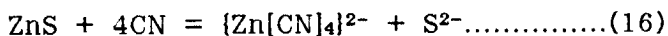
Thus excess CN^- or O_2 has to be added in order to replace that which is used up in the side reactions.

The retarding effect of impurities like sulphide may be two fold that is: the consumption of cyanide and oxygen from the solution to give thiocyanates and thiosulphates and the formation of insoluble aurous sulphide film on the gold which inhibits dissolution [31, 42].

4.2.2 EFFECT OF COPPER ON CYANIDATION

The copper content effect on the dissolution of gold can be very pronounced. The copper minerals dissolve in cyanide and cause excessive consumption of this chemical. The copper cyanogen complexes thus formed indirectly affect the dissolution of the gold.

Copper dissolves readily in cyanide solution, without the presence of free oxygen, with evolution of hydrogen and form a series of double cyanides, whose composition depends upon the amount of alkaline cyanide present in the solution. The general reaction can be represented by equation (18) below.

$$CuCN + XNaCN = Na_xCu(CN)_x..........(18)$$
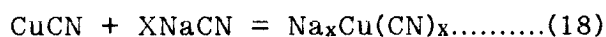
The complex $NaCu(CN)_2$ is only slightly soluble in water, tending to breakdown into CuCN [26]. Woolf et al., [35] state that the dissolving activity of a solution begins to decrease when its copper content is somewhere above 1.0%. The same workers however state that copper has little effect on extraction of gold and silver provided the solution contains enough cyanide ion.

Cuprocyanide solution hypothesis suggests that the

dissolution of gold and silver in the cuprocyanides

complexes is due to the presence of relatively small amounts

of cyanide ion resulting from the dissociation of these

complexes. As the ratio of total cyanide to copper decreases

in passing from $Na_3Cu(CN)_4$ to $NaCu(CN)_2$ the extent of this

dissociation decreases [32, 35, 42] and also the

dissolving effect. The chain of reaction indicating the

dissociation of cuprocyanide may be represented as in

equations (19a) and (19c).

$$Na_3Cu(CN)_4 \quad = \quad 3Na^+ \;+\; Cu(CN)_4^{3-}.........(19a)$$

$$Cu(CN)_4 \quad = \quad CN^- \;+\; Cu(CN)_3^{2-}.........(19b)$$

$$Cu(CN)_3 \quad = \quad CN^- \;+\; Cu(CN)_2^-.........(19b)$$
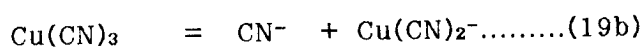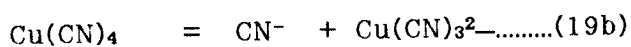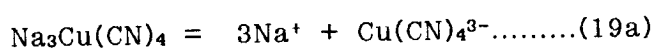
4.3.0 <u>CYANIDATION OF THE TELLURIDES OF PRECIOUS METALS.</u>

Cyanide solutions act very slowly on tellurides of gold and

silver but dissolve both elements whether in a fused

mixture or in native tellurides.

Thomson advocates an electrochemical theory of the stability

of the tellurides and suggests that dissolved oxygen or

oxidizing agents such as bromocyanide may assist by

oxidizing the telluride ion thus leaving the gold ion free

to form the aurocyanide complex [42].

The rate of dissolution of the gold is greatly increased by

the addition of bromocyanide. MacArthur and Forrest [27]

found that dilute cyanide solutions generally exercise a

selective action in dissolving gold and silver in whatever

form these may be present. The soluble sulphides may be rendered harmless by the addition of lead acetate, lead nitrate, litharge or mercury salts.

Johnston considers that auriferous tellurides yield their gold to cyanide if they are in a finely divided state and if excess lime is used. Appreciable amounts of arsenic or antimony in the material being leached result in low extraction of the precious metals in the cyanidation process. They decompose to some extent in alkaline cyanide solutions to form complex reducing compounds which retard or prevent gold dissolution [31, 32, 35, 42].

CHAPTER 5

EXPERIMENTAL WORK

5.1 ANODE SLIMES CYANIDATION EXPERIMENTS

The cyanidation experiments were done in five litre beakers,

The mechanical mixer was an IKA - Werk RW20 with a speed of 300

rpm. The laboratory air flowmeter was a platon gapmeter type

GTWK with an A10 unit scale, having airflow range 10-100

l/min. In the experiments agitation batch leaching in a

flat-bottomed agitator tank was simulated, to provide high

rates of mixing and consequently high rates of dissolution

due to: the large surface area exposed and the minimization

of the diffusion layer thickness, whilst maximising

reactants and products diffusion.

The mechanical mixer was used to promote mixing and prevent

settling of solids. Compressed air was used to maintain

effective pulp aeration and assist in mixing. In these

experiments, perfect mixing was maintained, to eliminate

short-circuiting and dead volume due to settlement of

solids. The apparatus set-up is as indicated in figure 7.

Copper anode slimes batches were leached in the above

apparatus under various conditions of airflow rate and

cyanide concentration to optimize leaching.

The leaching time ranged from one to six hours. In cyanidation

the principal solvent used is a cyanide salt, either sodium,

calcium, or potassium cyanide. Potassium cyanide is

Figure 7   CYANIDATION   APPARATUS,
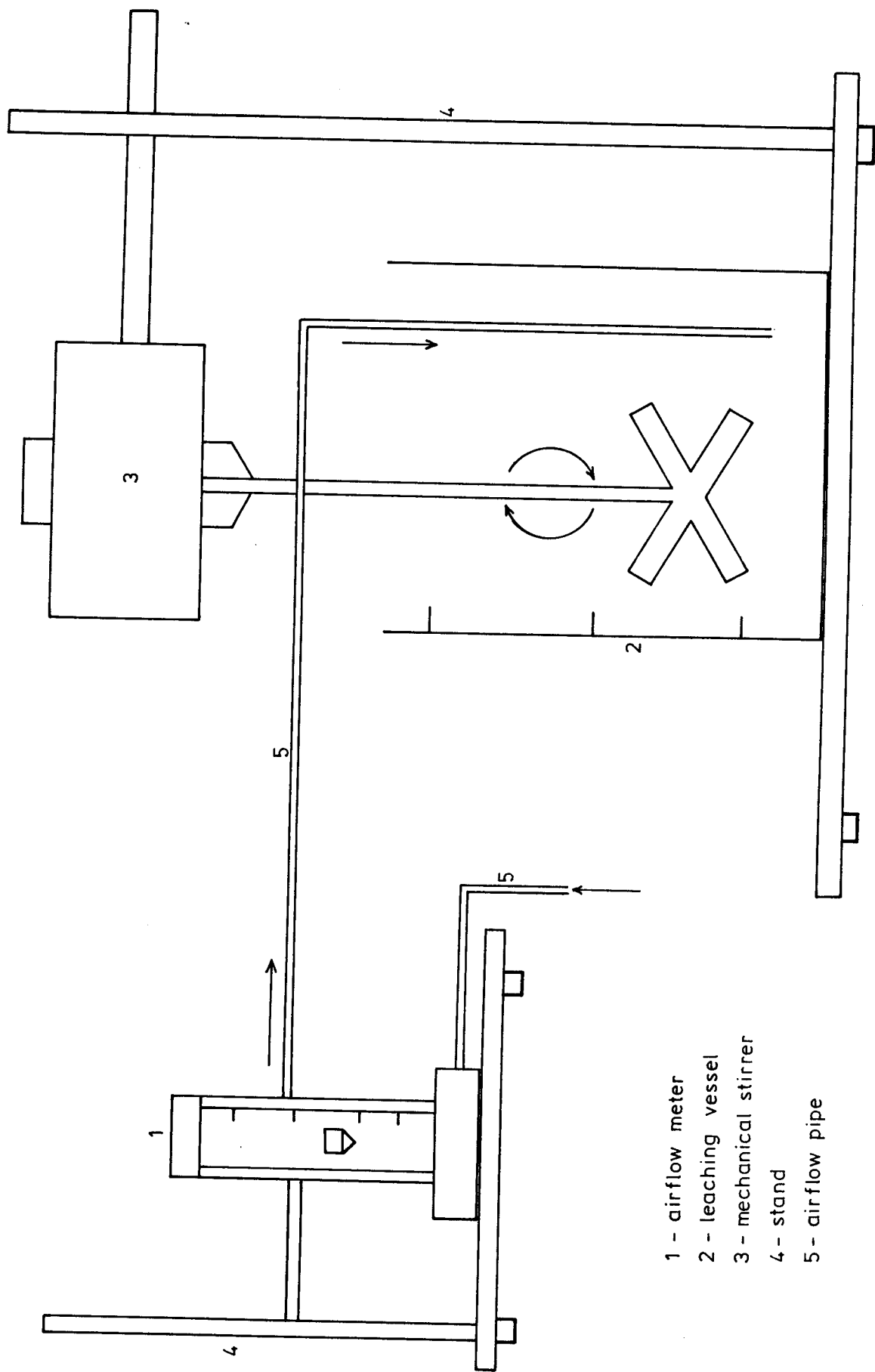
1 – airflow meter
2 – leaching vessel
3 – mechanical stirrer
4 – stand
5 – airflow pipe

frequently not used on large scale owing to the high price. However, during these cyanidation experiments potassium cyanide (KCN) was used as a solvent and protective alkalinity was obtained by sodium hydroxide (NaOH). Aeration of the pulp was effected by air, from the compressor. Cyanidation was carried out under room temperature.

The cyanide was initially dissolved in aqueous solution of pH 11, before adding to a leach vessel and continuously monitored by pH – meter.

In all the expeirments, the mechanical stirring rate was maintained at 300 rpm, no attempt was made to vary the rate as it was thought that variation in airflow rate inevitably augmented and varied the agitation of the pulp.

The pulp density was also held constant at 10% to facilitate dissolution to proceed rapidly. Therefore in all the experiments, pulp density, temperature, mechanical mixer speed, and pH were kept constant. The amount of dissolved gold, silver, and copper during cyanidation were determined periodically by atomic absorption spectrometer.

Only two parameters aeration and cyanide strength were varied. The reactive consumptions of cyanide and oxygen were not determined due to the limitation imposed by the colour of the solution to titration method, in the absence of CN^-ion and O_2 selective electrode probes.

The analysis of free CN^- was attempted by titrating with

standard 0.1N AgNO₃(silver nitrate solution), the end-point

marked by the appearance of a persistent yellow colour.

The limitation imposed by the brownish-yellow colour of the

anode slimes cyanidation liquor made it difficult to asssess

the end point, making the method unreliable. The main

objective of cyanidation of anode slimes was the dissolution

of precious metals gold and silver. Hence efforts were

concentrated on effecting optimum dissolution by

manipulating the two important parameters oxygenation and

cyanide strength.

5.1.1 SAMPLING.

The ideal measurement of the rate of leaching would have

been using on-line sampling and analysis.

During cyanidation the sample was periodically manually

scooped, filtered and analysed on the atomic absorption to

monitor the rate of dissolution. The main aim was to

optimize the dissolution of gold and silver from the copper

anode slimes by cyanidation and subsequently assess the

adsorption of these values on activated carbon.

5.1.2 ANALYTICAL METHOD.

The analysis of the cyanidation leach liquor was restricted

to atomic absorption spectrophotometry with its inherent

limitations as outlined earlier in the report.

Some of the analytical techniques which could be used to

determine gold, silver, selenium and copper are uv/vis

photometry, radio-isotope excited energy despersive x-ray
fluorescence spectrometry, inductively coupled plasma
spectrometry and ion selective potentiometry.

In the analysis of gold in cyanide leach liquor, atomic
absorption response is depressed by cyanide. Excess amounts of
iron, and copper also supress the results to some extent.
It is recommended that the cyanide be destroyed by fuming
with a mixture of sulphuric and perchloric acids prior to
analysis. The other interferences in the analysis of
•silver are mentioned in chapter three of this report.
Initially therefore, the cyanidation leach liquor was
analysed by atomic absorption without any pretreatment steps
and the results were recorded. Later on, to assess the
depressing effect of cyanide and consequently the
reliability of the results earlier obtained, two calibration
standards with the same gold concentration but different
matrix background were prepared. One with the cyanide
matrix background and the other being normal aqua-regia
atomic absorption standard.

The following, AA6 Varian Techtron AAS operating conditions
were used: wavelength:- 267.6 nm, spectral band pass:- 0.2,
lamp current:- 4mA, fuel flow (acetylene):- 4 AA units,
oxidant flow (air) :- 6 AA units, lamp intensity:- 2,
Typical sensitivity:-0.26.

The standards were prepared by the following procedure:
0.0346 grams spec pure gold was dissolved in aqua regia and

the volume made up to 100 ml with distilled water to make a 346 μg/ml concentration. From this stock solution two sets of standard concentration were prepared by pipetting calculated aliquots and making-up the volume with distilled water to make the following concentrations: 10, 20, 30, 40, μg/ml Au.

In one set, the solution were heated to near dryness and then made up to 100 ml again by strong cyanide solution (1 M). On aspirating the sample on AAS, a yellowish orange flame colour could be noticed, presumably as a result of the sodium/potassium from sodium hydroxide and potassium cyanide.

Measuring the absorbance of both standard solutions, a comparison of absorbance results was obtained, indicated in fig. 8.

From the foregoing, therefore the observation made was that the cyanide depressed the AAS absorbance read-out. By the extrapolation of the AAS calibration curves shown in figure 8, the absorbance read-out is zero at approximately 1.5 μg/ml Au of the cyanide matrix solution. From this observation it could be noted that, in the conditions employed, cyanide was found to have a slight depressing effect on the results. To verify these results further an excess amount of cyanide was added to these samples and the results compared with those obtained. It was found that the depressing effect remained, though slightly lower, approximately 1.2 μg/ml. Therefore,
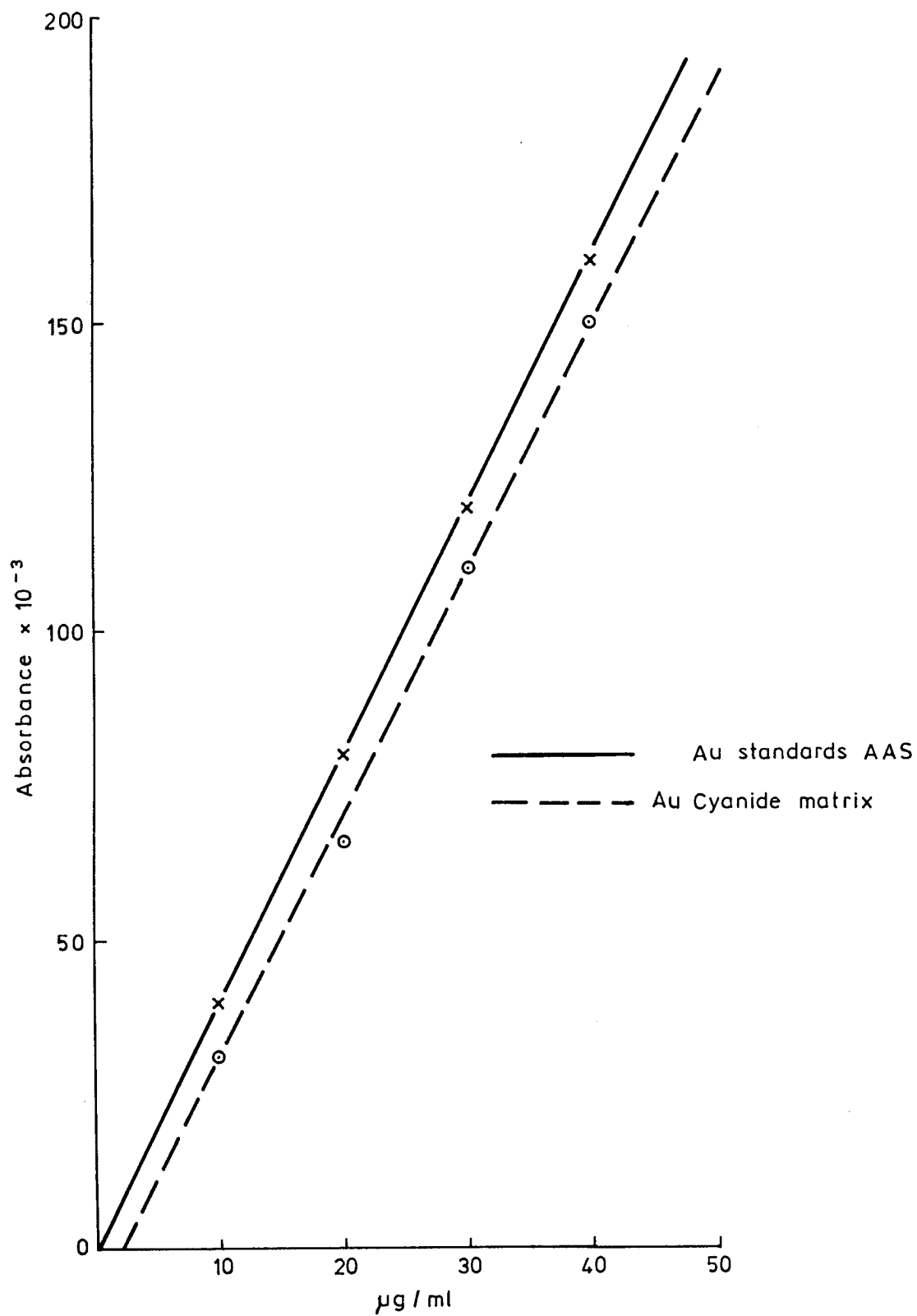
Fig. 8   AAS   calibration   curves

the depressing effect may be approximated to be in the region of 1.35 g/ml. This was adopted as a correction factor and used to adjust the results of the cyanidation experiments analysis (used to plot the results). The other method widely recommended is that of extracting the analyte element in the organic solvent methyl isobutyl ketone (MIBK) or di-isobutylketone (DIBK) and aspirating on AAS. This was not attempted because at the time of experiments the organic solvents were still on order and were not available.

5.2 EXPERIMENTS PROCEDURE

In the preliminary cyanidation experiments, Elsner's equation was used to calculate the stoichiometrical cyanide and oxygen requirements, as the basis of cyanidation. Initially, particle size analysis, mineralogical investigations, and chemical analysis of the anode slimes were carried out to facilitate the control of cyanidation experiments, as outlined earlier in the report. Theoretical oxygen requirement from the reaction equation 10, was calculated. Determination of the actual oxygen requirement needed the use of an oxygen probe to determine the rate of oxygen consumption in the anode slimes cyanidation during a series of cyanidation experiments. However the theoretically calculated flow rate served as an indicator in setting the airflow rate during the experiments. Airflow rates far in excess of the theoretically calculated were used in the experiments. Excess aeration was aimed to ensure adequate

supply of oxygen.

For silver dissolution, the stoichiometrical cyanide

requirement may be calculated from equation 10 as follows,

$$4Ag + 8KCN + O_2 + 2H_2O = 4 KAg(CN)_2 + 4KOH ....(10)$$
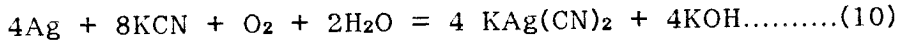
At standard temperature and pressure (STP), the number of

moles of KCN required to dissolve one mole of silver from

equation (-10) is given as

$$N_{KCN}/ N_{Ag} = 8/4 = 2 ....(i)$$

Where N_{KCN} = number of moles of cyanide

N_{Ag} = number of moles of silver

From equation (i) therefore two moles of KCN are required to

dissolve one mole of silver.

The general formula for calculating the number of moles is as

follows:

$$M/ RAM = N ....(ii)$$

where N = number of moles, M = amount of the material, and

RAM = relative atomic or molecular mass of the element

Hence the amount of cyanide required to dissolve the amount

of silver in the sample was calculated, from the following

values:

100 grams,of the sample with an assay value of 8.150% Ag.

The weight of KCN required = $[M_{Ag}/RAM_{Ag}].2 . M_{KCN}...(iii)$

$$= [8.150/108]. 2 . 65$$

$$= 9.818 \text{ grams}$$

The theoretical airflow rate was calculated by using the summary of the gas empirical laws of Boyle, Gay-Lussac and the hypothesis of Avogadro's equation / 23 /, at STP as follows

$$pV = NRT \dots \dots \dots (iv)$$

$$pV = N_{o2}RT \dots \dots \dots (iva)$$

The number of moles of oxygen (N_{o2}) required to dissolve one mole of silver(N_{Ag}) from equation 10 is given as;

$$N_{o2}/N_{Ag} = 1/4 \dots \dots (v)$$

Therefore the volume of oxygen (V_{o2}) required is expressed as,

$$V_{o2} = N_{o2}RT/P \dots \dots \dots (ivb)$$

Substituting the N_{o2} in equation (ivb) by equation (v) will be as follows,

$$V_{o2} = N_{Ag}.[1/4].[RT/P] \dots \dots (ivc)$$

The general equation for the conversion of the volume of oxygen in terms of atmospheric air volume, is given in the equation below,

$$V_{AIR} = V_{o2}.[100/21] \dots \dots (vi)$$

Ideal airflow rate (Q) is calculated as,

$$Q = V_{AIR}/Time \dots \dots \dots (vii)$$

For the one hour leaching time the volume of oxygen needed to dissolve the amount of silver in the sample was

calculated from equation (ivc):

$V_{O_2} = [8.150/108].[0.25]. [8.314 . 298/101325]$

$= 50 . 10^{-5} m^3$ of oxygen

The volume of air was calculated using equation (vi):

Volume of air $= V_{o_2} .[100/21] = 2.3 . 10^{-3} m^3$

The air flowrate was calculated from equation (vii)

Airflow rate $= 2.3 \times 10^{-5}/60 = 3.8 . 10^{-5} m^3$

The ideal amount of cyanide and oxygen required for the dissolution of gold is calculated from the stoicheiomentrical equation below,

$4 Au + 8KCN + O_2 + H_2O = 4 KAu(CN)_2 + 4KOH$
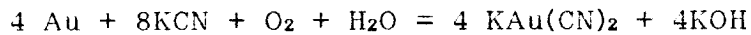
all the calculations were carried out in a similar manner as in the case of silver above.

Therefore weight in grams of KCN required to dissolve gold in the 100grams sample with gold assay value of 0.0758% is given below:

amount of KCN required $= [0.0758/196.9665].2. RAM_{KCN}$

$= 0.05$ grams

Theoretical oxygen required is obtained by equations (vi) to (vii) above.

$V_{o_2} = N_{Au} .[0.25]. [RT/P] = 3 . 10^{-5} m^3$

$V_{air} = V_{o_2} . [100/21] = 14 . 10^{-5} m^3$

Air flow rate $Q = V_{AIR}/t = 14 . 10^{-5} \text{ m}^3/60$

$$= 2.33 . 10^{-5} \text{ m}^3/\text{min}$$

5.3 EXPERIMENTAL RESULTS AND DISCUSSIONS.

In the initial cyanidation experiments a series of the copper anode slimes samples were leached at various cyanide strength for a period of two hours, after which samples were taken. The results of a series of these tests are given in the extraction curve, figure 9. The extraction curve shows that at 2% cyanide concentration, gold and silver extracted was 46% and 6% respectively. The amount of gold extracted was maximum, 62% at 5% KCN. On the other hand, silver dissolution continued to increase with increase in cyanide concentration.

The gold and silver extraction curves intersect at approximately 13.80% KCN with the recovery of 59%.

Further experiments were conducted at 2%, 10%, and 15% KCN, the leaching time was increased from 2 to 6 hours, and sampled hourly.

The results are shown in figures, 10, and 11. Gold and silver recoveries at 2%, 10%, and 15% KCN were 58%, 68%, 71% and 10%, 62%, and 74% respectively.

The gold recoveries did not vary greatly and were in the range of 62%, whilst silver recoveries varied significantly with increased cyanide concentration as indicated in figs. 10 and 11. It can be noted that much of gold dissolution was high

PH :　　　 11·8
Pulp density : 10%
Temperature :　25 ± 2°C
Leaching time : 2 hrs
Airflow rate : 0·01m³ /min

————— Au

— — — Ag
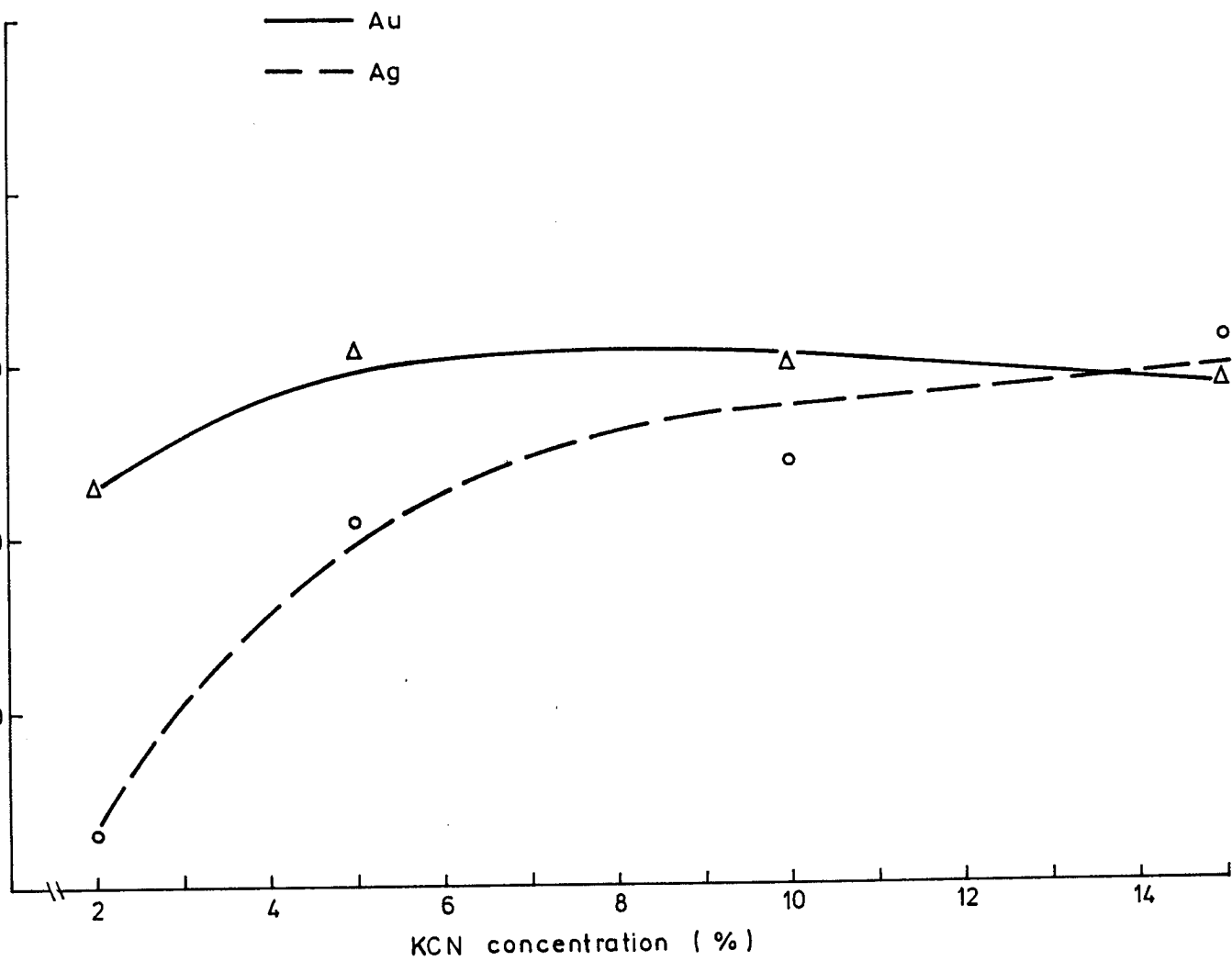
KCN concentration (%)

Fig. 9　　Silver and gold percent extraction at different cyanide concentration

PH : 11·5
Pulp density : 10 %
Airflow rate : 0·01 m³ / min
Temperature : 25 ± 2°C
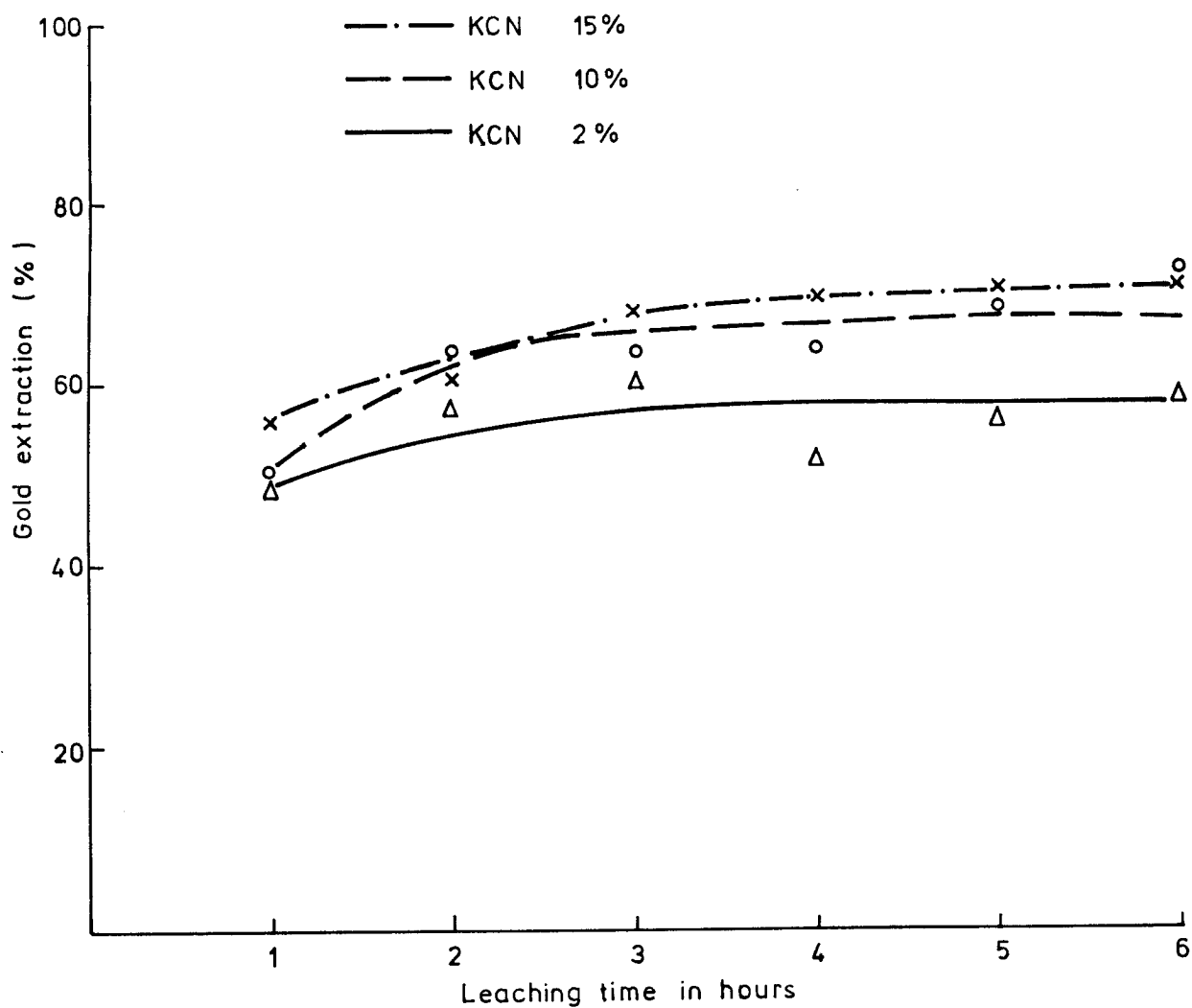
Fig.10   Gold extraction with time at different cyanide
         concentration

PH : 11·5
Pulp density : 10 %
Airflow rate : 0·01 m³ / min
Temperature : 25 ± 2°C
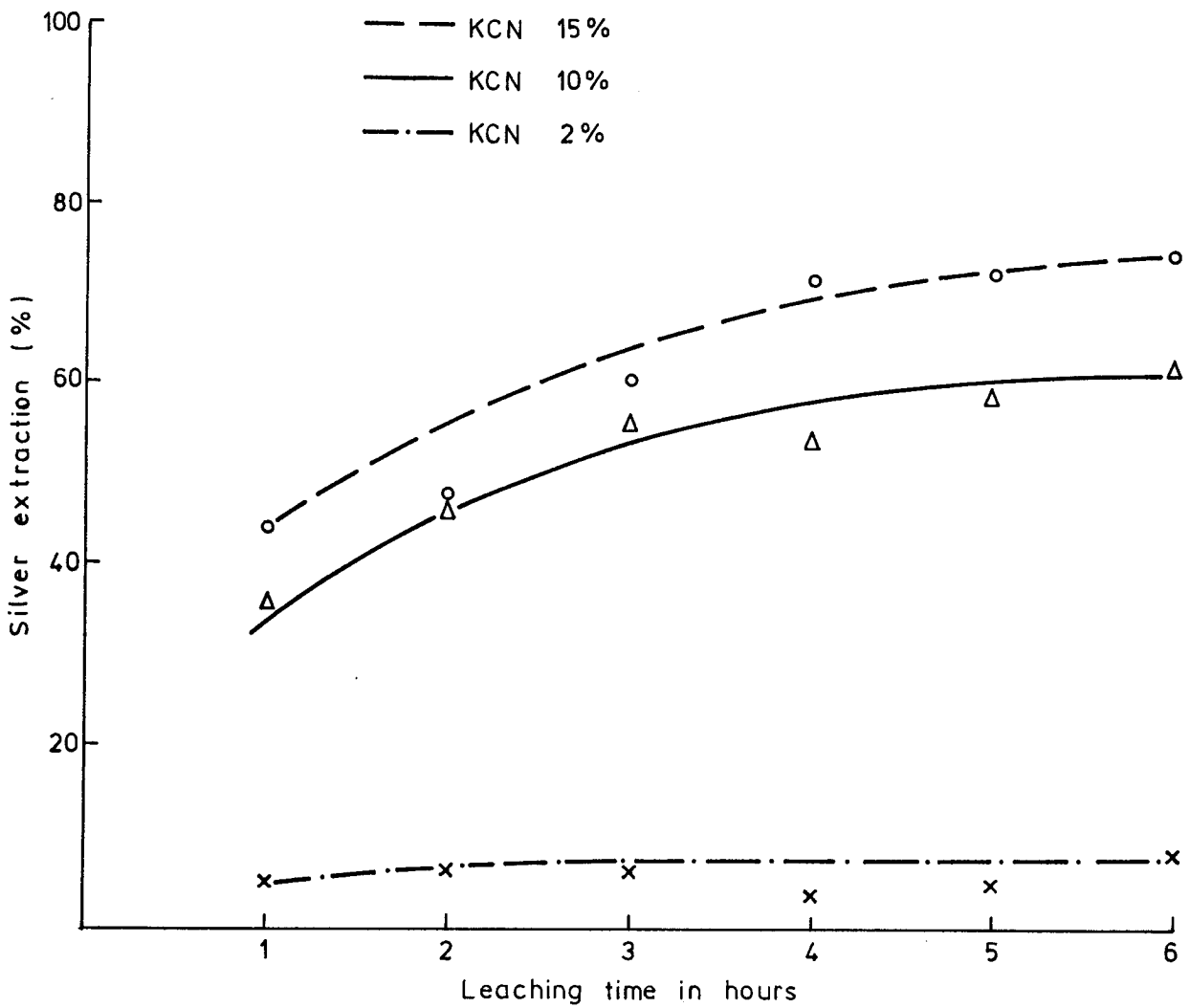
Fig.11   Silver extraction with time at different
cyanide concentration

in the initial stages(slope of these curves if extrapolated to zero on the graphs indicate the rate of dissolution), therefore the rate of gold dissolution was high in the initial cyanidation stages. This was similar to silver at high cyanide strength.

5.3.1 EFFECT OF INCREASED AERATION.

The high airflow rate was necessitated by the desire to effect the dissolution of precious metals as rapidly as possible. The increased airflow rate may have had a multiple effect on cyanidation conditions namely agitation, mass transfer, not easily quantifiable individually but which could be summed up in the overall effect of increased oxygenation of the pulp.

Hence the increased airflow rate on dissolution was investigated. A cyanide strength of 14% KCN was maintained at pH = 11.5

The airflow rate was increased from the initial 0.01 m³/min to 0.02 m³/min in the second test and to 0.03 m³/min in the third test. The results are shown in figures, 12, 13a and 13b.

Figure 13a and 13b indicate the results obtained by AAS using different flame oxidant. The results plotted in fig. 13a were obtained by nitrous-oxide/acetylene flame, whereas fig. 13b, results on the same sample, were obtained by air/acetylene flame.

PH : 11·5
Pulp density : 10 %
Temperature : 25 ± 2° C
Cyanide strength : 14 % Wt

——— 0·03 m³ / min ⎫
— — 0·02 m³ / min ⎭ Airflow rate
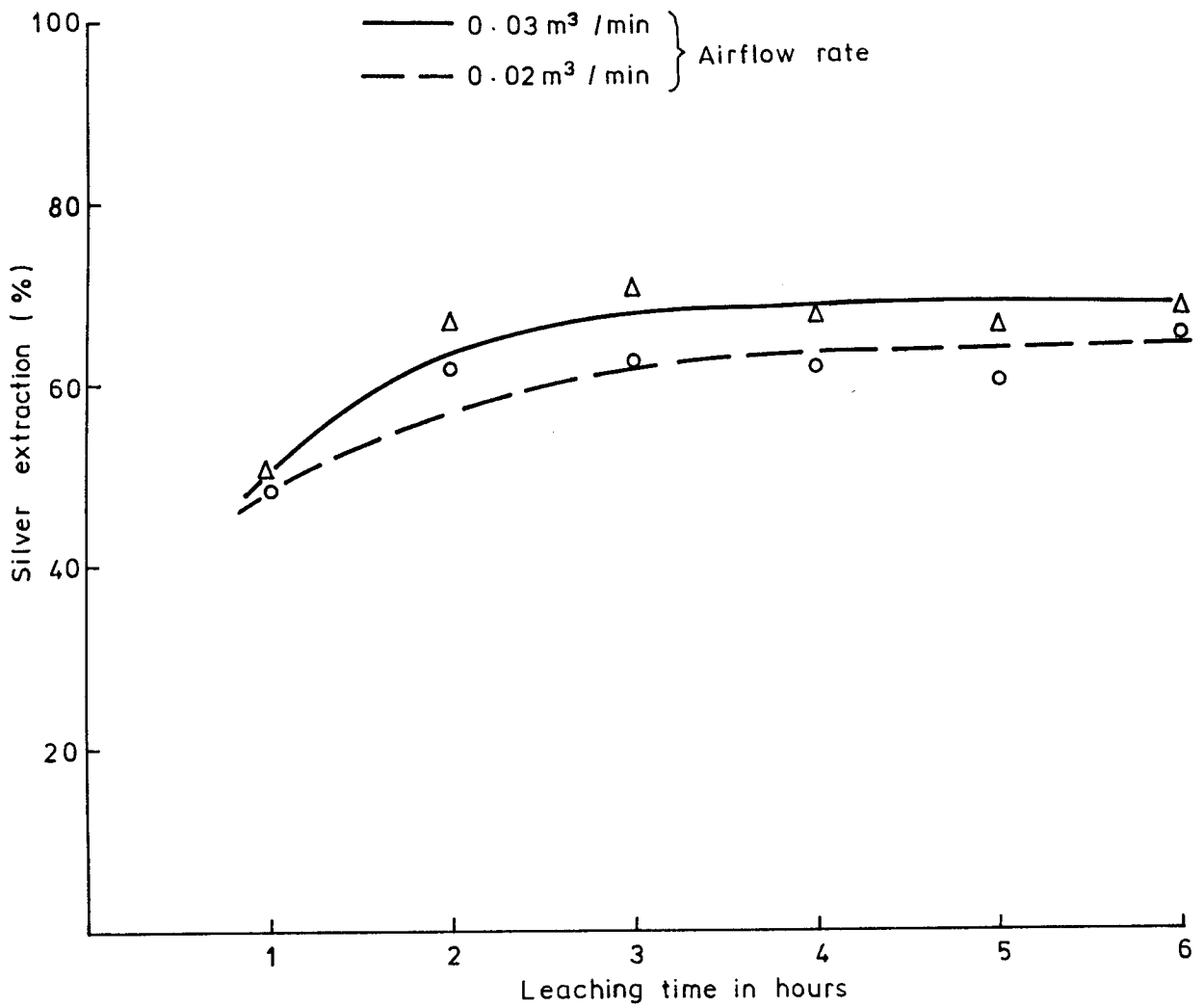
Fig. 12 Silver extraction at different airflow rates

PH :   11·5
Pulp density: 10 %
Temperature :   25 ± 2°C
Cyanide strength : 14 % Wt
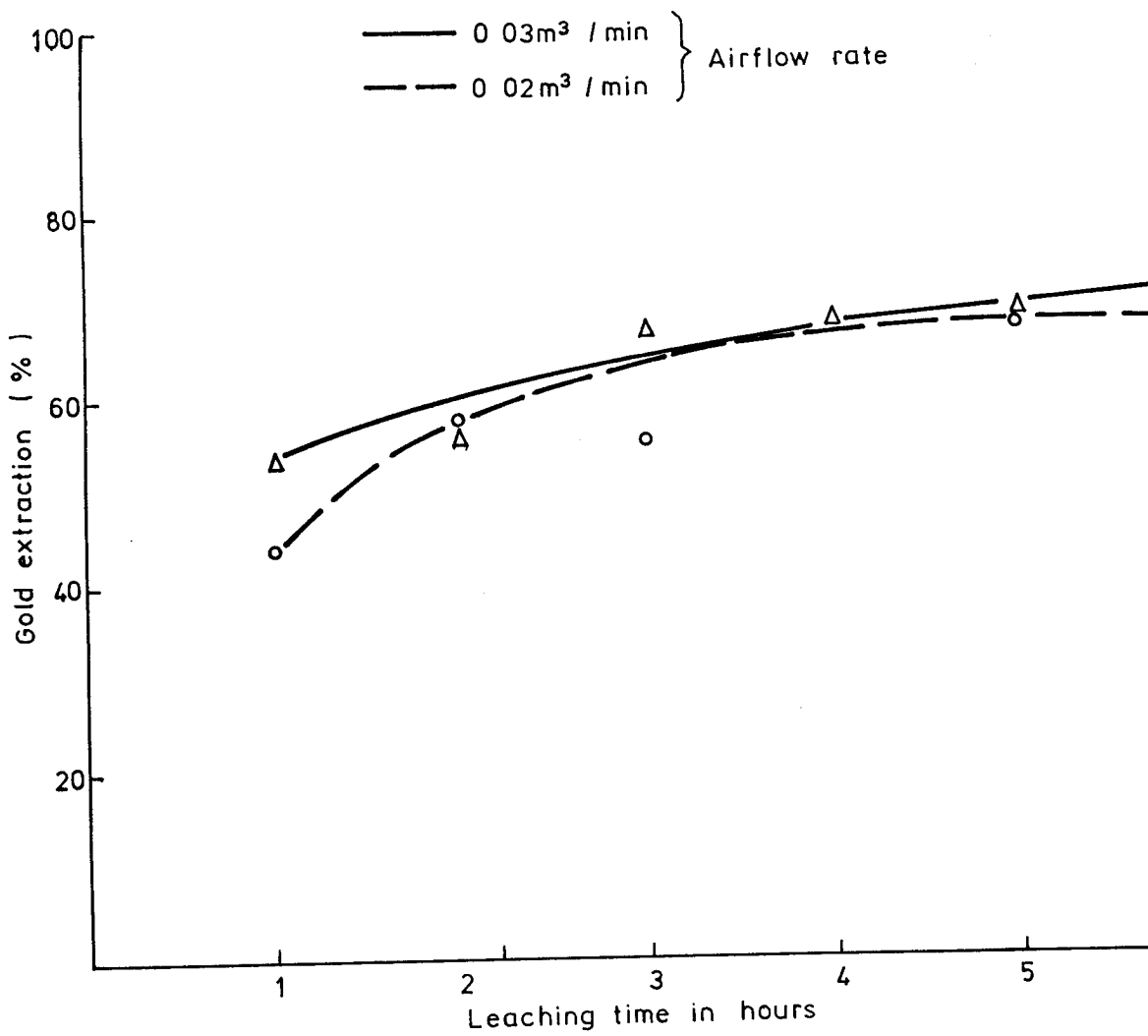
Fig.13a Gold extraction at different airflow rates
(Nitrous - oxide / actelylene flame. AAS analysis

PH : 11·5
Pulp density   10%
Stirring : 300 rpm
Temperature : 25 ± 2°C
Cyanide strength : 14% Wt

――― 0 03 m³ / min ⎫
                    ⎬ Airflow rate
― ― ― 0 02 m³ / min ⎭

Gold extraction (%)

Leaching time in hours
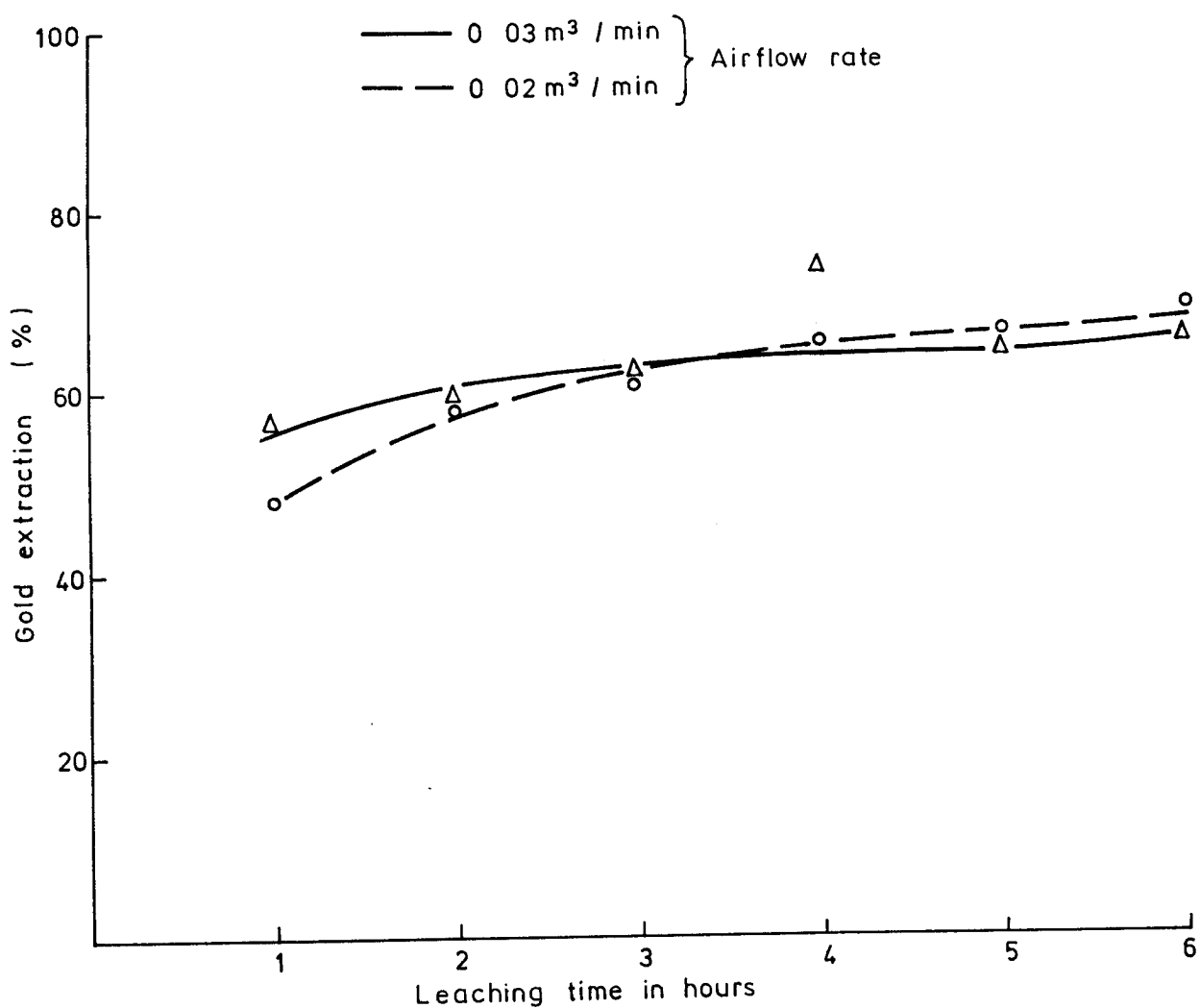
Fig.13b   Gold extraction at different airflow rates
(Air/ Acetylene flame. AAS analysis)

The increased aeration increased rate of solution in the
initial hours but there was only a slight increase in the
overall recoveries of the metals. In both cases, violent
agitation of the pulp could be observed, which seemed to
show that, excessive air was being bubbled into the pulp.
It is apparent from the curves that violent agitation of the
pulp increased only slightly the recovery of gold and
silver. This then indicates that the initial airflow rate
was sufficient for the dissolution of gold and silver. It
also implies that oxygen may not have been rate controlling
for the dissolution reaction. Higher flow rates of say 0.05,
0.08, 0.10 m³/min were not performed in these experiment
due to spillages caused by voilent agitation. However,
from these results it can be assumed that the higher flow
rates could result in increased extraction of gold and
silver and vice versa for low flow rates.

5.3.2 ROASTED ANODE SLIMES CYANIDATION

The roasted anode slimes were leached under the same
conditions as in the earlier experiments.

The slimes sample was roasted in the muffle furnace at 700°C
for four hours until no reddish/purple fumes were observed.

The chemical analysis of the anode slimes was as follows:

12.35%Ag, 0.12%Au, 1.65%Cu, 2.58%Se.

The roasted sample was ground in the laboratory Retsch cross-
beater mill fitted with 500µm sieve .

The percent recoveries are shown in figure 14. There was

PH :   11·5
Pulp density : 10%
Stirring :   300 rpm
Airflow rate : 0 01m³ / min
Temperature : 25 ± 2°C
Cyanide strength : 14% Wt
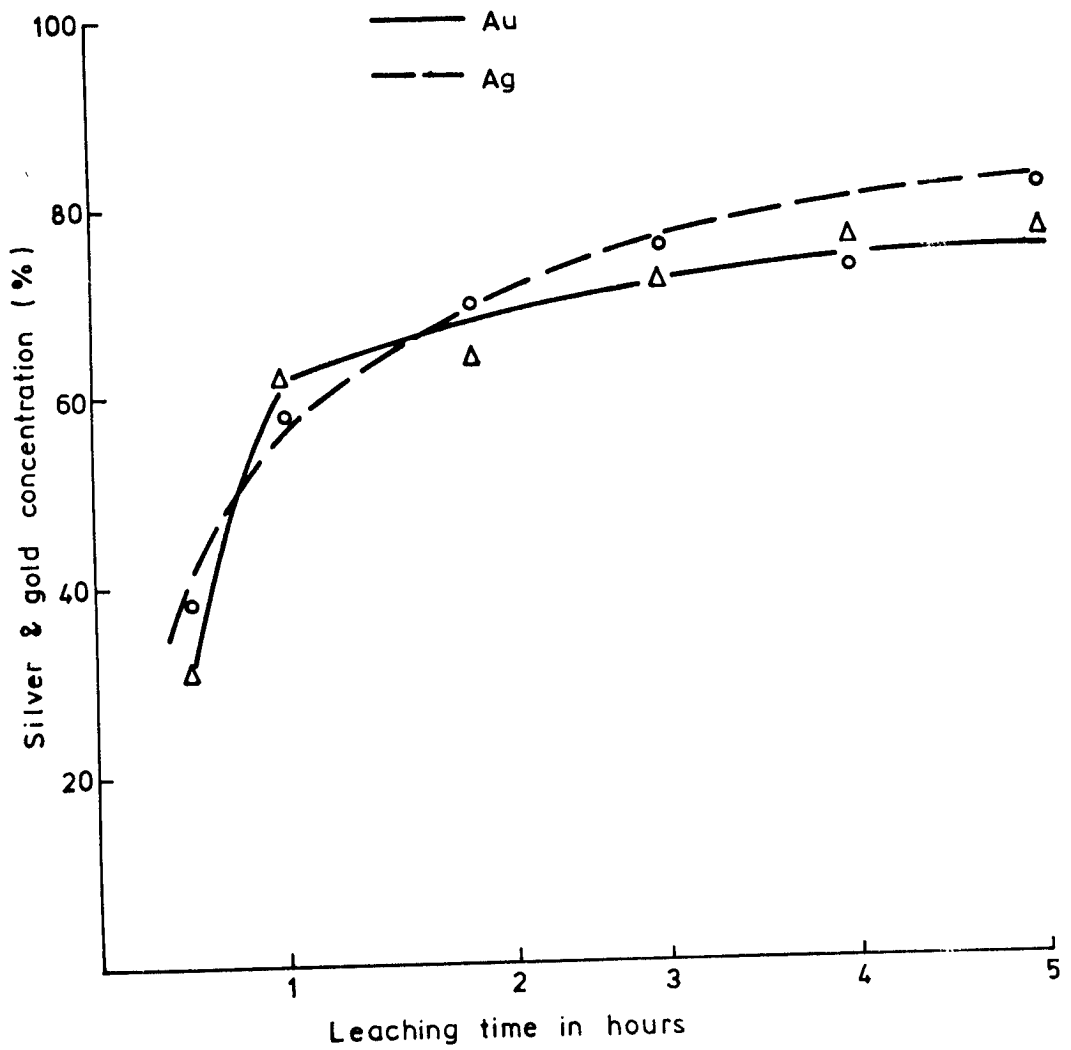
Fig. 14   Silver and gold extraction from deselenised slimes

considerable increase in the extraction of the metals, 77%

and 82% for gold and silver respectively.

This was attributed to the absence of decomposed selenides,

sulphides and other volatile constituents of the anode

slimes. The absence of these deleterious elements may have

improved cyanidation of gold and silver. The somewhat low

recoveries in the unroasted slimes may be attributed to

probable, insoluble films formed on gold and silver surfaces

and thus retarding dissolution, and the loss of the reactive

reagents (cyanide and oxygen) to these elements.

The x-ray diffractograms of the roasted slimes indicate the

presence of metallic silver, this could have been more amenable to

cyanidation than say silver compounds of naumannite (Ag_2Se)

or eucairite (CuAgSe). Gold is mostly suspected to be

occurring in native form, therefore its relative low

recovery must be attributed to other factors, for

example the formation of insoluble films on the gold surface

resulting from the dissolution of the other elements.

CHAPTER 6

LITERATURE REVEIW

ADSORPTION OF GOLD AND SILVER ON ACTIVATED CARBON

6.1 ADSORPTION

Adsorption is the accumulation of a solute at the interface and is a surface phenomenon. The solute is known as the adsorbate or adsorptive, while the solid which has adsorbed them is known as the adsorbent. There are two types of adsorption, physical adsorption with adsorption forces having the same nature as intermolecular or van der waals, forces, and chemical adsorption in which the adsorption forces have a chemical nature. Physical adsorption is always reversible whereas chemisorption is usually irreversible [40] .

The adsorption theories have mostly been developed basically by the study of gas adsorption on the solid and these theories have been applied to the study of solid-liquid adsorption.

The concept of physical adsorption has found wide application in industry and is the main subject in this thesis. Physical adsorption occurs spontaneously. The adsorptive tends to occupy the entire adsorbent surface but this is hindered by desorption. For every adsorptive concentration, there is a state of adsorption equilibrium, similar to the equilibrium between condensation and evaporation in the environment. At higher adsorptive concentration, the

greater is adsorption. It is also clear that the higher the temperature, the smaller, is physical adsorption. The effect of temperature on physical adsorption completely obeys the Le Chatelier-Braun principle because desorption, being a process opposed to adsorption, is accompanied with heat up take [48] .

To determine the amount of the adsorbed substance, it is necessary to experimentally find the adsorptive concentration in a vessel where adsorption is occurring prior to and after adsorption. The determination of the amount of an adsorbed substance is often very difficult owing to the small quantities of the adsorbate being measured. The amount of the adsorbed substance is often determined by the gain in weight of the adsorbent. The pore diameter of the adsorbent may affect adsorption either way. Comparatively large molecules of the adsorptive cannot penetrate into the narrow capillaries of the adsorbent, and the adsorption limit will be attained. When the pore diameter is small, the adsorptive may become like 'liquefied' (capillary condensation), and the amount of the adsorbed substance will be overestimated.

Adsorption may be expressed by several parameters:

(a)   the amount adsorbed per unit mass of adsorbent

(b)   the amount   adsorbed per unit surface = $mole/cm^2$. The quantity is merely surface concentration.

(c)   Gibbs' quantity Γ which represents an excess in the

number of moles of the adsorptive in the adsorbent unit surface area.

The dependence of the amount of the adsorbed substance (a) on equilibrium concentration at constant temperature, represented by a = f(c) are known as adsorption isotherms [30, 40] .

Adsorption may be characterized by various ways amongst which adsorption isotherms have been found to be the most important when investigating adsorption.

The adsorption isotherms show the relationships between, feed concentration, equilibrium adsorption and adsorbent surface. From adsorption isotherm data one obtains information on whether or not a particular recovery can be effected and obtain an approximation of the ultimate capacity of the carbon for application.

Isotherms are especially important in the investigation of adsorption. Typical isotherms of adsorption are schematically represented in fig.15. according to the classification of Brunauer, Deming, Deming and Teller [40].

FIG. 15   TYPICAL ADSORPTION ISOTHERMS CLASSIFICATION
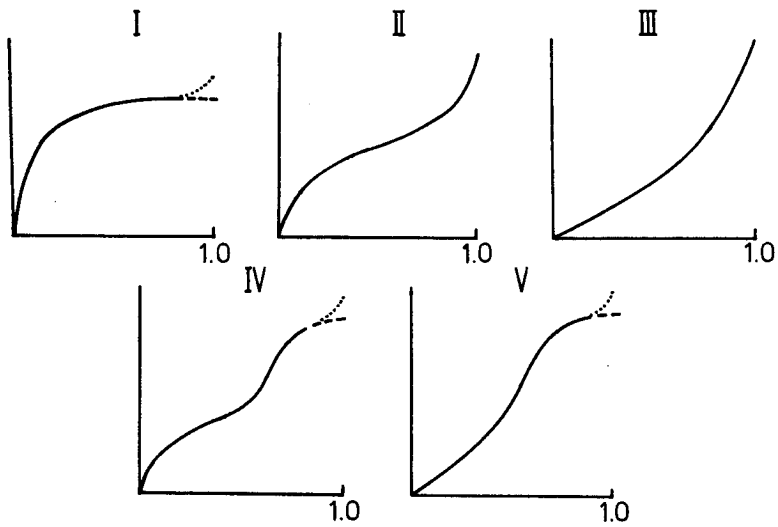
The five types of isotherm according to the classification of Brunauer, Deming, Deming and Teller:

Ordinates: Adsorption, x

Abscissae: Relative pressure at equilibrium, p/po

6.1.1 <u>ADSORPTION THEORIES</u>

There are several theories which attempt to clarify various
physical adsorption isotherms, among which are
monomolecular, polymolecular and the Brunauer, Emmett and
Teller (BET), adsorption theory. A sharp rise of the
isotherm at low equilibrium concentration gives an
indication of the difficulty of desorbing the adsorptive
from the surface.

The ideal isotherm of physical adsorption does not have any
sharp inflections which are sometimes characteristic of
isotherms of adsorption that is accompanied with chemical
interactions. This indicates that no chemical compounds of
the adsorbent and the adsorptive are formed in the course of
physical adsorption. Adsorption is dependent on temperature
as temperature rises, the quantity of equilibrium adsorption
decreases and, as a result, isotherms for high temperatures
are below the isotherms for low ones.

However, as temperature rises the adsorption limit(the
amount of the adsorptive per unit surface at the closest
packing of its molecules in the monolayer)does not change.
The adsorption limit is virtually independent of
temperature, and is determined only by the dimensions of the
adsorptive molecules.

When an adsorption isotherm is parabolic, for its analytical
expression, Baedeker and Freundlich proposed the following
emperical equation

$$a = X/m = kc^{1/n} \ldots\ldots\ldots\ldots(20a)$$

where X = amount of the adsorbed substance

m = mass of the adsorbent

c = equilibrium concentration

K and 1/n = constants.

For adsorption from solution, Freundlich's equation is as a rule written in the form.

$$a = x/m = \beta\ c^{1/n}\ \text{equilibrium}\ldots\ldots\ldots\ldots(20b)$$

where β = constant, which corresponds to constant K of the preceding equation, c = equilibrium concentration.

β usually varies within a wide range. Its physical meaning becomes clear if we take C = 1 then β will represent adsorption at the equilibrium concentration of the adsorptive that is equal to 1 mole/l.

The exponent 1/n in both equations is a proper fraction and characterizes the degree of approximation of an isotherm to a straight line.

The constants of Freundlich's equation may be easily found graphically by the isotherm plotted in logarithmic coordinates. For example, for adsorption from a solution, we have,

$$\log a = \log \beta + 1/n \log C \text{ equilibrium}\ldots\ldots\ldots(20c)$$

This equation is for a straight line [48, 40, 30] .

In proposing monomolecular adsorption theory, Langmuir noted

the following: i) that most adsorption is localized and caused by forces similar to chemical ones, ii) molecules are adsorbed on active centres which are present on the adsorbent surface, iii) owing to the small radius of action of adsorption forces, every active centre adsorbing the molecule, becomes incapable of further adsorption and as a result only a monomolecular adsorptive layer may be formed on the adsorbent surface. Adsorbed molecules are retained by active centres only briefly and there is dynamic equilibrium on these active centres. Langmuir did not take into account the forces of interaction between adsorbed molecules. Proceeding from the foregoing, Langmuir $\mathcal{L}$ 48 $\mathcal{J}$ presented a general equation for the isotherm of localized adsorption written as

$$ = \frac{max. \ P}{1/K + P} = \frac{max. \ P}{A + P} \dots\dots\dots(21) $$

Since the quantity of adsorption (a) is proportional to $\ $, Langmuir's equation may be represented as

$$ a = a_{max} \ K_p/(1 + K_p) = a_{max}P/(A + P)\dots\dots(21a) $$

where a_{max} the amount of the adsorptive (in moles) per unit mass of the adsorbent which corresponds to the filling up of all the active centres, $\ $ = surface concentration of the adsorptive, p = gas pressure, k = constant which does not depend on concentration and is invariable at a given

temperaure, A = quantity which is the inverse to the
equilibrium constant.

Hence in Langmuirs equation, both constants c_{max} or a_{max} and
K have a definite physical meaning. However, some cases of
physical adsorption cannot be explained by the theory of
monolayer adsorption, they require a fundamentally different
approach from the standpoint of polymolecular adsorption.
The theory advanced by Langmuir's has limited application
depending on the nature of the adsorbent and that of the
adsorptive. Langmuir's theory cannot be used to explain
fine-pored adsorbents owing to the additivity of the
dispersion forces. The constant a_{max} in this case would not
express capacity of a dense monolayer and correct results
would no longer be obtained and other adsorption isotherms
often found in practice do not fit into Langmuir's equation
[48].

To explain this, Polanyi proposed the theory of
polymolecular adsorption which is also called the potential
theory. Potential theory [40] notes that adsorption is
caused by purely physical forces and the adsorbent surface
does not have any active centres while the adsorption forces
act in the vicinity of the adsorbent surface and form near
it a continuous force field.

The principles of the polymolecular adsorption theory
assume a force field which originates at the adsorbent
surface and in many respects similar to the gravitational

field.

Adsorption forces act at comparatively great distances, distances which are greater than the dimensions of adsorptive molecules. The polymolecular theory proposes an adsorption volume which is filled with adsorptive molecules during adsorption.

Langmuir's monomolecular adsorption theory and Polanyi's polymolecular adsorption theory are both applicable depending on the nature of the adsorbent, the adsorptive and the conditions of adsorption.

Polanyi's theory is applicable to phenomena of purely physical adsorption. Polanyi's theory does not make it possible to derive the adsorption isotherm equation. Langmuir's theory covers, though with certain limitations, the phenomena of both physical and chemical adsorption. However Langmuir's theory cannot be used to explain adsorption of fine pored adsorbents which have narrowing pores as earlier outlined. It is difficult therefore to apply Langmuir's equation to adsorption by fine pored adsorbents which have pores with narrow spaces. Therefore a more general equation of Langmuir's and Polanyi's concepts was attempted by Brunauer, Emmett and Teller to describe the isotherms of different shapes by a single equation known as the BET equation which gives analytical expression of the isotherms. It appears to represent the general shapes of the actual adsorption isotherms. The BET equation for [30,

48] polymolecular adsorption isotherm may be easily reduced to a linear one as given below.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{P}{P_0} \quad \ldots\ldots\ldots(22)$$

Where V = the volume of gas and V_m = the volume of gas required to form a complete unimolecular adsorbed layer.

P = pressure of gas and P_0 = the equilibrium pressure of gas.

When only one layer is adsorbed on the surface, the equation reduces to the Langmuir's type of equation (22a) given below.

$$\frac{P}{V} = \frac{P_0}{C V_m} + \frac{P}{V_m} \quad \ldots\ldots\ldots(22a)$$

The equation (22a) is for type I isotherm and (22) is for type II isotherm shown in fig. 15 [30, 40].

6.1.2 ADSORPTION RATE.

The rate of physical adsorption on porous adsorbents may often be retarded due to the time taken for the adsorptive molecule to penetrate into pores. Initially adsorption is practically proportional to time because the adsorbent surface is free from the adsorptive. Once adsorption equilibrium has been established, adsorption no longer depends on time and the appropriate segments of curves are almost parallel to the time axis [48]. The equation for

the adsorption rate is usually given as

$$da/dt = k(a_{equil} - a_t) \ldots\ldots\ldots(23)$$

where a_{equil} = amount of the adsorbed substance that

corresponds to adsorption equilibrium under given conditions

a_t = amount adsorbed by time t, k = equation constant.

From this equation it can be noted that the closer the

system is to equilibrium the slower is adsorption. The

constant k depends on the area of the adsorbing surface and

on the adsorptive diffusion coefficient.

The adsorption of a solute occurs more slowly than that of a

gas because a decrease of the concentration in the boundary

layer can be restored only by diffusion which is generally

rather slow in a liquid [48]. To establish adsorption

equilibrium more rapidly the system is often stirred.

The amount of a substance (a) molecularly adsorbed by one

gram of an adsorbent from a solution is usually calculated

by the equation (24) below,

$$a = (C_0 - C_1) v/m \ldots\ldots\ldots(24)$$

where C_0 and C_1 = initial and equilibrium concentrations of

the adsorptive (a). m = amount of carbon. v = volume of

the solution

6.2.0 <u>RECOVERY OF PRECIOUS METALS BY ADSORPTION PROCESS</u>

The use of activated carbon adsorption process for the recovery of precious metals from the cyanidation process forms a very important part of the diverse and extensive field of activated carbon adsorption process applications. The activated carbon adsorption process is used to recover gold from solution under two conditions. One is the application in which the solution is an integral part of an ore slurry and in the other nominally clear solutions are treated. This occurs in a number of adsorption vessels in series. Either the pulp or the solution, flows continuously from the first to the last while the carbon flows countercurrent from the last to the first tank. The carbon movement is intermittent and is nominally moved out only once per day. Hence the gold and silver values of the solution decrease as it proceeds down the train of tanks to give a barren value in the last tank.

The carbon, during its contact with the adsorbate, also adsorbs other products that tend to poison the carbon seriously reducing its activity. The gold and silver recovery from nominally clear solutions is usually performed in a series of upflow bed contactors.

The rate equation determined for carbon loading used to model the countercurrent flow carbon-in-pulp process is as follows,

$$C_c - C_c(I) = kC_s t^n \ldots\ldots\ldots\ldots (25)$$

where C_c = concentration of gold on the carbon at time t,

$C_c(I)$ = concentration of gold in incoming carbon, K=equilibrium

constant, C_s = concentration of gold in solution at time t, t =

time, n = order of dependence on time determined for each

ore for the rate equation,

Taking in account mass balance of the carbon adsorption

plant would give the following relationship.

$$C_s(I)/C_s(i) = [1 + K(M_c/F_c)^n + F_c/F_s]^t \ldots\ldots (26)$$

Where $C_s(I)$ = concentration of gold in incoming solution,

$C_s(i)$ = concentration of gold in solution in stage i, M_c =

mass of carbon, F_c = flow rate of carbon, F_s= flow rate of

solution, r = rate, k = rate constant.

This is known as the 'Kn' model and is the rate equation

most commonly used to date for the design of carbon-in-pulp

plants [43].

With constant gold concentration in the solution the

following equation can be used to describe the rate of gold

loading onto the carbon.

$$r = k(KC_s - C_c) \ldots\ldots\ldots\ldots\ldots (27)$$

It has been shown that adsorption is under film diffusion

control until the carbon has reached 60 to 70% of its

equilibrium loading value, hence the need for the system to be

stirred. A rate expression based on this classical film
diffusion rate was proposed [43] as.

$$r = (A_c/V_s)k_t \rho_s(C_s - kC_c) ....(28)$$

where A_c = area of carbon, V_s = volume of solution, K_t =
transfer coeffecient, ρ_s = density of solution.

A branched pore adsorption model in which the mechanism of
adsorption is assumed to be multi-step with different
diffusion mechanisms for macro and micro pores was also
proposed [43].

Various workers have used either Freundlich or Langmuir's
models in order to describe the equilibrium adsorption data.
A number of factors have a significant effect on the loading
of carbon. In plant operations carbon has a retention time
within the adsorption tanks of 10 days, whereas the
pulp/solution is in contact with the carbon in each tank for
one hour. Adsorption isotherms show that there is an inter-
relationship between the number of factors i.e input assay
of feed, carbon feed, and carbon activity [8, 43].

6.3 GOLD AND SILVER ADSORPTION MECHANISM ON ACTIVATED CARBON

Early worker Green 1913,[18] postulated a reduction
mechanism for the adsorption of aurocyanide on carbon. The
reduction agent was assumed to be carbon monoxide occluded
on the carbon surface. He proposed that aurocyanide complex

was reduced and adsorbed as metallic gold. Feldtmann [19]

proposed that gold was adsorbed as carbonyl aurocyanide

complex (AuCN-CO(CN)$_2$. Allen [42] advanced that gold

cyanide was adsorbed as KAu(CN)$_2$, which was discounted.

Gross and Scott [42] proposed the adsorption of the following

at low pH,

$Au(CN)_2^- + H^+ = Au(CN)_S + HCN$

$Ag(CN)_2^- + H^+ = Ag(CN) + HCN$

$K[Au(CN)_2] + H_2O + CO_2 = H[Au(CN)_2] + KHCO_3$
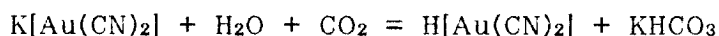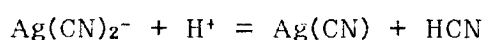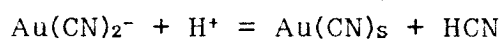
It was thought that highly insoluble AuCN and AgCN were

precipitated on the carbon.

Numeruos publications have appeared subsequently in which

the mechanism advanced involves adsorption of $Au(CN)_2^-$

anions.

Garten and Weiss proposed [43, 10] the adsorption of

aurocyanide and silver cyanide to be due to the

electrostatic attraction of $Au(CN)_2^-$ anions to positively

charged carbonium sites, which implied the oxidation of

Au(I) to Au(III).

Kuzminykh and Tjurin [9, 10] postulated that $Au(CN)^-$ is

retained on the carbon together with an equivalent amount of

an alkali cations such as K^+, Ca^{2+} or Na^+, which is held on

the carbon electrostatically.

It was generally established that the degree of gold and

silver adsorption is strongly dependent on the nature and

concentration of the spectator cations present in the

adsorption medium and that gold cyanide cannot be adsorbed on the carbon in the absence of stabilizing cations such as Na^+ and Ca^{2+}.

A mechanism that involves the adsorption of gold as a metal dicyanoaurate complex $M^{n+}[Au(CN)_2]_n$, was advanced [43]. In support of this hypothesis, it was claimed that when the cation of the complex M^{n+} is a divalent alkaline earth metal, the complex is bound more firmly to the carbon than when M^{n+} is a monovalent alkali metal cation. It was also found that the strength of adsorption of the $M^{n+}[Au(CN)_2]$ adsorbate followed the sequence Ca^{2+}, Mg^{2+}, H^+, Li^+, Na^+, K^+. Cho et al., like Garten and Weiss,[9, 43, 10] suggested that the mechanism for gold cyanide adsorption involved an electrostatic interaction between $Au(CN)_2^-$ anions and positively charged sites on the surface of the carbon. They found that as the loading of silver on the carbon was increased, the zeta potential of the carbon became more negative. This led to the postulate that the adsorbate was an anion, $Ag(CN)_2^-$.

Cho and Pit's investigation concluded that the $Ag(CN)_2^-$ anion is adsorbed in accordance with an ionic solvation-energy theory that accounts for the specific adsorption of anions on metal electrodes. According to this model, the degree and type of ionic hydration are the principal factors that determine specific adsorption. A weakly hydrated anion such as $Ag(CN)_2^-$ will be specifically adsorbed on the carbon

surface after losing some of its primary hydration water molecules, whereas some anions with a large number of strongly bound water molecules in their primary hydration shells for example CN^- will not be specifically adsorbed and will therefore remain in the outer part of the electrical double layer. The capacity for the $Ag(CN)_2^-$ anion is considerably higher than for the CN^- anion. It was also found that the small, highly hydrated Na^+ cation is adsorbed on carbon only if it is present in solution with $Ag(CN)_2^-$ anion. It was found that an increase in the concentration of K^+, Na^+ and Ca^{2+} ions in solution enhances the adsorption of silver cyanide.

To account for these ionic strength effects, it was proposed that the Na^+, K^+ and Ca^{2+} ions are non-specifically adsorbed on the silver cyanide complex, which in turn is specifically adsorbed on the carbon surface and that these ions provide additional sites for the adsorption of anions such as $Ag(CN)^{-2}$ and CN^- multilayer adsorption.

The deleterious effect of the free CN^- anion on the adsorption of the $Ag(CN)^{-2}$ anion is believed to be related to competitive ion-specific adsorption on the cation sites between the $Ag(CN)^-$, and CN^- anions.

The capacity of carbon for gold cyanide is about three times higher than for silver cyanide. This was attributed to the large ionic radius of gold compared with that of silver consistent with the solvent-energy theory [43].

Graboosk et al, investigation indicated that the

adsorption of gold is accompanied by reduction of the

$Au(CN)^{-2}$ complex to metallic gold.

It was considered that the role of carbon as the reducing

agent was in accordance with the reaction shown in the

equation below, where $C_xO...Na$ represents the oxidised

surface of the carbon with an adsorbed cation;

$$Na_2Au\ (CN)^2 + C_x + 2NaOH = C_xO..Na + Au(0) + (CN)^2Na + H_2O....(29)$$
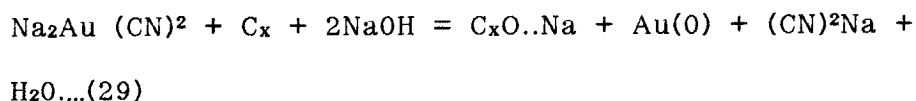
Investigation by McDougall et al, $\lceil 10 \rfloor$ using X-ray

photoelectron spectroscopy showed that the adsorption of

gold cyanide on carbon was in two stages: adsorption of

aurocyanide complex and the partial reduction of Au(I) to a

mixture of Au(I) and Au(0) in cluster type compounds.

Later study by Tsuchida, Ruane and Muir

showed that,the initial adsorption comprise an ion-pair

aurocyanide species involving charge-separated carboxylate

and chromene type active groups on the carbon surface. If Ca^{2+}

or Mg^{2+} is present, then the ion-pair formed with

carboxylate group would have a net positive charge and ion-

pair with further $Au\ (CN)^{-2}$.

McDougall et al [9, 10] support the view that Au(I) is

partially reduced to a mixture of Au(I) and Au(0) in

cluster-type components.

Furthermore, it is well known that activated carbon readily

In view of the limited adsorption capacity of carbon for
metal cyanide complexes, this adsorption has a detrimental
effect on gold adsorption by virtue of the selective
displacement observed. The selective adsorption metal
cyanide complexes onto activated carbon appear to relate to
the solubility and charge of the adsorbed complex concerned.
While the less soluble monovalent complexes of gold ,silver
and copper have all been shown to be strongly adsorbed by
carbon the more soluble divalent and trivalent, tricyano and
tetracyano complexes (e.g. Cu, Zn and Ni) are weakly
adsorbed, whereas the very soluble hexacyano and octacyano
complexes (e.g. Co and Fe) are not adsorbed to any marked
degree.

The adsorption of copper on carbon appears to play a unique
role in possibly aiding gold adsorption in some instances
via its ability to catalyse the oxidation of free cyanide.
Under typical plant conditions copper is present as
$Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ complexes and as such is weakly
adsorbed.

6.5 DESORPTION THEORY

The elution (or desorption) of the gold and other metals
adsorbed onto activated carbon is achieved in practice by
one of three main procedures, as follows:

(1)   the Zadra (or Homestake) method in which a hot caustic
       cyanide solution or eluant is circulated through an

elution column and one or more electrowinning cells,

(2)   the Anglo American Research Laboratory (AARL)

procedure, which involves pretreatment of the carbon by

a hot caustic cyanide solution prior to elution with

hot deionized water in a single pass through the

column, and

(3)   the organic solvent procedures, which are variations of

(1) or (2), in which the eluant contains large amounts

of organic solvents like methanol, ethanol, or

acetonitrile.

Detailed descriptions of these procedures are given in the

literature [43].

CHAPTER 7

EXPERIMENTAL WORK

ADSORPTION-DESORPTION OF GOLD AND SILVER CYANIDE

7.1 EXPERIMENTAL DESIGN

The adsorption experiments were done by using the mechanical flask shaker type SF1 with facility for clamping 8 flasks. Figure 16a shows the front view of the apparatus.

The activated carbon sample used in the adsorption tests was screened prior to use. A size range of -8 to +14 mesh size screened activated carbon was washed in de-ionised water to remove the fines. It was then dried in an oven at 100° C - 110° C and cooled in a dessicator prior to use in the adsorption experiments. De-ionised water was preferred to tap water to avoid contamination.

The adsorption experiments were based on the assumption, that adsorption rate is initially proportional to the adsorbent free surface and that the subsequent adsorption rate is rather slow and therefore of little practical interest. This more realistically simulated the carbon-in-column (CIC) plant operation practice, rather than equilibrium loading capacity. The residence time in the CIC contactors seldom exceeds one hour, thus adsorption experiments for a period of one hour were investigated and residence times of twenty four hours were also investigated.

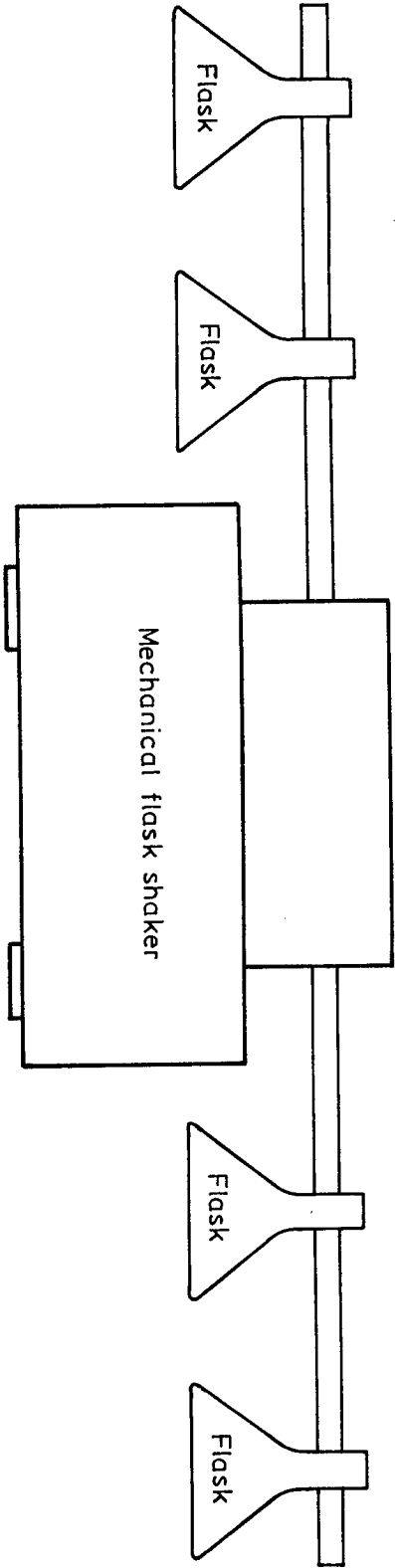The data for plotting adsorption isotherms were obtained by

FIG. 16a. FRONT VIEW OF THE ADSORPTION APPARATUS

treating fixed volumes of the cyanidation leach liquor with
a series of known weights of carbon. The activated carbon-
liquid mixture was agitated in flasks using the mechanical
shaker for a fixed time at constant temperature to establish
rapid adsorption. After the activated carbon had been
removed by filtration, the residual solution was analysed by
atomic absorption spectrophotometry (AAS).

From these measurements, the data necessary to plot
isotherms were calculated.

The loaded metal complexes of gold, silver and copper per
unit weight of the carbon are also tabulated. In a liquid
phase application, the transfer of the adsorbate from the
bulk solution to the carbon particle must proceed through at
least two stages:

(1) The transfer of the adsorbate molecule from the bulk liquid
to the surface of the carbon particle and (2) migration of the
adsorbate from the surface of the carbon to the adsorption
site within the particle. It is known from kinetic
experiments [43] that step 1 is appreciably more rapid
than step 2 and the latter is the rate determining step.

In preliminary experiments, fixed volumes of the roasted
anode slimes leach liquor were contacted with a unit weight of
carbon for one hour and the adsorption was noted.
Subsequently adsorption experiments, in which fixed volumes
of roasted anode slimes cyanidation leach liquor were
treated with various amounts of activated carbon, were

conducted.

The concentration of silver in the roasted anode slimes liquor was very high in the range of 5400-7000ppm which was beyond the analytical limit of AAS and could only be noted by diluting the leach liquor. Therefore this made it difficult to note the changes in silver concentration during the adsorption test in relatively small amounts(grams) of activated carbon. Large amounts of activated carbon were also not suitable for the determination of the adsorption of gold owing to the small concentrations of gold in the leach liquor. Thus a compromise was found by diluting the leach liquor ten times for the purpose of determining silver adsorption. However the changes in gold concentration(gold adsorption) were noted with undiluted leach liquor.

The pH 11 of the cyanidation leach liquor was maintained during the adsorption experiments. Adsorption was carried out at room temperature(25 $\pm$ 2° c). The temperature was not controlled in a thermostated bath largely because in CIC contactors the adsorption is carried out at room temperature (atmospheric temperature in the case of unenclosed CIC circuit). Therefore CIC conditions were simulated in the experiments.

The determination of the nature of the adsorbed species was attempted by XRD and XRF. The results are discussed in the report.

suspended particles.

Different weights of the oven dried activated carbon were transferred to laboratory flasks.

To each flask 100ml of the leach liquor from a graduated cylinder was added, the flasks were closed with stoppers and were then clamped to the shaker. The mixture was agitated for the chosen contact time. The same volume of leach liquor was added to a flask without carbon and subjected to the same procedure in order to obtain blank readings.

After the contact time had elapsed the samples were filtered and the filtrate was analysed on atomic absorption spectrophotometry to determine the residual concentration of the filtrate.

The determination of the amount of an adsorbed substance on AAS is difficult as small quantities are being sought. Careful analysis was imperative since a slight error in quantitative analysis could result in a large difference when plotting adsorption isotherms.

Therefore analysis of residual concentration on AA6 Varian Techtron atomic absorption spectrophotometry was done on average three times. The AAS was optimised before every run and the average results were used in the data analysis.

An automated on-line laboratory analyser, for determination of gold and silver, with a print-out facility for plotting adsorption curve, would have been ideal for analysis.

The solution samples used in these experiments were obtained

from the cyanidation of the roasted anode slimes experiments. The fresh activated carbon samples used in the experiments were obtained from Zimbabwe Minerals Development Corporation, Gold Mines Division in Zimbabwe.

7.2 DESORPTION EXPERIMENT PROCEDURE

The desorption procedure used in these tests is similar to the Zadra-type elution system.

The known amounts of loaded carbon samples from the adsorption tests were dried at 90° c- 100° c and transferred to the 250ml laboratory flasks. To each flask was added 50ml (0.2M NaOH + 0.5M NaCN) caustic cyanide solution. The flasks were then submerged in the thermostated water bath. These flasks were tightly closed to simulate a pressurized vessel. The temperature of desorption was set at 98° C. Tap water was used to maintain the thermostated water bath level.

The simplified apparatus used in the desorption tests is given in figure 16b.

7.3 RESULTS AND DISCUSSIONS

The adsorption experiments were done several times using different feed concentrations and the typical adsorption data are presented in this report. The residual concentration of gold, silver, and copper in the solution was plotted against amount of activated carbon. Figure 17 shows these results. The adsorption of silver was more pronounced.

FIG. 16b   THERMOSTATED DESORPTION APPARATUS
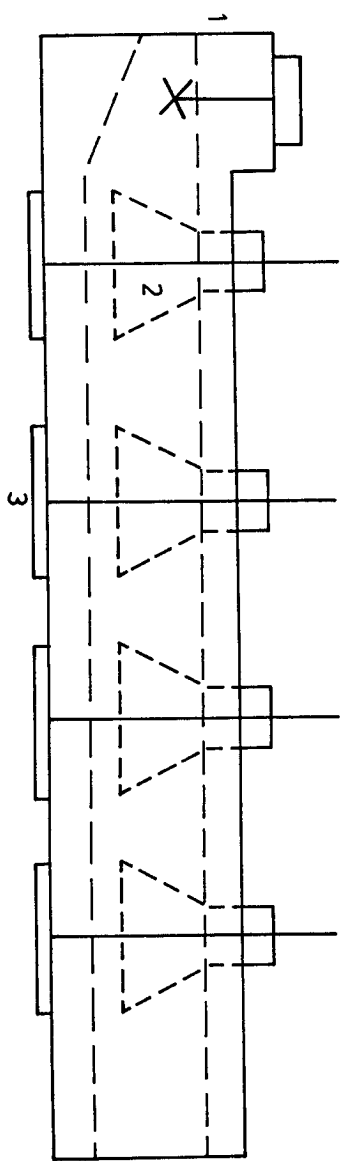
1. Thermostated water bath

2. Flask

3. Stand

Various curves of the adsorption of silver, gold and copper are presented in figures 18, 19,and 20 repectively. These curves show the adsorption profiles of these metals after one hour and twenty four hours residence time. They indicate the change in the concentration of the metals in solution against the amount of carbon. It can be noted from these curves that the higher the concentration the more is the adsorption. The results of the typical loading capacity of metals on the carbon for one and twenty four hours residence time are presented in table 4. on page 114 to page 116. Gold had the lowest concentration in the cyanidation leach liquor and its adsorption was measured against small amounts of activated carbon to determine its adsorption profile. The detection of the change in concentration of góld was very difficult owing to the small amounts of this metal in the cyanide leach liquor. However the loading capacity of gold was generated after several repeats of the adsorption experiments. The adsorption of copper had a different profile which indicated low adsorbability of copper.

The loading of gold, silver and copper on to the carbon surface was investigated using different feed concentrations to assess the effect on the loading capacity. The data generated were used to plot adsorption isotherms given in figures 21 and 22 on page 117 and 118, gold and silver respectively. It can be noted from these isotherms that the adsorption of gold and silver is appreciably high at high

concentration and rather low at lower concentrations, which shows that, at lower concentration more time would be required to adsorb the same amount of metal complexes as at higher concentration. Copper was of interest in the experiments to determine its adsorbability and therefore its competition for the available adsorption surface on the carbon, with gold and silver. Copper dissolves in cyanide solution but the predominant complex change is from $Cu(CN)_2^-$ to $Cu(CN)_3^{2-}$ to $Cu(CN)_4^{3-}$ as the cyanide to copper ratio is increased. The copper cyanide complex in the solution depends on the mole ratio of CN/Cu.

The copper adsorption isotherm data are also tabulated in table 4 and indicate that the amount of copper adsorbed per unit weight appears not to vary significantly with an increase in the adsorption surface.

The adsorption of copper onto the carbon could be explained as being due to probable breakdown of the higher copper complexes which are least adsorbed. This may be caused by the assumed depletion of free cyanide in the solution due to the surface reaction on the carbon resulting in either the adsorption of CN^- or the oxidation to CNO. Therefore this could have resulted in $Cu(CN)_4^{3-}$ breaking down (to maintain equilibrium in CN^- concentration) to $Cu(CN)_2^-$ which is sufficiently adsorbed on to the carbon.

The shape of the adsorption isotherms of silver and gold in figure 21 and 22 are similar to the type I of the typical

isotherms presented by Brunauer, Deming, Deming and Teller.
The adsorption curves of gold and silver were rather similar
and followed freundlich adsorption isotherm model.

These isotherms indicate the relationship between the amount
of carbon, the concentration of the metal complexes, and
retention time to the amount of metal complex adsorbed per
unit weight of activated carbon. It may also be noted that
at high concentration more metals of gold and silver are
loaded on the carbon. The 'Kn' model could be
used to explain this relationship
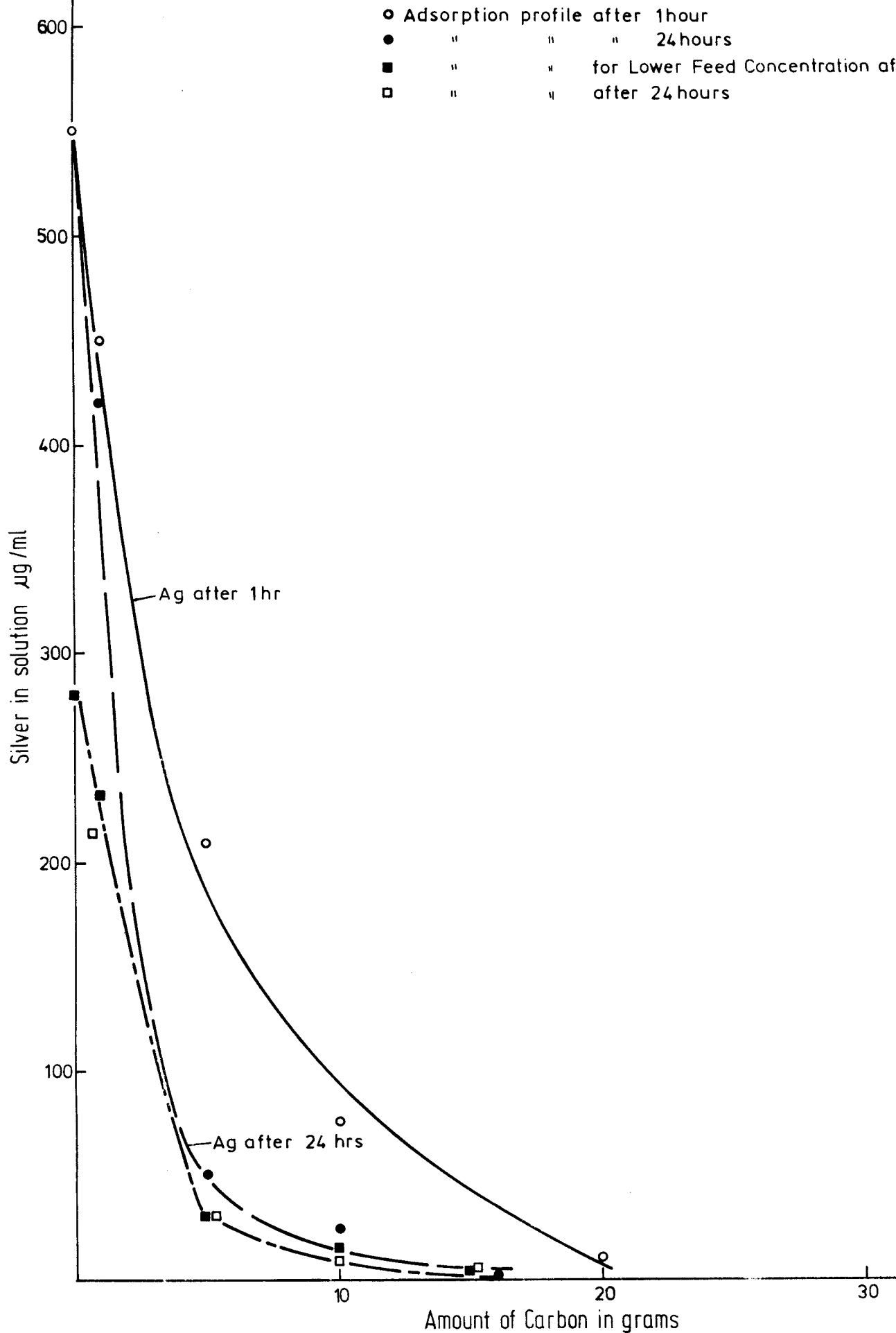
FIG. 18 ADSORPTION OF SILVER FROM ANODE SLIMES CYANIDAT
LIQUOR ON VARIOUS AMOUNTS OF CARBON
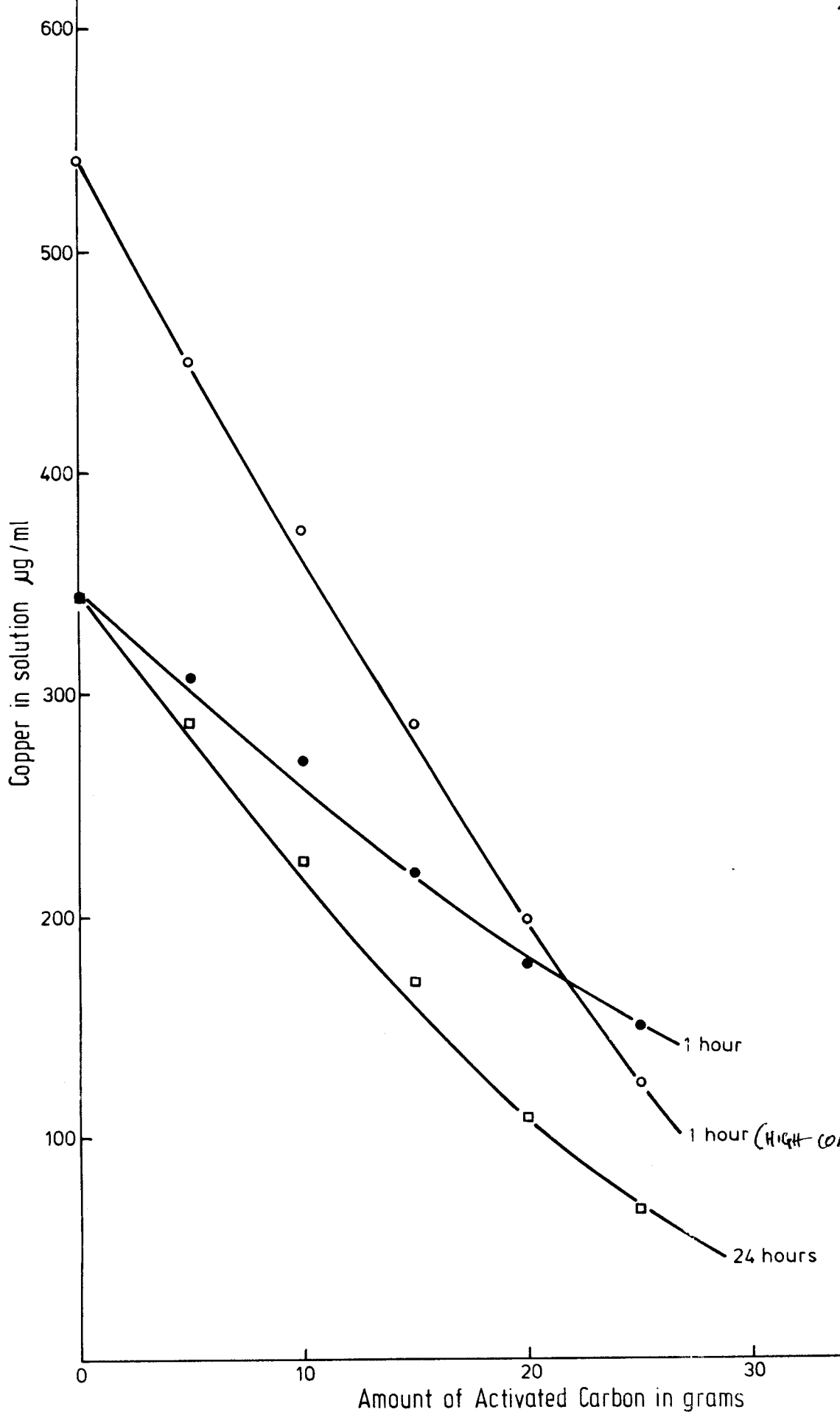
FIG. 20 ADSORPTION OF COPPER FROM ANODE SLIMES
CYANIDATION LIQUOR ON VARIOUS AMOUNTS OF CA

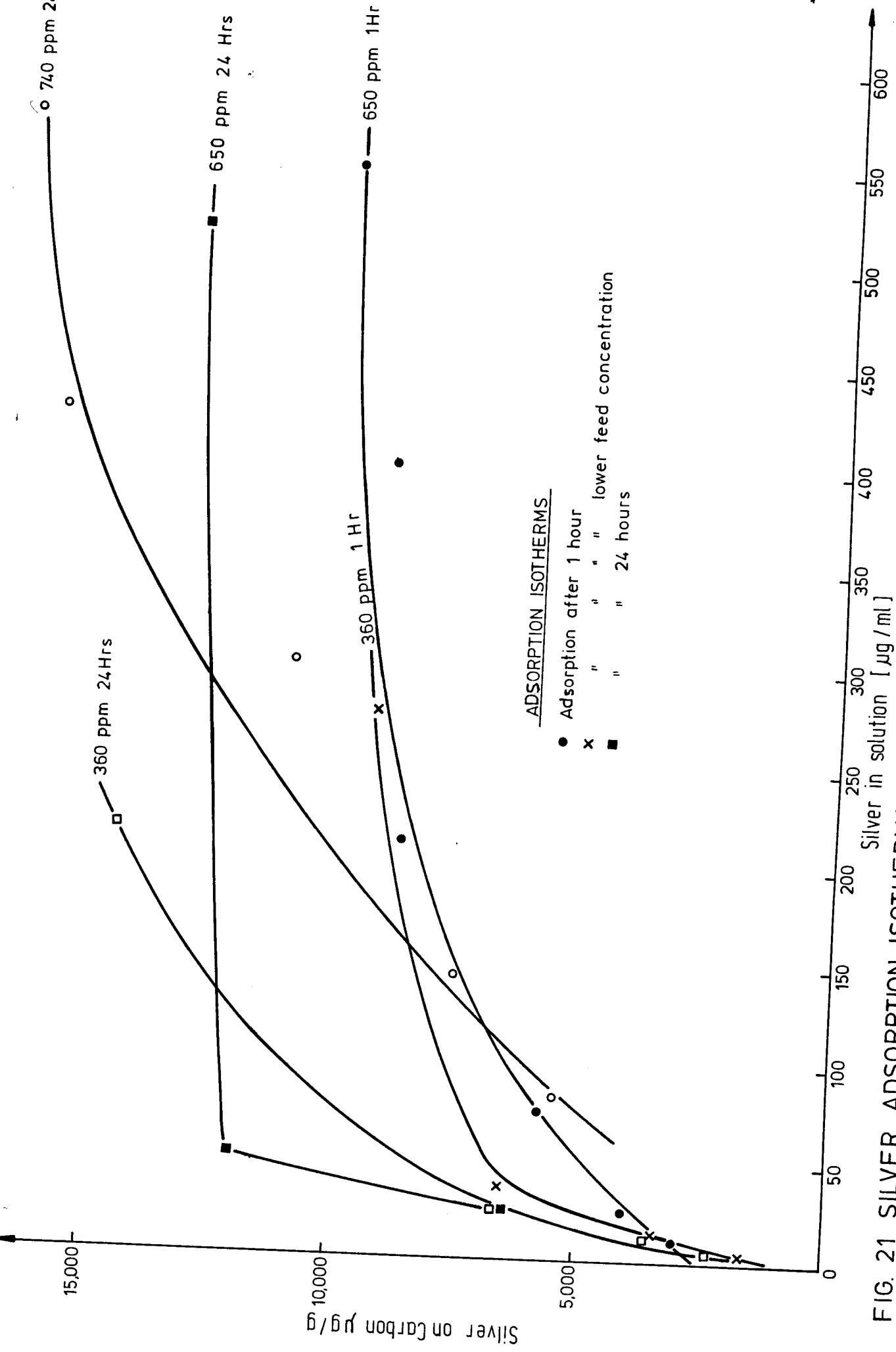TABLE 4. SILVER, GOLD AND COPPER ADSORPTION ISOTHERMS DATA

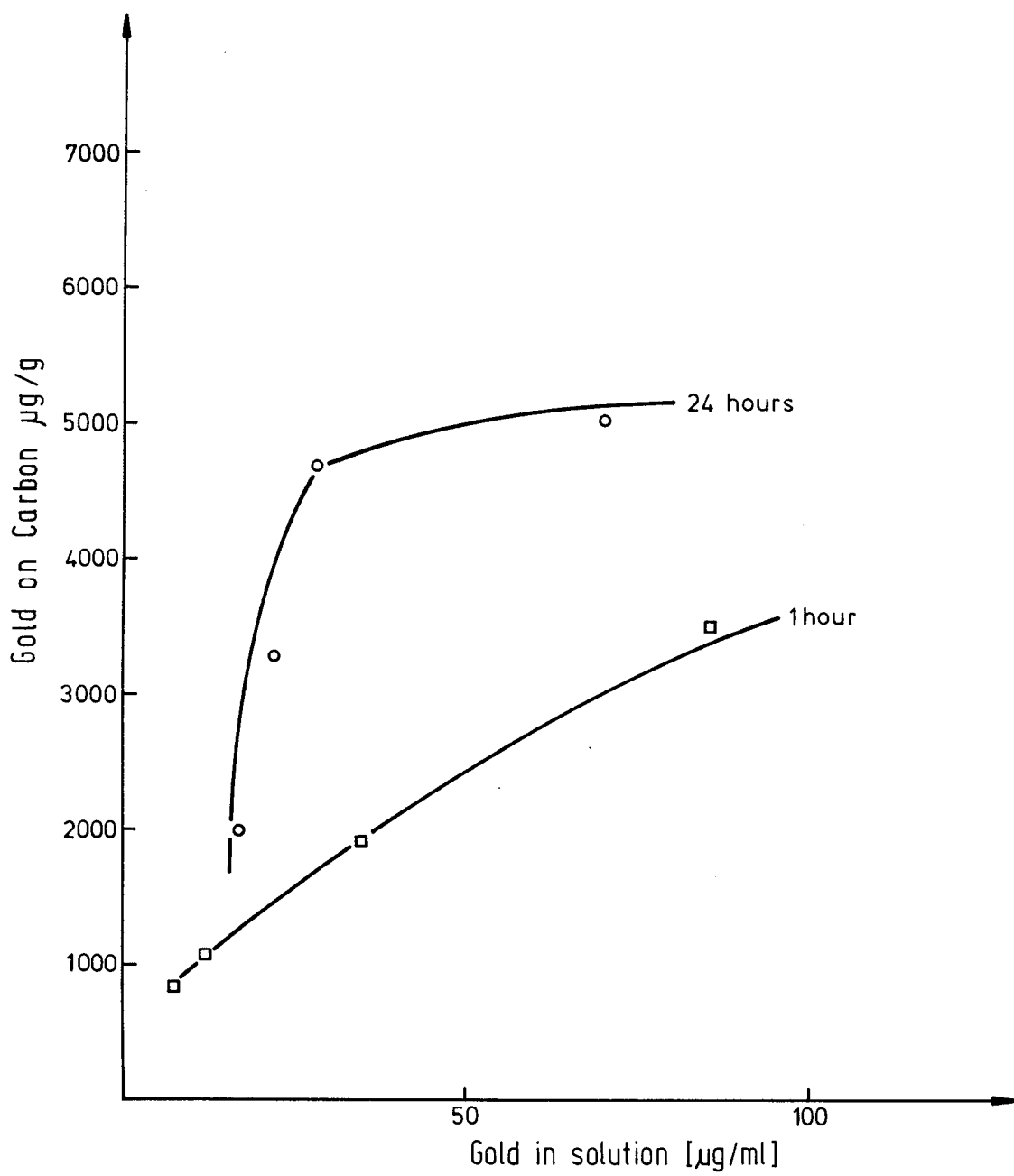FIG. 21 SILVER ADSORPTION ISOTHERMS

FIG. 22 GOLD ADSORPTION ISOTHERMS

The x-ray diffractogram of the blank carbon showed no patterns indicating the amorphous nature of the activated carbon. The XRD of the loaded carbon indicated patterns, an indication of the presences of crystalline substance occluded or adsorbed by the carbon.
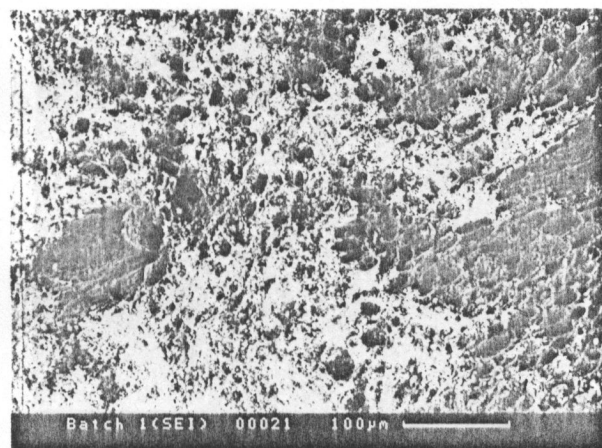
Peaks of the following; AgCN, KAg(CN)$_2$, KAg(CN)$_3$, K$_3$Ag(CN)$_4$, AuCN, and KAu(CN)$_2$ metal complexes of silver and gold, formed during cyanidation of the silver and gold material, were sought on the XRD pattern. However no peaks of the known sought for crystalline complexes of silver and gold were present. McDougall et al view that Au(I) is partially reduced on the carbon to a mixture of Au(I) and Au(O) in cluster-type compounds of the type Au(CN)$_x$. This could also probably explain the patterns on the x-ray diffractograms of the adsorbed carbon. The x-ray fluorescence scans of the same sample of the loaded activated carbon washed in 0.1M HCl showed the presence of gold and silver elements as shown in figure 23 of the appendix. The sample of loaded carbon was heated in a mixture of 1.0% NaOH and 0.1% cyanide solution,(widely used for desorbing gold and silver from loaded activated carbon) to dryness and presented for XRD analysis. The x-ray diffractogram obtained given in figure 24 in the appendix, showed peaks of gold and silver. This meant that the adsorbed gold and silver complex was broken down to metallic form. X-ray diffractometry does not record the ionic complex

phases, therefore deducing from the results it can be said ·
that, the gold and silver species could likely be adsorbed
as either charged complex compounds (ionic complexes) or in
a stiochiometry involving fractional valency. Hence it is
proposed, from these XRF and XRD studies, that gold and
silver is adsorbed according to the mechanism suggested by
Garten and Weiss, similar to the that proposed by Cho et al,
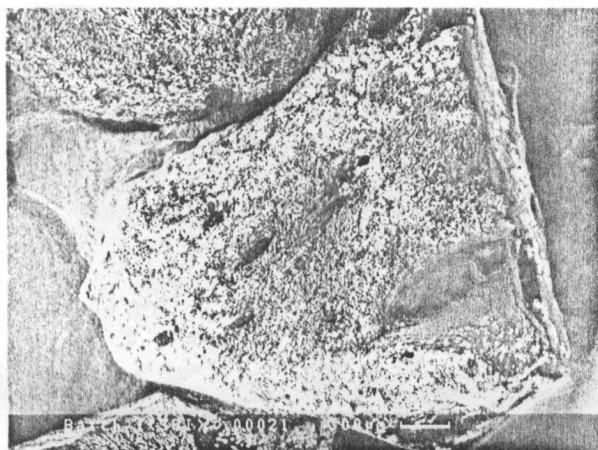which involves electrostatic attraction.

The adsorbed(loaded) and the fresh activated carbon samples
were viewed under Scanning Electron Microscope(SEM) as shown
in figures 25 and 26. The loaded and free regions of the
activated carbon were viewed ta higher magnification using
SEM as shown in figure 25. In general these photomicrographs
indicate the density of adsorption on the activated carbon
surface. The adsorbed gold and silver shows light on the
loaded samples. Surface texture and location of the
adsorbate are all clear as indicated on the prints. There
are different densities of adsorbate in different region as
shown on the prints and there are also remarkable variations
in texture. The adsorbate appears to favour the clear
surfaces rather than holes or depressions. The loaded carbon
adsorbs selectively on specific features and in specific
areas but the texture of these features are not easily
reproduceable. The apparent variation in area selectivity
from particle to particle may explain the variation in
loading levels in the adsorption test. However, there seems
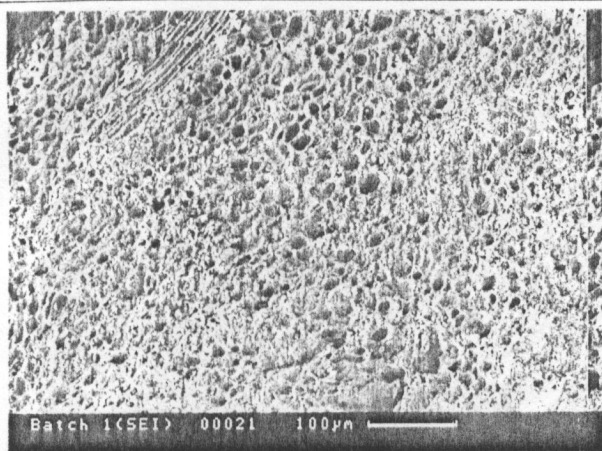
C. UNADSORBED REGION
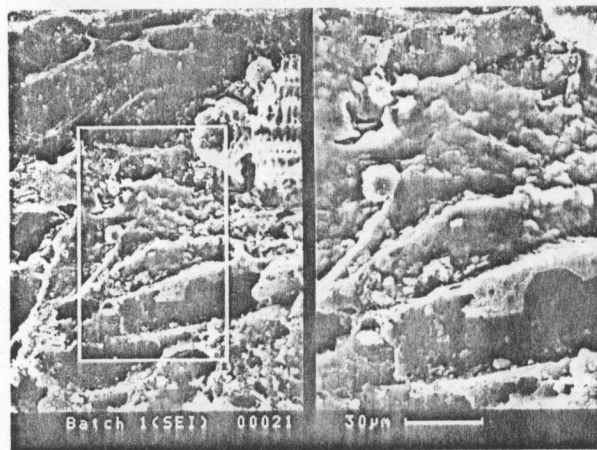

D. HIGHLY ADSORBED SURFACE

B. ADSORBED REGION
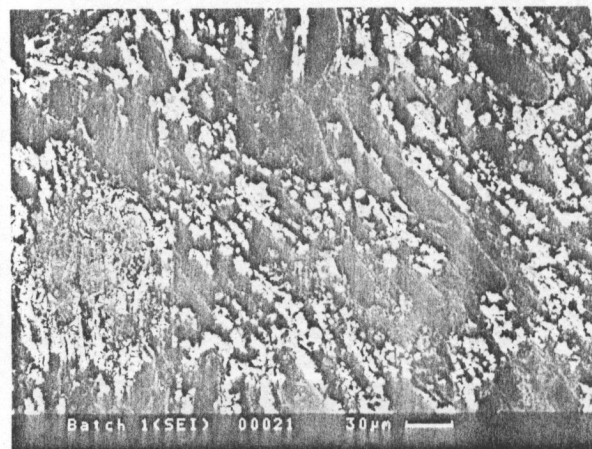
E. MEDIUM ADSORBED SURFACE

A. SOME ADSORBED AND UNADSORBED REGIONS
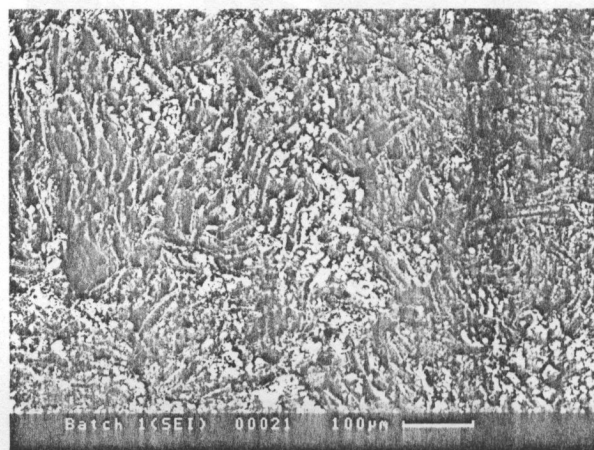
F. LOW ADSORBED SURFACE

FIGURE 25. SCANNING ELECTRON MICROSCOPE PHOTOMICROGRAPH OF THE ADSORBED ACTIVATED CARBON.

122
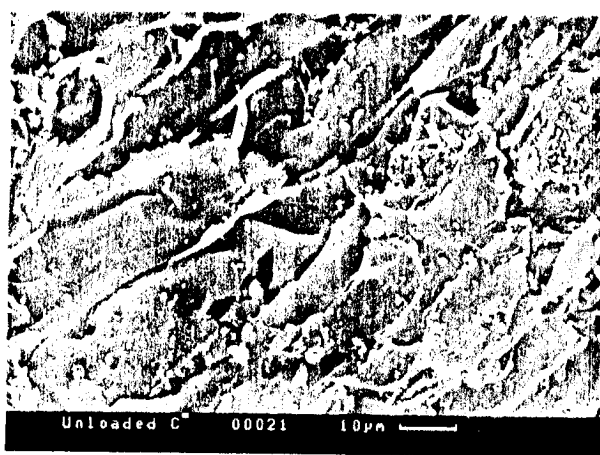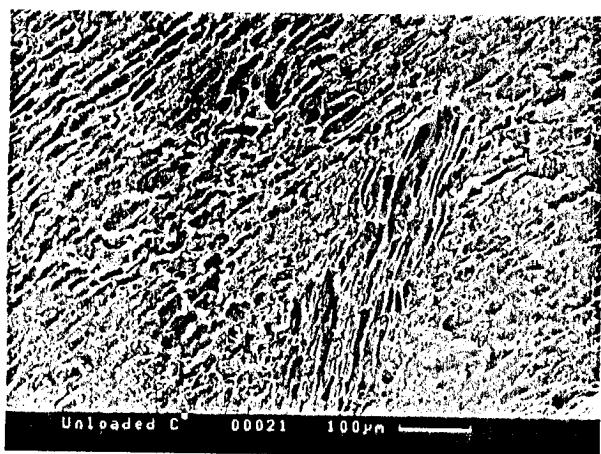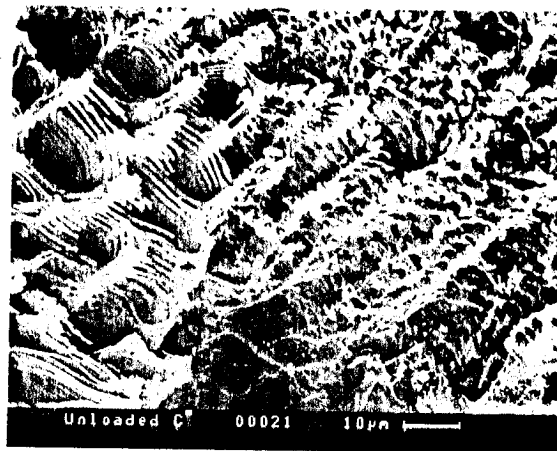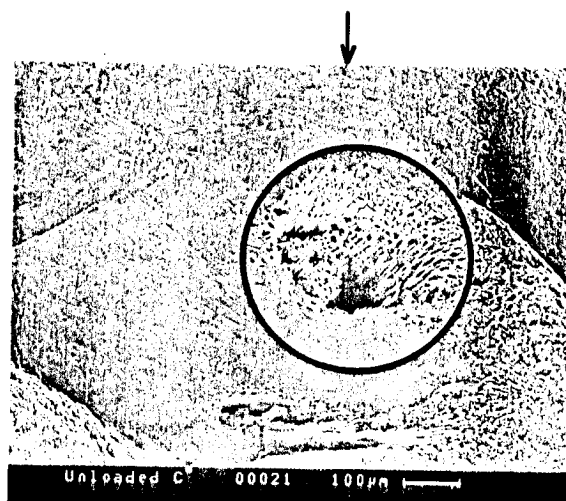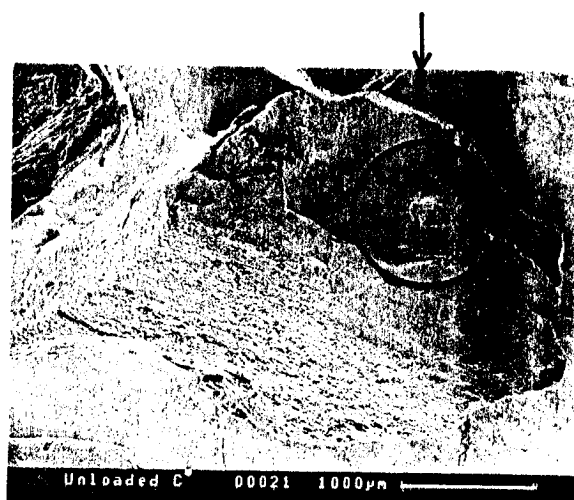
FIGURE 26. SCANNING ELECTRON MICROSCOPE PHOTOMICROGRAPH OF FRESH ACTIVATED CARBON

The desorption test were carried out on selected amounts of the loaded carbon and the typical desorption data are tabulated in table 5. These results show consistent high desorption of silver and indicates that silver desorbs more easily than gold.

TABLE 5. SILVER, GOLD AND COPPER DESORPTION DATA.

Silver desorption data

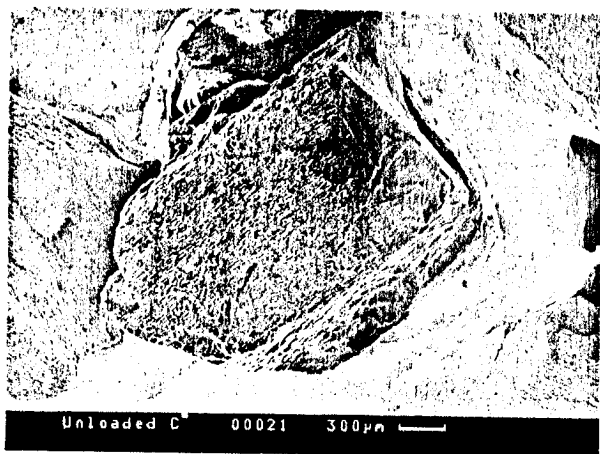| Amount of carbon	Ag adsorbed per unit weight	Total amount of Ag on the carbon	Concentration of Ag in solution desorption solution	Total amount of Ag desorbed	Ag per unit weight desorbed carbon
M	g/g	g/g	g/ml	g	g/g
			190		
			244		
			855		
			1004		

Gold desorption data

Amount of carbon	Au adsorbed per unit weight	Total amount of Au on the carbon	Concentration of Au in liquid desorption solution	Total amount of Au desorbed	Au per unit weight desorbed carbon
M	g/g	g/g	g/ml	g	g/g
		2.900	30		
	5.500	5.000	35	2520	
	2.000	2.000	39.5	1980	
	2.700	2.700	43.5	2120	

	amount of gel unit weight	Total amount of Cu on the solution	concentration of Cu in final adsorption solution	amount of Cu adsorbed	Cu per unit weight adsorbed solution
N	-g/2	-g/3	-g/m.	-g	-g/g
	500	4,000	85	3200	100
	700	9,000	188	7000	115
	1000	12,000	181	19030	130
	1100	15,000	402	20100	145
	1500	20,000	5.1	20500	170

7.3.1 DISCUSSION OF THE PROPOSED FLOWSHEET

From the foregoing studies a flowsheet has been proposed as
shown in figure 29.

The flowsheet represents details on what was achievable
under the circumstances. Some feature of the flowshet , for
example re-pulping and dump residual leaching stages are the
proposed further addition to the flowsheet for the
anticipated maximum recovery of the residual gold and
silver in the cyanidation tailings.

This flowsheet is a basically hydrometallurgical process
and represents a rather simplified model of the proposed
alternative anode slimes treatment route to the conventional
process. In this flowsheet the use of various acids, as
used in the other process and their adverse effects as
earlier outlines, have been eliminated.

The preliminary stage in this process is the roasting of the
anode slimes in the muffle furnace at an average temperature
of 700°C. This is largely to remove selenium and decompose
selenium related compounds. The reasons for this are
twofold to eliminate the deleterious effects of selenium
during the cyanidation of anode slimes and to enable the
recovery of selenium.

The subsequent stage of cyanidation is rather important as
high recovery at this stage would mean negligible loss in
tailings. in the single cyanidation stage indicated in

fig.29 the following parameters yielded the optimum results: pH 11, cyanide strength 14%wt, mechanical and air agitation, and the rate of deration $0.01m^3$/min.

The adsorption stage is mainly the function of desired loading of the metals on the carbon and the metal content. in the effluent. This would then be used to determine the activated carbon charge, the retention time and the cyanidation leach solution flowrate. The amount of gold and silver loaded on the activated carbon in this adsoprtion stage depended upon, the concentration of these metals in the leach solution, the retentionn time and the carbon charge.

The final stage of desorption-electrowinning could be effected by various proven methods. However, in this test work desorption was carried out using the Zadra desorption method.The elution solution comprised a mixture of 0.2M NaOH and 0.5M NaCN at temperature of 98°C.

FIG. 27 PROPOSED ANODE SLIMES FLOWSHEET

D - Residual Leaching Dump
F - Activated Carbon Recycle / R
E - Electrowinning Loaded Liquor
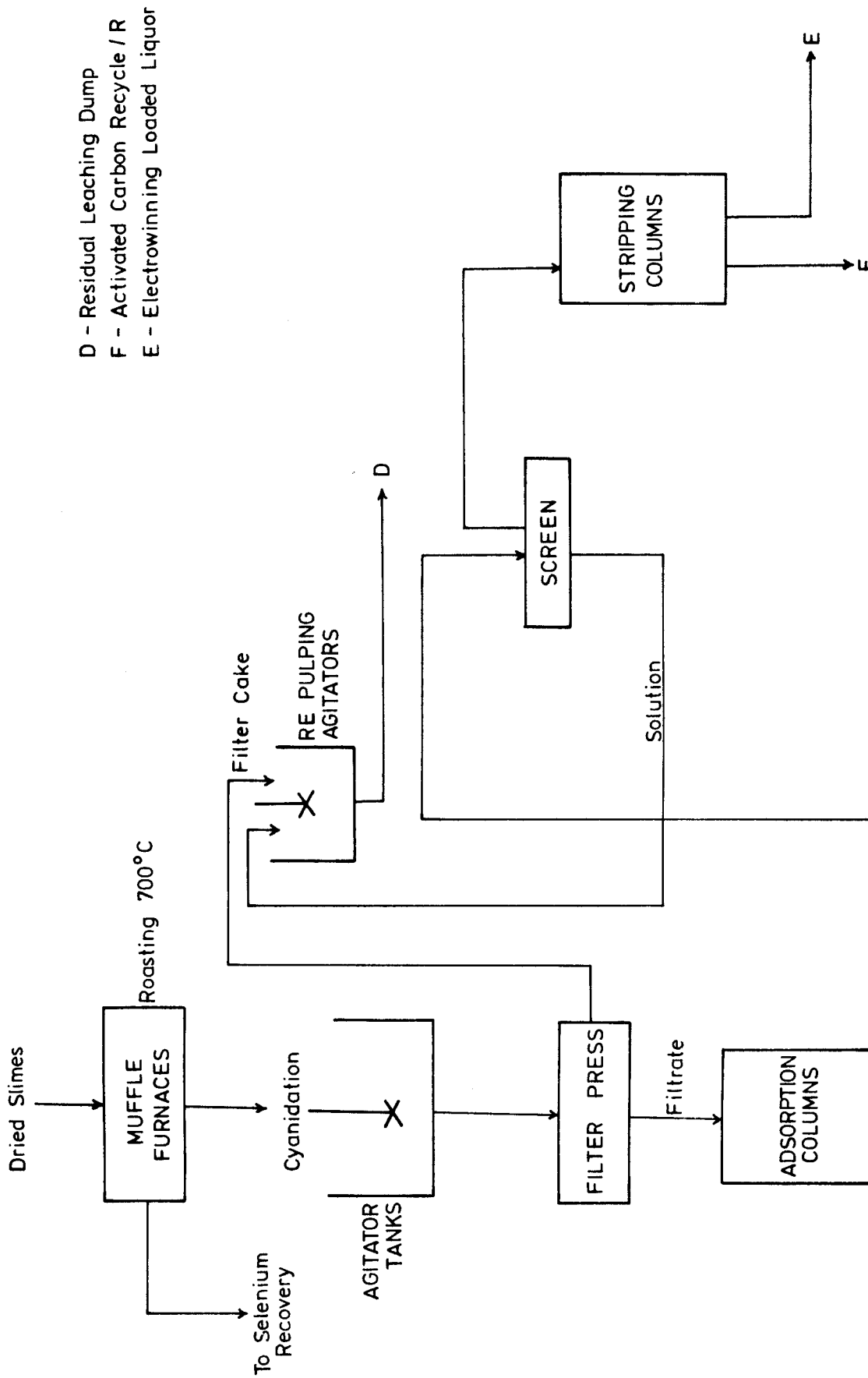
SUMMARY, CONCLUSION AND RECOMMENDATIONS

SUMMARY AND CONCLUSION

The cyanidation process for extracting precious metals(gold
and silver) from copper anode slimes (by product of copper
refining) was investigated. The recovery of these precious
metals from cyanidation solution by adsorption on activated
carbon has been studied. This was to assess the cyanidation
and adsorption process as a potential alternative recovery
process to the conventional metallurgical flowsheet
presented in this report. The technique used in the study
included size classification, mineralogical and chemical
analysis. This formed the basis of cyanidation and
adsorption investigations.
The analytical techniques used in the studies were a
combination of x-ray fluorescence spectrometry, x-ray
diffractometry, atomic absorption flame spectrophotometry,
volumetric and gravimetric analysis.

The surface features of the fresh and adsorbed activated
carbon were studied using scanning electron microscope.

From the x-ray fluorescence spectrometry, the copperbelt
anode slimes were found to consist minor and major elements.
The minor elements were tellerium, magnesium, chlorine,
cobalt, calcium, bismuth, antimony, and nickel. The major
elements were gold, copper, selenium, silver and silicon.
The mineral phases identified from x-ray diffractograms were
chloragyrite, nuamannite, quartz, berzeliant, cuprite and

selenium.

The size classfication showed that, particle size of anode slimes was in the range of -53μm to +600μm and 50.6% wt was less than -75μm.

From the cyanidation tests, the recovery of silver was found to increase with an increase in cyanide concentration. Recoveries of 82% and 77% of silver and gold respectively were achieved during the cyanidation of roasted anode slimes.

Adsorption isotherms of gold, silver and copper have been generated. From these isotherms, an approximation of the loading capacity of gold and silver on the activated carbon has been obtained. The dependence of adsorption of silver and gold on, the amount of carbon, the retention time and the concentration of silver and gold in solution, has been noted.

The results obtained on several adsorption experiments show a high consistent adsorption of silver. The loading of approximately 15,000g/t Ag and 5,000g/t Au was achieved. Gold loading on the activated carbon is much less than silver owing, largely, to the difference in concentration of these metals in the solution. Copper is the least adsorbed, though its adsorption is significant. Generally the adsorptiopn of silver and gold is higher than copper.

Information of the nature of the adsorbed species of gold

and silver on the carbon has been done by x-ray diffractometry
From these diffactograms no peaks of the known crystalline
complex of gold and silver have been identified.
Surface texture and location of the adsorbate on (gold,
silver and copper) on the carbon were noted on the scanning
electron microscope prints. The surface feature of the fresh
activated carbon showed a highly irregular surface.

From the foregoing studies the following general conclusions
can be made:

a) The extraction of gold and silver from anode slimes is
feasible, though at high cyanide concentration.

b) The separation of silver and gold from the complex
mixture obtained from the cyanidation of anode slimes can
be achieved by activated carbon adsorption process.

c) The amount of metals adsorbed per unit weight of
activated carbon depend on the, amount of carbon(surface
area available), the concentration of gold and silver in
solution and retention time. The adsorption of these metals
relate to the 'Kn' adsorption process design model, which
could be used for the design of the multi- stage adsorption
process.

d) From the x-ray diffractograms of the adsorbed carbon,
gold and silver species were proposed to be adsorbed as

ionic complexes in line with the adsorption mechanism proposed by Garten and Weiss, similar to Cho et,al.,[43] involving electrostatic attraction of gold and silver cyanide complex on to the carbon surface and subsequently reduced on the carbon to stiochiometry involving fractional valency.

RECOMMEDATION

A scale up of the cyanidation and adsorption experiments must be carried out. Multi-stage adsorption test should be tried to simulate plant operations. These experiments would focus on extraction of silver and gold against cyanide concentration.

Several other parameters, for example the activated carbon charge (kg/m^3), the desired loading, the retention time, type of agitation and flow rate would have to be determined. Therefore a model similar to the 'Kn' adsorption process design model should be used to aid the design of these multi-stage adsorption tests.

This would enable a comprehesive evaluation of cyanidation and adsorption process, for use on industrial scale.

APPENDICES

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