

APPLICATIONS OF MINERAL CHARACTERISATION
AND PROCESS RESEARCH
TO THE DEVELOPMENT OF BENEFICIATION TECHNOLOGY
FOR THE MINERALS INDUSTRY

C.W. NOTEBAART

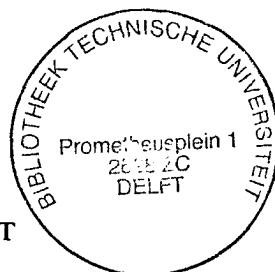
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PROEFSCHRIFT



**TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE TECHNISCHE UNIVERSITEIT DELFT,
OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF.DRS. P.A. SCHENCK,
IN HET OPENBAAR TE VERDEDIGEN
TEN OVERSTAAN VAN EEN COMMISSIE
AANGEWZEN DOOR HET COLLEGE VAN DEKANEN,
OP DONDERDAG 15 DECEMBER 1988 TE 10.00 UUR**

DOOR

CORNELIS WILHELMUS NOTEBAART

**MIJNINGENIEUR
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Dit proefschrift is goedgekeurd door de promotor

Prof. ir. W.P.C. Duyvesteyn

Aan mijn ouders

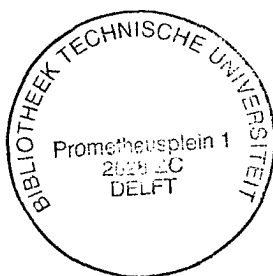
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Aan Astrid en Richard

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CONTENTS

INTRODUCTION	1
PART ONE	3
1.1. Mineralogy and metallurgy.	3
1.2. Treatment of oxide copper ores in Zambia.	13
1.2.1. General.	13
1.2.2. Flotation of oxide ore at Rokana.	15
1.2.3. Process development for the treatment of cupriferous mica ores.	17
1.3. Dense medium separation of oil shale.	35
1.4. High intensity magnetic separation.	40
1.5. Concluding remarks.	49
1.6. References.	51
PART TWO - PAPERS	55
2.1. Ore minerals of the Zambian Copperbelt.	55
2.2. Libethenite at the Rokana Mine, Kitwe, Zambia.	73
2.3. The nature of cupriferous micas from the Chingola area, Zambian Copperbelt.	89
2.4. Metallurgical treatment of Chingola cupriferous mica ores.	105
2.5. Design of mixer-settlers for the Zambian copper industry.	125
2.6. Commercial processes for copper.	145
2.7. Determination of the separation efficiency in dense medium separation of porous materials using magnetic tracers.	187
2.8. Improved selectivity in high intensity magnetic separation of Mount Pleasant wolframite flotation concentrate.	197
SUMMARY	225
Samenvatting	228
Dankwoord	231
Curriculum vitae	232
Notes on authorship	233

INTRODUCTION

A large variety of ore beneficiation techniques exists. Flowsheets in operating plants range from very simple with relatively few processing steps to highly complex, involving many stages of mineral separation and extraction of valuable components by hydro- or pyrometallurgical processes. Each ore is different and requires separate flowsheet development. Although standard flowsheet types may be applied for certain ores the details should be based on the results of metallurgical testwork. During the normal course of investigations the ore is first characterised by mineralogical analysis to determine the types of ore and gangue minerals, their associations and grain sizes to estimate the required degree of comminution for liberation of the valuable minerals. Based on the results of this study possible alternative treatment methods are considered. A program of metallurgical testwork is then carried out to assess the amenability of the ore to one or more of these alternative processing routes. If the results are sufficiently promising a feasibility study is conducted, involving detailed testwork on a laboratory-scale, which may or may not be followed by piloting to generate data for a final economic analysis and plant design.

In all these stages of the project, mineralogy or more generally materials characterisation, plays an important role. Metallurgical problems can often be anticipated or explained by mineralogical analysis of the feed, separation products, precipitates, leach residues, slags etc. Appropriate action can then be taken. The availability of "in house" process research facilities together with mineralogical support can result in substantial benefits to a mining company. The feedback between operations and the research group will provide an invaluable build-up of expertise. It is evident that such facilities are costly and usually only large mining companies can sustain them.

The interaction between mineralogy and metallurgy forms the central theme of this thesis, which is divided into two parts. The first part commences with a general section in which the importance of mineralogy

in metallurgical processing is illustrated by means of examples of applications in mineral dressing, hydrometallurgy and pyrometallurgy. Gold processing is separately treated in view of its current importance. This section is followed by an overview of research work in various areas of mineral processing in relation to the central theme. The details of this research work are contained in a series of published articles which, supplemented by recent work, forms the second and main part of the thesis.

PART ONE

1.1. Mineralogy and metallurgy

One of the classic papers on applied mineralogy in the mineral industry deals with the Zambian Copperbelt [1]. The usefulness of mineralogical support has been recognized there by the metallurgists in an early stage and resulted in the formation of strong research groups in the two mining companies (Nchanga Consolidated Copper Mines Ltd and Roan Copper Mines Ltd) over the years. Most of the work was related to the operating plants and geological exploration activities. Also elsewhere in the world the importance of mineralogical support to metallurgical process operations and to flowsheet development for new ores was increasingly recognized.

During the past two decades the number of publications related to applied mineralogy steadily increased. The development of image analysis techniques, in combination with an electron microprobe [2], or with a scanning electron microscope (SEM) with X-ray detection [3] made quantitative mineralogy a very powerful tool in metallurgical investigations. Not only quantitative data on mineral composition but also the degree of locking of individual minerals and the relative proportions of the components in locked particles can be determined with the more sophisticated systems. Also optical image analysis [4] has been extensively applied in metallurgical studies. Other developments occurred in thermal analysis (TGA, DTA), hot-stage microscopy and X-ray diffraction equipment (e.g. high temperature).

Cathodoluminescence microscopy can sometimes be applied in case determination of particular minerals is problematic in reflected light microscopy. For example the unwanted phosphate mineral apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{Cl}, \text{F})$) in iron (hematite- Fe_2O_3) concentrates can be easily detected with luminescence microscopy [5] and thus its mode of occurrence can be studied (intergrowths with hematite).

For the study of coatings of one mineral on another mineral Auger electron spectroscopy (AES) in combination with electron spectroscopy for chemical analysis (ESCA) has been applied. Hagni [5] investigated the cause of flotation of pyrite (FeS_2) into a molybdenite (MoS_2) concentrate. The AES and ESCA analysis showed that a very thin coating of molybdenite occurred on these pyrite grains, explaining their flotation behaviour.

The "gold rush" of the 1980's posed its own mineralogical and metallurgical problems. The diversity of gold ore types is remarkable and has been discussed by Ypma [6] in relation to dissolution and re-deposition processes under various conditions. The location of gold minerals in ore samples, usually native gold or electrum (Au,Ag), requires special consideration. Although native gold has very distinctive optical properties in reflected light, its location in ore samples is not always that simple. If the gold is relatively coarse, the occurrence of such grains is rare. In alluvial gold pre-concentration by gravity separation is possible, but for samples from hard rock deposits several polished sections may have to be scanned before a single coarse gold grain is encountered. Gold associated with sulfide minerals, pyrite or arsenopyrite (FeAsS), may be even more difficult to locate. For example at Carlin, Nevada, gold occurs in a spheroidal pyrite in relatively high concentrations (up to 6 kg/t), but could not even be detected with a scanning electron microscope. It occurs either as a solid solution in the pyrite or as inclusions smaller than $0.2 \mu\text{m}$ [7]. Automated location of rare grains of gold in polished sections requires special techniques. If such grains are small, complete area scanning of the polished section is needed. The standard method with the electron microprobe using characteristic X-rays is relatively slow and if several polished sections would have to be scanned the analytical time would be prohibitively long (in the order of one or more days). To speed up the analysis use can be made of the electron backscatter signal, which is dependent on the average atomic number of the mineral being scanned [2,8]. Once high-atomic number phases have been located, further

quantitative analysis with characteristic X-rays can then be carried out.

Applications of mineralogy in various areas of mineral beneficiation are outlined below.

Flotation

Mineralogical analysis is extensively applied in flotation research, in metallurgical testing for flowsheet development and in the analysis of flotation circuit performance. Liberation analysis forms an important part of such studies. Particle flotation rates depend on the type of mineral and on the degree of liberation. This can be illustrated by an analysis of copper sulfide flotation in the rougher-scavenger circuit at the Luanshya concentrator in Zambia. The first two cells in a bank produce a rougher concentrate and the next four cells a scavenger concentrate, which is recycled to the rougher feed. Chalcopyrite (CuFeS_2) and bornite (Cu_5FeS_4) are the main copper-bearing minerals and are associated with cobaltiferous pyrite. Quantitative mineralogical data for this circuit have been provided by Rixom and Kostic [9]. From these data the cell recoveries for the different sulfide minerals have been calculated and are given in Table 1. First order flotation kinetics (rate constant k) are assumed. The mass fraction of a mineral remaining in the tailings (R_t) of N perfectly mixed flotation cells with residence time t is given by [10]:

$$R_t = (1 + k \cdot t)^{-N}$$

A plot of the logarithm of the fraction of non-floated mineral versus cell number should give a straight line. Such a plot for the Luanshya data is shown in Fig. 1a. It can be seen that the data points for the first 2-3 cells approximately fall on a straight line, but significant deviations occur down the bank. This is a well-known phenomenon [10]. Locked particles with smaller rate constants are recovered mainly in the scavenger section. This is confirmed by the liberation data given by

Flotation	Cumulative recovery, %			Ratio free:locked copper sulfides in concentrate
	chalcopyrite	bornite	pyrite	
1	65.3	53.7	29.7	97:3
2	89.7	81.4	45.2	95:5
3	94.5	85.6	57.4	87:13
4	97.5	91.9	70.8	78:22
5	98.2	96.0	73.5	84:16
6	98.3	96.4	74.9	88:12

Table 1. Flotation recoveries of chalcopyrite, bornite and pyrite along a rougher/scavenger bank in the Luanshya concentrator, Zambia (calculated from [9]).

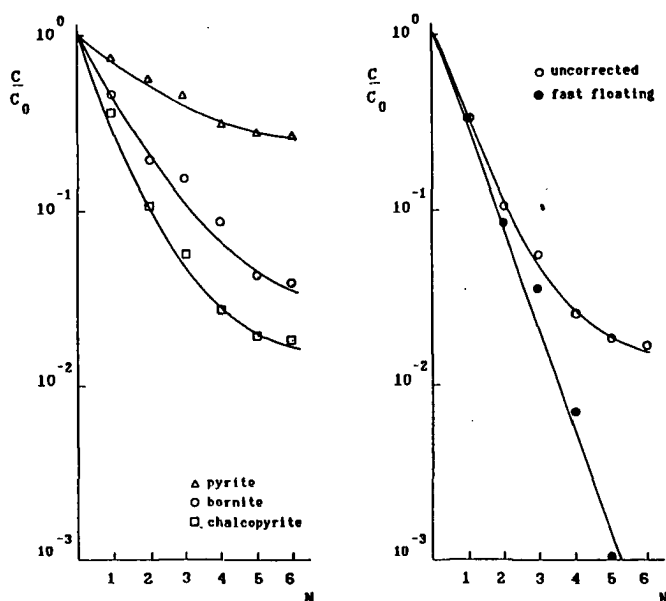


Fig.1. Flotation kinetics of ore minerals in the rougher/scavenger circuit of the Luanshya concentrator, Zambia (based on [9]).
a. overall values b. chalcopyrite - fast floating fraction.

Rixom and Kostic (Table 1). However, locking may not be the only cause of lower rate constants, but in each size fraction of valuables a proportion of material with lower rate constants can occur [10], due to unsuccessful preparation of the surfaces. Also in the very fine sizes ($< 20 \mu\text{m}$) the proportion of slow floating material is observed to increase. A distribution of rate constants may thus exist. Determination of such a distribution function is problematic, although the much improved image analysis techniques could facilitate this. Kelsall [11] found that in many cases an approximation could be made by assuming the presence of fast and slow floating fractions, resulting in a two rate constant model. For a flotation bank with N cells the recovery would then be [10]:

$$R = \phi[1-(1+k_s)^{-N}] + (1-\phi)[1-(1+k_f)^{-N}]$$

where ϕ is the proportion of slow floating mineral in the feed, and k_s , k_f are the rate constants of the slow and fast floating fractions respectively. These two rate constants can be estimated from data for cells near the feed and tailings end of a flotation bank. The data from Rixom and Kostic [9] show that there is a very slow floating fraction of chalcopyrite and bornite as the tailings grade of the last two cells hardly changes. This very slow floating material is all $< 20 \mu\text{m}$ and predominantly locked. Calculations were made using the two-rate constant model for the three sulfide minerals. First the slow floating fraction was determined by assuming that only slow floating mineral particles float in the last cell and the following equation was solved:

$$R = (C_5 - C_6)/C_5 = 1 - (1 + k_s t)^{-1}$$

where C_5 and C_6 are the concentrations of sulfide mineral remaining in cells 5 and 6 respectively. Evaluation of this equation gives $k_s t$. The fraction of slowly floating mineral in the feed can be evaluated from the expression for the recovery of slow floating material in the first 5

cells (it was assumed that only slow floating material remains in the last cell). Thus:

$$R = (\phi - C_s/C_0)/\phi = 1 - (1 + k_s t)^{-5}$$

where C_0 is the feed concentration. The fraction of slowly floating mineral retained in each of the cells is then calculated from:

$$C/C_0 = \phi(1 + k_s t)^{-N}$$

where C_0 is the feed concentration. Subtracting these values from the total amount of the mineral component retained in each cell gives the fractions of fast floating material. These are plotted for chalcopyrite in Fig. 1b and show the expected straight line relationship for the two component model. The data for bornite show more scatter, which may be due to the original mineralogical analysis or to the flotation conditions (a reduction in flotation rate is observed in the first cells of the scavenger circuit), but no operational data are given. The fast floating rate constant for each of the sulfide minerals could be determined from the data for the first cell corrected for slow floating material from the following equation:

$$R = (1 - \phi - C/C_0)/(1 - \phi) = 1 - (1 + k_f t)^{-1}$$

However, as the residence time in the flotation cells at Luanshya is not given, only the relative rate constants of the three sulfide minerals can be calculated from the above equation. They are:

$$\begin{aligned} k_{f, \text{chalcopyrite}} : k_{f, \text{bornite}} &= 1.5:1 \\ k_{f, \text{chalcopyrite}} : k_{f, \text{pyrite}} &= 2.7:1 \end{aligned}$$

The flotation rates of free particles thus decrease in the order chalcopyrite-bornite-pyrite. In other operations on the Zambian Copperbelt the cobalt mineral carrollite (CuCo_2S_4) is also present and observations indicate that this mineral floats faster than the

associated pyrite but slower than bornite. Knowledge of relative flotation rates of different minerals and composite particles might be utilized for optimum circuit design in differential flotation.

The study of plant flotation tailings is very important for performance analysis. The occurrence of free grains of valuable minerals may point to operational problems. Most commonly, losses in well-operated flotation plants are due to locked particles, which have low flotation rates. Finer grinding may not always be economic. An interesting example is the loss of copper in the tailings of the Phalaborwa concentrator in South Africa [12], due to the rare mineral valleriite $(4(\text{Fe,Cu})\text{S} \cdot 3(\text{Mg,Al})(\text{OH})_2)$ which occurs as very thin smears on gangue particles.

The deportment of precious metals to the various flotation products can be of great economic importance and should be carefully assessed in flowsheet development for new ores and in existing operations. Gasparrini [13] mentions a few case studies. One of these relates to a copper-zinc ore, in which silver used to report to the copper flotation concentrate, but then gradually started to float into the zinc concentrate or was lost into the tailings. It appeared that the silver was contained in two minerals, i.e. tetrahedrite $((\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13})$ and pyrargyrite $(\text{Ag}_3\text{SbS}_3)$. The tetrahedrite floated with the copper minerals, but the pyrargyrite, which occurred in parts of the orebody with lower copper contents, floated with the zinc minerals. This indicates that a detailed mineralogical analysis of samples from various parts of the orebody and discussions with metallurgists could have anticipated these problems. A very detailed study on the deportment of various trace metals in the flotation circuit of Brunswick Mining and Smelting Corporation, Canada was carried out by Petruk [14]. Here silver occurred mainly in tetrahedrite and galena. Losses in the tailings were due to either relatively large free grains ($> 26 \mu\text{m}$) or very small grains ($< 1 \mu\text{m}$), or due to locked particles.

Hydrometallurgy

The leaching behaviour of ores or mineral concentrates can be studied by mineralogical analysis of samples taken at different time intervals. For example in studying the dissolution mechanism of sphalerite (ZnS) in acidic chloride solutions Jansz [15] showed a pronounced difference in the leaching rate of different crystal planes. In the same study the leaching rate of galena was found to be reduced dramatically when the lead concentration was increased above 35 g/l, corresponding to the limit of solubility of PbCl_2 . Mineralogical analysis showed that the partially leached galena particles were covered by a rim of solid lead chloride.

Another example is the leaching of the uranium mineral brannerite in the Beaverlodge mill in Canada [16]. The brannerite in the so-called refractory ore consists of various types, some of which are complex mixtures of actual brannerite (theoretically UTi_2O_6 , but here containing $\text{Pb}, \text{Ca}, \text{Si}, \text{Fe}, \text{Al}, \text{V}$), leached "brannerite" and material partially converted by metamictisation to uranoanatase. These three "brannerite" types have different U:Ti ratios. Relatively low extraction percentages were experienced in leaching experiments with sodium carbonate as leachant. Mineralogical analysis showed that this was due to locking of part of the brannerite to the gangue mineral chlorite.

Mineralogical techniques have also been applied to a number of other operational problems such as the study of scale formation during leaching operations [16] or crud formation in solvent extraction settlers. The latter problem has been quite serious in the Chingola plant in Zambia after taking out the pressure sand filters on the pregnant liquor due to mechanical failure. A large part of the crud in fact was gypsum, due to supersaturation of the leach liquor with calcium. Experiments have subsequently been conducted with pilot-scale sludge clarifiers in an attempt to reduce the calcium supersaturation by using gypsum seed in the sludge.

Pyrometallurgy

Several applications of mineralogy to roasting testwork have been reported. In the reduction roasting of chalcopyrite aimed at avoiding sulfur dioxide emissions, optical microscopy, SEM, electron microprobe and X-ray diffraction techniques have been used to study the reaction mechanism [17]. The roasting of auriferous pyrite is discussed in the following section on gold processing.

Mineralogical analysis of smelter slags provides essential information in addition to chemical analysis. Early investigations in this area were done by Edwards, who studied copper slags and lead blast furnace slags from operations in Australia [18,19]. A detailed study on slags from ferrochromium smelting in a submerged arc furnace was conducted by Oosthuyzen en Viljoen [20] to obtain information on the nature of chromium and iron losses. They found that unreacted chromite (FeCr_2O_4) was the main contributor to these losses.

Mineralogical support is also essential in the re-processing of slags. An example is the INCO matte separation process, in which converter matte is slowly cooled and discrete phases of Cu_2S and Ni_3S_2 are formed together with a Cu-Ni alloy phase [21]. After removing the alloy by magnetic separation, the copper and nickel sulfides are separated by flotation with diphenyl guanidine as the collector at pH=12.4. The matte cooling rate determines the grain size distribution of the sulfides, which can be studied by reflected light microscopy.

Heerema [22] relates differences in internal structure of fired iron oxide pellets to the crystallinity of the magnetite in different ores. Variations in microporosity of such pellets may have an effect on the subsequent reduction process.

Of considerable importance is also the study of refractory bricks with respect to operational problems, such as premature failing.

Gold processing

A substantial increase in gold mining and processing activities occurred worldwide as a result of the high gold prices. This in turn greatly enhanced research and development in this area, not only in conventional technology but also in processes which might be potential alternatives to cyanide leaching. Much attention is now being directed to the refractory gold ores, in which the gold is associated with sulfides, mainly pyrite or arsenopyrite.

Mineralogical analysis can provide considerable support in considering the various processing options for a particular gold ore. Coarse free gold ($> 50 \mu\text{m}$) is usually recovered by gravity separation, followed by amalgamation or direct smelting. Cyanide agitation leaching times for such coarse gold would be prohibitively long. Ores with fine free gold (sulfide content $< 2\%$) are generally leached, either in tanks or in heaps. The gold is then recovered from the leach liquors by carbon absorption (carbon-in-pulp or carbon-in-leach processes) followed by stripping, electrowinning and smelting, or alternatively, by cementation onto zinc powder and smelting of the precipitate (Merrill-Crowe process). The presence of carbonaceous material can be problematic as it may absorb part of the leached gold (so-called preg robbing), which then reports to the tailings. Mineralogical investigations in support of metallurgical testing of such ores are quite important and have been extensively applied at Carlin, Nevada [7,23,24]. It was shown that a particular type of carbonaceous material absorbed gold 3-4 times faster than activated carbon, but had a 3-5 times lower loading capacity than the latter [24]. If preg robbing carbonaceous material occurs in the ore, the carbon-in-leach process would be preferred to the carbon-in-pulp process so that there is virtually no time lag between extraction and absorption.

The refractory gold ores require pre-treatment. Roasting of auriferous pyrite or arsenopyrite will form a porous hematite calcine which is then amenable to cyanidation. However, the gold extractions depend very much on the roasting conditions. Studies by Arriagada et al [25] showed that the specific surface area has a maximum at a roasting temperature of around 450°C. At higher temperatures this decreased due to sintering effects. The occurrence of arsenic is of special concern in such operations in view of environmental legislation. At Carlin, where refractory gold is associated with spheroidal pyrite, a chlorination treatment is applied to oxidize the pyrite prior to cyanidation [23].

The degree of surface exposure of free gold in cyanide leaching is of importance and can be determined by mineralogical analysis. However, at Carlin the gold in the oxidic ores is very fine ($< 5 \mu\text{m}$) and yet a fine grind is not required, due to the relatively high permeability of the host rock to cyanide leach liquors.

The occurrence of small quantities of the iron sulfides pyrite and arsenopyrite in oxidic gold ores usually presents no problem in cyanide leaching. However, the iron sulfide pyrrhotite (Fe_{1-x}S) consumes cyanide, forming thiocyanate. A chemical analysis of the ore would not distinguish between these iron sulfides and a mineralogical analysis is thus essential. Copper minerals, antimonite (Sb_2S_3) or the arsenic sulfides realgar (AsS) and orpiment (As_2S_3) are also cyanide consumers or cyanicides as they are commonly referred to.

1.2 Treatment of oxide copper ores in Zambia

1.2.1. General

Zambia is the world's fifth largest copper producer with a total in the order of 500 000 tonnes/year. Cobalt, which occurs in some of the copper orebodies, is also important, the total production being around 4000 tonnes/year. The copper sulfide ores contain chalcopyrite, bornite and

chalcocite as the main minerals, which vary in proportion in the individual deposits. The mineral carrollite is the main source of cobalt. The sulfide orebodies have been oxidized to various extent, forming a range of secondary copper oxide minerals. The minerals of the Zambian Copperbelt ores are described in some more detail in section 2.1.

The largest oxide orebody on the Zambian Copperbelt occurs near the town of Chingola. Smaller ones are located near Chillilabombwe, Kitwe, Luanshya and Ndola. Malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) is the major oxide copper mineral in most cases and may be associated with smaller amounts of chrysocolla ($\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$), pseudomalachite ($\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$), cuprite (Cu_2O), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), libethenite ($\text{Cu}_2(\text{PO}_4)(\text{OH})$) and cupriferous mica (K,Mg,Fe,Al-silicate).. The processing of such ores differs depending on local conditions, the exact mineral composition of the ore, the size of the orebody and on available treatment facilities. Flotation of oxide minerals is applied to concentrate the oxide copper minerals prior to further processing. The flotation concentrate is either fed directly to the smelter in the case of the small orebodies near Kitwe, at Mindola and Rokana Area E, or leached followed by solution purification and electrowinning, as at Chingola. Oxide copper flotation tailings, both from current operations and from dumps at Chingola are processed in a leach-solvent extraction-electrowinning plant.

For the so-called refractory oxide copper ores, which do not respond well to flotation the TORCO process (acronymous for Treatment Of Refractory Copper Ores) was developed in Zambia [26]. This chlorination process, which was discovered by accident in 1923 during roasting experiments on Chilean ore, has a long history of process problems, mainly of mechanical nature. Several plants, which were built in various parts of Africa (Rhodesia, Congo, Mauretania), were shut down after having operated for only a short time. Only in Zambia the TORCO plant was successful and is still in operation today. In the TORCO process the oxide copper ore is heated in a fluidized bed reactor to around 800°C

and then mixed with coal and salt. The salt reacts with the gangue silicates and water and forms HCl, which chlorinates the copper. The copper chloride is reduced by hydrogen and metallic copper deposits on the coal. The copper-coal composite particles are then separated from the gangue by conventional flotation. Near Chingola extensive reserves of low-grade refractory ores occur, in which the copper is contained in micaceous minerals.

A considerable amount of research work was conducted toward beneficiation of the oxide copper ores in various areas of the Zambian Copperbelt and is summarized in the following sections.

1.2.2. Flotation of oxide ore at Rokana

In the exploration stage of the development of various small oxide deposits at the Rokana mine near Kitwe (Area E) mineralogical examination of a large number of drillcore samples and grab samples was carried out to obtain a good insight into the distribution of the various oxide copper minerals with respect to future mineral processing. In addition samples of low-grade ore ($< 3\%$ Cu) from the small open pit at Mindola, also near Kitwe, were investigated (the higher grade ores at Mindola (3-5%) were being processed by the TORCO plant in Kitwe). The mineralogical composition of these samples varied considerably. Particularly the ore at Mindola contained much chrysocolla in addition to malachite. In these orebodies the mineral libethenite occurred in unusually high concentrations in some borehole samples, and occasionally was in fact the predominant copper mineral. It was anticipated that this mineral would have similar flotation properties as the other copper phosphate mineral pseudomalachite, which occurred in minor quantities near Chingola and did not respond well to sulfidisation in the oxide flotation circuit. This was confirmed by laboratory flotation tests, which showed that the libethenite recoveries were low: in the range of 20-40% and similar to pseudomalachite. Although locally abundant, libethenite proved to be only a very minor to accessory constituent of the total ore. Composite drillcore samples, in which malachite was the

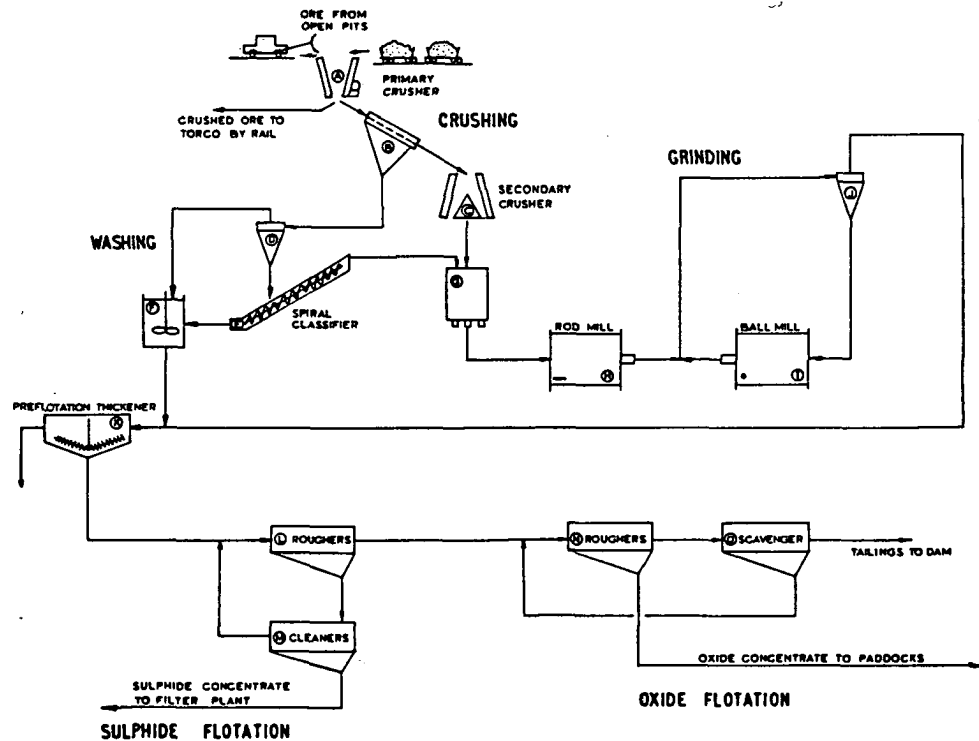


Fig.2. Flowsheet of the Rokana oxide concentrator.

major mineral, responded reasonably well to flotation (recoveries 55-85%). On the basis of this flotation testwork, which was extensively supported by mineralogical analyses, a decision was made to build an oxide flotation plant at the Rokana site in Kitwe. The general flowsheet of the Rokana oxide concentrator is given in Fig.2. The ore is crushed and ground to 80% -74 μm . The sulfide minerals (mainly chalcopyrite and bornite) are first floated with potassium amyl xanthate as the collector. The copper sulfide flotation tailings are then conditioned with sodium hydrosulfide and the sulfidized copper oxide minerals are floated with potassium amyl xanthate in combination with an allyl amyl xanthate (Cyanamid S3302) as the collectors. Both flotation concentrates are fed to the Rokana smelter. Examination of plant flotation products confirmed that most of the libethenite reported to the final tailings.

Chrysocolla is the most abundant refractory copper mineral in the open pits at Mindola and Area E and this determines to a large extent the flotation performance in the plant.

In subsequent investigations in these two open pits the libethenite appeared to be localized in certain zones. An unusual variety of crystal shapes was observed (section 2.2).

1.2.3. Process development for the treatment of cupriferous mica ores.

Mineralogy

The micaceous ores are particularly difficult to treat. The copper-bearing mica minerals were usually designated cupriferous vermiculite, in view of their exfoliation on rapid heating. However, the vermiculite mineral structure *sensu stricto* is found only in relatively small quantities near Luanshya and Kitwe. The vermiculite from the Roan Antelope Mine (now called Luanshya mine) near Luanshya has been studied in some detail by Bassett [27]. In the largest refractory ore deposit, near Chingola, the cupriferous mica mineral is quite different. In view of the envisaged future treatment of the low-grade Chingola refractory

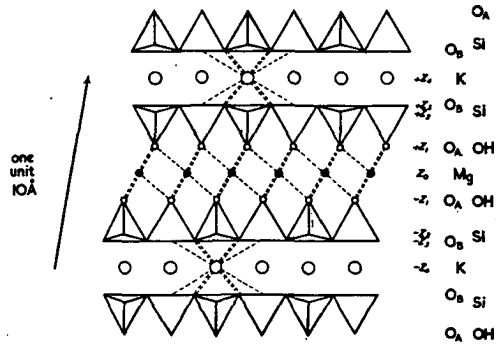


Fig.3. Structure of phlogopite projected on (010).
 O_A and O_B are at the vertices of the silica tetrahedra [28].

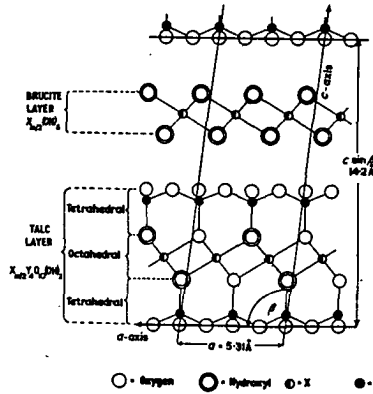


Fig.4. Structure of chlorite projected on (010) [29].

ore (average grade 1.23% Cu) a detailed mineralogical study of the micaceous minerals (section 2.3) was undertaken in close relationship with metallurgical testwork (section 2.4).

The micaceous minerals are sheet silicates. The silica tetrahedra are arranged with their bases in a plane along a (pseudo)hexagonal pattern with their apices all located on one side of the plane. In the basic mica structure two of such silicate sheets are orientated with their apices pointing towards each other with a layer of octahedrally coordinated cations sandwiched in between (Fig.3). The central layer alternatively can be considered as a hydroxyl layer: a brucite layer - $\text{Mg}_3(\text{OH})_6$ in phlogopite, $\text{Fe}_3(\text{OH})_6$ in biotite, or a gibbsite layer - $\text{Al}_2(\text{OH})_6$ in muscovite with four of the six hydroxyls replaced by oxygen atoms of the silica tetrahedra. Biotite and phlogopite form a series in which isomorphous substitution of Fe and Mg occurs. The fundamental three layer unit is often referred to as the talc layer in view of its structural similarity to the mineral talc. Due to substitution of silica by aluminium the sheets have a negative charge, which is compensated by ions in the space between successive talc layers (interlayer). In vermiculite these ions are hydrated, whereas in the proper micas such as phlogopite and biotite potassium ions occur, which are unhydrated. In chlorite (Fig.4) the interlayer space contains predominantly bivalent (Mg,Fe) or trivalent ions (Al,Fe), which are octahedrally coordinated to hydroxyl ions (referred to as trioctahedral or dioctahedral respectively). The talc layer in chlorite can also be predominantly dioctahedral or trioctahedral. Isomorphous substitutions of bivalent by trivalent ions and vice versa occur in both layers, resulting in net electrical charges, which should be compensated.

In the Chingola deposits of cupriferous mica ores three different micaceous mineral components occur: a phlogopite (non-copper bearing), a colourless chlorite (also non-copper bearing) and an interstratified mica, in which the copper actually occurs. This interstratified mica consists of a more or less regular alternation of structural units of phlogopite (10 Å basal spacing) and of a mineral with a 14 Å basal

spacing. It was demonstrated (section 2.3) that this 14 Å component is different from the discrete colourless chlorite, which also has a basal spacing of 14 Å. The copper appeared to be located in the 14 Å component of the interstratified mica. Contrary to these findings, Bassett [27], and in particular Jebson [30] who studied the Chingola micas in some detail, did not recognize that the 14 Å peaks in the X-ray diffractogram actually belong to the non-cupriferous colourless chlorite.

Based on X-ray diffraction studies, heat treatment, leaching and ion exchange experiments (section 2.3) it was concluded that the copper is coordinated to hydroxyl ions in the interlayer of the 14 Å component of the interstratified mica, i.e. as in the interlayer of a chlorite. However, considering the exfoliation property and the differences in certain characteristics from proper chlorites an intergradient structure was suggested for the interlayer of this 14 Å component, containing "chloritic" areas with $\text{Cu}_3(\text{OH})_6$ and "vermiculitic" areas with hydrated ions (section 2.3). Such intergradient structures were known to occur in various soils, in which aluminium hydroxyl complexes are absorbed by clay minerals [31].

A similar intergradient structure was recently also proposed by Ildefonse et al [32] for a cupriferous mica associated with the Salobo copper deposit in the Carajas mining district, Para State in Brasil. In the weathering zone of this deposit a cupriferous 14 Å mineral and a cupriferous interstratified biotite-14 Å mineral occurs. The cupriferous mineral components, i.e. the 14 Å layer in the interstratified mineral and in the distinct 14 Å mineral have very similar characteristics to the 14 Å layer in the interstratified mica at Chingola. The Brazilian micas also do not expand when treated with ethylene glycol. Heat treatment shows lattice contraction from 14 Å to 10.6 Å only above 400°C as for the Chingola micas but unlike the cupriferous vermiculite from the Roan deposit described by Bassett [27], which shows disappearance of the 14 Å reflection below 300°C. Cu-K α absorption edge spectroscopy on the Brazilian mica indicated that the copper is bivalent and occurs in 6-fold coordination, the energy spectrum being very similar to that of

$\text{Cu}(\text{OH})_2$. Ildefonse and his coworkers also conclude that an intergrade (=intergradient) structure in the intersilicate layer explains best the observed characteristics. They mention that the copper hydroxide has the lepidocrocite ($\gamma\text{-FeOOH}$) structure with distorted octahedral sites due to the Jahn-Teller effect, rather than the brucite structure normally encountered in the intersilicate layer of chlorite. According to these authors this structural difference might explain the incomplete occupancy of the intersilicate layer by the copper species resulting in the intergradient structure. However, consideration should also be given to the requirement for compensation of the negative charge on the talc layers, i.e. by hydrated ions in the interlayer.

Processing - general considerations

The mineralogical study indicated the difficulty of extracting the copper from the Chingola micas relative to the proper cupriferous vermiculites from other locations on the Copperbelt. The leaching characteristics of the micaceous materials are detailed in section 2.4. Of particular interest was the mineralogical study of the micas during various stages of leaching. The leaching of copper progressively changed the interlayer of the 14 Å component of the interstratified mica. After prolonged leaching lattice contraction could be induced by immersion in 1 N KCl, as is also shown by proper vermiculites, indicating that the "chloritic" copper hydroxide structure, which had prevented such lattice contraction, had been broken down.

Various methods of pre-concentration of the mica were studied, the main objective being to reduce the gangue acid consumption, particularly of the dolomitic sections in the orebody. Flotation proved to be the most promising technique (section 2.4). Desliming followed by flotation with cocoamine acetate as the collector gave a good mica concentrate (80-90% mica). However the loss of copper in the slimes was considerable (15-20%) and therefore flotation was unlikely to be applied in practice as the amount of very high acid consuming ore located during a subsequent borehole survey was not that high. Remarkable was the

peculiar grade-recovery relationship obtained in the flotation experiments (Table 2), which contrary to what happens normally, showed flotation of low grade material first. Detailed mineralogical analysis of mica flotation concentrates, collected at short time intervals, provided the explanation. The non-copper bearing micaceous minerals (phlogopite and colourless chlorite) appeared to float considerably faster with the cocoamine acetate than the cupriferous interstratified compound. The slight decrease in the cumulative grade due to the last concentrate (Table 2) was due to incipient flotation of non-mica gangue minerals.

For the treatment of such low grade ores (average grade 1.23% Cu) the TORCO process is too expensive. The fuel consumption for drying and segregation is estimated to be 2.6 GJ per tonne of ore [33], which would amount to 211 GJ per tonne of copper contained. For comparison the energy cost for a leach/solvent extraction/electrowinning process would be around 55 GJ/t.Cu [34]. The TORCO process would require a much higher ore grade (estimated to be at least in the range 3.5-5% Cu) for it to be economically viable. It was considered that the most promising treatment route for the micaceous ores was leaching, followed by solvent extraction and electrowinning (section 2.4). The leaching should be done at elevated temperature. Gangue acid consumption is important for the process economics. From data by Holmes and Fischer [35] a gangue acid consumption of 4.7 kg/t is calculated for the leaching of tailings from normal Chingola ores, which is 12% of the total operating costs of a leach-solvent extraction process. For the cupriferous micas the average gangue acid consumption is likely to be much higher as indicated by values for three ore samples in Table 3.

Solvent extraction

At the time, in the early seventies, copper solvent extraction was still rather novel technology. Only two SX plants were operational: at the Ranchers Bluebird Mine and at Cyprus Bagdad Copper both in Arizona. However, also in Zambia a decision had been made to treat current

Concentrate	Cum. grade % Cu	Cum. recovery % Cu
1	1.20	15
2	2.15	32
3	3.20	56
4	3.75	79
5	3.90	87
6	3.55	96

Table 2. Grade-recovery figures for the cationic flotation of cupriferous mica ore from Chingola.

Feed	Leach temp. °C	Acid tenor g/l	Leach time hr	Grade % Cu	Extraction % Cu	Acid consumption kg/t	
						total	gangue
Ore 1	50	50	6	1.05	77	15	3
Ore 2	50	50	6	1.85	79	67	45
Ore 3	50	50	6	2.04	87	69	41
Tails	20	10	2	0.69	78	13	5

Table 3. Acid consumption figures for three mica ore samples and Chingola concentrator tailings.

flotation tailings and some reclaimed material from old tailings dams using SX [35,36]. During the period when the project on the cupriferous mica ores was carried out the Chingola tailings leach solvent extraction plant came on stream. The availability of this technology evidently contributed to the selection of the final flowsheet for the micaceous ores. In view of the large reserves of these low grade ores and the commitment of the then available processing capacity for current tailings, an expansion of the SX plant would be necessary. This extra capacity could then be utilized first to reclaim the old tailings dams at a higher rate and subsequently for the processing of the micaceous ores.

In the original concept of the plant expansion the addition of extra solvent extraction streams was envisaged. Based on the operating experience with the existing plant a testwork program was initiated to improve mixer-settler design for implementation in the new plant. In particular the stability against phase inversion from organic to aqueous continuity in the extraction mixers had to be improved. Although aqueous phase continuity results in lower actual aqueous in organic entrainment, flotation of dispersion fragments occurs when the Chingola extraction mixer-settlers operate in this mode, resulting in gross carry-over of aqueous phase and thus impurity elements into the electrolyte circuit (section 2.5). Another objective was to improve the extraction stage efficiencies. Experimental work related to the mixer design was conducted in the laboratory, on the pilot plant at Chingola (a scaled down version of the Tailings Leach Plant with a feed capacity of 3 t/hr tailings) and on the main plant. Certain aspects of the mixer scale-up were investigated by a team at the University of Bradford who collaborated in the project.

The testwork resulted in the design of a three-stage mixer with a six-bladed Rushton mixing impeller [37] (Fig.5) in each compartment. The stability against phase inversion was achieved by separating the pumping and mixing functions, so that surges in one of the phase flows would not cause local changes in phase ratio as might be the case for the existing

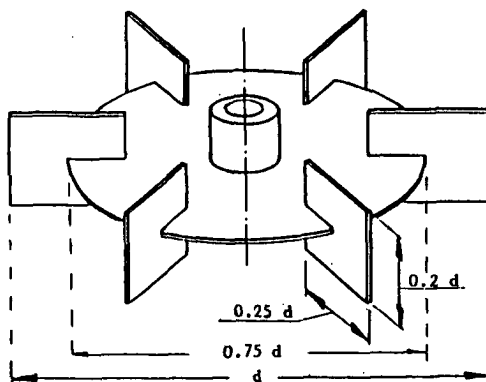


Fig.5. Rushton impeller.

Davy McKee pump-mix impeller, but instead the mixer volume would act as a buffer. An increase in stage efficiency was expected by compartmentalizing the mixer and using the scale-up criterion of constant mixing power input per unit volume instead of constant impeller tip speed as for the design of the existing mixer. It was expected that the use of this scale-up criterion would also result in an increased stability against phase inversion as there would be less tendency to hold-up segregation. The power input per unit volume (P/V) for a fully baffled mixer is expressed by [37]:

$$P/V \propto N_p^3 D^2$$

where N_p is the power number (-), which is constant under turbulent conditions, N the impeller speed (s^{-1}) and D the impeller diameter (m).

If constant tip speed is used as the scale-up criterion then:

$$ND = \text{constant}$$

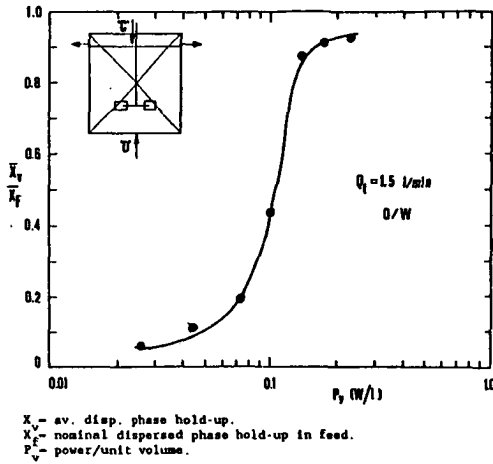


Fig.6. Relationship between average dispersed phase hold-up and power input per unit volume (modified from Grile [38]).

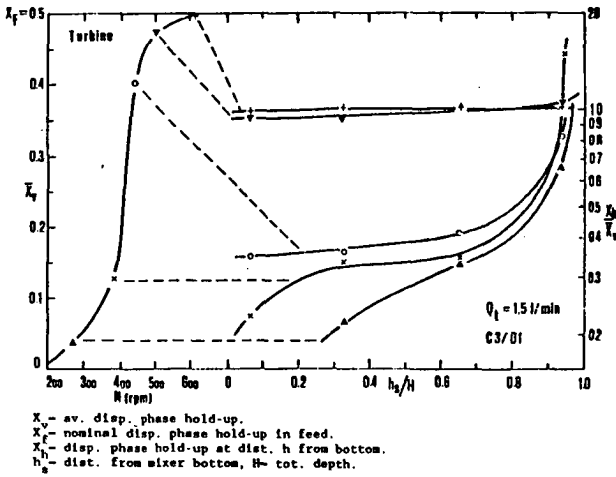


Fig.7. Variation of hold-up of dispersed phase with vertical distance in the mixer for different average hold-up values [38].

Thus in scaling up from size 1 to size 2 for geometrically similar mixers combination of the two above expressions gives:

$$(P/V)_2 = (P/V)_1 (D_1/D_2)$$

The power input per unit volume thus decreases with increasing mixer size as the ratio of the impeller diameters. Although no power input data for the original mixers are available, an estimate can be made. It is assumed that for a pilot-scale mixer of 0.76 m^3 (Chingola pilot plant) a mixer power input of 0.75 kW/m^3 is needed for the required extraction stage efficiency. Scale-up to the tailings leach plant Davy McKee mixers (100 m^3) using constant tip speed would then give an estimated power input per unit volume of 0.15 kW/m^3 . Initial experiments in a 20 l laboratory mixer indicated that phase segregation occurred at a power input of about 0.15 kW/m^3 (section 2.5). In a subsequent study Grilc [38] found that at a power input between 0.1 and 0.2 kW/m^3 the hold-up of the dispersed phase decreased (Fig.6). Segregation of hold-up then also occurred (Fig.7 - only data for oil in water dispersion are given). Local accumulations could then induce phase inversion. This critical power level is similar to that estimated above for the Chingola mixers. It should be noted that the Davy McKee pump-mix impeller geometry (radial back-swept blades) is different from the Rushton turbine used by Grilc. Furthermore no data on scale-up of hold-up or hold-up segregation to large mixer sizes are available. However, hold-up segregation may well occur at the relatively low power input of the Chingola mixers, which have a strong tendency to phase inversion when operating in the organic continuous mode (phase ratio 1:1). Accumulation of aqueous phase in the lower areas could easily result in complete inversion to aqueous continuous. In such cases a bottom discharge would improve stability to some extent as shown by Grilc. Any hold-up segregation disappears rapidly with increasing impeller speed and thus the conservative scale-up using constant power input per unit volume is likely to have a positive effect on stability against phase inversion.

A prototype mixer was designed and tested in one of the four SX streams in the Chingola plant. The performance met the requirements: the stage efficiency in the first extraction stage, where the mixer was tested increased from 88% to 95% and organic phase continuity could be maintained at an organic:aqueous ratio as low as 0.7:1, which had not been possible with the existing pump-mix impellers. Up to now this prototype has been in use as a production unit.

The settlers were designed based on detailed pilot-scale experiments, supplemented by tests with a dam baffle in one of the large settlers in the plant to confirm the scale-up criterion of constant specific dispersion flow. Details of the mixer-settler testwork and design are given in sections 2.5 and 2.6.

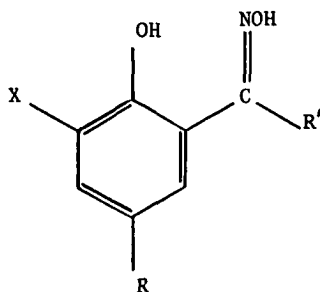
Apart from the mixer-settler design testwork a considerable amount of work was conducted on new extractants, mainly on laboratory scale but later also in the pilot plant. This resulted in the first commercial application of a copper extractant other than LIX 64N, i.e. Shell SME 529. Prior to piloting and plant implementation the SME 529 and LIX 64N were compared on an economic basis using laboratory equilibrium isotherms. Previous work with LIX 64N had shown that the performance of a continuous circuit could be predicted from extraction and stripping isotherms using the McCabe-Thiele construction. This formed the basis for the comparison of the two extractants. As their equilibrium characteristics differed, a real comparison should be done on equal metallurgical performance so that the required extractant tenors could be compared on a direct cost basis. For a three-stage extraction, two-stage strip circuit, organic to aqueous phase ratios of 1:1 and 4:1 in extraction and stripping respectively and an appropriate LIX 64N tenor McCabe-Thiele constructions, using the two isotherms in combination, gave a particular copper extraction percentage. As the isotherms for SME 529 differed, it was unlikely that the available ones would give the same extraction percentage of copper. However it was found that an isotherm could be "scaled-up" within limits, i.e. the organic copper tenors corresponding to certain aqueous tenors could be

varied in proportion to a specified change in the maximum loading. This scale-up of the isotherms was carried out until a combination of isotherms was found which would give the same copper extraction percentage as that obtained with LIX 64N. The metallurgically equivalent extractant tenors could then be directly compared.

The determination of the metallurgical equivalence of SME 529 and LIX 64N, the resulting economic comparison and a successful pilot plant test led to the introduction of SME 529 in the Chingola Tailings Leach Plant. SME 529 has worked very satisfactorily until the production was stopped by Shell. Henkel now produces this extractant under the name LIX 84.

Subsequently various new, more effective copper extractants were developed: the Acorga P-5000 series [39] and the recent "M" series of extractants [40], and the Henkel extractants based on LIX 860 such as LIX 622 and LIX 864. Table 4 presents a summary of these extractants. Many of these are based on strongly chelating basic oximes to which a modifier is added. Such modifiers can weaken the extractant strength, so that effective stripping is possible and the extractant utilisation is improved (P-5000 series, LIX 622), and/or affect other properties such as iron rejection, entrainment and crud formation (M series - Table 5). The formulation of extractants now allows considerable flexibility and is dependent on local conditions and requirements.

The stronger chelating power of the new Acorga and Henkel extractants allows reduction in the number of stages, or an increase in the throughput for an existing plant. This can be illustrated by means of McCabe-Thiele constructions on equilibrium isotherms of Acorga P-5300 and P-5100, for which a computer program (SXBAL) was written by the author. This program consists of two parts: isotherm curve fitting and the actual McCabe-Thiele construction. The extraction isotherms are



Basic extractants:

R	R'	X	Reagent
C ₉ H ₁₉		Cl	LIX 70
C ₉ H ₁₉	H	H	P-50
C ₁₂ H ₂₅	H	H	LIX 860
C ₉ H ₁₉	CH ₃	H	SME 529/LIX 84
C ₉ H ₁₉		H	LIX 65N

Derived formulations:

Basic reagent	Modifier	Commercial extractant	Manufacturer
P-50		P-5000	Acorga
P-50	nonyl phenol	P-5100	"
P-50	nonyl phenol	P-5300	"
P-50	tridecanol	PT-5050	"
P-50	alcohol*	M.5615	Acorga
LIX 860		LIX 860	Henkel
LIX 860	tridecanol	LIX 622	"
LIX 860	LIX 64N	LIX 864	"
LIX 860	LIX 84	LIX 984	"
LIX 65N	LIX 63	LIX 64N	"
LIX 84		LIX 84	"

* Composition not disclosed. Other alcohols and esters can be used in formulations of M-series extractants.

Table 4. Copper extractants for acid systems [40].

Modifier ¹	Entrainment ² , ppm		Crud mm/hr	Cu-Fe selectivity ³ , ratio in extract
	Org. in aq.	Aq. in org.		
Alcohol 1	147	675	1.6	736
Alcohol 2	313	792	3.4	515
Alcohol 3	73	467	2.2	976
Ester 1	300	1125	14.0	971
Ester 2	53	25	0.6	1210

- 1) composition not disclosed. 2) organic phase continuity.
3) aqueous phase: 3 g/l Fe, 3 g/l Cu, pH=2.

Table 5. Properties of some extractants from the Acorga M-series [40].

fitted by nonlinear regression using the following function:

$$Y = A(1 - e^{-BX}) + C(1 - e^{-DX})$$

where Y= organic Cu tenor (g/l), X= aqueous Cu tenor (g/l) and A,B,C,D are the parameters. The strip isotherms are simple straight lines. The program section with the McCabe-Thiele construction is based on an earlier version developed in Nchanga Consolidated Copper Mines Ltd, Zambia. The program also allows scaling of the isotherms to determine the organic tenor required to give a certain raffinate Cu tenor. The calculated extraction percentages using P-5300 for a pregnant liquor with 6 g/l Cu, pH=2 (spent electrolyte 30 g/l Cu, 180 g/l H₂SO₄) in a circuit with three or two extraction stages and two strip stages, as a function of the phase ratio in extraction are given in Table 6. The McCabe-Thiele construction for an extraction phase ratio (O/A) of 1.4:1 is shown in Fig.8 for three extraction stages and two strip stages. It can be seen that the third stage hardly functions. In two extraction stages 92% Cu extraction can be achieved at a phase ratio (O/A) of 1.4:1. With the more powerful P-5100 an even smaller total number of stages could be used. The McCabe-Thiele constructions for a pregnant

Phase ratio O/A	Extraction % Cu	
	3 extr.-2 strip	2 extr.-2 strip
1.0:1	88.3	81.0
1.2:1	95.0	88.0
1.4:1	96.8	91.5
1.6:1	97.5	93.2
1.8:1	97.8	94.2
2.0:1	98.0	94.8

Table 6. Copper extraction by P-5300 as a function of extraction phase ratio for circuits with 2 or 3 extraction stages and 2 strip stages.

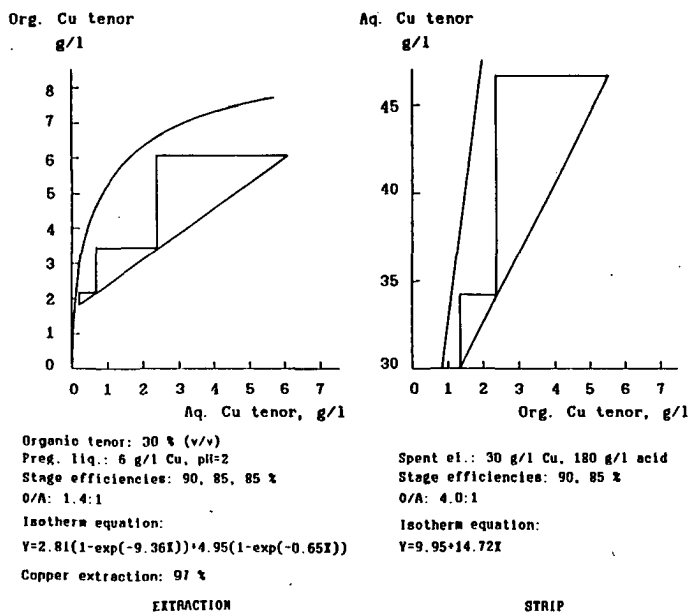


Fig.8. McCabe-Thiele construction on P-5300 isotherms for a circuit with 3 extraction-2 strip stages.

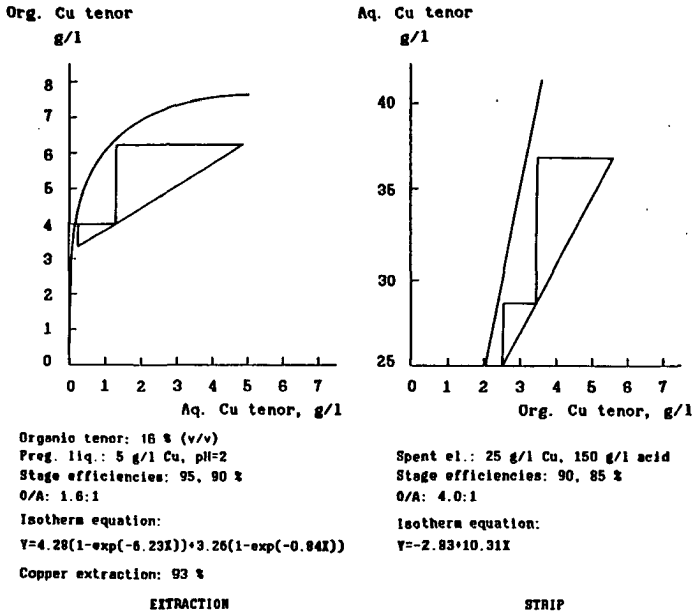


Fig.9. McCabe-Thiele construction on P-5100 isotherms for a circuit with 2 extraction-2 strip stages.

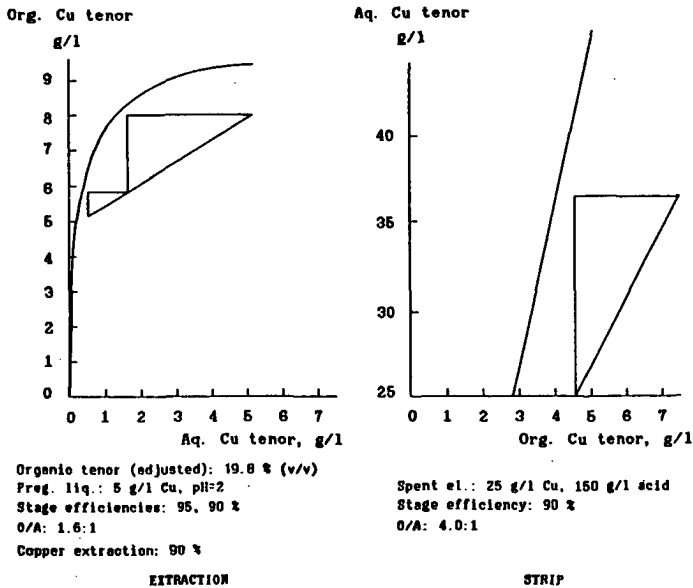


Fig.10. McCabe-Thiele construction on P-5100 isotherms scaled to give an extraction of 90% Cu for a circuit with 2 extraction-1 strip stages.

Company and location	Start-up date	Method of leaching	Production rate, mt/annum	Feed composition		Extractant	Diluent	No. of streams	Aqueous flow rate per stream, m ³ /h	Staging	
				Cu tenor g/l	pH					Extract	Strip
Cyprus Bagdad, Arizona	1970	Dump leach	6,500	1.1	2.0	LIX 64N HS	Kernac 470B Chevron IES	4	190	4	3
Zambia Consolidated Copper Mines, Zambia	1974	Agitated tank leach of tailings	100,000-120,000	5	1.9	ACORGA PT-5050 LIX 864/984	Escaid 100/ LSGO	4	750	3	2
Pinto Valley Copper Co. (Miami), Arizona	1976	In-situ leach	4,200	0.8	2.0	LIX 865	Philips SX-7	2	320	3	2
Cerro Verde, Peru	1977	Dump leach	33,000	2.7	2.0	LIX 64 NHS LIX 860	Local kerosene	4	280	3	2
Inspiration CC Co., Arizona	1979	Heap ferric cure leach	45,000	5.5	1.8	ACORGA M-5615 ACORGA P-5100	Chevron Ion Exchange solvent	1	1020	2	2
Asarco Ray Mine (formerly Kennecott), Arizona	1980	Dump leach Heap leach	39,000	5.0 0.96	1.8 2.2	ACORGA M-5397	Exxon 200	1 2	680 680	2 1	2 1
Soc. Min. Pudahuel, Chile	1980	Thin layer leaching	15,000	3.0	1.9	LIX 864	Escaid 100	3	200	2	1
Cia Minera de Cananea, Mexico	1980	Dump leach	12,700	2.5	2.0	ACORGA M-5615 ACORGA P-5100 LIX 622	Hydrosol 1000	1	730	2	2
Centromin, Cerro de Pasco, Peru	1980	Mine water	6,000	1.0	2.0	ACORGA P-5100 ACORGA M-5615	Local kerosene	2	360	3	2
Pinto Valley Copper Co. (Pinto), Arizona	1981	Dump leach	7,000	0.6	2.1	LIX 864	Philips SX-7	2	700	2	2
Cyprus Casa Grande (was Noranda Lakeshore), Arizona	1981	In-situ leach Roast leach	6,000 40,000	1.5 9.0	1.6 1.9	ACORGA P-5100	Philips SX-1	1 1	450 500	1 2	2 2
BHAS, Port Pirie, S. Australia	1984	Cl/SO ₂ /O ₂ agitated tank leach	3,500	35.0	1.5	ACORGA P-5100	Shellsol 2046	1	20	2	2
Phelps Dodge, Burro Chief, Tyrone, New Mexico	1984	Dump leach	39,000	2.6	2.0	LIX 984	Philips SX-7	2	910	2	1
CODELCO-El Teniente, Chile	1985	Mine water	5,000	1.2	3.0	ACORGA PT-5050 LIX 864	Escaid 100	1	340	2	2
Sunshine Mining, Idaho	1985	Agitated tank	2,800	8.0	2.0	ACORGA PT-5050	Chevron IES	1	46	3	2
Magma, San Manuel, Arizona	1985	Dump/in situ leach	46,000	1.7	2.0	LIX 622	Chevron IES	4	820	2	1
Gibraltar Mines, Canada	1986	Dump leach	6,000	1.0	2.0	ACORGA PT-5050 ACORGA P-5100	Shellsol 160	1 1	690 690	2 1	1 1
Phelps Dodge, Morenci, Arizona	1987	Dump leach IOS plant Central S.W. plant	43,000 21,500 9,000	1.9 1.9 0.4	2.0 2.0 2.5	LIX 984 LIX 984 ACORGA M-4560	Philips SX-7 Philips SX-7 Philips SX-7	2 1 1	1360 1360 2720	2 2 3	1 1 1
Tocopilla	1987	Heap leach	1,500	8.0	1.5	ACORGA PT-5050	Escaid 100	1	24	2	1
Cyprus, Sierrita	1987	Dump leach	4,300	0.6	2.5	LIX 984	?	5	90	3	2
CODELCO, Chuquibambilla, Chile	1988	In situ	80,000	6.0	2.0	ACORGA PT-5050	Shellsol 2046	1	1600	2	2
Roxby Downs/Olympic Dam, S. Australia	1988	Agitated tank	3,500	1.0	1.1	LIX 622	Shellsol 2046	1	410	2	1
Phelps Dodge, Chino	1988	Dump leach	41,000	1.8	2.0	ACORGA M-5640	Philips SX-7	2	1300	2	1

Table 7. Data on solvent extraction plants.
(courtesy Acorga Ltd).

liquor with 5 g/l Cu, pH=2 (spent electrolyte 25 g/l Cu, 150 g/l H_2SO_4) in a circuit with two extraction stages and two stripping stages is shown in Fig.9. The McCabe-Thiele construction for the P-5100 isotherm, scaled up to give a 90% Cu extraction for two extraction stages and one stripping stage, is shown in Fig.10. It can be inferred from Figs.9-10 that the stripped organic Cu tenor increases if the total number of stages is reduced. The copper inventory in the circuit then increases and this should be taken into account when comparing extractants. Optimisation is required for individual cases. Computer simulation using the SXBAL program, incorporated in a general mass balance program for the total circuit, including leaching and countercurrent washing could be of considerable help in evaluating the various process options, before any pilot plant or full scale tests are undertaken.

Data for all copper solvent extraction plants currently in operation are given in Table 7. It can be seen that since 1980 almost all new solvent extraction plants, built with the conventional countercurrent configuration, had no more than two stages in the extraction circuit and either one or two stages in the stripping circuit.

The availability of these powerful extractants has allowed the introduction of the Stage 3 expansion in the Chingola Tailings Leach Plant without having to add additional solvent extraction streams. Perhaps in a future expansion for the treatment of the micaceous ores extra SX capacity may have to be added.

1.3. Dense medium separation of oil shale.

The spatial distribution of valuable ore minerals or other components in a deposit may allow special processing options to be considered. An example of this is the utilisation of petrological data in the upgrading of the Tarfaya oil shale in Maroc by physical separation. In these oil shales the organic matter or kerogen, from which oil can be obtained, is segregated into distinct bands, resulting in density differences. By

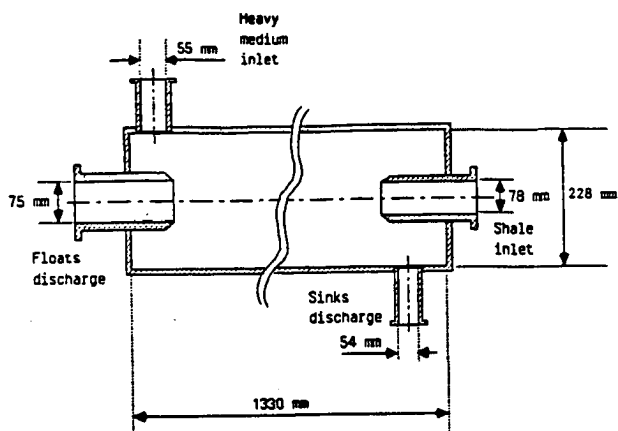


Fig.11. Dimensions of the Sala Dyna Whirlpool separator.

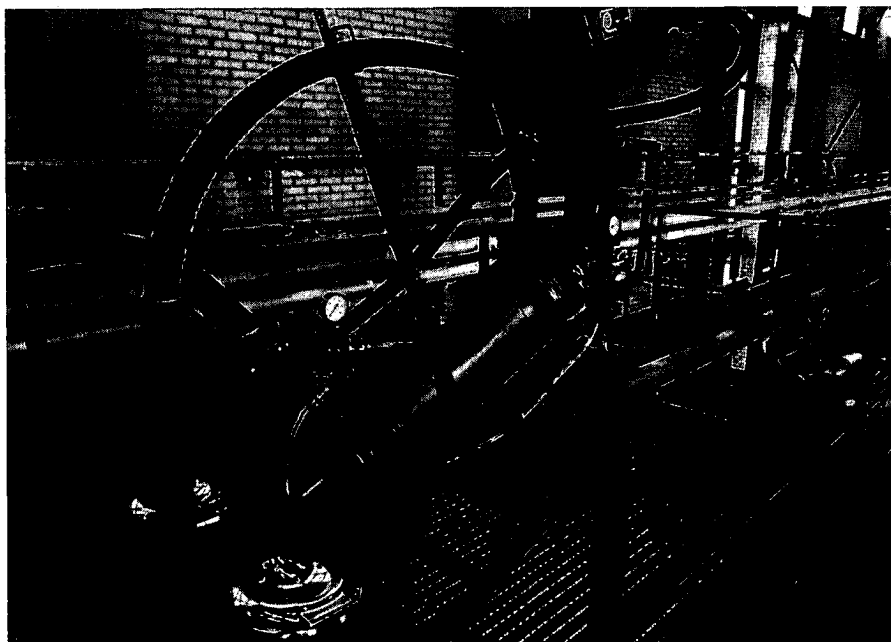


Fig.12. Pilot plant Sala Dyna Whirlpool separator.

crushing the shale to an appropriate size, shale fragments can be produced consisting predominantly of the material from either the kerogen-rich or kerogen-poor bands. Preliminary laboratory heavy liquid separation testwork indicated that the differences in density were small ($< 0.03 \text{ g/cm}^3$), but possibly sufficient for dynamic dense medium separation, which has a high separation efficiency, to be used.

During the laboratory testwork problems were encountered with the porosity of the shale. Absorption of heavy liquid (tetrabromoethane/toluene mixtures) by the shale caused fragments, which initially floated, to sink after some time. Pre-saturation of the shale with water alleviated the problem, but the resulting uncertainty in the separation results enhanced the need for testing on a larger scale.

Pilot-scale work was carried out using a Dyna Whirlpool separator. This is a cylindrical vessel (Fig.11,12), which is inclined at an angle of $12-25^\circ$ from the horizontal. It has two inlets, one is a short piece of pipe (vortex finder) in the upper end plate for the introduction of the feed material and the other is a tangential inlet for the dense medium, a suspension of magnetite (Fe_3O_4) in water. There are two outlets: an axial vortex finder in the bottom end plate, through which the light fraction (floats) is removed, and a tangential one near the upper end plate through which the heavy fraction (sinks) is discharged. The medium follows a predominantly spiral flow pattern, being discharged through the two product outlets. The medium flow generates an air core which extends throughout the separator along its axis. The separated light material concentrates at the surface of the air core and is discharged through the lower vortex finder. The heavy fraction is centrifuged out and concentrates near the wall of the vessel where it is directed toward the tangential sink discharge by the upward spiralling movement of the medium.

The general flowsheet of the plant is shown in Fig.13. The separation products are drained on the first section of a vibrating screen, which

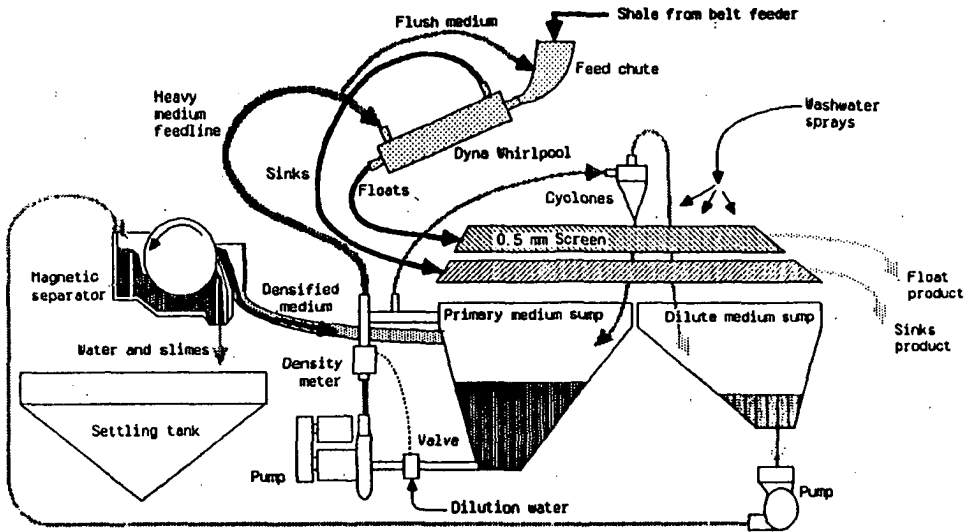


Fig.13. Dense medium pilot circuit.

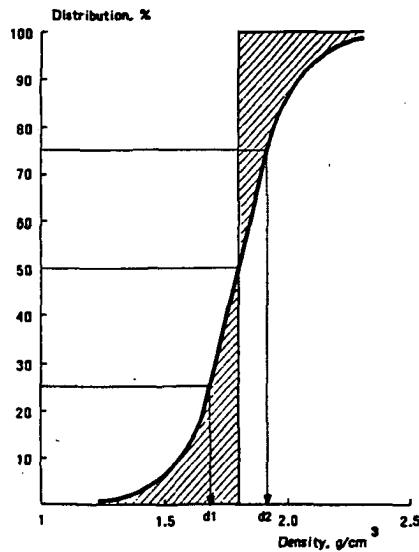


Fig.14. Example of a Tromp distribution curve.

is partitioned along its length to keep the two products separate. The drained medium gravitates to the medium pumpbox. On the second section of the screen the products are washed with spray water. The medium in the dilute washings is re-generated by magnetic separation. The separator has a total throughput of 4-5 t/hr shale.

For the evaluation of the efficiency of the Dyna Whirlpool separator generation of density distribution data was necessary. In standard practice this is done by heavy liquid analysis on the separator products and plotting the distribution percentage of material of a particular density to one of these products (say the heavy product or the sinks) versus density. The resulting curve, designated Tromp curve (Fig.14), has a characteristic S-shape. As a measure of the separation efficiency one uses the so-called Ecart Probable (E_p), which is defined as half the difference between the densities corresponding to distribution percentages of 75% and 25% [41]. However, in view of the porosity effects observed previously during the laboratory testwork it was anticipated that determination of the Tromp curve using classical techniques could lead to erroneous results. Therefore it was decided to use a tracer technique. It was realized that the tracers should be of the same average size as the shale particles: about 6 mm. To achieve acceptable accuracy in the Tromp curve large numbers of tracers had to be added. This required automatic tracer recovery and therefore magnetic tracers were developed for the density range of interest. Further details are given in section 2.7. The Tromp curve determined with the tracer method was significantly different from that determined with the classical heavy liquid analysis (see Fig.4 - section 2.7). An E_p value of 0.01 was determined by the tracer method, which demonstrates the efficiency of the Dyna Whirlpool.

The porosity problem encountered in this particular project resulted in the development of a very useful technique, which can also be applied in other dense medium separations, for example in coal preparation research. The tracer production method is very suitable for the manufacture of small tracers of relatively low density, which so far

presented a problem. For the application of such tracers in plant operations, installation of magnetic separators would be required. These might be simple static plate separators.

Recently Sentrex Engineering developed tracers which can be detected on line [42]. They are made of plastic and contain an alloy which emits a specific radio frequency signal when excited by an electrical field generated by a coil above the transport system.

1.4. High intensity magnetic separation

Mineral separation in magnetic fields has been applied since the last century. For a long period it was limited to the beneficiation of relatively strongly magnetic minerals such as magnetite and ilmenite (FeTiO_3). Drum separators with permanent magnets, operating either on dry material or on mineral pulps, were mostly used. For more weakly magnetic minerals, such as hematite or wolframite ($(\text{Fe,Mn})\text{WO}_4$), dry belt- or disc separators were employed in which the particles are presented in a monolayer and quite selective separations could be achieved. A recent review of these techniques is given by Svoboda [43]. However the grain size in these separators is limited to around $75 \mu\text{m}$. For smaller particles wet operation is required and thus much higher magnetic forces are necessary to overcome fluid drag forces. The magnetic force F_m on a particle in an inhomogeneous magnetic field is given by:

$$F_m = V\mu_o(K_p - K_1)|H|\text{grad}|H|$$

where μ_o is the magnetic permeability of the vacuum (N/A^2), K_p and K_1 are the volume susceptibilities of the particle and medium respectively (-), and H is the magnetic field strength (A/m). In order to achieve high magnetic forces on small particles of weakly magnetic minerals, high values of $\mu_o H \text{grad} H$, referred to as the force density, are required. A high gradient is obtained by using a ferromagnetic matrix, which

distorts the magnetic field, but its magnitude is limited by the saturation of the matrix material. This concept was first introduced by Frantz [44] who designed in 1932 a separator which consisted of a solenoid packed with steel ribbons. It was not until the 1960's that a considerable development in the area of high intensity, high gradient magnetic separation (HGMS) took place and much more powerful magnet systems became commercially available. Recently the first superconducting magnet system, manufactured by Eriez, has been installed for the purification of kaolinite. A number of other magnet manufacturers have developed such superconducting magnet systems and it is expected that more applications will be forthcoming. Some reluctance of utilising such sophisticated equipment in remote mining areas probably exists, although the system design has improved dramatically in recent years. In this respect the development of the new materials, which are superconducting at liquid nitrogen temperatures, is of interest. Although the current carrying capacity of these new materials is still low, it is expected that eventually much cheaper magnet systems will become available. Typical values of the force density for various magnet systems [45] are given in Table 8.

Device	$\mu_0 H \text{grad} H$ N/m^3
Belt separator	$5 \cdot 10^4$
Drum separator	$2 \cdot 10^5$
Induced roll separator	$8 \cdot 10^7$
Jones high intensity wet separator	$4 \cdot 10^9$
Conventional HGMS	$6 \cdot 10^{11}$
Superconducting HGMS	$2 \cdot 10^{12}$

Table 8. Magnetic force density values for different separator types [45].

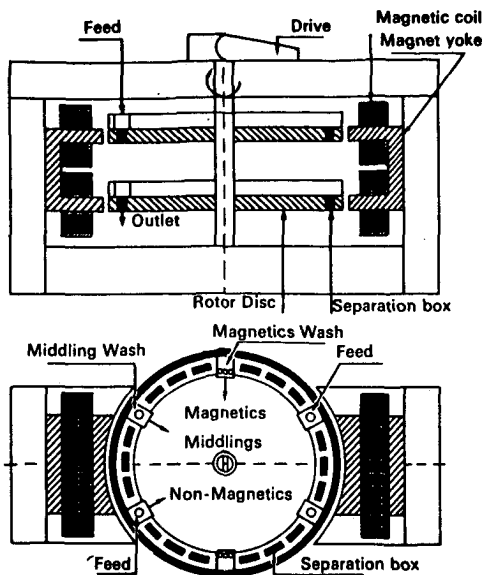


Fig.15. Jones high intensity magnetic separator [46].

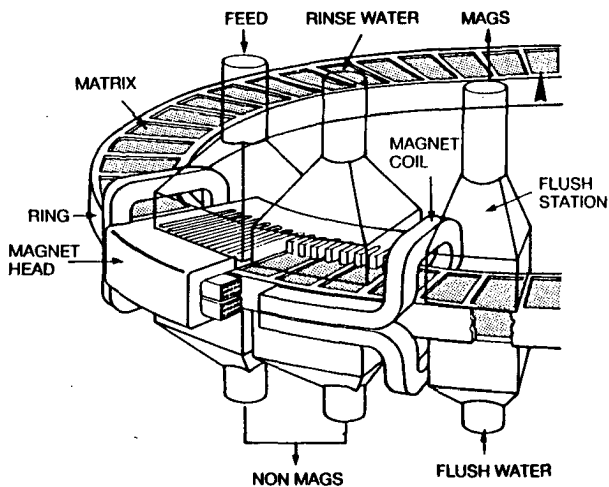
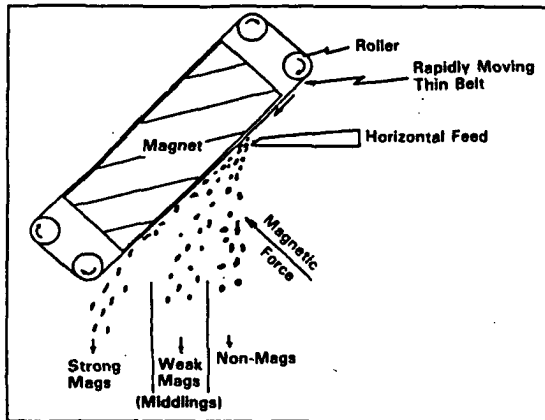


Fig.16. Sala high intensity, high gradient magnetic separator.
(courtesy Sala International).

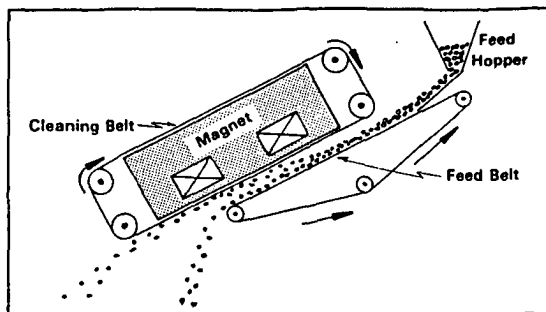
The main applications of HGMS are currently in the beneficiation of iron oxide ores (hematite) and in purification of kaolinite for the paper industry, in which small quantities of iron oxide minerals are removed. In the iron ore industry the Jones separator [46] (Fig.15) is mostly used. The matrix in this separator consists of grooved plates contained in compartments of a caroussel, which rotates through the magnetic field, generated by a conventional electromagnet. In the clay industry the separators are semi-continuous with a solenoid magnet system, containing a canister with stainless steel wool as the matrix (Eriez, Sala).

High mineral recoveries of weakly magnetic mineral particles can be achieved fairly easily with the powerful magnet systems available. However the selectivity in HGMS separation is not always sufficiently high. This may be one of the reasons that HGMS has not been applied more often in the mineral industry. The selectivity aspect was of considerable importance in the Mount Pleasant tungsten mine in Canada where HGMS was applied in the separation of wolframite from arsenic minerals in the final upgrading stages using a Sala caroussel separator with a solenoid magnet (Fig.16). In relation to this, testwork was conducted aimed at improving the selectivity. Full details of this work are given in section 2.8. It was found that significant improvements in the grade of the final wolframite concentrate were possible using split-size treatment of the feed. In subsequent research work actual capture profiles in the canister could be determined for the first time using a cryogenic technique and these provided a very good insight into the general selectivity problem. The research work on selectivity, which is still ongoing, may lead to improved separation techniques applicable to complex ores.

Three other recent system developments in high intensity magnetic separation, aimed at improving selectivity should be mentioned. Zhongyuan and Zhengnan [47] have used a vibrating matrix to reduce the amount of physically entrained quartz in a very fine wolframite magnetics ($< 5 \mu\text{m}$) product. They found an increase in WO_3 grade of the



a. Inclined fall separator.



b. Inclined lift separator.

Fig.17. Open gradient superconducting separators from Cryogenic Consultants Ltd [48].

magnetics from 8% to 35%. It should be noted that these investigators used stainless steel wool as the matrix, which is known to give poor selectivity due to high levels of mechanical entrainment (section 2.8).

Stadtmüller et al. [48] describe an open gradient dry magnetic separator in which high selectivity can be obtained. The magnet consists of a linear superconducting magnet ("race track" design) which is set at an angle so that the feed material can be introduced into the separation zone very close to the region of high field strength (Fig.17a). The magnetics are removed continuously by a fast moving thin belt, guided by rollers around the magnet system. The magnetic product, middlings (or weaker magnetic fraction) and the "non-magnetics" are separately collected by a splitter system. The tilting of the magnets also makes the splitter position less critical. Although high selectivity could be achieved with this set-up the capacity remained low (1-1.5 t/hr/m.width). By reducing the tilt and feeding the material on a second belt a system was obtained (Fig.17b) which has the inherent selectivity of for example a high intensity disc separator, but has a much higher capacity (10 tonne/hr/m.width) because of the high field strength. This separator looks very promising but as it is a dry technique there will be a lower size limit of around 45-75 μm .

The third system is the superconducting drum separator, developed by KHD Humboldt Wedag in Germany [49], which could be utilised wet or dry. In the dry mode high selectivity can be obtained by top feeding the material in a monolayer. The separation efficiency in a wet system will be comparable to a conventional drum separator, but its capacity will be much higher. This system has not yet been commercially applied and therefore no performance data are available. As this is also an open gradient separator, processing of very fine material (< 10-20 μm) will be much less effective than with high gradient, matrix systems. The construction of this drum separator is complicated in comparison to the above systems of Cryogenic Consultants, and thus much more expensive.

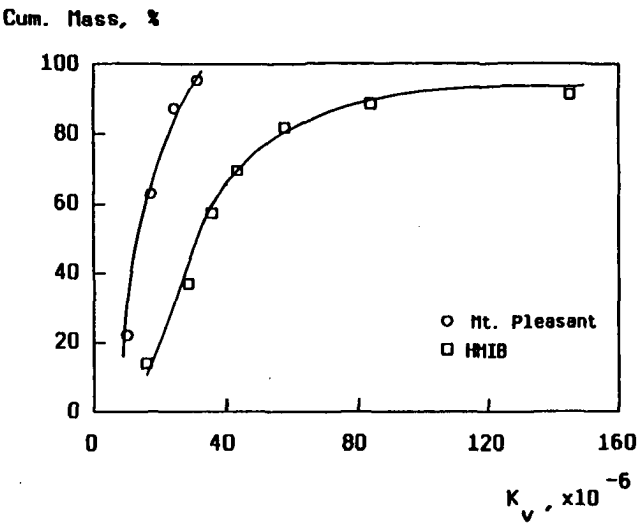


Fig.18. Distribution of magnetic susceptibilities for two arsenopyrite samples.

Origin	% Fe	Mass susceptibility $\times 10^{-9} \text{ m}^3/\text{kg}$
Ottawa, Oklahoma, U.S.A.	0.23	1.1
Broken Hill, Zambia	0.41	6.5
Brownley Hill, England	1.4	26.9
Nanisivik, Canada	3.9	66.5
Faro, Yukon, Canada	9.7	130.6
Broken Hill, Australia	11.6	177.8

Table 9. Magnetic susceptibility of sphalerite as a function of its iron content.

In magnetic separation characterisation of the mineral properties is very important, particularly in complex separations. Accurate measurement of susceptibilities is a first requirement. Literature data on susceptibilities are not always reliable, and inaccuracies may be related to impure materials. A considerable spread in magnetic susceptibilities for a particular mineral concentrate can occur. This may be caused by variations in chemical composition, for example the iron content in sphalerite (Table 9), or by intergrowths of mineral components such as pyrite and arsenopyrite. Examples of magnetic characterisation of two arsenopyrite concentrates are shown in Fig.18. The sample from Mount Pleasant is quite pure (96% arsenopyrite) and has a relatively narrow range in magnetic susceptibility. The other sample, a flotation concentrate provided by HMIB, Arnhem, The Netherlands, shows a considerably larger spread in magnetic susceptibility, which is at least partially due to locking with pyrite and small quantities of chalcopyrite.

The utilisation of changes in magnetic properties during phase transformations or differences in magnetic structure of minerals has considerable potential in mineral separation. The magnetising roast of chalcopyrite contained as an impurity component in lead and molybdenum sulfide concentrates is an example of the application of a phase transformation [50]. It appears that a copper ferrite is formed at temperatures above 280°C. Another interesting application of differences in magnetic properties at high temperatures has been described by Wada [51] in the separation of a ferri-ilmenite (FeTiO_3) from titanomagnetite ($(\text{Fe,Ti})\text{Fe}_2\text{O}_4$) which have Curie temperatures of around 200°C and 500°C respectively. A separation at 250°C will concentrate the titanomagnetite in a magnetic fraction leaving the ilmenite in the tailings. Apparently this process is being applied in the mill of the Toho Kinzoku Co. at Nishinoomote in Japan.

The possible use of differences in magnetic structure has been considered by the author for the separation of wolframite and hematite

from pre-concentrates produced from Hemerdon (Cornwall, England) ore. These two minerals have very similar magnetic susceptibilities at ambient temperature and are therefore difficult to separate with conventional technology. The best results were so far obtained with a dry high intensity disc separator. The difference in magnetic structure offers the possibility for an improvement in separation performance. Wolframite is paramagnetic, whereas hematite shows canted antiferromagnetism. In hematite the magnetic moments of the Fe^{3+} ions in the (0001)-plane are mutually parallel, but nearly antiparallel to those in alternate basal planes [52]. The deviation of exact parallelism (canting) results in a net magnetic moment. If the temperature is reduced to below -23°C the spin axis orientation changes from within the c-plane to parallel to the c-axis, and at the same time the canting is nearly eliminated making the mineral antiferromagnetic. As the magnetic moments then almost cancel out a strong decrease in the magnetic susceptibility of hematite occurs. This change in magnetic structure is known as the Morin transition [53]. On the contrary the susceptibility of wolframite increases with decreasing temperature according to the Curie law for a paramagnetic mineral.

The changes in susceptibilities of the Hemerdon wolframite and hematite with temperature are shown in Fig.19. The hematite shows a more gradual decrease as compared to a synthetic hematite, which has a sharp transition at about -23°C [53]. Such a gradual transition has also been noted for a natural hematite from Elba [54]. This may possibly be due to impurities and/or structural imperfections. At low temperatures the difference in susceptibilities between the Hemerdon wolframite and hematite is substantially larger than that at room temperature and this might offer the possibility of achieving enhanced selectivity between these two minerals.

The utilisation of special magnetic properties of minerals is a research area, which is largely unexplored, but certainly has considerable promise.

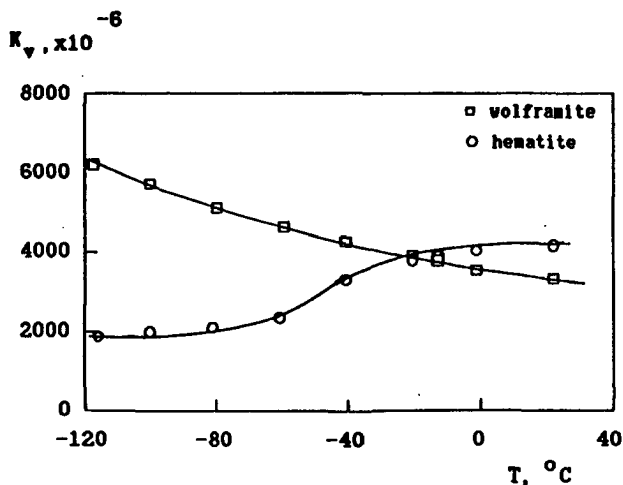


Fig.19. Magnetic susceptibilities of wolframite and arsenopyrite at low temperatures.

1.5. Concluding remarks

In the development of beneficiation schemes and for efficient plant operations quantitative mineralogy is an essential tool for the metallurgist. Important issues are listed below:

1. At an early stage in a new development project accurate mineralogical data should be generated from borehole composite samples covering the whole orebody. These should be studied by process metallurgists who then decide on the required testwork. Any future major changes in ore composition, possible related processing problems and the implications on plant output can then also be anticipated. Rapid means of metallurgical characterisation should be developed and/or refined, which can provide data for computer modelling.

2. During plant operations mineralogical data of important process streams should be routinely generated to monitor performance and to identify any operational problems which are not directly evident from chemical analysis.
3. In cases where processing performance is sensitive to changes in feed mineralogy analyses of advance mining samples in combination with routine metallurgical testing should be conducted [55].
4. The proper tools for carrying out these tasks should be further developed. In the coming years a great deal of research work will have to be conducted to relate the available quantitative mineralogical data to the behaviour of minerals or other materials in various processes.

It is evident that good interaction between metallurgists and mineralogists is required. The metallurgist needs to have adequate knowledge of mineralogy and the available techniques with their possibilities and limitations. He needs to be aware of mineralogical aspects in all stages of a project and in relation to all unit processes under consideration. On the other hand the mineralogist needs to be familiar with the metallurgy of various ores. He is usually the first, who studies geological samples from new prospects and thus at a very early stage he could already recognize potential problems and advise metallurgical testing.

In actual process research the importance of modern techniques of mineral characterisation and quantification is generally recognised. They provide the insight into process mechanisms required to develop more efficient beneficiation technology. As already mentioned in the preceding section, the study of specific mineral properties, such as magnetic structures, in relation to possible application in separation technology is an area which offers considerable scope.

Some of the sophisticated image analysis techniques and other instrumental methods require large capital investment and only few mining companies can afford them. It is expected that more analytical centres, such as for example CSIRO in Australia who provide facilities for image analysis with a SEM, will be established which can serve the mining industry.

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PART TWO - PAPERS

2.1. ORE MINERALS OF THE ZAMBIAN COPPERBELT

C.W. Notebaart and B.W. Vink

Geologie en Mijnbouw, 1972, 51, 337-345.

INTRODUCTION

A typical feature of the Copperbelt ore deposits is their stratiform character. Nine major mines are presently in operation (Table 1) and a few other deposits where exploration is being carried out, are known. All orebodies occur stratigraphically in one group, called the Lower Roan Group, which is the lowest member of the Precambrian Katanga System of metamorphosed sediments. The Katanga sediments were folded during the Lufilian orogeny and regionally metamorphosed mainly under greenschist facies conditions. They occur now as synclinal structures within the Basement Complex. The dip of the orebodies is related to the structural deformation and ranges from shallow to steep, and locally overturning of strata has occurred.

The main orebodies are associated with shaly and quartzitic rocks, but conglomerates and dolomitic rocks also occur. The mineralisation is essentially the same in all sulfide orebodies: the major minerals being chalcopyrite, bornite, chalcocite and pyrite. Where the orebodies are cobalt bearing, carrollite and cobaltiferous pyrite are the major cobalt minerals.

There is a zonal arrangement of the primary sulfides in most of the deposits, generally from barren through chalcocite, bornite, chalcopyrite and pyrite.

The relative proportions of the major sulfide minerals vary from deposit to deposit. They are listed in Table 1 for the mines presently in operation.

Mineral	Beluba	Bwana Mkubwa	Chambishi	Chibuluma	Chillila- bambwe	Mufulira	Nchanga/ Chingola	Roan Antelope	Rokana/ Mindola
Chalcopyrite	xxxx	x	xx	xxxx	x	xxx	x	xxxx	xxx
Bornite	xx	xx	xxxxx	xx	xxx	xxxx	x	xx	xx
Chalcocite	x	xxx	xx	x	xxx	xx	xxx	xx	x
Co-pyrite	xx	-	-	xx	-	-	-	-	xxx
Carrollite	xx	-	-	x	x	-	x	-	xx
Malachite	xx	xxxx	xx	-	xx	x	xxxx	xx	x
Cuprite	x	x	x	-	x	x	x	x	-
Native copper	trace	trace	-	-	x	x	x	trace	trace
Pseudomalachite	trace	x	x	-	x	-	xx	x	x
Chrysocolla	trace	x	trace	-	x	-	xx	x	trace

x 1-5% xx 5-20% xxx 20-40% xxxx 40-70% xxxxx > 70%

Table 1. Relative abundances of the major copper and cobalt minerals in the copper producing mines on the Zambian Copperbelt.

Near the surface, the primary sulfide orebodies are oxidised and leached. The depth of oxidation varies greatly, the average being in the order of 50-70 m. Locally, partial oxidation of the sulfides is found at depths of 800 m. In general a zone of supergene enrichment exists between the primary sulfides and the oxidation zone.

In the following mineral descriptions the attention paid to each mineral is disproportionate to its relative abundance in the Copperbelt ore deposits. In general, more details are given on relatively rare ore minerals than on the common ore minerals, which have been described previously in a number of papers on Copperbelt ore deposits.

SULFIDE MINERALS

Chalcopyrite, CuFeS_2 . - In most sulfide orebodies on the Copperbelt, chalcopyrite is the main source of copper and is almost without exception of primary origin. It occurs mainly as disseminated grains, the size of which is related to the grain size of the host rock. In some orebodies where considerable migration and recrystallisation of the sulfides took place, chalcopyrite is found in vein-like masses (Rokana South orebody, Baluba, Roan Antelope). The chalcopyrite in some orebodies shows complex growth twinning. The twinning lamellae have, on occasions, a typical oleander leaf shape, which appears to be an indication of relatively high temperature. More rarely translation twinning occurs near shear fractures. In the Rokana South orebody chalcopyrite seldom contains exsolution lamellae of cubanite. In the Mindola, Baluba and Roan Antelope orebodies chalcopyrite is found as exsolution lamellae in bornite. Chalcopyrite frequently replaces carrollite as thin veins, following the parting and cracks in the latter. At Chambishi secondary chalcopyrite is found as transition rims, which occur at the contact between primary bornite and secondary chalcocite (Fig.1).

Bornite, Cu_5FeS_4 . - Bornite is the secondmost important primary sulfide copper mineral on the Copperbelt. It occurs as disseminations in the hostrock, often forming simple contacts with chalcopyrite and chalcocite. Chemical analyses of various types of bornite show that the iron content ranges from 8 to 11%. In polished sections the colour of the bornite varies from bright orange to dark pinkish brown. The orange bornite at Rokana apparently forms a metastable solid solution with chalcopyrite, which sometimes exsolves along polishing scratches during preparation of the polished sections. Massive bornite from the 530-level in the Mindola orebody is distinctly anisotropic and frequently shows polysynthetic twinning lamellae. Some of the bornite from Mindola and Baluba contains very regular exsolution lamellae of chalcopyrite along the {111}-planes.



Fig.1. Secondary chalcopyrite (medium grey) partly as veins in primary bornite and partly as rims around primary bornite at the contact with secondary chalcocite. Chambishi mine.

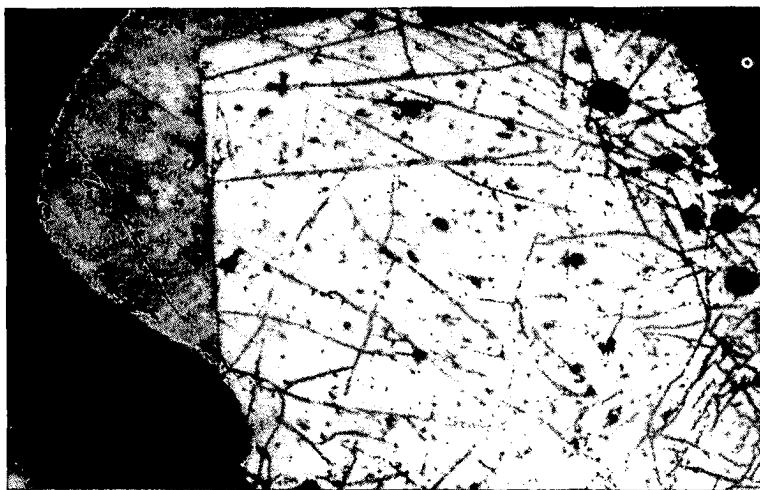


Fig.2. Subhedral carrollite veined by digenite and surrounded by bornite (medium grey). Nchanga mine.

Idaite, Cu_3FeS_4 . - *Idaite*, originally described by Frenzel [1] as an intermediate alteration product of bornite, has been found recently in several ore specimens from the Nchanga mine. No previous mention of its occurrence in Copperbelt ores has been made. The *idaite* from Nchanga is similar to bornite in colour, but shows a distinct reflection pleochroism from brownish orange to greyish yellow. It is easily distinguished from bornite by its enormous anisotropism. *Idaite* occurs as small rounded inclusions in bornite, occasionally associated with minute specks of chalcopyrite. The bornite is being replaced by lamellar chalcocite and digenite. Textural relationships indicate that the *idaite* has been formed prior to the replacement of bornite by the supergene sulfides.

Chalcocite, Cu_2S . - The most important chalcocite concentrations are found at Nchanga and Chililabombwe, where virtually all the chalcocite is of supergene origin, replacing the primary sulfides, thereby increasing the copper content (zone of supergene enrichment). Both primary and secondary chalcocite occur in the Roan-Muliashi Basin (Roan Antelope and Baluba) and Mufulira "A".

Carrollite, Co_2CuS_4 . - In all cobalt-bearing orebodies on the Copperbelt, carrollite is the major source of cobalt. Analyses of several carrollite samples from different orebodies, checked microscopically for absence of chalcopyrite, gave Cu and Co values of 20% and 38% respectively, i.e. close to the ideal composition. Electron microprobe studies on carrollite from Chibuluma [2] confirm the formula Co_2CuS_4 . Hills [3] also found that at Chibuluma the predominant cobalt mineral is carrollite. Electron microprobe analyses on carrollites from the Rokana South orebody by Richards [4] show that the copper content in carrollite varies from 1.9% to 20.2%, which would indicate a series between carrollite and linnaeite*.

Carrollite occurs as disseminated anhedral to subhedral grains, associated with chalcopyrite and/or bornite. Replacement of carrollite

* A.E. Annels et al (Miner. Deposita, 1983, 71-88) report a variable Cu content (11.5-22.0%) in carrollites from Chambeshi SE. Carrollites from Baluba and Chibuluma assayed close to 20% Cu.



Fig.3. Euhedral carrollite containing exsolution lamellae of pyrrhotite. Concentrations of mackinawite (bright white) occur at the carrollite grain boundaries. The carrollite is surrounded by chalcopyrite. Part of a grain of Co-pentlandite is visible (bottom right). Rokana South orebody.

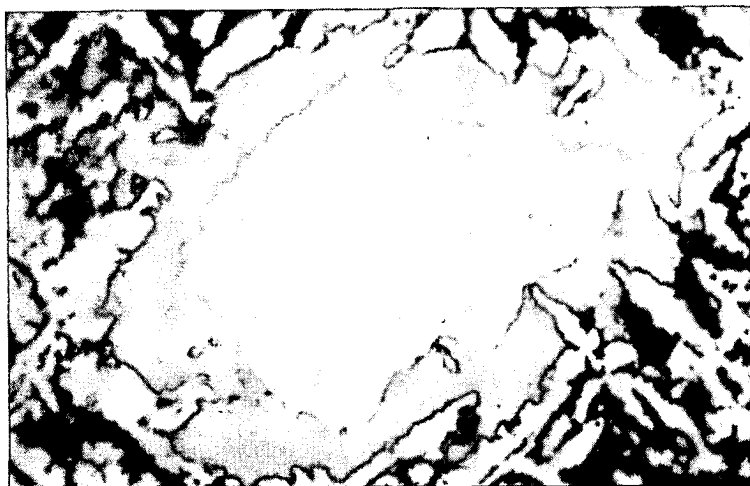


Fig.4. Digenite (medium grey) replacing carrollite and chalcopyrite (centre). Nchanga mine.

by chalcopyrite, digenite (Fig.2) and bornite is common and takes place along parting and fractures in the carrollite (Rokana, Mindola).

Occasionally large euhedral carrollite crystals up to 5 cm across are found at Chibuluma. In an ore specimen from the 790-level in the Rokana South orebody euhedral to subhedral carrollite crystals contain exsolution lamellae of pyrrhotite along the (111)-planes (Fig.3). At the contact of the pyrrhotite lamellae and the carrollite with the surrounding chalcopyrite, concentrations of mackinawite occur. These are possibly formed as a reaction product between the chalcopyrite, pyrrhotite and carrollite. Also at Rokana carrollite is infrequently found as exsolution lamellae in pyrrhotite, associated with cobalt-pentlandite. The majority of the carrollite is formed earlier than the chalcopyrite. However, in ore specimens from the 1970-level in the Rokana South orebody a second generation of carrollite has been observed. This carrollite replaces chalcopyrite as irregular veins.

Linnaeite, Co_3S_4 . - Etching tests on carrollite from Chibuluma [3] showed that some grains were composed of two phases, which have been identified as linnaeite and carrollite. Richards [4] mentioned the occurrence of linnaeite, containing small quantities of copper, from the Rokana South orebody.

Pyrite, FeS_2 . - Cattierite, CoS_2 . - Pyrite occurs widespread in most sulfide orebodies. An interesting and economically important feature of some Copperbelt pyrites is their cobalt content. The cobaltiferous pyrites belong to the isomorphous series pyrite-cattierite. It appears that cobalt and iron are interchangeable over the whole range of compositions from FeS_2 to CoS_2 . The pure endmember cattierite has been described by Kerr [5]. O'Meara [6] mentioned the occurrence of cattierite from the 890-level in the Rokana South orebody. At Baluba and Rokana the cobalt percentages of most pyrites vary from 0 to 8%. Intermediate members of the pyrite-cattierite series have been reported from Chibuluma [7]. In polished sections some pyrites from the Rokana South orebody show distinct, irregular colour zones, varying from creamy



Fig. 5. Bornite (dark grey) containing a vein composed of tellurobismuthite (white) and a greenish strongly anisotropic mineral (tetradymite?). Chalcopyrite occurs as exsolution lamellae. Mindola.

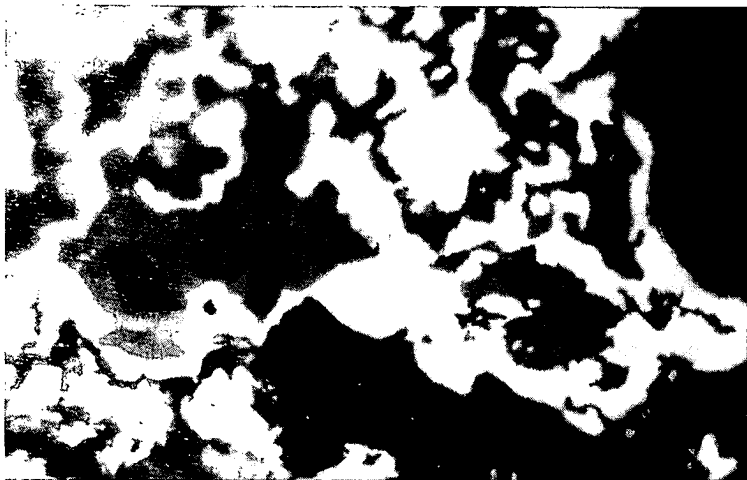


Fig. 6. Rickardite (medium grey), surrounded by weissite (light grey) and melonite (white). Mindola mine.

white to pinkish brown, and showing slight differences in polishing hardness and reflectance. Electron microprobe analysis [4] showed that the darker, brownish zones contained more cobalt than the lighter ones.

Hills [3] carried out a detailed study on Chibuluma cobaltiferous pyrites and found that both the magnetic susceptibility and reflectance decrease with increasing cobalt content. There appears to be no significant relationship between the cobalt percentage and the microhardness. X-ray diffraction studies on pyrites with different amounts of cobalt [7] revealed a linear relationship between the $d(511)$ -spacing and the cobalt content of the pyrite.

Pyrite occurs mainly as disseminated, subhedral to euhedral crystals up to 3 cm in diameter. In the Rokana South orebody octahedral pyrite crystals, having a distinct brownish tint in a polished section, are often associated with small amounts of native bismuth and bismuthinite. Textural observations clearly indicate that pyrite normally is the first crystallized sulfide, followed by carrollite and chalcopyrite, although overlapping occurs to a variable extent. It appears that the high-cobalt pyrite is usually formed later than the cobalt-poor pyrite. Graphic intergrowths of pyrite and carrollite occur at Chibuluma and were probably formed as a result of replacement of pyrite by carrollite along its crystallographic directions.

Covellite, CuS . - Covellite is a common, though very minor mineral in most sulfide orebodies. The bulk of the covellite is of supergene origin and replaces chalcopyrite, bornite and chalcocite.

Digenite, $\text{Cu}_{1.8}\text{S}$. - Digenite is found in minor quantities in ores from the Roan-Muliashi Basin, the Chambishi-Nkana Basin, Nchanga and Chililabombwe. Most of it appears to be of secondary origin and is associated with chalcocite, carrollite, and bornite. Digenite, replacing carrollite from the centre, is relatively common at Nchanga and Chililabombwe (Fig.4).

Pyrrhotite, Fe_{1-x}S . - Pyrrhotite is an accessory sulfide in the vein ores of the Rokana South orebody. It occurs as disseminated grains and aggregates of grains, associated with chalcopyrite, cobalt-pentlandite, pyrite, carrollite and mackinawite. Occasionally pyrrhotite is found as stringers, following the chalcopyrite grain boundaries. Very rarely it is enclosed as orientated lamellae in carrollite. Small quantities of pyrrhotite are found in the Basement rocks at Roan Antelope.

The pyrrhotite from Rokana frequently contains exsolution lamellae of pentlandite parallel to the basal plane marked by the pyrrhotite parting. Etching shows that the pyrrhotite is composed of a light coloured hexagonal form, which contains darker coloured monoclinic lamellae. The proportions of the two pyrrhotite modifications vary, but it appears that on the average the hexagonal form is slightly more abundant than the monoclinic form.

Pentlandite, $(\text{Fe},\text{Ni})_9\text{S}_8$, *Cobaltpentlandite*, $(\text{Co},\text{Ni},\text{Fe})_9\text{S}_8$. - Small quantities of cobaltpentlandite are found in the sulfide veins of the Rokana South orebody. It occurs as small irregular masses enclosed in chalcopyrite and as minute exsolution lamellae in pyrrhotite. A quantitative electron microprobe analysis on two cobaltpentlandite samples from the Rokana South orebody by Richards [4] showed that they contained 63% Co. The cobaltpentlandite is replaced by mackinawite and chalcopyrite. Replacement of pentlandite by mackinawite takes place along the grain boundaries and occasionally along the cleavage directions.

Mackinawite, $(\text{Fe},\text{Co},\text{Ni})_9\text{S}_8$. - Recently the occurrence of mackinawite in the Rokana South orebody was confirmed by X-ray diffraction (Notebaart [8]). Mackinawite is found mainly as small worm-like inclusions in chalcopyrite. Some ore specimens contain rectilinear veinlets of mackinawite, which frequently cross the chalcopyrite grain boundaries. This indicates that the mackinawite replaces the chalcopyrite and is not an exsolution product.

Millerite, NiS . - Millerite is found very rarely as exsolution lamellae in carrollite. Small exsolution blebs are occasionally found in pyrrhotite from the Rokana South orebody.

Bismuth, Bi , *Bismuthinite*, Bi_2S_3 . - Trace amounts of native bismuth, invariably associated with bismuthinite have been found in ore specimens from the Rokana South orebody. The bismuth minerals are often associated with octahedral pyrite (probably with high cobalt content) in which they occur as small, irregular inclusions with or without chalcopyrite.

Bismuth is a harmful impurity in refined copper. It makes the metal brittle and thus unsuitable for wire drawing.

Tellurobismuthite, Bi_2Te_3 . - Recent studies of massive bornite specimens from the 530-level at Mindola revealed the presence of small inclusions and veinlets, composed of a high reflecting, strongly anisotropic mineral which was identified as tellurobismuthite by X-ray diffraction. This mineral has not been reported previously from the Copperbelt. It occurs principally as small rounded masses, surrounded by a greenish, strongly anisotropic mineral, which has not yet been identified (tetradymite?). The latter mineral also forms thin, irregular veinlets in the bornite (Fig.5) frequently crossing the chalcopyrite exsolution lamellae. The tellurobismuthite from Mindola undoubtedly replaces the bornite.

Melonite, NiTe_2 . - In the uranium ore deposit at Mindola, melonite is found as small disseminations and as irregular veins traversing subhedral uraninite crystals.

Rickardite, Cu_7Te_5 , *Weissite*, Cu_{2-x}Te and *Vulcanite*, CuTe . - Rickardite, with its characteristic purplish red and violet colours, occurs at Mindola, as irregular masses, surrounded by weissite and melonite (Fig.6). The copper tellurides replace melonite and have been formed probably by reaction between melonite and later chalcopyrite and digenite. Small inclusions in rickardite and weissite, with enormous bireflectance from white to greyish blue, are probably vulcanite.

Wittichenite, Cu_3BiS_3 . - This mineral was identified by Hills [3] in ore samples from Chibuluma, where it occurs as radially segmented inclusions in bornite. Annels [9] mentions wittichenite from the Nkana North Limb Prospect, where it is found as lath-shaped inclusions in bornite.

Cubanite, CuFe_2S_3 . - Cubanite is found as exsolution laths in chalcopyrite from the Rokana South orebody, and is associated with mackinawite and cobaltpentlandite.

Cobaltite, CoAsS . - Cobaltite, being replaced by chalcopyrite has been found in the carbonaceous shales in the Rokana South orebody, and was identified by electron microprobe analysis [4].

Molybdenite, MoS_2 . - In the Rokana South Orebody molybdenite is found as irregular masses, replacing chalcopyrite. Small amounts of molybdenite were also reported from Chibuluma and the Nkana North Limb Prospect.

Galena, PbS and *Sphalerite*, ZnS . - Both minerals are extremely rare.

Uranium minerals. - A small uranium deposit was located at Mindola in the 4-shaft barren gap. The predominant radioactive mineral is *uraninite*, UO_2 , which is associated with minor amounts of *brannerite*, $(\text{U,Th,Ca})[(\text{Ti,Fe})_2\text{O}_6]$ and *coffinite*, $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$. The uranium minerals occur as small disseminations and as larger masses throughout the host rock. Under the action of ground water these minerals have been altered locally to *uranophane*, $\text{Ca}(\text{UO}_2)_2\text{Si}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ and *gummite*, which is an oxidation and hydration product of uraninite. *Metatorbernite*, $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is found as small, well developed tabular crystals in vugs and lining rock fractures at Nchanga, Chililabombwe and Bwana Mkubwa. Bowie [10] reports the presence of *meta-autunite*, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and *phosphuranylite*, $\text{Ca}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ at Chibuluma. Small amounts of the hydrated and hydroxylated uranyl sulfates *zippeite* and *johannite* are reported from Roan Antelope, where they occur as efflorescences on the walls of mine workings.

OXIDE COPPER MINERALS

General

Near the surface the sulfide orebodies are oxidised and leached by meteoric water. In this zone the sulfide minerals are generally completely altered. From descending copper-containing solutions, new copper minerals were deposited in the lower levels. Below the groundwater level secondary sulfides, mainly chalcocite, were formed, with minor cuprite and native copper, resulting in an increase in copper content, thus forming a zone of supergene enrichment. Lowering of the groundwater level resulted in renewed oxidation of the primary and supergene sulfides, forming a mineral assemblage of which cuprite and native copper are typical.

The depth of leaching is a function of the resistance of the host rock to weathering processes. The more resistant rocks have sulfides even in the outcrop. In general, however, the orebodies are leached near the surface with only trace amounts of copper. In the case of the Chibuluma ore deposit, this totally leached zone is represented by a gossan extending to a depth of over 40 m.

The "oxide" copper minerals include oxides, carbonates, sulfates phosphates, and silicates.

Malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$. - Malachite is the major source of copper in the oxide orebodies on the Copperbelt. The main occurrences are at Chingola (Nchanga), Chililabombwe and at Chambishi.

The well-known ornamental malachite is common in Katanga, Zaire, but virtually absent on the Copperbelt, although specimens of high quality, ranging up to 15 cm across, have been found at Mindola, Chambishi and at Bwana Mkubwa.

At Mindola malachite occurs rarely as well developed twinned crystals in vugs. In the Nchanga open pit malachite is sporadically found as pseudomorphs after azurite crystals.

Alteration of sulfides to malachite is a relatively fast process. This was suggested by the weathering of fresh Baluba sulfide ore, containing 0.035% acid soluble copper, present as malachite. After 18 months exposure to atmospheric conditions, the same ore contained 0.18% acid soluble copper, occurring as distinct grains up to 100 μm across.

Azurite, $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$. - The main occurrence of azurite is in the Chingola open pit, where it is found as rounded compact masses of radiating crystals, frequently containing a core of malachite. It is possible that the rounded masses of azurite retain moisture over a long period, permitting the core to alter to malachite. Azurite is occasionally observed as idiomorphic, short prismatic crystals.

Copper, Cu. - Native copper is locally abundant in the partially oxidised zones of supergene enrichment. It is associated with chalcocite, cuprite and malachite. At Nchanga and Mufulira masses of native copper, weighing over 100 kg, have been recovered. Native copper, occurring as large solid masses, is most unwelcome in milling practice, because it will not crush, due to its ductility.

Cuprite, Cu_2O . - Cuprite is common in all oxide orebodies and can be abundant locally. An example is Muliashi South, the western extension of Roan Antelope, where cuprite accounts for approximately 75% of the total copper in the oxide zone. It is mainly found in the lower parts of the oxidation zone and occurs as earthy masses, intergrown with malachite and Fe-oxides. At Nchanga occasionally octahedral crystals and felty growths of minute crystals (chalcotrichite) are found.

Tenorite, CuO . - This is a very minor copper mineral in most of the oxide orebodies. Normally it occurs as fine-grained earthy material, intimately intergrown with cuprite, Fe-oxides and/or wad. Very rarely coarse-grained, polysynthetically twinned tenorite forms a crust around malachite grains (Nchanga).

Pseudomalachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$. - In oxide orebodies the mineralisation can change abruptly over short distances. A typical example is the occurrence of pseudomalachite. This mineral, although widespread in most oxide orebodies, is often concentrated in some beds, and can be virtually absent in directly overlying or underlying beds (Roan-Muliashi Basin, Chingola open pit). As the name indicates, pseudomalachite is in appearance very similar to malachite, but it displays a distinct bluish-green tint compared with malachite.

Breccias composed of malachite fragments cemented by later pseudomalachite are commonly found at Chambishi. In the Chingola and Mindola open pits, pseudomalachite occurs as small globules, lining cavities in the host rock. In the Chambishi open pit and at Mindola it is found in botryoidal masses. Pseudomorphs of pseudomalachite after libethenite are occasionally observed at Chingola.

Libethenite, $\text{Cu}_2(\text{PO}_4)(\text{OH})$. - Libethenite occurs in small amounts in most oxide orebodies, associated with pseudomalachite and malachite, mainly as well-developed rhombic crystals, up to 1 cm. In the Mindola open pit acicular, or lath-shaped crystals are also found.

Cornetite, $\text{Cu}_3(\text{PO}_4)(\text{OH})_3$. - This rare copper phosphate was first reported from Bwana Mkubwa. Later small quantities have been found at Nchanga. Cornetite is a common mineral at Kalengwa, a copper deposit 320 km southwest of the Copperbelt, where it occurs as dark blue, minute crystals, lining rock fractures. It has subsequently also been found at Kansanshi, 200 km west of the Copperbelt.

Chrysocolla, $\text{CuSiO}_3 \cdot n\text{H}_2\text{O}$. - *Chrysocolla* is locally abundant and particularly well-known from Nchanga. It occurs as solid masses, up to 40 cm across, varying in colour from pale green to sky blue, depending on the hydration state. It is sometimes found as veins, containing a central part of chalcedony (Nchanga), clearly indicating its deposition from a silica gel.

Bisbeeite, $\text{CuSiO}_3 \cdot \text{H}_2\text{O}$

Dioptase, $\text{CuSiO}_2(\text{OH})_2$

Shattuckite, $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$

Plancheite, $\text{Cu}_8\text{Si}_8\text{O}_{22}(\text{OH})_4 \cdot \text{H}_2\text{O}$

These copper silicates are rarely found in the Copperbelt orebodies. *Bisbeeite* and *shattuckite* were reported from the oxidation zone of the Chililabombwe mine, where they are associated with *chrysocolla*.

Shattuckite is found as pale blue aggregates of radiating crystals (Nchanga). *Dioptase* has been reported only from Nchanga, *plancheite* from Nchanga and Mufulira.

Chalcanthite, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Brochantite, $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$

Antlerite, $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$

Chalcanthite is present as a secondary formation in underground mine workings. *Antlerite* is found in association with *sphaerocobaltite* at Nchanga. *Brochantite* occurs in trace amounts in most oxide orebodies.

Cupriferous Wad, - Wad is a common oxidation product in most oxide orebodies. It occurs as earthy black masses, in fissures and often interleaved in mica flakes. Purified wad concentrates from Baluba contain up to 20% Mn, 10% Co and 20% Cu. X-ray diffraction showed that all these materials are amorphous. The Cu/Co/Mn ratios change over very short distances, sometimes within a few centimeters.

Cupriferous micas, K,Mg,Cu,Fe,Al-silicates - In virtually all Copperbelt oxide orebodies, low-grade micaceous copper ores, from which the copper is difficult to extract by conventional methods, are present in large quantities. The cupriferous micas are generally called cupriferous vermiculite. Basset [9] concluded that the copper is firmly fixed in the intersilicate layer of the vermiculite. A later investigation on cupriferous mica ores from Anglo American mines by Jebson [7] showed that these micas are composed of regularly interstratified layers of biotite and cupriferous chlorite (*editorial note*: conclusions mainly derived from the behaviour of the associated discrete chlorite, which was subsequently shown to be non-cupriferous - section 1.2.3 and 2.4). All Copperbelt cupriferous micas show exfoliation properties. Jebson attributed the exfoliation to the Cu-OH bond which is weaker than the corresponding Mg-OH bond in normal non-exfoliating chlorites. Exfoliation appears to take place in two stages, corresponding to the two major stages of water loss during heating as shown by TGA curves. The considerably lower cation exchange capacity of cupriferous micas compared with that of the normal Mg-vermiculite indicates that the copper bonding is different from that in a normal vermiculite. This can be explained by the fact that the Cu-OH bond in a chlorite is stronger than the Cu-H₂O bond in a Cu-vermiculite. From Bassett's and Jebson's investigations it appears that the Copperbelt cupriferous micas form a mineralogically heterogeneous group, including vermiculite, hydrobiotite and cupriferous "chlorite". Subsequent work (section 1.2.3 and 2.3) has shown that at Chingola the copper is contained exclusively in the intersilicate layer of an interstratified phlogopite - 14 Å compound and is probably coordinated to hydroxyl groups.

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2.2. LIBETHENITE FROM THE ROKANA MINE, ZAMBIA

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The Mineralogical Record, 9, 1978, 341-346.

INTRODUCTION

Libethenite, $\text{Cu}_2(\text{PO}_4)(\text{OH})$, is well-known to mineral collectors as occurring in small, olive-green crystals, generally less than 0.5 cm, and often well developed. The orthorhombic crystals show few forms; typical are the prism (110) and the dome (011). The crystal habit is usually short prismatic or elongated along the a-axis; occasionally the two dominant forms are similar in size and combine into a pseudo-octahedron. The chemical composition is generally close to the ideal composition. Dana [1] mentions that a small amount of arsenic may replace phosphorous, but that no metals substitute for the copper. However, Guillemin [2] found that a substantial portion of the copper can be replaced by zinc. Zincian libethenite occurs very rarely in the oxidized zone of the Pb-Zn orebody at the Broken Hill mine, Kabwe, Zambia and differs considerably in appearance from its copper equivalent: it has a characteristic pale greenish blue color and occurs mainly as minute spheres and incrustations. The common type of libethenite has been found in most open pits and several underground workings in the Zambian Copperbelt. However, the specimens recently discovered at the Rokana mine are extraordinary in size and variety of habits.

GEOLOGY AND OCCURRENCE OF LIBETHENITE

The Zambian Copperbelt (see Figs 1-2) covers an area of about 50 by 250 km and, together with the adjacent area in Shaba province (formerly Katanga) in Zaire, forms one of the richest copper mining regions in the world. Many of the mines in this region have a history of ancient copper mining going back as far as 400 A.D. Copper was discovered by European prospectors in the early years of this century and two mines started

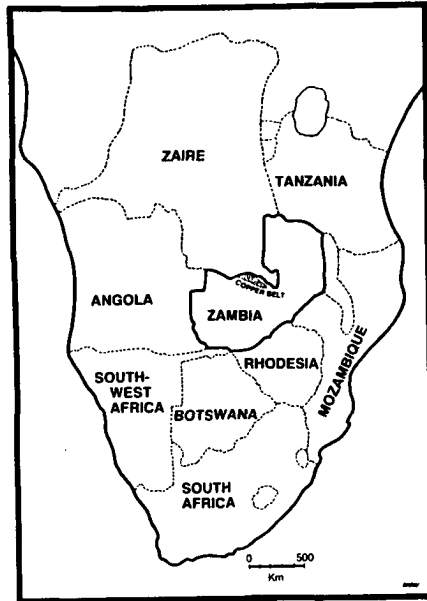


Fig.1. Location of Zambia and the Copperbelt.

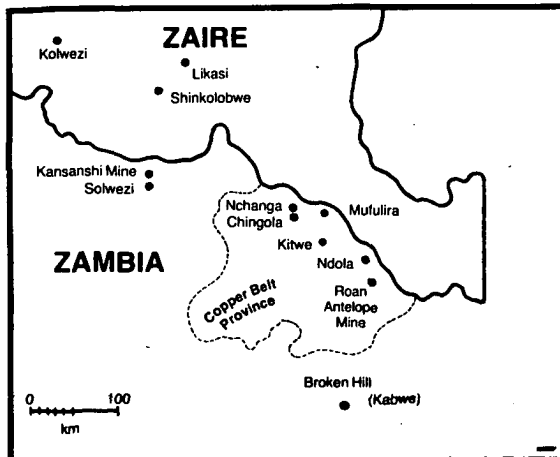


Fig.2. Location of important mines and towns on the Zambian Copperbelt.

production before the First World War: Kansanshi and Bwana Mkubwa. Production at Roan Antelope, Rokana, Mufulira and Chingola did not start until the early 1930's. Since then expansion has been very rapid and presently Zambia's yearly copper production of 680 000 tonnes is the fifth largest in the world. A total of 11 underground mines and eight open pits are operated on the Copperbelt by the two large mining companies, Nchanga Consolidated Copper Mines Limited and Roan Consolidated Mines Limited.

The copper orebodies are stratiform and occur in the Lower Roan group of the Katanga system of sediments which were deposited during Precambrian times. These Katanga sediments were folded and regionally metamorphosed, forming a mineral assemblage representative of the greenschist facies. Typically the orebodies occur in carbonaceous shales, argillites, quartzites and dolomites. Chalcopyrite and bornite are the major primary copper sulfides and carrollite is the main source of cobalt. In the oxidation zones of these orebodies the major oxide copper minerals are malachite, chrysocolla, pseudomalachite, cuprite, cupriferous wad and azurite. Generally a zone of supergene enrichment with chalcocite as the major copper sulfide lies intermediate between the primary sulfide mineralisation and the oxidation zone.

The Rokana deposit consists of the Mindola, Central and South orebodies. Underground mining produces sulfide ore. Two relatively small open pits in the oxidation zone of these orebodies are presently in operation: Area E and Mindola, both near the town of Kitwe (Fig.2) and approximately 10 km apart. Additional open pits may be developed in this area in the future. The sequence of sedimentary rocks is rather similar at both localities, a typical stratigraphic section being:

- | | |
|--------------------------|--------------------------------------|
| 1. Hangingwall argillite | 6. Schistose ore |
| 2. Porous sandstone | 7. Footwall conglomerate |
| 3. Cherty ore | 8. Ore formation: approximately 10 m |
| 4. Banded sandstone | with an average grade of 2.4% Cu. |
| 5. Low-grade argillite | |

The strata have an approximate northwest strike and dip to the southwest at 30°. The Mindola and Area E open pits follow the strike over lengths of 1.0 km and 0.5 km and have been excavated to depths of 120 m and 65 m respectively.

Libethenite has been fairly common in the upper levels of the Ore Formation in both open pits. Generally it occurred in vugs as small, but well-developed short prismatic crystals or as groups of thin, blade-shaped crystals on massive malachite and pseudomalachite, which lined the walls. When mining progressed to deeper levels the two remarkable occurrences of libethenite were encountered in the Hangingwall argillite. The host rock has since been largely removed as waste during continuing mining operations. Although libethenite is still encountered in the deeper levels, it is generally of inferior quality compared to that found in the higher levels. The Hangingwall argillite is a fine-grained medium to dark grey rock and has an average thickness of about 10 m in both pits. In the Mindola open pit the argillite is more weathered and thus considerably softer than that in the Area E open pit. The rock is composed of fine-grained quartz, microcline and oligoclase (in places weathered to kaolinite), green biotite and smaller quantities of muscovite, dolomite and anhydrite. Tourmaline, rutile and zircon are accessory minerals. Some sections contain concentrations of dolomite, usually as lenses but sometimes as bands parallel to the bedding planes. The libethenite occurs in vugs of widely different dimensions (1 to 10 cm across) scattered throughout the argillite. The origin of these vugs is still largely a matter of conjecture. As indicated above, the argillite in certain sections, notably the underground mine at Mindola and the northern part of the nearby open pit, contains lenses of dolomite. Leaching of the dolomite by acidic solutions, percolating downwards from the higher levels in the oxidation zone of the orebody, could have formed the vugs. Many of the vugs are empty; others, particularly at Mindola, are partially filled with a whitish clay-like material composed of kaolinite (60-80%) and residual rock forming minerals (20-40%) such as quartz, iron oxide, tourmaline, rutile and mica (generally weathered to vermiculite). It is possible

that this white filling is a weathering product of the argillite, surrounding the original carbonate aggregations, the feldspar being transformed into kaolinite and the other mineral constituents largely unaltered (except mica). A more detailed study of the profiles of the weathering zones in both localities would be required to provide further evidence as to the origin of these vugs.

The occurrence of libethenite in the vugs is very erratic and its crystal habit may change dramatically over short distances, both horizontally and down the dip of the argillite. In large sections of the exposed argillite the vugs are completely devoid of libethenite, but may contain some malachite, pseudomalachite and chrysocolla. The occurrence of libethenite and the other copper minerals does not seem to be related to the size of the cavity or texture of the argillite. The secondary copper minerals do appear to be restricted to a few meters of argillite, immediately above the top ore member - the Porous sandstone. The upper part of the argillite, although it may be vuggy, is notably barren.

CRYSTAL MORPHOLOGY

The libethenite crystals in both open pits show the simple basic forms: the prism m $\{110\}$, the dome e $\{011\}$, the bipyramid s $\{111\}$ and the pinacoids a $\{100\}$ and b $\{010\}$ (Fig.3). The different relative development of these forms, combined with certain parallel growth phenomena, results in the remarkable variety of crystal habits in these two localities. The typical olive-green libethenite colour is shown mainly by the very thin, acicular and blade-shaped crystals, while others are greenish black to black in hand specimens. Crystals generally are between 0.5 and 1.0 cm; the larger crystals (1.5 to 3.0 cm) shown in some of the photographs are exceedingly rare.

The most characteristic libethenite crystals in the Mindola open pit occurrence are the pseudo-octahedron and short, stubby types, elongated along the a axis. The pseudo-octahedron (Fig.4) is formed by equal

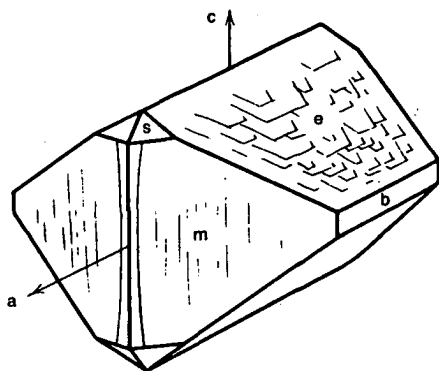


Fig.3. Drawing of a libethenite crystal from Rokana. Forms: m $\{110\}$, e $\{011\}$, s $\{111\}$, b $\{010\}$.

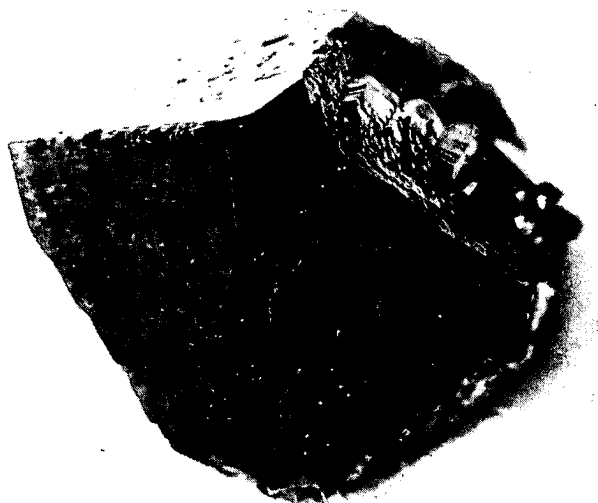


Fig.4. Pseudo-octahedral crystal of black libethenite (1.5 cm across) with pronounced stepping on e $\{011\}$ (right side). Mindola open pit.



Fig.5. Stubby black libethenite crystal (1.5 cm long) elongated along the a-axis. Mindola open pit.

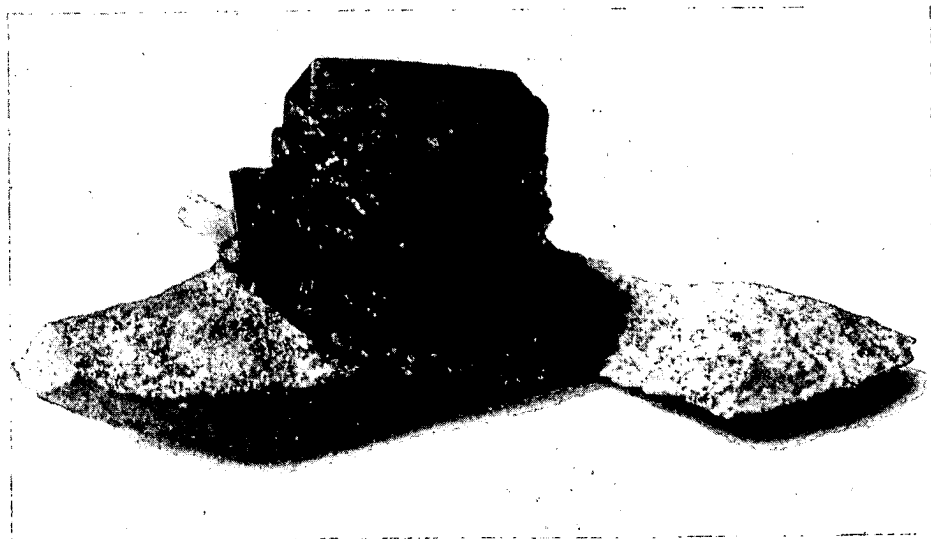


Fig.6. A 2 cm long libethenite crystal similar to that in Fig.5. Mindola open pit.



Fig.7. A "saddle" shaped libethenite crystal (2.5 cm) showing curved and stepped e {011} planes. Mindola open pit.

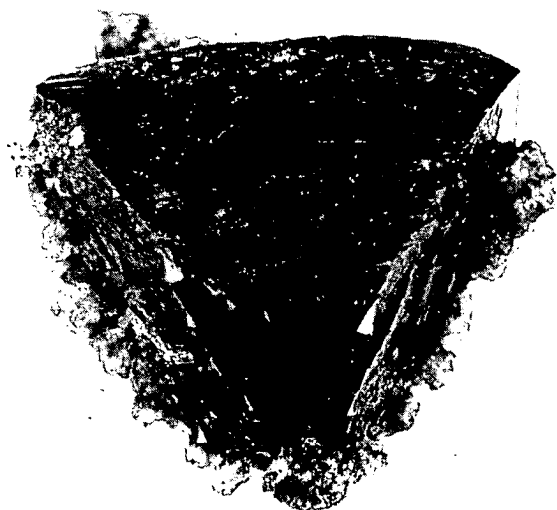


Fig.8. Large libethenite crystal (3 cm across) with curved m {110} faces. Mindola.

development of the dominant forms {011} and {110}, the apex being modified by the small, but sharp {111} plane. A characteristic feature is the slight, smooth curvature of the prism faces, which reduces the luster, even in small crystals. The {011} plane usually shows a bright reflection although in the larger crystals the surface is rough due to development of sub-parallel individuals (Fig.4). On the crystals elongated along the a axis the {011} faces dominate. Double termination by prism faces results in a "saddle" type which is restricted to the Mindola open pit. Well-developed "saddles" possess a length to width ratio of 2:1. The {011} faces are composed of sub-parallel individuals which are slightly rotated around the a axis. A fine example is the large crystal (2.5 cm long) in Fig.7.

Crystals which resemble an octahedron are found occasionally in Area E. A very large crystal (3 cm across) with prominent stepping and curvature of the prism faces is shown in Fig.8.

In 1974 some 30 by 50 meters of bedding surface of the argillite was exposed in the north end of the Mindola open pit. The rock was flaggy and closely spaced cavities were common, which frequently contained delicate sprays of acicular libethenite crystals not more than 1 cm in length (Fig.9). There was a period then, when this type was practically the only one to be found. More recently, as mining has progressed to lower levels, the acicular form has become more scattered in the argillite. Closer examination of these sprays reveals that the needles are actually blade-shaped, this becoming more pronounced with an increase in size. The blades are elongated along the c axis, usually taper near the top, and are terminated by two small, sharp dome faces. The elongated vertical plane is slightly curved and striated; it is probably not the prism {110}, but a poorly developed pinacoid {100}. Toward the base of the small blades the vertical surface becomes progressively more disrupted or deeply striated and rounded, often exhibiting a pale olive-green, mantle-like coating. A group of interconnected clusters of blades is shown in Fig.10. The larger blade-shaped crystals (Fig.11), typical of Area E, are better

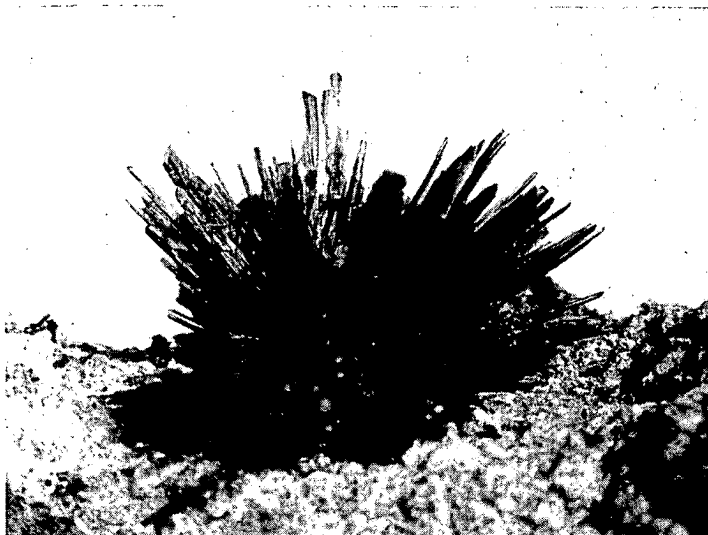


Fig.9. Spray of bladed libethenite crystals in a cavity in the argillite. Mindola.

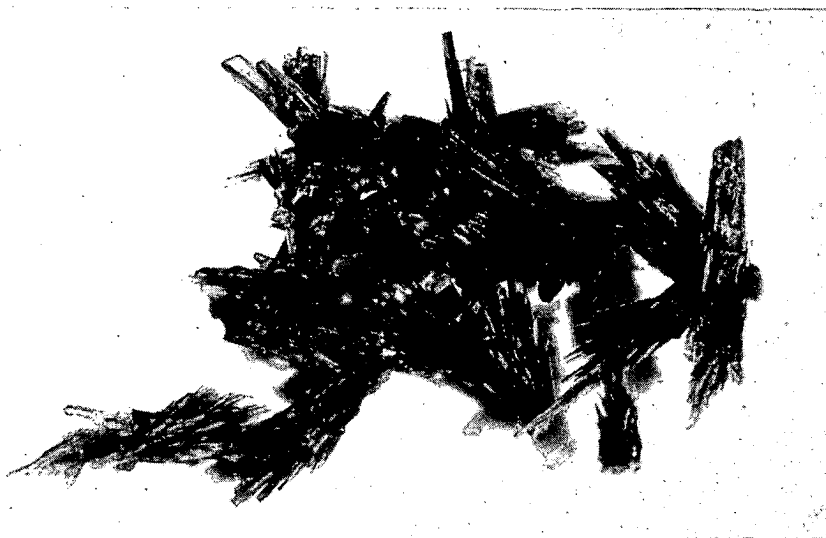


Fig.10. Interconnected cluster of minute libethenite crystal blades. Mindola open pit.

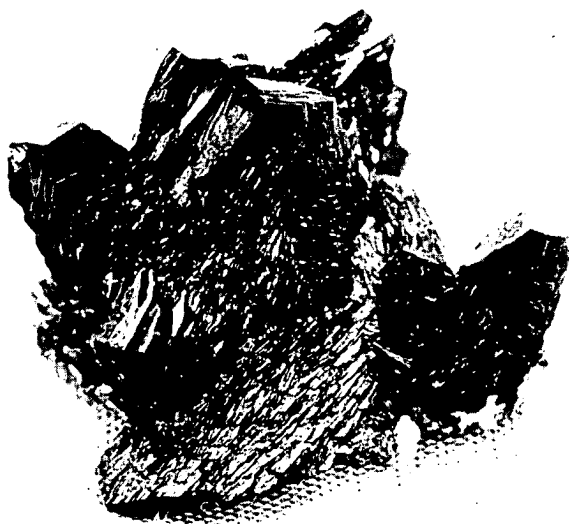


Fig.11. Blade-shaped black libethenite crystals.
Area E open pit.

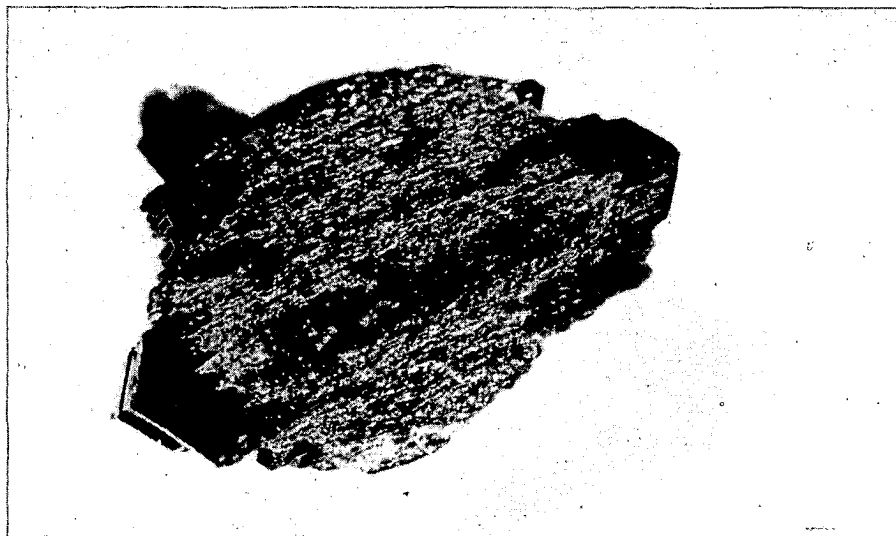


Fig.12. Doubly terminated crystal of black libethenite
with pale green central zone. Area E open pit.

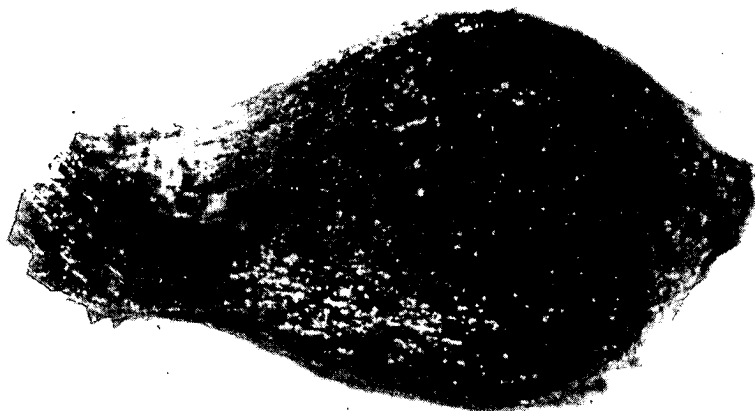


Fig.13. Pear-shaped form composed of many sub-individual crystals in parallel growth. Area E open pit.

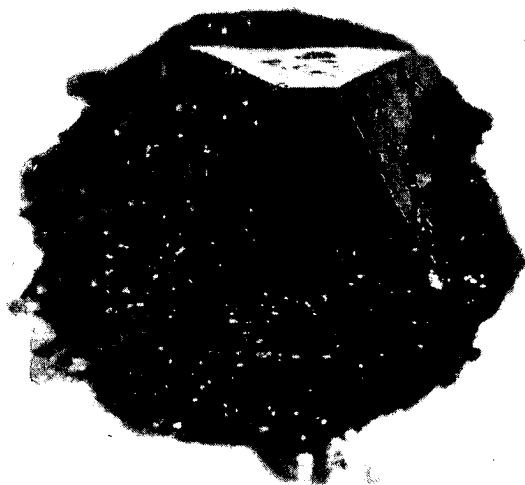


Fig.14. Black libethenite crystal protruding from a tapered base of finely packed blades. Area E open pit.

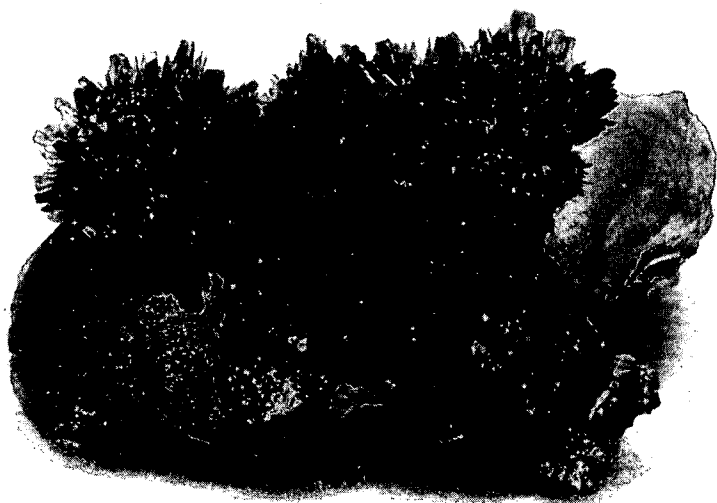


Fig.15. Malachite nodule topped by clusters of short prismatic libethenite crystals. Mindola open pit.



Fig.16. Prismatic libethenite crystal with parallel growth of sub-individuals. Area E open pit.

characterised as prismatic. In the Area E open pit double-terminated, blade-shaped or long prismatic crystals are occasionally found with a typically grooved and lighter coloured central portion (Fig.12).

An unusual pear-shaped habit (Fig.13) has been found in the Area E pit. It appears to be composed of densely packed, very thin blades, which are rotated around a common c axis, resulting in a fairly smooth surface with an almost circular cross-section. In cases where the crystal is attached to the wall of the cavity in the argillite by a flat base, the resulting shape is a cone. Similar, but smaller, more elongated and spindle-shaped crystals with small, well-developed dome faces, sometimes at both ends, are encountered more frequently in this locality. Another type consisting of a tapering base of packed blades topped by well-defined terminal forms, found in Area E, is illustrated in Fig.14.

Prismatic crystals with an almost square cross-section are found in both localities, and usually occur in clusters (Fig.15). A larger prismatic type, found in Area E, shows a very typical, deep grooving of the prism, extending into the dome faces, which gives the impression of the crystal being strongly weathered (Fig.16). The grooves are due mainly to spacing between sub-parallel individuals.

A characteristic crystal habit for Area E, which indeed is restricted to this locality, is illustrated in Fig.17. The crystals are elongated along the c axis and show well-developed, sharp dome $\{011\}$ faces. The prism faces, however, are composed of smaller individuals, which are rotated around the c axis with a sub-parallel arrangement of the $\{110\}$ faces, resulting in a very characteristic curved form (Fig.17). Reflections from the small prism faces of these sub-individuals are relatively sharp and result in a sparkling appearance of these crystals. Some of the largest specimens found had crystals of this peculiar habit. A group of 3 to 4 individuals can be as much as 5 cm across, but these are rare. The large, sharp dome faces in Fig.17 are not always

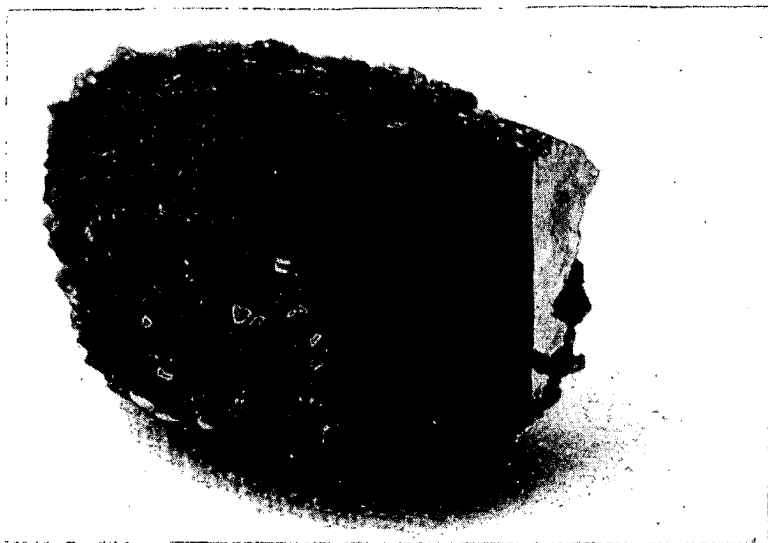


Fig.17. Crystal of black libethenite elongated along the c-axis showing many subindividuals. Area E open pit.

well-developed, and in fact are often absent; the crystals are then tapered at both ends.

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2.3. CUPRIFEROUS MICAS FROM THE CHINGOLA AREA, ZAMBIAN COPPERBELT

C.W. Notebaart

Transactions of the Institution of Mining and Metallurgy, 87,
1978, Section B, B74-78.

INTRODUCTION

Extensive deposits of low-grade micaceous ores are closely associated with the mixed oxide-sulfide ores in the Chingola area of the Zambian Copperbelt. Total reserves have been estimated at 237 000 000 tonnes at an average grade of 1.23% Cu. A hydrometallurgical treatment route for these ores has been developed [1].

The copper deposits at Chingola occur in Precambrian metasediments of the Lower Roan Group, a subdivision of the Katanga System. These metasediments are folded and form an asymmetric syncline, plunging to the west. The largest deposits of low-grade cupriferous mica ores are located in the gently sloping south limb of the main Nchanga syncline and occur in the Dolomitic Schist and the Upper and Lower Banded Sandstone formations. In the schistose areas of all formations the rock is generally soft and poorly coherent. The cupriferous micas are associated with small quantities of malachite, chrysocolla, pseudomalachite and cupriferous wad. Detailed information on the distribution of micaceous ores was given by Freeman [2].

The first study of Copperbelt cupriferous mica ores was made by Bassett [3], who investigated mica samples from the Roan Antelope mine (now Luanshya mine) and one sample from the Chingola (Nchanga) Banded Sandstone. He demonstrated convincingly that in the Roan samples the copper occurred in the intersilicate layer of a vermiculite. Bassett [3] and Jebson [4] found that the mica from Chingola behaved more like a chlorite. In connection with metallurgical testwork the present study

was initiated to obtain further information on the nature of the micas from the various ore formations at Chingola.

EXPERIMENTAL

The micas from a composite trench sample (N1) from the Upper Banded Sandstone, covering a strike length of 150 m in the Nchanga open pit at Chingola, were studied in detail. Limited comparative studies were made on seven composite grab samples from the same formation, taken such that the major part of its exposure in the open pit was represented. Also mica samples from boreholes through the various formations in both the existing open pit and the projected eastern extension were investigated.

Mica fractions were prepared by use of a Frantz magnetic separator, and subsequently purified by heavy liquid separation. All mica samples were checked microscopically for impurities prior to chemical analysis, and if necessary, further purified by hand picking. Where X-ray peak intensities were required the samples were ground to $< 44 \mu\text{m}$ and the $-44+10 \mu\text{m}$ fractions were used for analysis. In most cases orientated samples on glass slides were employed. X-ray diffractograms were obtained with a Philips diffractometer, which operated at 30 kV and 30 mA and used Ni-filtered $\text{CuK}\alpha$ radiation. For infrared analysis 0.1 mg or 0.3 mg of $-10 \mu\text{m}$ mica was pressed with 300 mg KBr in a 1 cm diameter disk and the absorption spectrum was recorded on a Perkin Elmer 457 grating spectrophotometer.

X-RAY AND CHEMICAL ANALYSIS

X-ray analysis showed that, in general, three different micaceous minerals were present, i.e. a biotite-phlogopite type mica with a basal spacing of 10 Å, an interstratified compound with a basal reflection of 12 Å, and a 14 Å type. Chemical analysis showed the 10 Å mica to be phlogopite with an iron content of 5.1% (Mg:Fe ratio 4:1) and less than

0.1% Cu. The 14 Å type proved to be a colourless chlorite and microchemical analysis showed that it contained no copper. The interstratified mica consists of regularly alternating 10 Å layers (phlogopite) and 14 Å layers (chlorite or vermiculite phase). This interstratification results in a new repeat distance of $10+14 \text{ Å} = 24 \text{ Å}$ and consequently the (00k)-reflections occur at $24/k \text{ Å}$. The observed (00k)-spacings are typically 12.03 Å, 8.40 Å, 6.02 Å, 4.93 Å, 4.14 Å, 3.49 Å, 3.03 Å, 2.71 Å, 2.47 Å and 2.03 Å. The 24 Å reflection is of very low intensity and only rarely detectable. The diffraction peaks of the interstratified mica are invariably broader than those of the associated phlogopite and chlorite. This is probably due to a certain long range disorder and/or slight deviation from a regular alternation of 10 Å and 14 Å layers.

Chemical analysis of a large number of mica samples from various locations in the Nchanga open pit and from boreholes that cover the eastern extension showed that the copper percentages varied from 0.1% Cu to 8.0% Cu with an average of 2.5% Cu. The cupriferous micas show considerable variation in colour, which ranges from yellowish green to pale brown. No simple relationship exists between the colour of the mica and its copper content. Generally, the green and yellowish green micas are high in copper (up to 8%), but some of the golden brown micas analysed 4% Cu. These colour variations are likely to be related to the oxidation state of the mica.

EXFOLIATION

Exfoliation during rapid heating to 300°C is characteristic of vermiculite and is not shown by normal chlorites. It is generally assumed that heating causes formation of water vapour in the intersilicate layer of the vermiculite, which results in a pressure build-up and subsequent buckling of the silicate layers. Exfoliation is shown by all Copperbelt cupriferous micas which, as a result, were commonly designated cupriferous vermiculite. The volumetric expansion of

Copperbelt cupriferous mica on heating is, however, in the order of 100 times less than that of a Mg-vermiculite. Some mica samples from the dolomitic sections in boreholes in the eastern extension of the Nchanga open pit did not exfoliate during heat treatment. X-ray diffraction of these samples showed the presence of phlogopite and chlorite, but no interstratified mica. All non-exfoliating micas have a very low copper content (0-0.4% Cu). These observations suggested that only the interstratified mica does exfoliate. To confirm this a bulk mica concentrate was heated to 300°C and the exfoliated and non-exfoliated mica fractions were separated by heavy liquid (tetrabromoethane-acetone mixture). Comparison of X-ray diffractograms showed that the light fraction of exfoliated mica consisted mainly of the interstratified mica, whereas phlogopite and chlorite constituted the heavy fraction. As expected, the interstratification peaks showed considerable broadening and a decrease in height after exfoliation. Chemical analysis of the exfoliated and non-exfoliated fractions showed that virtually all the copper was contained in the interstratified mica. This was further indicated by the direct relationship between total mica copper content and the abundance of the interstratified compound found in the analysis of borehole samples.

LATTICE CONTRACTION

As the 14 Å layer of the interstratified mica is formed during weathering of primary phlogopite in the oxidation zone of the orebody, the intersilicate layer of this 14 Å layer is the most likely site of the copper. Structurally, it could be similar to the 14 Å minerals chlorite or vermiculite. One of the diagnostic criteria used to distinguish between these two minerals is their behaviour during treatment with solutions that contain K^+ or NH_4^+ ions. Immersion of a vermiculite in a 1 N KCl solution results in lattice contraction from 14 Å to 10 Å (in a direction perpendicular to the layers). The hydrated bivalent ions in the intersilicate layer of the vermiculite are replaced by unhydrated K^+ ions, the radius of which is smaller than the exchanged

bivalent ions with their hydration shells. As a result lattice contraction occurs and a structure develops similar to that of phlogopite, which also has a basal spacing of 10 Å. The strong cation-hydroxyl bond in the intersilicate layer of a chlorite prevents replacement of these cations by K^+ ions and therefore the chlorite lattice does not contract. Treatment of the cupriferous interstratified mica with KCl or NH_4Cl did not result in lattice contraction; in this respect the mica is similar to a chlorite. Attempts were made to extract the material from the intersilicate layer in the 14 Å component of the interstratified mica by various techniques, i.e. boiling in 1 N KOH, treatment with citrate solutions and immersion in 1 N NH_4F . The first two methods proved to be unsuccessful. Treatment with 1 N NH_4F for one hour caused contraction of the 14 Å layer to 10 Å, corresponding to a peak shift from 12 Å (second order interstratification peak) to 10 Å. After removal of the interlayer material the mica should then respond to re-expansion by replacement of the ammonium ions by hydrated bivalent ions. Immersion of the contracted mica in solutions of $CuCl_2$ or $CaCl_2$ caused in each case a peak shift from 10 Å to the original value of 12 Å. The 12 Å peak of the re-expanded mica was invariably stronger than that of the untreated mica, probably because of the change in structure from a chlorite to a vermiculite type. A re-expanded Cu mica showed lattice contraction when treated with KCl or NH_4Cl at room temperature. The 10 Å peak of the contracted mica was not symmetrical, but tailed off towards higher d -values, which indicated partial contraction of some of the 14 Å layers. During treatment with NH_4F 60% of the copper was leached from the interstratified mica. The 14.4 Å peak of the non-cupriferous chlorite did not change in position or intensity during NH_4F treatment.

LEACHING OF MICA SAMPLES WITH SULFURIC ACID

Leaching testwork [1] on mica concentrates from the Banded Sandstone formation showed that, with 50 g/l H_2SO_4 , at ambient temperature high copper extractions could be obtained only after prolonged treatment.

Leaching rates increased considerably at elevated temperature, with a metallurgical optimum at around 70°C. X-ray analysis of mica samples, leached at constant acidity, for various times or at different acid tenors, showed considerable changes in the intensities of the interstratification peaks as leaching progressed. The intensity of the 12 Å peak showed in all cases a strong increase to a maximum followed by a decrease at higher copper extractions. The 8.01 Å and 4.93 Å peaks generally showed a reduction in intensity. Typical data are shown in Fig.1. The phlogopite and chlorite peaks did not show significant changes in intensity during leaching. All leached samples showed lattice contraction when immersed in 1 N KCl, i.e. the 12 Å peak of the interstratified mica shifted to 10 Å.

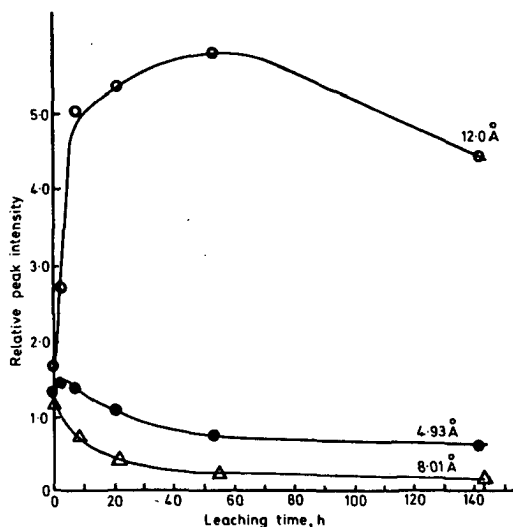


Fig.1. Variation in intensity of interstratification peaks during leaching with 50 g/l. H_2SO_4 at 25°C.

HEAT TREATMENT

Differential thermal analysis (DTA) of mica samples from the Upper Banded Sandstone and Dolomitic Schist formations (Fig.2) showed no endothermic peaks below 300°C; Mg chlorites are similar in this respect. Vermiculites have up to three well defined endothermic peaks in this region, which indicates a stepwise dehydration of the interlayer cations. The cupriferous micas showed a small endothermic peak at 310°C, which corresponds to the exfoliation temperature. This peak may correspond to the third vermiculite peak (250-300°C), which was attributed by Walker and Cole [5] to the loss of the majority of remaining water molecules in the single-sheet structure that formed part of the octahedral shell around the cation. A broad endothermic peak occurred at 600-625°C, similar to that shown by chlorites, and would correspond to the dehydroxylation of the intersilicate space in the 14 Å layers of the interstratified mica and the associated colourless chlorite. This dehydroxylation reaction starts between 400°C and 500°C. An endothermic peak, or sometimes two, closely spaced, was observed at 820°C, and is attributable to dehydroxylation of the silicate layers. At 860-880°C a small exothermic peak, due to recrystallisation to olivine, spinel and tenorite occurred [4].

Thermogravimetric analyses (TGA) by Jebson [4] (Fig.3) showed a weight loss of 1% at 300°C, which corresponds to the exfoliation temperature and the small endothermic DTA peak. A significant weight loss (3-6%) occurred between 400°C and 500°C, followed by a further 1-3% between 600°C and 700°C that corresponds to the shoulder observed on the DTA peak at 680°C. In the case of Mg chlorites the dehydroxylation reaction starts at 500-600°C, i.e. significantly higher than for the cupriferous micas.

X-ray analysis of heated mica concentrates showed that the 12 Å peak did not change in position up to 400°C, but a decrease in intensity occurred above 300°C. Between 400°C and 500°C the 14 Å layer gradually contracted to 10 Å (Fig.4). At 450°C the basal spacing is 12.6 Å, which corresponds

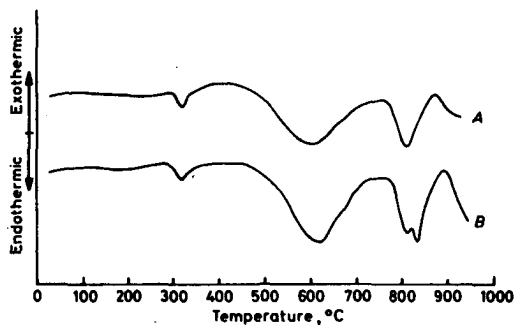


Fig.2. Differential thermal analysis curves for mica samples from the Upper Banded Sandstone (A) and Dolomitic Schist (B) formations.

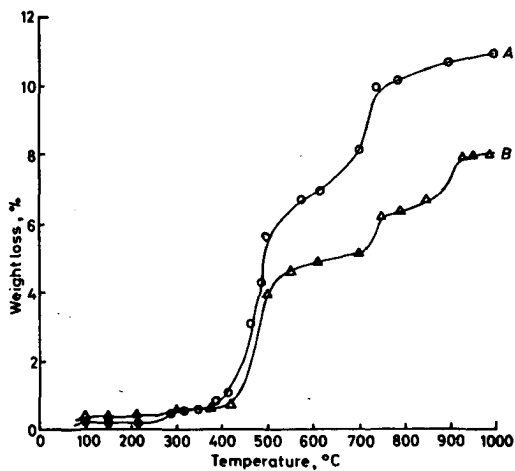


Fig.3. Thermogravimetric analysis curves for mica samples from the Dolomitic Schist (A) and Upper Banded Sandstone (B) formations.

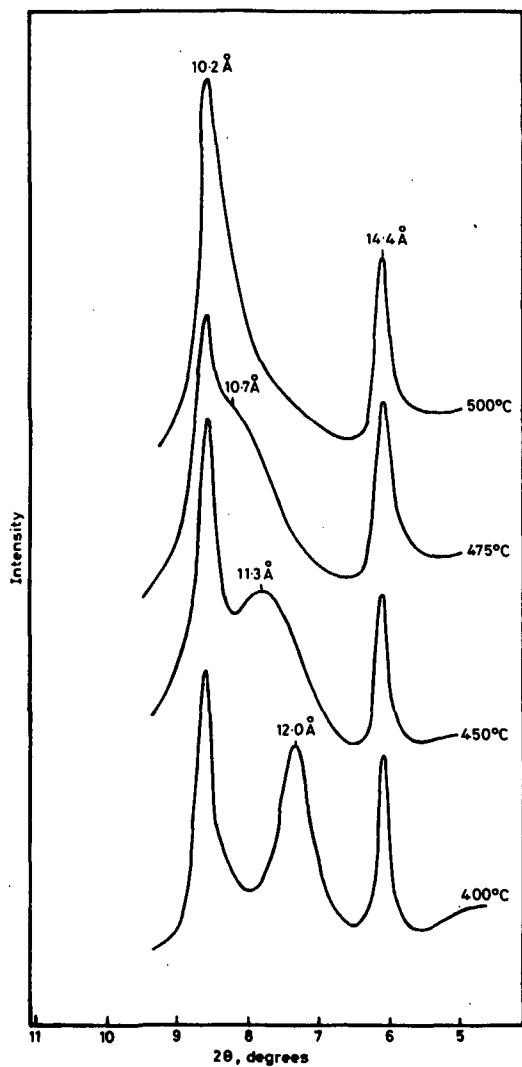


Fig. 4. Lattice contraction of interstratified mica (12.0 Å peak) during heating. (phlogopite - 10.2 Å peak). (non-cupriferous chlorite - 14.4 Å peak).

to a peak shift from 12.0 Å to 11.3 Å, and at 500°C lattice contraction is essentially complete. The 10 Å peak has now increased in intensity, but tails off to higher d-spacings, which indicates partial contraction of some of the layers; this tail persists to temperatures as high as 650°C.

The temperature range at which lattice contraction occurs corresponds to that of the dehydroxylation of the intersilicate layer (Fig.3). Dehydroxylation of chlorites occurs at higher temperatures (500-600°C) and does not result in lattice contraction, whereas vermiculites contract at lower temperatures (300-400°C). No lattice contraction of the interstratified mica heated between 300°C (exfoliation temperature) and 400°C can be induced by immersion in 1 N KCl, which indicates that no important structural changes in the 14 Å layer occur in this temperature interval.

INFRARED ANALYSIS

Infrared analysis of a mica concentrate from sample N1 showed, in the region of OH stretching vibrations, a small narrow band at 3695 cm^{-1} , due to phlogopite, a broad band at 3560 cm^{-1} and one at 3420 cm^{-1} (Fig.5). The latter two have been attributed [6] to OH groups in the brucite layer of a chlorite. The 3560 cm^{-1} band is also observed for vermiculites formed by oxidative weathering of micas [7] and has been assigned to hydroxyl groups associated with vacancies in the octahedral layer.

Heating of the Chingola mica showed that the absorption band at 3420 cm^{-1} decreased in intensity between 200°C and 300°C (Fig.5), probably because of loss of water in the intersilicate layer (exfoliation). The absorption bands at 3560 cm^{-1} decreased in intensity relative to the 3420 cm^{-1} band above 400°C and eventually disappeared at a temperature just above 500°C (Fig.5). Between 450°C and 500°C the small band at 3695 cm^{-1} and that at 685 cm^{-1} disappeared. The temperature range of

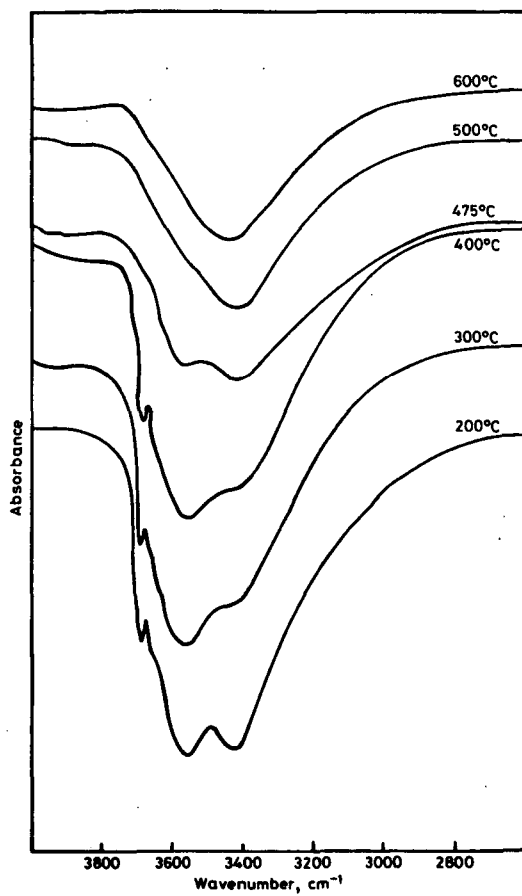


Fig.5. Infrared absorption spectrum in the region of OH stretching vibrations for a mica sample from the Upper Banded Sandstone (N1) heated to various temperatures.

400-500°C corresponds to that at which dehydroxylation of the intersilicate layer takes place (Fig.3).

For purposes of comparison a series of synthetic interstratified micas was produced by immersion of phlogopite from Phalaborwa, South Africa, for five days at 90°C in 1 N CuCl_2 , 1 N MgCl_2 and six solutions of intermediate compositions. The synthetic micas showed a 12 Å interstratification peak, which increased in intensity with increasing Cu:Mg ratio, the 6 Å peak showing an inverse relationship. All synthetic micas showed contraction after immersion in 1 N KCl, which indicates that the expanded layers are of a vermiculite type. The mica formed by leaching with 1 N MgCl_2 showed, apart from a sharp band at 3700 cm^{-1} due to phlogopite, absorptions at 3450 cm^{-1} and 3360 cm^{-1} (Fig.6). With

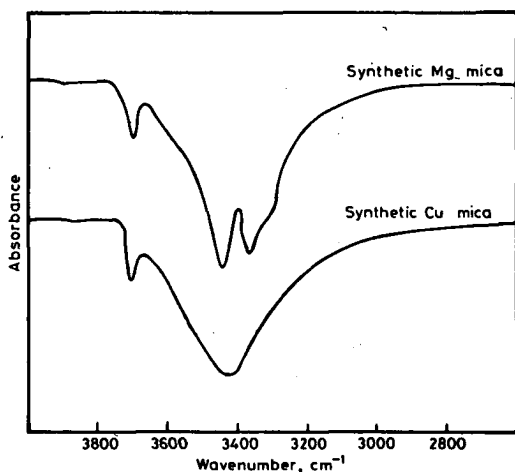


Fig.6. Infrared hydroxyl absorption of synthetic Cu- and Mg-interstratified mica.

increased Cu:Mg ratio in the aqueous solutions the band at 3360 cm^{-1} decreased in intensity but did not change in position. The pure Cu mica showed significant differences: the band at 3360 cm^{-1} had disappeared and that at 3450 cm^{-1} shifted to 3430 cm^{-1} to form one broad band (Fig.6). The naturally occurring cupriferous micas show considerable differences in the absorption spectrum. They miss the band at 3360 cm^{-1} , which is probably due to loosely bound water in the intersilicate layers of the synthetic Cu/Mg vermiculites. This band, however, is also absent in the spectrum of the synthetic pure Cu mica and probably indicates stronger coordination of the H_2O molecules to the copper. The band at 3560 cm^{-1} is absent in the synthetic micas. Substantial oxidation, which could form this vacancy band, would not, however, have taken place during the laboratory leaching of the phlogopite with $\text{CuCl}_2/\text{MgCl}_2$ solutions. It is evident that infrared analysis does not provide decisive information on the structure of the intersilicate layer of the Chingola cupriferous micas.

DISCUSSION

The experimental data show that the copper in the Chingola micas is restricted to an interstratified mica, which consists of regularly alternating $10\text{ \AA}$ layers (phlogopite) and $14\text{ \AA}$ layers. The copper is incorporated in the $14\text{ \AA}$ layer and is difficult to extract by conventional sulfuric acid leaching processes [1]. DTA and TGA and the failure to induce lattice contraction by K^+ saturation or heating to 300°C show that the $14\text{ \AA}$ layer has predominantly the characteristics of a chlorite, with the copper octahedrally coordinated by OH groups. It was found, however, that heating of the interstratified mica to $400\text{--}500^\circ\text{C}$ caused lattice contraction to $10\text{ \AA}$; this is not shown by Mg chlorites. This probably reflects differences in bond strength between Cu-OH and the Mg-OH in the brucite layer. If the Cu-OH bond is broken, either by immersion in NH_4F or after prolonged leaching with H_2SO_4 , lattice contraction can be induced.

Exfoliation on heating to 300°C points to the presence of some hydration water in the intersilicate layer of the 14 Å layer, and thus to an intergradient structure. The possibility of a complete series between copper vermiculite (Cu-H₂O bonding), which occurs at Roan Antelope mine, and copper chlorite (Cu-OH bonding) at Chingola (Nchanga) was considered by Bassett [3]. An apparent intermediate type is his sample RA5, in which 14 Å micas occur but no interstratified compounds. DTA showed distinct endothermic peaks between 100°C and 200°C, which indicated vermiculite. Yet potassium saturation caused only a reduction in intensity of the 14 Å peak, which indicated chlorite. This does not necessarily imply an intergradient structure; vermiculite and chlorite may occur separately and the latter need not be cupriferous. This is the case in Chingola, where non-cupriferous chlorite occurs frequently interleaved with the cupriferous mica. Judging from Bassett's X-ray data [3], this non-cupriferous mica (14 Å peak) also occurred in his sample from the Nchanga Banded Sandstone, but was not recognized as such. Study of mica samples from different locations in the various formations in the Chingola ore deposit showed no types similar to those encountered at Roan, which all gave the characteristic DTA peaks of vermiculite in the range 100-300°C. The Chingola mica is therefore considered to be basically different from the Roan copper vermiculites, i.e. the intersilicate space is predominantly occupied by the octahedral Cu-OH layer, although a small amount of hydration water is present. The Chingola mica should thus be termed an interstratified phlogopite-cupriferous chlorite. This cupriferous chlorite can be converted into a Cu vermiculite, of the Roan type, by first breaking the Cu-OH bond by treatment with NH₄F and then re-expansion in a CuCl₂ solution. Bassett [3] mentioned that if a copper mica is prepared by leaching of biotite in a pure CuCl₂ solution no lattice contraction takes place during treatment with KCl, and suggested that Mg ions should be present to allow K⁺ ions to enter the interlayer space. Bassett's synthetic mica would in this respect be similar to the Chingola cupriferous mica. His data, however, show that, when this mica is heated, lattice contraction occurs at a temperature of < 300°C. None of the Chingola micas contracts below 400°C. The micas synthesized in the

present study, even the pure Cu mica, all showed lattice contraction after immersion in 1 N KCl. The Chingola interstratified mica thus differs from any synthetic copper mica produced so far. The occurrence of the micas suggests that they are formed during weathering conditions, as is the case for the Roan Cu vermiculites. Possibly, differences in Eh, pH and solution composition may be factors that affect copper coordination in the interlayer space.

Cupriferous hydrobiotite from Ukaparinga, Australia, has been described by Henley and Brown [8]. This mica consists of randomly interstratified biotite and 14 Å layers. Potassium saturation and heating to 200°C also do not result in lattice contraction. The DTA curves, however, show distinct endothermic vermiculite peaks at 100°C and 220°C. The Australian cupriferous hydrobiotite is thus different from the Chingola micas, but more similar to the Roan Antelope cupriferous vermiculite.

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2.4. METALLURGICAL TREATMENT OF CHINGOLA CUPRIFEROUS MICA ORES

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INTRODUCTION

Cupriferous mica ores were identified at Chingola in the early 1950's. In the years following it became evident that vast reserves of low-grade micaceous ores, in which the majority of the copper is incorporated in a mica-type structure, existed in the Chingola area. Owing to their poor response to normal methods of metallurgical treatment and to the difficulties of visual recognition, the full significance of these deposits was not appreciated until after 1954, when mining of the Nchanga open pit commenced. Other deposits of cupriferous mica, although not so extensive as those at Chingola, were found in various parts of the Copperbelt: at Luanshya (Roan Antelope [1]), Rokana, Baluba, Konkola (Fitwaola) and Chambishi. In the upper levels of the oxidation zones of these orebodies predominantly micaceous ores occur; with increasing depth these grade through mixtures with malachite, pseudomalachite, chrysocolla and cuprite down to sulfide ore. In most cases the depth of the oxidation zone ranges from 30 to 70 m and the tonnage of actual micaceous ore is very limited.

The cupriferous mica deposits at Chingola occur in separate stratigraphic units adjacent to normal mixed oxide-sulfide orebodies and extend down to depths in excess of 300 m. The position of the three formations - the *Dolomitic Schist*, the *Upper Banded Sandstone* and the *Lower Banded Sandstone* - in relation to the conventional orebodies is shown in Table 1, which gives the stratigraphic column at Chingola.

A typical section across the Nchanga open pit (Fig.1) shows how the Dolomitic Schist must be removed as overburden before stripping the conventional ores in the lower part of the Upper Banded Shale and the Feldspathic Quartzite, which constitute the Nchanga upper orebody. This, in turn, leaves the Upper Banded Sandstone open with only the thin Pink Quartzite (conventional ore) separating it from the Lower Banded Sandstone. These three formations have together been estimated to contain some 237 000 000 t of ore with an average copper content of 1.23%.

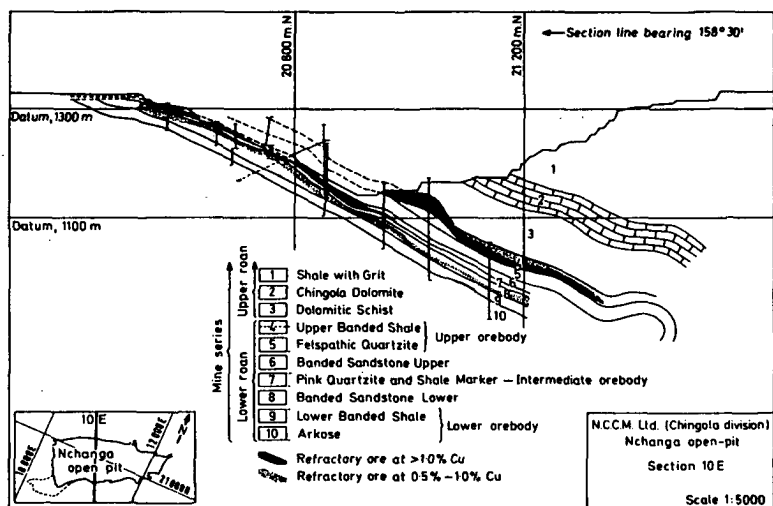


Fig.1. Section across the Nchanga open pit.

Much of the Dolomitic Schist has now been removed and stockpiled. A large part of the Upper Banded Sandstone will also be removed and set aside during the next few years to recover the Pink Quartzite. It is evident, therefore, that a large part of the micaceous ore could be delivered to a treatment plant for little more than the transport cost.

MICACEOUS OREBODIES

The *Dolomitic Schist* formation consists of quartz-mica schists and micaceous dolomites. The thickness varies from 20 to 30 m and the copper content ranges between trace and 2.4%, but considerable tonnages of this ore assay at more than 1.0% Cu. In the *Upper Banded Sandstone* micaceous sandstones, quartz-mica schists with occasional dolomite-phlogopite rocks occur. The formation becomes more dolomitic with depth. The copper content of the various rock types is in the range 0.5 - 1.5%. The *Lower Banded Sandstone* is separated from the Upper Banded Sandstone by the Pink Quartzite and Shale Marker and consists of greyish brown, medium-grained micaceous sandstone, interbedded with siltstone and mica-rich seams. The thickness of the Lower Banded Sandstone formation varies from 10 to 50 m (average about 20 m). The copper content is between 0.4% and 0.8%.

MINERALOGY

Mineralogical analysis of a large number of mica samples from different localities in the Chingola area showed the presence of three different types: a cupriferous interstratified mica, a colourless non-cupriferous chlorite, and phlogopite. The colour of the cupriferous interstratified mica varies from pale brown to yellowish green. In general, the greenish micas have the highest copper content (up to 7%), but some of the golden brown micas are also rich in copper (up to 4%). The micaceous ores

System	Series	Group	Formation	Member	Thickness, m	Lithological		
Katanga	Kundelungu	Lower Kundelungu	Superficial deposits	—	0—50	Clay, mud, sand and soil		
			Calcareous sandstone	—	?	Calcareous, sandstone and shale		
			Kakontwe limestone	—	?	Limestone, dolomite and calcareous shales		
			Grand tillite	—	?	Tillite, shales and conglomerate		
		Mwashia	—	—	?	Calcareous phyllite		
			Argillite	—	?	Dominantly argillaceous with arenites and dolomites	Intruded by gabbro and diorite of unknown age	
	Upper Roan	Dolomite	—	0—60	White crystalline massive dolomite			
		Dolomitic Schist	—	0—40	Scapolitic dolomitic schist arenites and dolomites			
	Mine	Lower Roan	Upper Banded Shale	—	6—37	Pale grey banded shale, dolomitic in part		
			Feldspathic Quartzite	—	15—37	Beige to white massive feldspathic quartzites		
			Upper BSS	15—30	Quartz mica schist, dolomitic in part			
			Banded Sandstone	Pink Quartzite	5—6	Pink to brown well sorted feldspathic quartzite		
			Shale Marker	0.5—2	Pale grey argillite			
			Lower BSS	12—30	Quartz sericite schist			
			Chert Marker	0—6	Iron stained cherty quartzite			
			Lr. Banded Shale	12—27	Blue grey carbonaceous banded shale			
			Transition	0—15	Quartzose phyllites			
			Arkose	0—150	Grey to pink coarse arkose			
			Basal Conglomerate	0—50	Angular to sub-rounded boulders up to 2 m in diameter			
			Unconformity					
Pre-Katanga			Muva	Quartzite and quartz—chlorite schist				
Assumed unconformity								
Granitic rocks								
Assumed intrusive relationship								
	Lufubu	Kafue garnetiferous chlorite schist						

Table 1. Stratigraphic column at Chingola.

contain small quantities of conventional oxide copper minerals: malachite, pseudomalachite and chrysocolla. In some areas these minerals contribute significantly to the total copper content.

The cupriferous micas have been the subject of considerable study in an attempt to improve understanding of the nature of the copper in the mica structure and to point the way to optimum extraction methods. Bassett [1] carried out the first detailed examination of the cupriferous micas from the Zambian Copperbelt. He found that in samples from the Roan Antelope mine the copper occurred in vermiculite and in interstratified biotite-vermiculite. Bassett [1] also studied a single sample from the Chingola Banded Sandstone, which showed distinct chlorite characteristics. This was later confirmed by Jebson [4].

Extensive investigations [5] of cupriferous micas from various formations at Chingola has confirmed Bassett's findings. It appeared that the copper occurred exclusively in an interstratified mica, which consisted of regularly alternating 10 Å layers (phlogopite) and 14 Å layers. This interstratification could be deduced from the positions of the various X-ray diffraction peaks. A regular sequence of 10 Å layers and 14 Å layers results in a new basic repeat distance of 24 Å. The basal reflections should now occur at d-values of $24/k$ Å ($k = 1, 2, 3, \dots$), i.e. at 24 Å, 12 Å, 8 Å, 6 Å, 4.8 Å, etc. The observed d-spacings occur close to these values.

The cupriferous interstratified mica exfoliates when heated rapidly to 300°C. Exfoliation experiments in combination with X-ray analysis showed that the interstratified mica exfoliated but not the associated chlorite and phlogopite. Thus, it was possible to separate the exfoliated interstratified mica from the other mica types by heavy liquids. Chemical analysis of the two mica fractions showed that the copper occurs only in the interstratified mica, probably in the 14 Å layer, which could be a vermiculite, chlorite or intergradient chlorite-vermiculite. Exfoliation is a characteristic of vermiculite and the Copperbelt mica was therefore generally referred to as a cupriferous

vermiculite. Exfoliation, however, is the only property that the 14 Å layer has in common with a normal vermiculite. All other experimental data, such as differential thermal analysis, the failure to induce lattice contraction by potassium saturation and its low cation-exchange capacity, pointed more towards a chlorite. During heating, however, lattice contraction to 10 Å occurred at 500°C, and in this respect the 14 Å layer differs from a normal chlorite.

The combined evidence indicates that the 14 Å layer is predominantly chloritic, i.e. the copper is coordinated to hydroxyl groups. Some loosely bound water appears to be present and causes exfoliation during heating. The Chingola copper-bearing mica can thus be termed an interstratified phlogopite-cupriferous chlorite.

The cupriferous mica was formed during weathering of primary phlogopite. Potassium ions in half of the phlogopite layers were exchanged by hydrated bivalent ions, such as magnesium and copper from descending solutions, causing layer expansion from 10 Å to 14 Å.

TREATMENT OF MICACEOUS ORES FOR EXTRACTION OF COPPER

In view of the large tonnage of the micaceous ores at Chingola, and the low cost of recovery of these ores to a treatment plant, it has long been evident that the only bar to successful economic exploitation of the ores was the lack of a suitable treatment and extraction method. Over the past 20 years treatment of these ores has been the subject of a large number of investigations and many different processes have been examined.

As was noted above, the ores consist primarily of a weathered and highly friable schist, together with irregular and minor patches of harder sandstone or dolomitic rock. Washing on shaking screens followed by

cyclone separation at about 300 μm is sufficient to disintegrate most of the mica aggregates. When treated in this way, between 70% and 90% of the ore reports in the undersize fraction; this undersize fraction contains almost all the cupriferous mica in the ore, the copper in the oversize fraction being mainly a mixture of the more common oxide copper minerals.

Owing to its fine sizing, comparatively little grinding energy is required to prepare the ore for treatment by agitation leaching, or by flotation; but the fine sizing would not be beneficial for treatment by any percolation leaching method.

Recovery of the copper by pyrometallurgical means was generally ruled out. Even if the pure cupriferous mica could be separated from the ore, its grade on an overall basis would be unlikely to exceed 5% Cu. At this grade the concentrate could not bear the cost of smelting, although it might be able to bear the cost of heating to a somewhat lower temperature. Separation of cupriferous mica from the other micas present would, in any case, be almost impossible. Some concentration has been achieved in the laboratory by dry magnetic separation, but this could hardly be expected to form the basis of a commercial process.

Treatment of a mica concentrate by a smelting route has therefore been largely discounted. With the exception of the TORCO process, the development of which was primarily aimed at treating the Chingola micaceous ores, all extraction routes examined have involved winning of copper from the mica by leaching. Leaching of the micaceous ores has not been particularly attractive, however, owing to a number of adverse factors affecting either the capital or operating cost of a leaching operation.

High-impurity dissolution

All acid-leaching methods extract, in addition to copper, significant quantities of magnesium, iron and aluminium from the mica. Until the

Conditions, g/l H ₂ SO ₄	Temp., °C	Time, h	Cu extrac- tion, %	Mg/Cu	Fe/Cu	Al/Cu	Acid consumption, kg/t
<i>Sample A (Cu, 1.85%; Mg, 6.0%; Fe, 4.0%; Al, 5.8%; Mn, 0.27%; Ca, 0.65%)</i>							
5	30	8	51	0.15	0.13	0.09	26
25	30	8	61	0.27	0.17	0.10	29
10	50	6	70	0.29	0.15	0.11	40
50	50	6	79	0.33	0.19	0.32	67
<i>Sample B (Cu, 1.05%; Mg, 5.3%; Fe, 4.0%; Al, 5.5%; Mn, 0.40%; Ca, 0.15%)</i>							
5	30	8	35	0.08	0.10	0.12	2.2
25	30	8	45	0.08	0.12	0.11	4.5
10	50	8	62	0.09	0.16	0.16	12.4
50	50	6	77	0.14	0.43	0.19	15.5
<i>Sample C (Cu, 2.40%; Mg, 6.2%; Fe, 3.3%; Al, 7.1%; Mn, 0.25%; Ca, 0.70%)</i>							
5	30	8	62	0.12	0.05	0.08	16.4
25	30	8	71	0.14	0.15	0.11	25.7
10	50	6	79	0.17	0.13	0.12	33.0
50	50	6	87	0.30	0.39	0.25	68.7

Table 2. Sulfuric acid leaching of Chingola micaceous ores.

development of solvent extraction methods for copper solution treatment, these impurities rendered subsequent treatment both difficult and expensive.

High acid consumption

The iron, magnesium and aluminium dissolved from the mica all consume acid in acid-leaching processes, with consequent high acid cost (unless such acid can be regenerated). Some areas of the Dolomitic Schist also

contain significant quantities of dolomite, which increase the gangue acid consumption yet further.

Slow reaction rate

Except under conditions that yielded total disintegration of the mica, the leaching rate of the mica was particularly slow in comparison with other oxide copper minerals. This can be attributed to the strength of the Cu-OH bond in the 14 Å layer of the mica. At ambient temperatures with 5% sulfuric acid, very many hours of contact time were required to obtain copper extractions in excess of 80%.

Laboratory agitation leach test results on a number of samples of micaceous ore, at 30°C and 50°C, are given in Table 2. To examine the leaching of the pure cupriferous mica more closely a sample (200 g) was magnetically separated from the -150+44 µm fraction of sample B (see Table 2) - the leaching test results are given in Table 3. It is apparent that for copper extractions of up to 80 - 85% the gangue acid consumption per gram of copper extracted does not vary greatly. If either acid concentration, leaching time or leaching temperature, however, is increased to give extractions in excess of 85%, the acid consumption rises very rapidly. It is postulated that this rapid rise of gangue acid consumption reflects the partial breakdown of the mica structure.

It was evident that acceptable leach extractions could be obtained either by extended leaching times, or by high acid tenor leaching solutions, or by elevated temperatures, or by a combination of all three. It was further evident that the acid consumption by gangue was primarily a function of the copper extraction percentage, irrespective of the leaching conditions used to obtain that extraction (see Fig.2) - this was particularly so for low extractions. At copper extractions in excess of 75% major lattice breakdown has taken place and the acid consumption follows copper extraction less closely.

Acid concentration, g/l H ₂ SO ₄		5								20								50							
Temperature, °C	Time, h	Cu	Co	Mg	Al	Fe	Mn	Ca	g Acid/ g Cu	Cu	Co	Mg	Al	Fe	Mn	Ca	g Acid/ g Cu	Cu	Co	Mg	Al	Fe	Mn	Ca	g Acid/ g Cu
25	1	8.8	1.6	0.17	0.04	0.5	4.5	8.7	3.1	8.6	3.8	0.1	0.3	1.2	8.6	11.1	4.1	14.6	4.3	0.2	0.4	1.1	9.5	6.3	3.9
	2.7	14.2	1.6	0.2	0.3	0.7	5.7	11.4	3.2	20.2	4.2	0.3	0.4	1.4	13.4	16.7	3.5	22.7	4.4	0.2	0.6	1.4	9.6	12.6	3.4
	7.3	26.8	3.1	0.3	0.5	1.2	11.4	13.3	3.1	29.6	7.0	0.4	0.9	2.1	18.6	16.8	3.3	39.7	7.1	1.0	1.8	3.0	19.3	16.9	4.6
	19.7	54.4	6.1	0.7	0.9	2.5	19.0	19.0	3.2	53.0	9.9	0.9	1.5	3.2	27.8	25.3	3.5	57.1	9.7	1.2	2.1	3.9	27.5	17.6	4.1
	53.1	70.3	6.3	1.1	1.4	2.9	20.5	33.0	3.4	78.2	15.4	1.3	2.6	5.1	40.9	17.5	3.8	81.3	13.8	1.4	2.3	6.0	36.8	33.8	4.1
	143.1	86.5	14.3	2.1	2.3	4.6	39.0	35.2	3.8	90.7	16.4	3.5	4.8	11.4	57.8	26.7	5.6	91.2	21.4	7.7	8.1	17.4	71.1	41.8	9.0
45	1	23.9	3.3	0.2	0.4	1.2	10.5	22.2	2.9	33.8	5.9	0.5	0.9	1.8	15.0	11.1	3.5	41.2	8.3	1.6	2.3	4.1	27.9	57.1	5.3
	2.7	44.7	6.3	0.5	0.8	2.1	20.0	21.1	3.1	55.0	9.2	1.3	2.0	3.9	29.3	22.2	4.5	61.1	13.8	2.7	3.7	7.2	38.1	44.4	5.9
	7.3	64.0	9.8	1.2	1.6	3.2	28.6	66.7	3.7	76.2	12.3	1.8	2.9	6.2	41.9	8.6	4.6	88.2	19.0	4.3	6.0	8.7	62.5	50.0	6.2
	19.7	71.4	10.5	1.3	1.9	3.8	32.4	55.6	3.6	90.6	20.7	4.4	7.0	14.7	57.1	45.5	7.4	99.0	26.1	12.2	11.1	26.8	82.4	40.0	11.8
85	0.37	48.6	6.1	1.3	1.4	3.0	23.8	54.3	4.3	68.4	12.4	4.3	4.4	10.7	46.5	36.4	6.8	82.0	19.7	11.7	9.7	19.7	69.1	40.0	10.6
	1	72.2	12.4	2.8	3.3	5.5	47.8	39.8	5.3	89.0	17.3	5.4	5.0	19.6	65.1	4.6	9.3	99.0	31.3	37.4	32.5	37.0	83.3	40.0	29.4
	2.7	89.1	18.0	4.2	4.6	10.2	62.2	13.8	6.0	92.5	21.4	6.8	8.0	21.6	64.2	14.8	9.5	99.0	38.6	31.8	25.9	45.5	89.4	17.8	24.7
	7.3	94.1	22.0	7.0	7.1	14.1	84.4	11.7	8.3	95.2	36.7	24.8	22.5	38.3	93.3	12.9	24.7	99.0	50.0	44.2	30.8	54.5	91.3	28.6	34.1
	19.7	98.5	32.2	10.9	11.3	18.0	88.9	10.1	11.2	99.9	45.9	33.8	32.7	47.6	98.3	8.9	30.1	99.0	55.2	54.8	38.9	63.5	92.0	15.8	39.4

Table 3. Elemental extractions and acid consumption for pure micas.

Additional grinding had little effect on acid-leaching rates: the reason for this has not yet been confirmed, but it is probably due to selective grinding of the non-mica particles.

The use of high-acid tenors of the leaching solutions was not particularly favoured, due to the problems involved in recovery of the copper from such solutions without neutralizing the acid, the cost of which would be prohibitive. The recent development of copper solvent extraction reagents LIX 70 [6] and P-1 [7] which are capable of extracting copper efficiently from such high-acid solutions, has gone part of the way towards facilitating their use. Problems still exist, however, in the stripping of such solutions without the use of an acid tenor in strip solution too high to be altogether suitable as advance electrolyte for copper electrowinning.

Considerable attention was therefore given to the two alternative methods for obtaining adequate copper extraction. If high temperatures were used, reaction time was short (a matter of a few hours), and the process lent itself to agitation leaching with countercurrent thickening for solid-liquid separation. Owing to the long retention time and consequently high capital cost involved, agitation leaching was not favoured for extraction at ambient temperatures. It appeared that the only leaching method that could compete at ambient temperature was percolation leaching, either in vats or in a shallow heap.

Percolation leaching was studied in some detail and a number of drawbacks emerged. First, the percolation rate through the micaceous ores was generally rather low - of the order of $50 \text{ l/m}^2/\text{hr}$. Secondly, the percolation rate appeared to be highly variable and difficult to predict, even for samples from the same ore source; the method of loading percolation columns or vats also had a major effect on percolation rate, probably due to the plate-like nature of the mica particles. Thirdly, channelling and overleaching of parts of the bed took place before the reaction was complete in other parts. As a result, higher gangue acid consumptions and impurity dissolution were

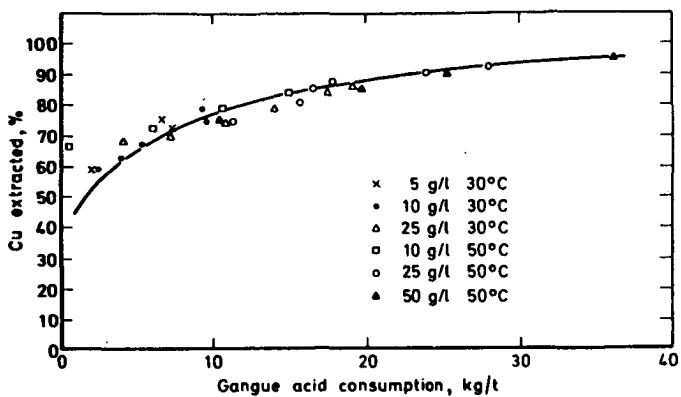


Fig.2. Typical relationship between copper extraction and gangue acid consumption for micaceous ore.

	Mass %	Grade % Cu	Distribution % Cu
Slimes	10.84	2.40	9.6
Concentrate	51.82	4.44	85.3
Tailings	37.34	0.37	5.1
Feed	100.00	2.70	100.0

conditions: pH=7.5, collector-cocoamine: 125 g/t
4 stages, flot. time: 4.5 min.

Table 4. Flotation of Dolomitic Schist.

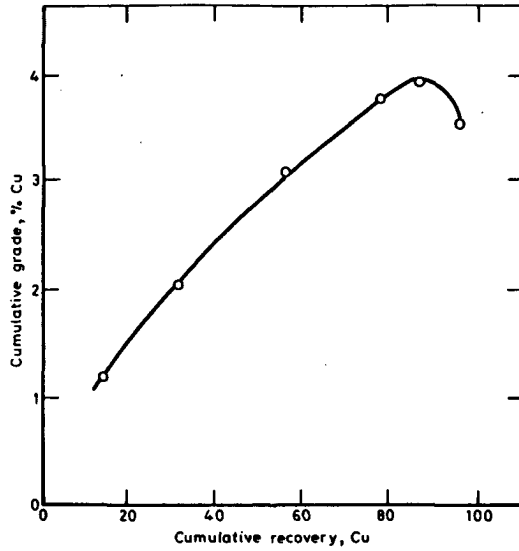


Fig.3. Grade-recovery relationship for mica flotation.

experienced than would have accompanied an equivalent copper extraction in agitation leaching. It therefore became evident that hot dilute acid leaching was probably the most economic direct leaching method. Although the operating cost incurred in heating the pulp was high, the small size of the leaching plant required and the improved control of the leaching reaction with the use of agitation leaching swung the balance in favour of this method of operation.

ALTERNATIVES TO DIRECT LEACHING OF MICACEOUS ORES

The main drawbacks to direct leaching of micaceous ores are the high acid consumption per unit of copper recovered and, until the recent development of solvent extraction for upgrading and purifying copper solutions, the impurities, magnesium, iron and aluminium, which dissolved together with the copper. Three main alternative methods of extraction have been examined.

TORCO Process

The TORCO process was originally developed with a view to treatment of the Chingola micaceous ores. At the time significant tonnages of micaceous ore grading $> 2\%$ Cu had been confirmed. Much of the pilot testwork on the TORCO process was carried out on this ore in the small pilot unit at Chingola [8]. The ore was shown to be totally amenable to the TORCO process: elemental copper concentrates grading $> 60\%$ were produced at recoveries in excess of 85%.

The TORCO process was subsequently tested on a semi-commercial scale (500 t/day) at the Rokana mine in Kitwe, using ore from Mindola [9]. This ore, although containing significant proportions of cupriferous mica, also contained malachite, azurite, cuprite and cupriferous wad and assayed 3.5 - 5.0% Cu. This TORCO plant proved a technical and economic success.

Fuel, however, is a major part of the cost of the TORCO process, and fuel prices in Zambia have escalated acutely over the past 10 years. When the TORCO process was first developed, high-grade coal was being delivered from Wankie colliery to the Zambian Copperbelt at K5/t [10]. The present delivered cost of rather lower calorific value coal from Maamba colliery is some K30/t. Similarly, heavy fuel oil has increased in price from K19/t to K68/t during the past 18 months. Other operating costs have also risen, and, despite the increase in the selling price of

copper, the TORCO process could not now be commercially successful on the Chingola micaceous ores.

Preconcentration of Mica by Flotation

Although it was realized that much of the gangue acid consumption was due to the mica, it was believed that some benefit might be obtained from preconcentration by flotation. The capital cost of the leaching and solid-liquid separation sections of an agitation leaching plant would be largely a function of the tonnage of material treated. Rejection of a significant tonnage of the material would therefore reduce this capital cost. Moreover, a number of areas of the Upper Dolomitic Schist were known to be contaminated with dolomite, increasing the gangue acid consumption. There were, therefore, potential benefits from preconcentration.

Exploratory tests demonstrated the feasibility of flotation of the various micas, although the presence of slimes was generally detrimental. A number of collectors, both cationic and anionic, were examined. The most promising of these were the amines of vegetable origin, particularly cocoamine. Table 4 presents the results of a typical laboratory flotation test with cocoamine acetate as the collector on a sample of the upper Dolomitic Schist.

It was essential to remove a proportion of the fine slimes prior to flotation. Flotation of the bulk ore resulted in lower concentrate grades and lower recoveries. Rejection of approximately 10% weight in slimes, containing most of the $-20\text{ }\mu\text{m}$ fraction, yielded the optimum results. Owing to the comparatively fast flotation of the noncopper-bearing micas, grades of the initial concentrate fractions were always low, giving rise to the type of grade-recovery curve shown in Fig.3.

Despite the comparative success with the micaceous schist, where almost all the copper is present as cupriferous mica, it became apparent, when

a number of other samples were examined, that preconcentration by flotation could only provide a partial solution. The disadvantages were rejection of at least 10% of the contained copper in a slime fraction and poor recovery of conventional oxide minerals. In many places small quantities of malachite, pseudomalachite and chrysocolla occur within the micaceous ores. Testwork showed that, in general, flotation of these minerals with the cocoamine acetate was very slow and recoveries were poor. This had the effect of reducing the overall recovery of much of the available ore by 10-20%.

The copper losses incurred in pre-flotation were generally, therefore, too high to compensate for the reduction in tonnage for leaching, the rejection of dolomite leading to lower acid consumption. Parts of the micaceous schist may, however, contain sufficient dolomite for pre-flotation to be an attractive step prior to leaching.

Exfoliation Prior to Leaching

The acid consumption in leaching the cupriferous micas has been shown to be primarily due to the need to break down the mica to contact the copper with the leaching agent (sulfuric acid). It has also been shown that the copper-bearing mica exfoliates on heating rapidly to 300-400°C. It was originally believed that this exfoliation might facilitate copper extraction and reduce the acid consumption in leaching.

Tests were therefore carried out in which the mica was leached with sulfuric acid after exfoliation. Little change was observed in the leaching characteristics of the material as a result of the exfoliation. The mineralogical examinations had shown that exfoliation at temperatures up to 500°C did not result in breaking the copper-hydroxyl bond; it may be concluded that the leaching rate is controlled primarily by structural properties rather than by diffusion.

A number of other, less important, alternatives were examined. Ammonia leaching was found to be ineffective except on particle sizes of less

than about 20 μm . Oxidation pressure leaching converts iron and aluminium to either oxide or basic sulfate, thereby reducing the acid consumption; unfortunately, the decreased acid consumption due to iron and aluminium is accompanied by an increased magnesium extraction. Magnetic separation was also considered. The cupriferous mica could be separated by high intensity dry magnetic separation, but the overall copper recovery was not particularly good, due to the presence of small, but significant, quantities of other oxide copper minerals, which reported to the non-magnetic product.

FLWSHEET OF THE PROPOSED DIRECT LEACHING PROCESS

The main process step in the treatment of the Chingola micaceous ores has been largely confirmed as a hot (60-70°C) agitation acid leach, producing solution for concentration and purification by solvent extraction. The pregnant solution to solvent extraction is expected to have the following compositional range, depending on the the rate of raffinate recirculation: Cu 2-4 g/l; Mg 1-3 g/l; Al 0.5-1.5 g/l; Fe 0.8-3.0 g/l; and Mn 0.2-1.5 g/l.

Two methods of preconcentration are still under consideration. The first is the separation of a coarse fraction by wet screening at 1 cm after coarse crushing. It has been shown that this fraction contains little cupriferous mica but most of the conventional oxide copper minerals (malachite, pseudomalachite, chrysocolla, azurite). This fraction could be treated by the present flotation plant, followed by leaching in the new Tailings Leach Plant [11,12]. The second method is flotation of mica from the Dolomitic Schist.

If preconcentration is excluded, the final flowsheet is envisaged to be as in Fig.4. The main process steps involved are: crushing, both primary and secondary; washing on washing screens and in trommels; grinding of the small oversize fraction; pre-leach thickening; primary leach in pachucas to neutralize acid from secondary leach to produce solution at pH 2-2.5 for copper solvent extraction; hot secondary leach (acid

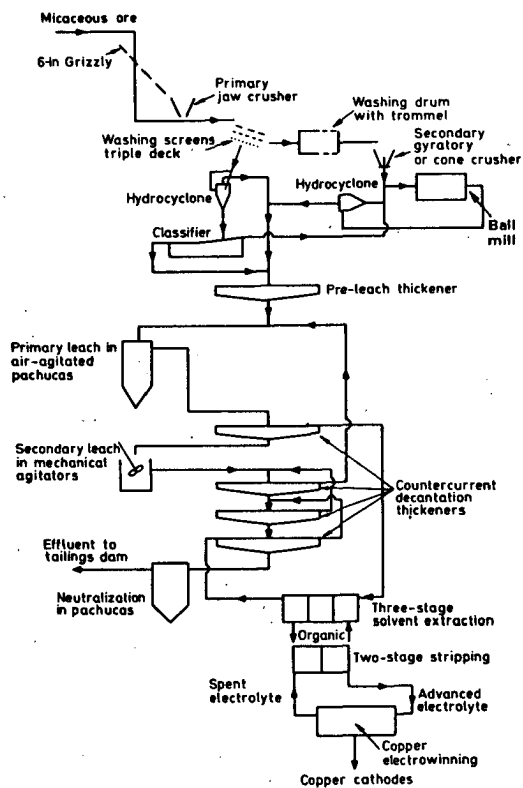


Fig.4. Proposed treatment route for micaceous ore.

strength about 50 g/l H_2SO_4) in mechanical agitators; washing in countercurrent thickeners; solvent extraction; electrowinning; and neutralisation of effluent.

During the next year or two experience will be gained in the operation of the new Tailings Leach Plant at Chingola. With the development of new and improved solvent extraction reagents, and increasing experience of electrowinning from high-purity electrolyte ex-solvent extraction, it may well be that the capacity already installed in the solvent extraction and electrowinning sections of the Tailings Leach Plant will also suffice for the additional copper from leaching of the Chingola micaceous ores. The main drawback to early implementation of this process is the large quantity of sulfuric acid required. It is envisaged that this will eventually be provided from additions to the smelter gas collection and acid manufacturing facilities of the Zambian Copperbelt.

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2.5. THE DESIGN OF MIXER-SETTLERS FOR THE ZAMBIAN COPPER INDUSTRY

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INTRODUCTION

The use of mixer-settlers in continuous liquid-liquid extraction processes dates back to the beginning of this century. A two-stage mixer-settler unit, which maintained gravity flow of both phases by level differences was used by Barstow; the Holley unit had additional control of interstage flows by valves. These and other types, used to about 1950, are reviewed by Morello [1]. In a later design, the Windscale contactor, used in the uranium purification process [2], flows also depend on gravity. In order to overcome the disadvantage of large organic depths, required in gravity flow mixer-settlers, various types of pumping arrangements, either internal or external, have been introduced for interstage transfer of the phases. The "pump-mix" mixer-settler was developed by Coplan et al [3] in 1954. Large-scale mixer-settlers were first employed for the recovery of uranium from leach solutions in the early 1950's. In these plants both pump-mix systems and external pumping were applied [4]. The settlers in these plants are generally of the conventional gravity type, either rectangular or circular in shape. Only recently, new settler designs have been developed and applied industrially by I.M.I. [5] and Lurgi [6]. In these settlers various types of physical aids have been introduced to increase the capacity.

Extensive studies on the performance of the Windscale mixer-settler and scale-up procedures have been conducted by Lowes et al [2]. The

classical study of scale-up procedures by Ryon and co-workers [7], relating to uranium extraction from leach liquors, is still used as the basis for mixer-settler design.

The application of solvent extraction in the copper industry began with the development of the LIX extractants by General Mills Inc. (now Henkel Corp.). The first commercial plant using LIX 64N was designed and built by Bechtel for Ranchers Corp. at Bagdad, Arizona [8], and commenced operation in 1968. Davy Powergas Ltd in conjunction with Nchanga Consolidated Copper Mines Ltd (NCCM) introduced new concepts in mixer design for the Tailings Leach Plant, Chingola, Zambia which was commissioned in 1974 [9,10]. The most recent development in mixer-settler design for the copper industry is the Holmes and Narver Inc. low profile mixer-settler [11], used in the Cities Service plant in Arizona. The use of multi-compartment mixers in this design offers two advantages: firstly, conditions approaching plug flow are achieved in the mixer, and secondly, due to the reduced mixer depth, elevated settlers can be avoided.

During the two years of operation of the Chingola Tailings Leach Plant it became evident that, although overall performance was very satisfactory from an economic point of view, considerable scope existed for improvement. With a future expansion of the Tailings Leach Plant in mind and in view of the possibility of applying the leach-solvent extraction route also to the treatment of other oxide orebodies in Zambia, it was decided to continue operation of the solvent extraction pilot plant at Chingola [10] to widen the general knowledge of copper solvent extraction and in particular to develop and improve mixer-settler design and scale-up procedures. Concurrently, NCCM initiated a cooperative research project with the University of Bradford, England, to study the chemistry of the LIX 64N system and mixer-settler design.

Design of the Tailings Leach Plant expansion, designated Stage 3, is now in progress. An additional 700 000 tonnes of tailings per month, reclaimed from the existing dams, will be treated.

The proposed solvent extraction circuit consists of three streams, each treating a maximum of $1000 \text{ m}^3/\text{hr}$ of pregnant liquor. From experience gained in the operation of the Tailings Leach Plant, three major areas in mixer-settler design, requiring further study, were identified:

Stage efficiency

The stage efficiencies in the solvent extraction circuit are low, in the region of 80 - 90%, and significantly lower than those in the pilot plant, in spite of a 10°C higher operating temperature in the commercial plant. This necessitated a critical assessment of the scale-up criterion of constant tip speed used in the design of the Tailings Leach Plant.

Phase stability

In order to minimize entrainment, it is necessary to operate with organic phase continuity and to ensure stability against phase inversion. During aqueous continuous operation, entrapped air tends to float dispersion fragments up into the organic phase, resulting in a high rate of carry-over of leach liquor impurities and solids from the dispersion band into the electrolyte circuit. This phenomenon has not been observed when operating in the organic continuous mode. Previously, it has been generally accepted that mixer-settlers should operate with organic phase continuity in order minimize organic in aqueous losses. It is interesting to note, however, that contrary to this belief, the organic in aqueous entrainment levels in pilot plant and full-scale operations are not higher for aqueous phase continuity than for organic phase continuity, and may in fact be somewhat lower.

Organic phase continuity has been found difficult to maintain in the Tailings Leach Plant mixers at a phase ratio of 1:1. It would be

necessary to operate at phase ratios (O/A) higher than 1.2:1 to prevent phase inversion to aqueous continuity. This, however, is difficult to achieve mainly due to pumping and piping restrictions. The presence of significant quantities of suspended solids (gangue minerals and gypsum) in the aqueous phase could be a contributing factor to the phase stability problems experienced.

Settler capacity

Because of the difficulty in predicting operating temperature, and the uncertainty regarding the use of specific throughput as a scale-up criterion for settlers very much larger than any in operation at that time, the Tailings Leach Plant settler design was conservative. This resulted in considerable settler overcapacity and, as a consequence, dispersion bands are wedge shaped. When operating in the organic continuous mode the dispersion band in the extraction settlers extends only over approximately two thirds of the settler length. Under aqueous continuous conditions the dispersion band covers less than half of the extraction settler area.

EXTRACTION AND MIXING STUDIES

Having established the critical areas, the objectives for an extensive mixing and extraction study could be defined:

- a. determination of maximum stage efficiencies compatible with acceptable entrainment levels.
- b. establishing the requirements for maintaining organic phase continuity..
- c. a critical comparison of the two commonly used mixer scale-up criteria: constant tip speed and constant power input per unit volume.

Observation of small mixers suggested that phase inversion is initiated in areas of low intensity of agitation. It seemed therefore that configurations in which power is more evenly distributed throughout the mixer volume, than is the case in the existing pump-mixer designs, were to be preferred. As a consequence it was decided at an early stage to investigate a mixer configuration in which the mixing and pumping functions of the impeller were separated.

A turbine impeller with six flat blades was chosen for comparison with the single and double shrouded turbines, which have been employed in copper solvent extraction plants. This turbine, extensively studied by Rushton [12], has been used in solvent extraction, although not in copper systems. The experimental work was conducted in tanks of square cross section with an without baffles.

Four tank sizes were used:

- a 3.5 l laboratory mixer in which the effect of impeller size, baffle arrangement and phase inlet configuration on stage efficiency, entrainment and stability against phase inversion were studied.
- a 20 l and a 780 l mixer, operating in parallel on leach liquors from the pilot plant, in which power correlations were determined and scale-up criteria compared.
- an 8000 l mixer, in which power correlations and vortex formation were studied in the absence of mass transfer.

In work involving mass transfer, copper was extracted from aqueous solutions containing sulfuric acid by a solvent comprising LIX 64N in Escaid 100, usually at a concentration of 20% by volume and at ambient temperature. The experiments were carried out under conditions of aqueous phase continuity and mostly at a phase ratio in the dispersion of 1:1. Measurements of entrainment and phase stability in the 3.5 l

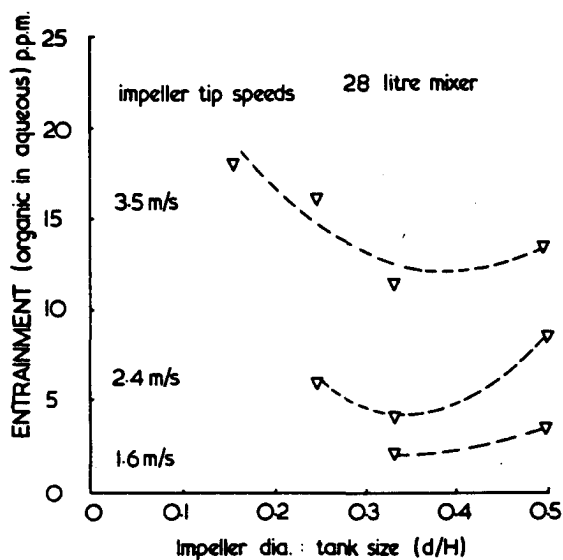


Fig.1. Entrainment and impeller: tank size ratio.

Impeller size cm	Impeller speed r/min	Stage efficiency* %
5.1	1250	87
7.6	833	85
10.2	625	85

* Stage efficiency = $\frac{C_f - C_o}{C_f - C_e}$

where: C_f = Cu tenor of the aqueous feed stream
 C_f = Cu tenor in the aqueous exit stream
 C_e^o = equilibrium Cu tenor

Table 1. The effect of impeller diameter on extraction efficiency.

mixer were made in the absence of mass transfer using 20% LIX 64N and water with 2 g/l H_2SO_4 added.

Extraction Characteristics

A series of batch extraction tests was conducted in the 3.5 l square tank, using a range of impeller sizes (5, 7.5, 10 cm) and impeller speeds; the findings were checked in continuous flow. It was found that at a constant tip speed the stage efficiency is independent of impeller size (Table 1). On the other hand organic in aqueous entrainment, at constant tip speed, varied with impeller diameter, showing a decrease with impeller size down to an impeller/tank size ratio of 1:3 (Fig.1). A further decrease in impeller diameter gave increased entrainment levels. It is interesting, therefore, to note, that the generally accepted design practice of employing an impeller diameter of one third of the tank diameter, seems to correspond with the optimum with respect to entrainment generation.

Scale-up criteria for extraction were examined by comparing the performance of the 20 l and 780 l mixers, operating in parallel on pilot plant liquor. Aqueous feed conditions varied over a wide range, which was partly due to deliberate changes in the leach circuit operating parameters, and partly due to normal operating variability.

In the first series of experiments, extraction performance of the two mixers was compared under conditions of equal power consumption per unit volume. Considering the variation in aqueous feed composition over an eight hour run, comparison should only be made between pairs of simultaneously determined stage efficiencies. A t-test on 136 pairs of such determinations showed no significant difference in stage efficiency at a confidence level of 95%. Average stage efficiencies for different power inputs and operating conditions are presented in Table 2.

A second series of tests comprising 74 pairs of stage efficiency determinations was conducted at two tip speeds. Again each of the runs

Phase ratio O/A	Power input HP/m ³	Aqueous composition g/l		Av. stage efficiency %	
		Cu	H ₂ SO ₄	780 l mixer	20 l mixer
1.0	1.0	3.8	3.2	88.9	86.6
1.0	0.7	3.5	3.8	82.7	80.9
1.0	0.7	2.5	4.1	83.4	83.2
1.0	0.3	3.6	2.7	77.8	76.2
1.5	1.0	1.0	8.0	76.6	76.3
1.5	0.7	0.75	7.9	75.2	76.9

Table 2. Comparison of stage efficiencies at equal power input.

Tip speed m/s	Av. stage efficiency %	
	780 l mixer	20 l mixer
1.667	83.0	89.8
2.000	88.9	93.1

Table 3. Comparison of stage efficiencies at equal impeller tip speed.

extended over eight hours; the aqueous composition varied around the mean of 4.3 g/l Cu and 1.0 g/l H_2SO_4 .

A t-test showed that the difference in performance of the two mixers was significant. In all except two cases, stage efficiencies in the small mixer were higher than those in the large mixer. Average results are given in Table 3. This data shows that for the flat-blade turbine, constant power input per unit volume adequately predicts the stage efficiencies in mixers of various sizes, and that at constant tip speed, lower stage efficiencies would be achieved in a large mixer than in the small experimental mixer.

As a conclusion of this testwork the following mixer design procedure is proposed:

1. The tip speed for the required stage efficiency is determined in a laboratory mixer.
2. At this selected tip speed the optimum impeller/tank diameter ratio with respect to entrainment is determined in the same vessel under continuous flow conditions.
3. The scale-up from the laboratory mixer to commercial size is carried out using geometric similarity and equal power input per unit volume.

Mixing Characteristics

It is evident from the foregoing sections, that accurate power prediction for large-scale mixers is of prime importance to the designer. In view of this, studies of power correlation were conducted for all available mixer sizes.

The experiments showed that for a square mixer box, the power number changes with Reynolds number and therefore predictions of power

consumption in large-scale mixers is difficult, if not impossible. With the addition of two baffles, however, the power number became independent of Reynolds number and of mixer size. Over the range in mixer volumes of 20 l to 8000 l a power number of 6.5 was determined. It is somewhat anomalous that a slightly lower power number (5.0) was found in the 3.5 l laboratory mixer, indicating that mixers below a certain size should not be used in scale-up experiments. Experiments with four vertical baffles showed no further changes in power characteristics, indicating that with two baffles, fully baffled conditions had already been reached. This is also illustrated by the elimination of vortex formation in the 8000 l mixer with the installation of two vertical baffles. Elimination of vortex formation was more difficult in the smaller tanks; in the 3.5 l laboratory mixer vortices and air entrainment could not be avoided without the use of a top baffle.

The instability against phase inversion in Tailings Leach Plant mixers has been difficult to reproduce in pilot plant and laboratory mixers. The occurrences of phase instability in the smaller-scale mixers have, however, always coincided with high suspended solids or gypsum concentrations. Testwork has shown that other factors such as power input per unit volume and phase inlet configuration are also important.

The power per unit volume in the Tailings Leach Plant mixers is considerably smaller than in the pilot plant mixers, since the design was based on constant tip speed. In addition, circulation in the lower part of the mixers is poor and segregation of the phases may take place. A tendency towards phase segregation in the 20 l and 780 l mixers has been observed at power inputs below 0.2 hp/m^3 . In order to investigate the effect of improved mixing conditions on phase stability it was decided to remove the draught tube, which conveys the two phases to the eye of the centrally located, double-shrouded impeller, from one of the Tailings Leach Plant mixers. This could conveniently be done in the last extraction stage. In this way the power input is utilised for mixing only and circulation in the lower part of the mixer is greatly improved. As a result of this modification it has been possible to operate with

organic phase continuity for periods of several weeks, whereas for the same phase ratio (O/A = 1.1:1) it has not been possible to maintain organic phase continuity in a corresponding, unmodified mixer in one of the other streams. It is concluded from these results that the improved mixing tends to increase stability against phase inversion. The fact that the two phases are no longer introduced into the impeller eye, but at considerable distance from the high shear zone in the mixer, may also have contributed to the improvement in phase stability. The proposed mixer configuration with a flat-blade turbine, will ensure adequate circulation and the scale-up criterion of constant power input per unit volume will provide an agitation intensity far exceeding that at which phase segregation has been observed.

Entrainment is also an important consideration in mixer design. In the pilot plant no significant differences in entrainment levels have been observed for different impeller types. However, information about entrainment at different scale of operation is currently very limited. Studies of entrainment characteristics in the 3.5 l mixer showed a significant influence of inlet arrangement. In one case the aqueous phase (to be dispersed) was introduced by an extended inlet to the impeller region with the organic phase brought into a region distant from the impeller. With this inlet combination high levels of entrainment are observed. A high aqueous to organic ratio in the impeller eye region apparently causes high levels of organic entrainment. If, instead, the continuous phase is introduced into the eye of the impeller, or both phases are introduced separately at the base level of the mixer, the entrainments of organic (continuous) phase are significantly lower. It has also been observed that, during the tests which were conducted in the organic continuous mode of operation, any air entrainment was associated with high levels of organic entrainment.

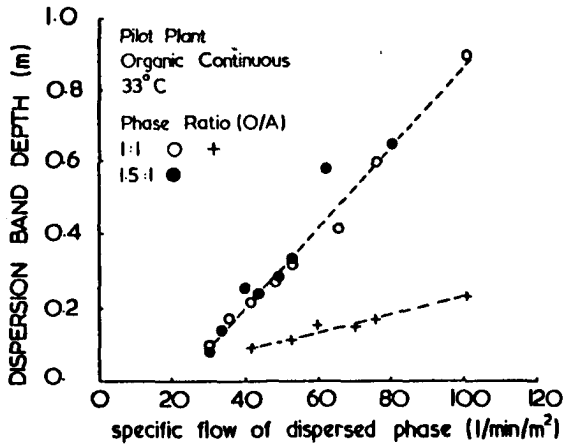
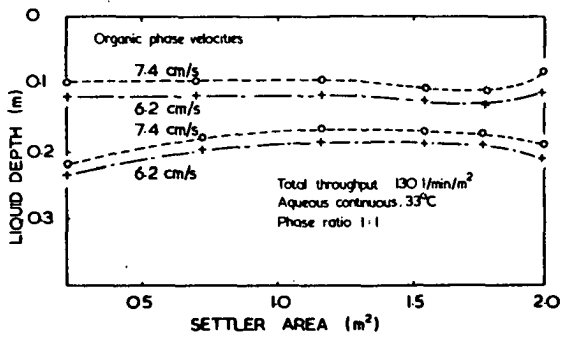


Fig.2. Dispersion band characteristics.

Fig.3. Dispersion band profile.
(aqueous continuous)

SETTLER STUDIES

The two main considerations in settler design are:

- a. The functional relationship between dispersion band depth and throughput of dispersed phase per unit of horizontal settler area.
- b. The critical linear velocity in the clear organic phase above which aqueous entrainments increase sharply.

When generating design information, the difficulty experienced by the experimental worker is that the above two factors cannot be determined simultaneously in a laboratory-scale settler. It can be shown that, for equal specific flows and depths of clear organic phase, the ratio of linear velocities in the organic phase in settlers of different sizes equals the ratio of their lengths. Consequently, in order to obtain simultaneously similarity in velocities and specific flows, the lengths of the experimental and commercial settlers should be the same. To fulfil this requirement at least partially, an existing pilot plant settler (4.2 m^2 settling area) was converted into a 12.6 m long and 0.3 m wide channel by installing two length-wise baffles. Most of the design testwork was conducted in this settler. Comparative work was carried out in a laboratory settler and in one of the Tailings Leach Plant settlers, where facilities for varying the settling area by means of a moveable dam baffle had been installed.

Pilot Plant Testwork

Most of the testwork was carried out in the channelled settler under conditions simulating the first extraction stage in the Tailings Leach Plant Stage 3 circuit. The composition of the leach liquor feed averaged 3.3 g/l Cu and 1 g/l H_2SO_4 . The extractant tenor was 23% v/v LIX 64N in Escald 100 and the operating temperature was 30°C in most experiments.

Phase ratios (O/A) of 1.0:1 and 1.5:1 were investigated. To vary the settling area, dam baffles could be introduced at various positions along the settler length.

Relationship between dispersion band depth and specific settler flow

In all pilot plant experiments the relationship between dispersion band depth and specific flow is distinctly linear within the range of determinations. However, individual determinations of this relationship showed marked variations in the slope of the line, representing data points, as is shown in Fig.2. It was not possible to relate these variations to measured changes in operating parameters and it is believed that factors such as changes in the nature of the suspended solids particles and possibly static electricity contribute to the phenomena observed. The testwork also showed that the dispersion band depth is dependent only on the flow of dispersed phase per unit settler area and is thus independent of the phase ratio.

It should be pointed out that in the laboratory experiments the functional relationship between dispersion band depth and specific settler flow was distinctly exponential (exponent generally greater than 2). The present pilot-scale and large-scale data, however, could only be described by either a linear relationship or an exponential relationship of lower exponent.

Effect of linear velocity

In the unmodified settlers, at low specific flows the dispersion bands were generally of constant thickness throughout the settler length, whereas in the channelled settler operating at the same specific flows, wedge-shaped dispersion bands were observed. This difference can be explained by the high linear velocity of the dispersion in the channelled settler, the wedge providing the driving force for dispersion flow. At higher specific flows, where the dispersion band is thicker and the linear velocity of the incoming dispersion consequently lower, the

wedge shape is less pronounced. At the dam baffle the profile of the dispersion band is influenced by the linear velocities of the clear phases. This effect becomes increasingly significant at deep dispersion bands, i.e. low depth of clear phases at constant total liquid depth in the settler. Typical dispersion band profiles determined under organic and aqueous phase continuity are shown in Figs 3-4. Under organic continuous conditions, the upper surface of the dispersion band curves upwards at high linear velocities in the clear organic phase, which ultimately results in flooding. When operating in the aqueous continuous mode, both the upper and lower dispersion band surfaces curve strongly, respectively upwards and downwards at the dam baffle at all linear velocities. This difference in profile between aqueous and organic continuous dispersion bands could be explained by differences in dispersion viscosity.

The relationship between linear velocity and aqueous entrainment in the clear organic phase was separately determined at various specific flows, by adjusting the interface position. In this way the depth of the clear organic phase could be varied independently of other parameters. Under organic continuous conditions, sharp increases in aqueous in organic entrainment were generally observed at linear velocities between 6 cm/s and 9 cm/s. Typical results are shown in Fig.5. There is no apparent correlation between the critical linear velocity and dispersion band thickness.

Effect of temperature on dispersion band depth

Experiments at different temperatures clearly illustrated the importance of this parameter in settler design. When the pilot plant temperature was increased from ambient (25°C) to the operating temperature of the Tailings Leach Plant (33°C) the dispersion band thickness was halved.

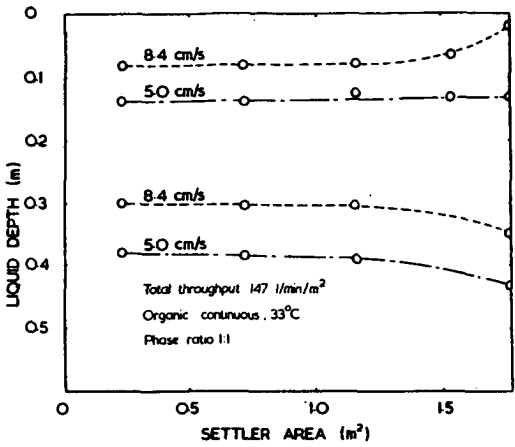


Fig.4. Dispersion band profile.
(organic continuous)

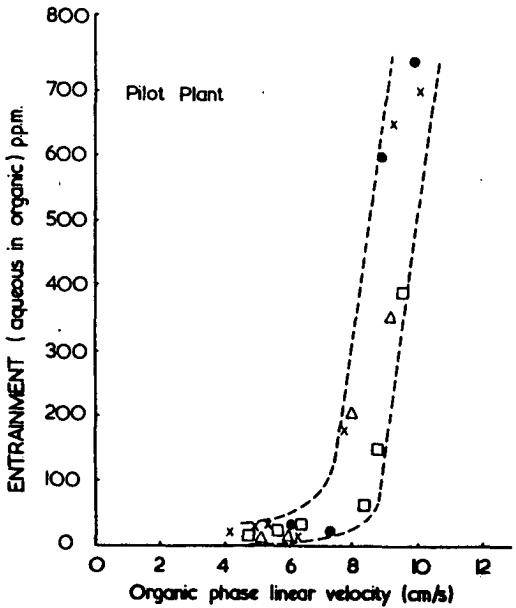


Fig.5. Entrainment and linear velocity.

Coalescence aids

Physical coalescence aids have been extensively studied. Although in certain cases substantial reductions in dispersion band volume could be achieved, a decision was taken not to use coalescence aids for the expansion of the Tailings Leach Plant, due to the uncertainty related to suspended solids level and the severity of gypsum encrustation.

Scale-up

To assess the validity of the scale-up criterion of constant specific settler flow, comparative testwork was conducted on the pilot plant and in one of the Tailings Leach Plant extraction settlers. This work was conducted under conditions of aqueous phase continuity due to the instability of organic continuous dispersion in the large-scale mixer. At a specific settler flow of 60 l/min/m^2 (total flow, O/A = 1:1) the dispersion band in the pilot plant channelled settler and in the Tailings Leach Plant settler stretched over only two thirds of the settler length. At a specific flow of 220 l/min/m^2 an average dispersion band depth of 24 cm was observed in the large settler; the corresponding figure for the pilot plant was 26 cm.

These data demonstrate the validity of the scale-up criterion under conditions of aqueous phase continuity. For the design of the settlers in the Tailings Leach Plant expansion it was assumed that this scale-up criterion is also valid for organic phase continuity.

DESIGN CONSIDERATIONS

From the results of the mixing and extraction studies it was considered possible to achieve significant improvements in stage efficiencies and phase stability, if a flat-blade turbine were to be used in preference to a pump-mix impeller. Other testwork had confirmed the significant advantage of plug flow in mixers and it was therefore decided to employ

multicompartment mixers. Prior to finalizing the design, it was decided to construct a large-scale prototype mixer to further investigate the entrainment and phase stability characteristics. This mixer will operate in conjunction with an existing Tailings Leach Plant settler.

The dimensions of each of the three compartments were fixed at 2.9x2.9x4 m with two vertical baffles of 0.3 m fitted to the centre of opposite walls. An impeller/tank size ratio of 1:2.6 was chosen which would minimize regions of poor agitation and which approximately corresponds with minimum entrainment generation. External pumps are required if non-pumping turbines are used. It is intended to test power inputs varying from 0.7 hp/m³ to 1.0 hp/m³. At the time of finalizing this paper the prototype had not yet been commissioned.

In selecting the design parameters for the Stage 3 settlers, a very important consideration has been the minimizing of organic inventory costs. For determination of settler area requirements, organic inventories have been calculated for a number of specific settler flows, using the steepest line, relating dispersion band thickness and specific settler flow (Fig.2), i.e. representing the most unfavourable conditions. The results showed that for these particular conditions only a small reduction in settler organic inventory could be achieved by operating at high specific flows. Furthermore, although the settler data was generated over a period of two months, some uncertainty still exists in the maximum slope of the line, relating dispersion band depth and specific flow. It was therefore decided to avoid the upper range of specific flows studied. As the design specific flow for the existing Tailings Leach Plant settler, 30 l dispersed phase/min/m², resulted in considerable overcapacity, a value of 45 l dispersed phase/min/m² was eventually chosen for the design of the Stage 3 settlers, both in the extraction and stripping stages. For a design flowrate of 1000 m³/hr/stream leach liquor, the required area per settler would be 370 m².

Once the settler area has been decided upon, the organic inventory becomes directly proportional to the depth of the clear organic phase. In order not to exceed the critical linear velocity, shallow clear organic depths can be achieved only by increasing the settler width. Calculations of organic inventory for settlers of different widths, showed that very substantial reductions can be achieved by increasing the settler width (Table 4). There are, however, several points to consider when designing very wide settlers.

- uniform distribution of dispersion into the settler.
- maintaining even flow within the settlers.
- a minimum clear organic depth is required to accommodate disturbances in the upper surface of the dispersion band, and small increases in dispersion band volume.

At present a settler width of 20 m is considered; for a settler area of 370 m^2 this would give a length of 18.5 m. Increasing the settler width even further is less attractive as the rate of reduction in organic inventory becomes relatively small beyond 20 m and the clear organic depth would become less than 20 cm, which is considered the minimum acceptable.

Settler width m	Settler length m	Minimum clear organic depth m	Organic inventory m^3
10	37.0	0.46	216
15	24.7	0.31	161
20	18.5	0.23	131
25	14.8	0.19	117

Table 4. Clear organic depth and inventory as a function of settler width.

CONCLUSIONS

It has been shown that laboratory tests are useful for examining the practicality of new ideas and for selecting promising combinations of operating variables from the large number of possible test conditions. However, for more precise plant design, pilot plant investigations are necessary because there are many aspects of plant performance associated with equipment size and feed stream composition that cannot be adequately examined in the laboratory. In particular, pilot plant work has shown the importance of linear velocity in the settler and established the scale-up criteria of constant specific throughput for the settler and constant power input per unit volume for the mixer.

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2.4. COMMERCIAL PROCESSES FOR COPPER

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INTRODUCTION

Hydrometallurgical extraction of copper from aqueous solutions with the use of cementation on iron was practiced in Spain as early as the middle of the eighteenth century [1]. In the nineteenth century leaching of oxidized copper either by natural or downward-percolating acid water or by artificially produced sulfuric acid was practiced in Russia and the United States, with the copper being recovered from solution by cementation. This method was generally found to be suitable for the lower-grade oxidized copper ores and residues that could not be extracted economically by direct smelting. It did depend, however, on the availability of adequate and inexpensive sources of acid and of iron scrap.

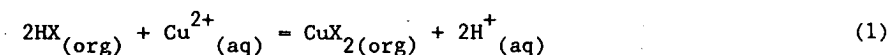
Sulfuric acid has almost always been favoured, as it can usually be produced easily from the sulfur of sulfide ore minerals. The advent of electrowinning for the recovery of copper from its acid sulfate solutions led to significant economies compared with cementation due to elimination of the necessity for iron scrap, regeneration of a part of the sulfuric acid for leaching, and the much greater value of the final product, cathodes, compared with copper cement powder. Despite these advantages, electrowinning only replaced cementation in a few places because of severe limitations on electrowinning as regards solution quality.

The development of solvent extraction reagents specific for copper in the mid-1960's allowed the improved economics of electrowinning to be applied to low-copper-tenor, impure solutions derived from many

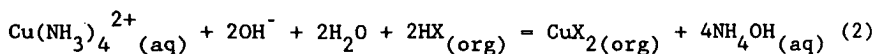
sulfuric acid leaching operations. Solvent extraction has also been applied to the recovery of copper from ammoniacal solutions produced by the ammonia leaching of chalcopyrite (Arbiter process [2]), scrap metal [3], and lead refinery drosses [41].

Solvent extraction in the two leach systems is based on the following exchange reactions:

Sulfuric acid leaching:



Ammonia leaching:



In copper extraction at low H^+ concentrations, both reactions proceed to the right, and thus the leaching medium - sulfuric acid or ammonia - is regenerated. The raffinate from the copper solvent extraction step are thus recycled to the leaching circuit.

The loaded organic in both cases is stripped with a solution high in sulfuric acid to reverse reaction (1) forming the feed to electrolysis. In the ammonia system contamination of the sulfuric acid electrolyte should be avoided and the loaded organic is thus washed thoroughly prior to stripping.

A typical schematic flow diagram for a copper solvent extraction plant is shown in Fig.1, in which the left-hand circle represents the leach circuit, the centre circle the solvent extraction circuit, and the right-hand one the electrowinning circuit.

The three main operations - leaching, solvent extraction, and electrowinning - need to be carefully integrated such that a maximum overall profitability is achieved. This needs detailed evaluation of the

interaction effects, and where conflicting requirements exist, determination of the best compromise. A brief outline of these interfacing problems is given in the following section.

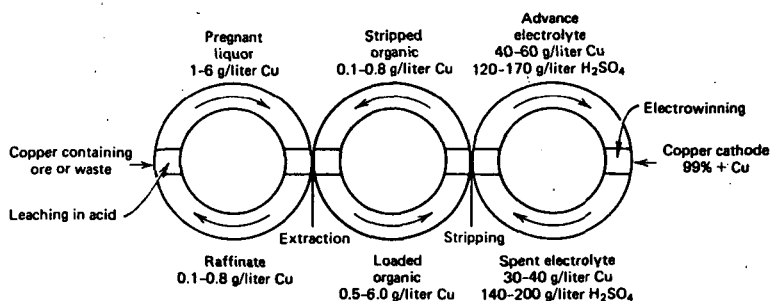


Fig.1. Diagrammatic representation of copper extraction by use of solvent extraction. The indicated copper tenors are typical of sulfuric acid leach circuits. For the ammonia leach system, the circuit would be similar, but the copper concentrations in the leaching solution are much higher.

CONSTRAINTS ON COPPER SOLVENT EXTRACTION PLANTS

Leaching operations

Acid leaching operations can be divided into two principal groups:

1. Percolation leaching, in which the solids are contacted by allowing leaching solution to flow through a static bed of solids.
2. Agitation leaching, in which a finely ground suspension of solids is agitated, more or less violently, together with the leaching solution.

Percolation leaching

In percolation leaching, acidified liquor is allowed to permeate and percolate through a static bed of ore, which may be contained within vats (as at the Kennecott Ray silicate leaching plant), may be piled in an open heap (Ranchers Exploration Co. [4] and Cyprus Bagdad [5]), or may be the ore-body itself in place (in situ leaching). Oxidized copper minerals are leached directly by acid; some sulfide minerals are leached by ferric sulfate, and by bacteria that oxidize iron and sulfur. Copper and acid tenors of pregnant liquor depend on many factors such as grade and type of mineralisation, acid tenor of feed liquor, iron tenors, and so on. Copper tenors of pregnant liquor are generally in the range 0.5-5 g/l, which is satisfactory for subsequent solvent extraction.

Where bacterial action is an important part of the leaching process, both metal and acid tenors in solution must be limited to avoid poisoning the bacteria; these limitations serve to restrict the free acid content of pregnant liquor to concentrations which are acceptable for solvent extraction. Toxicity of entrained organic in raffinate towards the leaching bacteria has been of concern, but there is no evidence that the levels of entrainment which are regarded as normal have any deleterious effects.

Where bacterial action is insignificant, high acid concentrations in the leach liquor will generally lead to higher copper recoveries, or faster leach kinetics. However, high free-acid concentrations in pregnant liquors should be avoided, as unfavourable solvent extraction equilibrium conditions may be created, leading to higher equipment and working costs; in the worst case, neutralisation of pregnant liquor might be required. However, this problem can usually be avoided by suitable design of the leach circuitry, and by ensuring that high acid liquors are largely neutralised by contact with fresh ore, in order to yield pregnant liquors suitable for solvent extraction.

In contrast with agitation leaching, the pregnant solutions from a percolation leach plant have very low suspended solids contents as a result of the filtering action of the heap of crushed ore; the problems of solution clarification and crud removal which characterize agitation leach/solvent extraction plants are therefore avoided.

Agitation leaching

In agitation leaching, finely ground copper ore particles are agitated in the acid leach solution; by contrast with percolation leaching, recoveries of copper to solution are much greater, but there is the added problem of solid-liquid separation and the losses caused by liquor entrainment. In both of the two important plants using agitation leaching, the NCCM Tailings Leach Plant in Zambia [6] and the Anamax Twin Buttes plant in Arizona [7], the first stage in solid-liquid separation is countercurrent washing in thickeners. This is comparatively cheap, but has the disadvantage that the resulting liquor may still contain some 50-500 ppm of suspended solids. Removal of these suspended solids either before solvent extraction by special clarifiers and/or filters, or during solvent extraction by special crud-handling facilities, poses a number of difficulties; these difficulties are frequently increased by supersaturation of the solution with calcium sulfate, derived from dolomite or calcite, which often occur to some extent in these oxidized copper ores.

The cost of agitation leaching plant is very largely a function of the volumetric flow in the plant. To reduce flows in the wash circuit, the incoming liquor flowrate is limited by maximising the density of the feed pulp. The wash flow rate is then selected such that the best compromise is reached between plant size and costs and overall copper recovery. A smaller washflow reduces leach-countercurrent decantation (CCD) equipment size but, for a given solvent extraction recovery, results in higher losses from the CCD circuit and thus lower overall recoveries. Reduced washflow also implies higher copper tenor in the pregnant liquor, resulting in high-acid tenors of interstage aqueous and

raffinate flows. This requires increased extractant tenors and possibly higher phase ratios, which increases the mixer-settler size and organic inventories. For very high pregnant liquor tenors, interstage neutralisation could even be required. Obviously for an existing plant, maximisation of washflow within the constraints of the equipment gives maximum recoveries both in the wash circuit and in solvent extraction.

Electrowinning

Copper electrowinning is carried out in an electrowinning cell containing inert lead alloy anodes and either copper starting sheets or rigid blanks of titanium as the cathodes. The electrolyte is a solution of copper sulfate in sulfuric acid. At the cathode, copper ions are reduced to copper metal, whereas oxygen is evolved at the anode.

The most important constraints are those pertaining to copper and acid content of the electrolyte. For satisfactory electrowinning, the copper content of the spent electrolyte should be not less than 25 g/l and preferably in the range 30-35 g/l. To avoid any risk of copper sulfate crystallisation, the copper tenor in the advance electrolyte should not exceed 60 g/l. To ensure maximum conductivity of the electrolyte, the free sulfuric acid content should not be less than 80 g/l. The acid content should be held at the minimum possible above this figure in order to minimise acid attack on the lead anodes. Experience has shown that the maximum practical acid concentration lies in the range 160-200 g/l.

To obtain maximum advantage from the process, the copper deposited should be as pure as possible. Many factors affect this purity, the most important of these are:

a. Density of deposit

A dense deposit with minimum entrained electrolyte requires copper tenors as indicated in the preceding paragraphs, a cathode current density of not more than 450 A/m^2 , addition of

small quantities of chloride ion, and of an organic surface active agent to depress nodular growth. The presence of an organic film on the surface of the electrolyte, such as arises from entrained organic from the solvent extraction, has been shown to cause a loose powdery deposit and is to be avoided if at all possible.

b. Impurity content of the electrolyte

Various impurities in the electrolyte affect the copper deposit in different ways. Bismuth and selenium are to some extent codeposited with copper. A high concentration of metal cations other than copper, such as magnesium or aluminium, reduces the mobility of the copper ion and reduces the density of the deposit. Solid particles in the electrolyte can be incorporated in the copper deposit by physical entrapment in pore spaces. In addition it could be possible that particles are attracted to the cathode by their positive zeta potential.

c. Anode degradation

Acid attack on the anode releases flakes of lead sulfate. The larger flakes may be physically incorporated in the cathode and are generally discovered during a quality inspection; these grossly contaminated cathodes are normally rejected. Fine flakes may be trapped in pore spaces and are subsequently overgrown with copper or are incorporated as a result of the electrokinetic phenomenon described previously.

Two other factors in electrowinning have an important bearing on the solvent extraction process:

1. Iron content of the electrolyte.

Iron in the electrolyte causes a reduction in current efficiency and its content must be kept at a minimum, preferably below 2 g/l. Good selectivity of the copper extractant against iron is thus an important requirement.

2. Acid mist evolution

The evolution of oxygen at the anode produces a fine acid mist. The most effective method of reducing this mist is to add a surface active agent to the electrolyte to induce a foam cover on the cell. Unfortunately, practically all such reagents either do not form a froth as a result of solvation by the entrained organic phase or reduce the organic-aqueous interfacial tension to the point where dispersion bands increase and a stable emulsion may be formed in the solvent extraction circuit. However, the proprietary reagent 7C 100, marketed by the 3M Company, has been used with some success at a number of operations in the United States. The alternative method of using single or multiple layers of polythene balls on the surface of the cell is much less effective.

Size of Copper Solvent Extraction Operations

The existing copper solvent extraction plants are an order of magnitude larger than any other type of solvent extraction plant presently in operation, as the following statistics will show:

Annual tonnage of metal produced in a single operation	5000-80000 tonnes/yr
Flowrate of pregnant liquor	200-3000 m ³ /hr
Surface area of solvent extraction plant	up to 50000 m ²

The large size of the plants brings particular problems, including (1) design of the solvent extraction equipment, typically mixer-settlers, (2) provision of adequate fire-fighting facilities, (3) provision of facilities for preventing accidental discharge to streams

or rivers, and (4) high capital cost of the organic inventory of the plant.

REAGENTS FOR COPPER SOLVENT EXTRACTION

Extractants

Of the reagents currently available and under consideration for copper extraction, most belong to the family of hydroxyoximes; exceptions being the Kelex reagents, based on 8-hydroxyquinoline, and LIX 34, which is 8-(alkarylsulfonamido)-quinoline [18]. The various reagents are listed in Table 1 with an indication of properties, uses and limitations.

The Henkel reagents LIX 64, LIX 63 and LIX 64N were the first to achieve commercial acceptance. During the early 1970's, LIX 64N became the standard extractant for copper solvent extraction. It consists of a mixture of LIX 65N, a hydroxybenzophenone oxime, and LIX 63, an aliphatic hydroxyoxime, which acts as a kinetic modifier. LIX 64N has a loading capacity of 0.25 g Cu/l/vol.% in kerosene at pH=2.0. LIX 64N tenors in kerosene up to 30% v/v can be used at temperatures below 40°C with satisfactory phase disengagement. The extraction isotherm of LIX 64N for a typical acid leach liquor is compared with those of other extractants in Fig.2.

LIX 64N is currently used for concentrating and purifying acid leach solutions containing up to 6-7 g/l Cu. For higher copper concentrations an alternative, stronger reagent would be recommended (e.g. LIX 70 series, LIX 622 or P-5100) because of the effect of increasing the hydrogen ion concentration in the later extraction stages.

In the ammoniacal leach system LIX 64N has very favourable extraction properties for copper. The loading capacity is higher than for sulfate solutions (0.3-0.4 g Cu/l/vol.%) and kinetics are fast [8]. Because of the uptake of free NH_3 , the loaded organic should be washed

Trade Name	Manufacturer ^a	Composition	Uses and Properties	Limitations
LIX63	1	5,8-Diethyl-7-hydroxy-6-dodecanone oxime	Kinetic promoter for other hydroxy oxime reagents	Low loading capacity on its own; degrades faster than other LIX reagents
LIX64	1	2-Hydroxy-5-dodecyl benzophenone oxime with added LIX63	Low tenor, low-acid copper solutions; replaced by LIX64N	Maximum concentration in kerosene of 10%; efficient for extracting from copper tenors exceeding 3 g/liter
LIX64N	1	LIX65N, with added LIX63	The standard reagent for low-medium copper tenor, acid leach solutions; also used for ammoniacal solutions	Slow-medium kinetics in acid solutions, poisoned by Co^{2+} in ammoniacal solutions
LIX65N	1	2-Hydroxy-5-nonyl benzophenone oxime	High-temperature extraction of copper	Too slow without kinetic modifier for normal operations
LIX70	1	Chlorinated LIX65N with added LIX63	Strong chelating agent for high-acid, high-copper solutions	Difficult to strip requiring acid tenors around 300 g/liter H_2SO_4
LIX71	1	Mixture of LIX64N and LIX70	Intermediate between LIX64N and LIX70	—
LIX73	1	Mixture of LIX64N and LIX70	Intermediate between LIX64N and LIX70	—
LIX34	1	8-(Alkaryl sulfonamido)quinoline	Similar to LIX64N but higher selectivity against Fe; may be stripped with somewhat lower-strength acid solutions	Comparatively high cost
LIX54	1	See Table 3 Chapter 24	Extraction from ammoniacal solutions, high copper loadings, good selectivity, loads no ammonia. Rapid kinetics. Strips with relatively weak H_2SO_4	Needs to be operated aqueous phase continuous. Fe loads in weak acid solution and is difficult to strip with H_2SO_4 .
LIX622	1	—	Strong chelate, high maximum loading, rapid kinetics	Requires high acid for stripping.
LIX6022	1	—	Weakened form of LIX622, similar to LIX64N but with rapid kinetics	—
SME 529	2	2-Hydroxy-5-nonyl acetophenone oxime	Higher maximum loading capacity than LIX64N; extraction similar to LIX64N, stripping easier	Slow kinetics, significantly slower than LIX64N

Table 1. Reagents available for copper extraction.

Trade Name	Manufacturer ^a	Composition	Uses and Properties	Limitations
SME 530	2	SME 529 with kinetic modifier	Similar to SME 529 but kinetics faster—similar to LIX64N	—
P50	3	Substituted salicyl aldoxime	Basis for reagents P5100, P5200, P5300, and PT 5050	—
P5100	3	P50 diluted with an equal part nonyl phenol	Strong chelate, high maximum loading copper, useful for high acid, high copper tenor solutions; rapid kinetics	Requires strong acid electrolyte for stripping; not compatible with rubber linings
P5300	3	One part P50 with three parts nonyl phenol	Chelating power weakened by nonyl phenol, maximum loading similar to LIX64N, favorable extraction isotherm but more difficult stripping as compared with LIX64N; faster kinetics than LIX64N	Not compatible with rubber linings
P5200	3	One part P50 with two parts nonyl phenol	Intermediate between P5100 and P5300	Not compatible with rubber linings
PT5050	3	Two parts P50 with one part tridecanol	Similar to P5100 but compatible with rubber linings	—
P17	3	Phenyl benzyl ketone oxime	Similar to LIX64N	Low solubility of copper complex in organic phase
Kelex 100	4	Substituted 8-hydroxy quinoline with isodecanol modifier	Extracts from high-copper-tenor, medium acid solutions, stripped by lower acid solution than most other reagents	Acid carry-over from strip solution, requiring acid wash stages; modifier required to assist phase disengagement
Kelex 120	4	Similar to Kelex 100 but with approximately 20% isodecanol	As Kelex 100 but better phase disengagement	As Kelex 100

^aManufacturer: (1) Henkel Corporation; (2) Shell Chemical Company; (3) Acorga Ltd.; (4) Sherex Chemical Company (previously Ashland Chemical Company).

Table 1. (Continued)

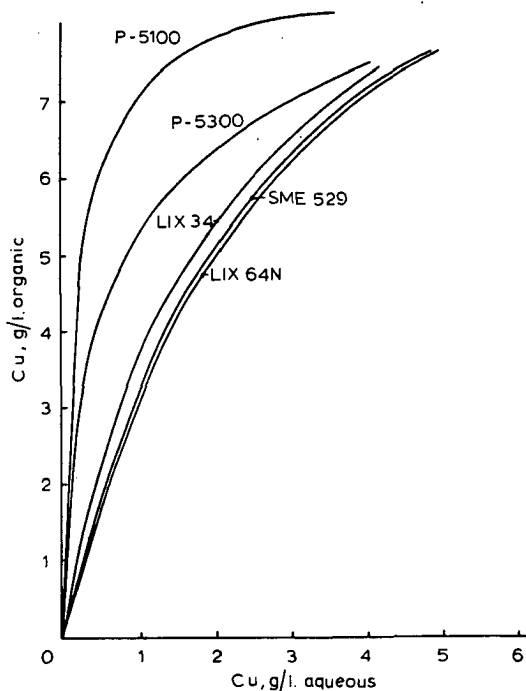


Fig.2. Extraction isotherms for various copper extractants.

prior to stripping to avoid contamination of the electrolyte. Nickel, cobalt (Co^{2+}), and zinc are co-extracted with copper. Nickel and copper can be subsequently separated by selective stripping or by copper cementation from the nickel strip liquors using nickel metal. Co-extraction of Co^{2+} should be avoided as the Co^{2+} oxidizes to Co^{3+} in the organic phase and forms a complex which is difficult to strip and consequently builds up in the loaded organic. Cobalt in the pregnant liquor should therefore be mainly in the cobaltic form, which is not extracted by LIX 64N. LIX 64N can also be used in the extraction of copper from chloride [9,10] and nitrate [11] solutions.

Since 1975, various other reagents have achieved wide commercial acceptance. The most important of these are the Acorga P-5000 series [13,14] including the reagent PT-5050. These Acorga reagents are all based on the reagent P-50, which is a substituted salicyl aldoxime. P-50 is a strong chelating agent, with a high maximum loading for copper and relatively fast kinetics. It is modified by the addition of nonyl phenol to yield the commercial reagents P-5100, P-5200 and P-5300. As the nonyl phenol causes degradation of natural and synthetic rubbers, its use should be avoided in plants which have any significant amount of rubber-lined construction. For such cases, the alternative reagent PT-5050 is available in which the nonyl phenol modifier is replaced by tridecanol. In other respects PT-5050 is similar to P-5100 in performance characteristics.

Henkel also developed a number of reagents with stronger chelating power and more rapid kinetics. LIX 70 was developed first; it is a strong chelating agent and extracts copper efficiently from relatively high acid solutions [15,16]. Subsequently the reagents LIX 622 and 6022 were marketed and are now in commercial use. They are similar in performance characteristics to the Acorga reagents P-5100 and P-5300, respectively. The strong chelating reagents, of which LIX 622 and P-5100 are typical, can be used for treatment of relatively high copper tenor liquors or for accomplishing extraction from low tenor liquors in fewer stages. They have the disadvantage, however, of requiring increased acid concentrations in the stripping solutions, and if these are higher than 180-200 g/l serious problems may arise in electrowinning due to more rapid attack on the lead anodes and to increased acid mist generation.

The improved kinetics of the newer reagents, compared with LIX 64N, permit satisfactory operation down to temperatures below 10°C. Previously a number of plants in the United States had to use some auxiliary heating in winter to maintain adequate kinetics.

The only other reagent that has achieved commercial recognition is the Shell Chemical Company SME 529 [12], which is similar to LIX 64N in performance, but with rather higher maximum loading capacity, balanced by somewhat slower kinetics. Shell Chemical Company also markets a reagent SME 530, which is similar to SME 529 but has a kinetic modifier.

Mention must be made of the Kelex series of reagents that were developed by the Ashland Chemical Company [17]. They are somewhat different from the hydroxyoxime family of reagents in that, while they extract particularly well from relatively high-copper, high-acid pregnant liquor, they do not require a very high acid concentration in the strip liquor. This could have been very useful were it not that these reagents also take up acid from the stripping solution and transfer it to the last extraction stage. Acid carry over may be prevented by adding wash stages, but this obviously complicates the circuit. Some problems of insoluble complex formation have also been noted with the Kelex reagents. So far they have not found commercial application in the copper industry.

Diluents

All copper solvent extraction plants presently in operation use kerosene with intermediate to low aromatics content (0-25%) as a diluent for the extractant.

The chemical composition of a diluent may affect the following extractant properties: loading capacity; equilibrium loading; kinetics; stability; selectivity; and phase disengagement.

Variations in these properties have been related to the solvency power of the diluent [19], which itself is related to the aromaticity. An increasing aromaticity may result in: (1) a reduced maximum loading capacity, but only at high aromatics content, (2) a decrease in equilibrium loading, (3) a reduced pH functionality at high aromaticity, (4) a decrease in kinetics, (5) faster phase separation, (6) a decrease

in stripping efficiency, (7) reduced selectivity of copper over iron, (8) improved copper chelate solubility, and (9) increased extractant stability [19-25]. These changes should be regarded only as trends. Not all extractants show changes in each of these properties, and not to the same extent. In fact, variation in aromaticity among diluents currently used in solvent extraction would appear to have very little effect on extraction properties.

The use of perchloroethylene as a diluent for LIX 64N has been investigated [26]. Comparison with Escaid 100 with the use of 10% v/v LIX 64N showed considerably faster phase disengagement, improved iron rejection, a better stripping efficiency and improved kinetics. Another advantage is that perchloroethylene is not inflammable. Perchloroethylene has a higher solubility in water and evaporates faster than the normal kerosene diluent. As perchloroethylene is approximately twice as expensive as normal kerosene, a diluent recovery system is required. Perchloroethylene has been used as a diluent in the Metal-Chem Plant, Mesa, Arizona, which is now closed. Settler specific flows of 387 l/min/m^2 could be achieved [3] that is 4-8 times as high as those for which most other plants were designed.

COPPER SOLVENT EXTRACTION EQUIPMENT DESIGN

All large-scale copper solvent extraction plants treating acid leach liquors with low to intermediate copper tenors use mixer-settlers, arranged for countercurrent extraction and stripping. The main reasons for choosing mixer-settlers instead of other contacting equipment are the high feed flow rates and the relatively slow kinetics of the copper extractants for low-pH sulfate solutions, requiring contacting times of 2-4 min per stage. The copper solvent extraction plants presently in operation on low copper tenor acid leach liquors have two to four extraction and two to three stripping stages.

Because of the nature of the hydrometallurgical processes treating low-grade copper ores or tailings, a development toward very large scale operations has taken place, with inevitable uncertainties in the scale-up of mixer-settlers. After the successful scale-up of the Ranchers Plant [4] from pilot plant data, decisions for construction of much larger plants were taken with more confidence. The first of these very large plants, treating low tenor leach liquors was built at Chingola, Zambia in 1974 [6]. This plant operated successfully and was followed by the large Twin Buttes plant [7] in 1976. However, years of operating experience on these plants highlighted a number of areas in which improvements in mixer and settler design could be made and led to changes in design concepts and scale-up parameters.

Mixer Design

The first commercial copper extraction plant at the Bluebird Mine in Arizona [4] uses circular mixer boxes with straight-bladed, top-shrouded impellers. Dispersion is pumped from the mixer by an axial flow pump to the far end of the settler, and the separated liquors gravitate to the appropriate mixers. With the exception of Ray Mines, all subsequent plants use pump-mix systems [27], in which mixing and pumping is done by the same impeller. The advantage of this system is that no external pumps are required. Recently, certain disadvantages of the pump-mix system were recognized and a new mixer was developed in which pumping and mixing are again separated [28].

In mixer design a compromise must be reached between the objectives of achieving the highest possible mass transfer and keeping entrainments as low as possible.

The main mixer types and configurations that are being used in operating copper solvent extraction circuits or that have been developed for planned treatment plants are described below

Davy McKee mixer

The Davy McKee pump-mix impeller [29-30] is double shrouded with back-swept blades, which were designed for minimum entrainment. It is centrally located in the mixer and the clear phases are introduced through a bottom feed box and a draft tube into the eye of the impeller. Recirculation, and thus mass transfer (Fig.3), is increased by setting the gap between the impeller and the draft tube at a maximum so that the pumping requirements are just met. The mass transfer may be further increased by attaching spoiler blades at the top and/or bottom of the impeller, although this effect is generally small. This increases the power input considerably and the drive mechanism should be designed to cope with this. Mixing vessels fitted with these impellers in the Chingola Tailings Leach Plant and the Twin Buttes Plant have a square cross section and do not have vertical baffles. Vortex formation and air entrainment are prevented by a top plate with a central hole through which the drive shaft passes and the dispersion is discharged.

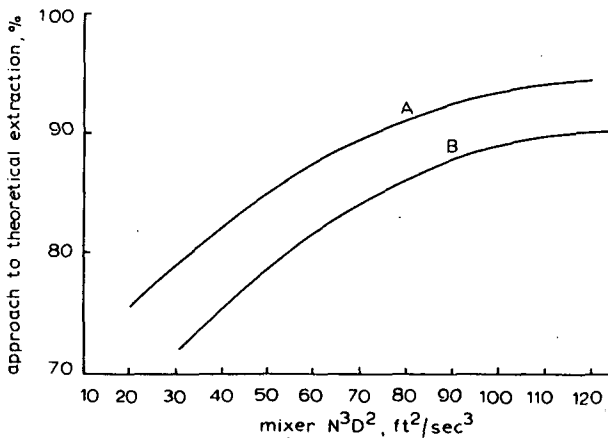


Fig.3. Effect of recirculation through the impeller zone [30].
(A= recirculation in mixer, B = no recirculation)

Holmes-Narver mixer

In the Holmes-Narver mixer design the pump-mix impeller is located at the bottom of the mixing vessel where the clear phases are introduced [31]. The impeller is top-shrouded and has six straight blades. Single-stage mixers using this impeller type have been installed in the Bagdad and Cyprus Johnson plants.

In this mixer design, recirculation, and thus redispersion and coalescence, does not occur. The bulk of the mass transfer takes place during the very short passage of the two phases through the impeller. The later Holmes-Narver design, the "low-profile" mixer [32], consists of three or more compartments in series (Fig.4). The first compartment contains their standard mixing impeller, located near the bottom. One or more additional mixing impellers are installed in the other compartments. The "low-profile" mixer offers the following advantages:

1. As compared to the single stage design, for a given mixer residence time and agitation intensity, mass transfer will be increased as a result of a greater plug flow component and redispersion by the additional mixing impellers.
2. A lower pumping head is required.
3. The lower elevation of the mixer-settler will reduce the cost of a support structure. It should be noted that room for piping is required and that if the mixer-settler is on ground level, some excavation work and a special drainage system may be required.

The low-profile mixer has operated satisfactorily in the Cities Service plant [32]. The stage efficiencies in the extraction circuit were 60% with agitation on one compartment and 75% with agitation in two compartments. It is understood that additional agitator mechanisms will be installed to further increase mass transfer.

NCCM mixer

The NCCM mixer [28] was designed for the expansion of the existing Tailings Leach Plant at Chingola and consists of three mixing compartments, each of which contains a turbine impeller with six straight blades (Fig.5) located at half height. Two vertical baffles in each compartment located on opposite walls prevent rotation of the dispersion and vortex formation, and thus no top baffle is required. The clear phases are separately introduced into the mixer, the organic phase through a central inlet, and the aqueous phase through a side inlet. The aqueous phase gravitates from one stage to the next, whereas the organic is pumped with external, axial flow pumps.

Two main considerations led to this mixer design:

1. Recirculation of dispersion through the impeller zone and thus redispersion and coalescence in the two previous mixer designs were considered inadequate. The centrally located Rushton impeller in the NCCM mixer gives a high recirculation rate of dispersion throughout the mixer volume.
2. Organic continuous dispersion proved highly unstable in the Davy McKee mixers in the Chingola plant, even at organic-to-aqueous (O/A) phase ratios as high as $O/A=1.6:1$ in extraction and $O/A=4:1$ in stripping. It is believed that this was due to:
 - a. The short residence time of the dispersion in the impeller zone. A sudden decrease in organic flow rate will result in an immediate deficit of this phase in the impeller zone and cause a local phase inversion from organic-to-aqueous continuity, which then may quickly spread throughout the mixer.
 - b. Accumulation of aqueous phase in the bottom part of the mixer. The gap between the double-shrouded impeller and the draught tube is probably not wide enough to permit sufficient recirculation.

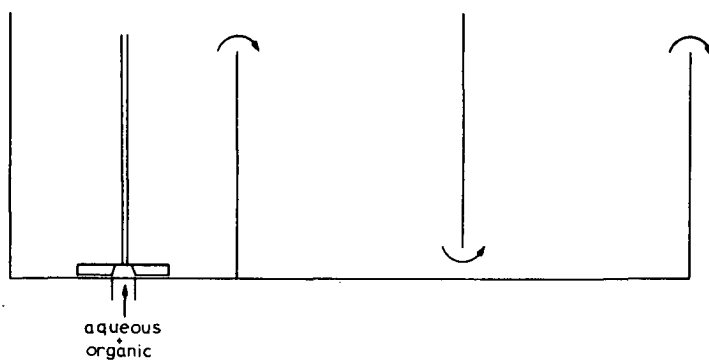


Fig.4. Holmes-Narver low profile mixer.

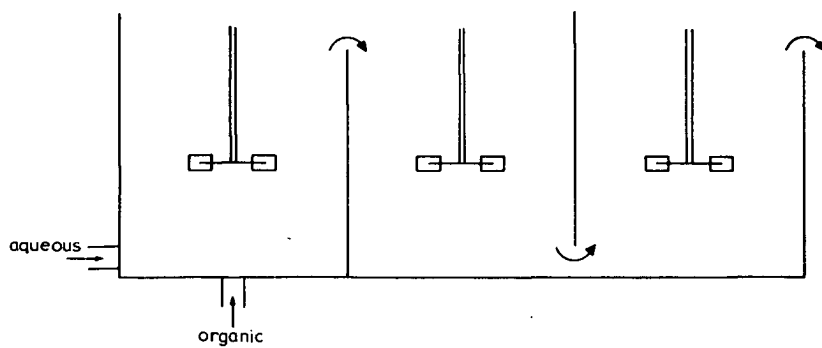


Fig.5. NCCM three-stage mixer.

Also, the power input per unit volume is probably insufficient (see section on mixer scale-up).

In the new mixer design, segregation of aqueous phase is prevented by much improved mixing in the lower half of the mixer and by the increased power input per unit volume as compared to the existing mixer. Phase stability is further improved by the separate introduction of the phases well away from the high shear impeller zone, so that the whole mixer volume acts as a buffer against surges in the continuous-phase flow rate.

A large-scale test mixer based on this design has operated successfully in the first extraction stage of one of the streams in the Chingola Tailings Leach Plant treating a dispersion flow of $1400 \text{ m}^3/\text{hr}$ (O/A ratio 1:1). The average stage efficiency in the first extraction stage was 95% at a total residence time of 3 min and a power input of $1 \text{ hp}/\text{m}^3$. Organic phase continuity could be maintained at a phase ratio as low as O/A = 0.7:1. Entrainment levels were comparable to those of the Davy McKee mixer.

Kenics mixer

The only known planned application of plug flow, static mixers is in Zaire for the treatment of impure leach liquors at Lulu and Shituru. This type of mixer is possible because of the high temperature of the pregnant liquor (60°C) produced in a leach circuit, in which the main feed constituent is roaster calcine. Kinetics of LIX 65N at this temperature are very fast. In view of the potential fire hazard at high temperature, a completely sealed mixer-settler system was chosen. Gecamines tested the Kenics static mixer successfully on a pilot scale. This mixer is essentially a pipe of which certain sections contain alternate right- and left-handed helical blades. These helical segments are positioned such that at their contact the edges are at 90°C , so that splitting of flows and changes in rotation direction of the liquid

flow occur. This generates a dispersion with a narrow drop size distribution and ensures efficient radial mixing.

Mixer-Scale-Up

In the design of mixers for very large copper solvent extraction plants the two criteria - constant tip speed and constant power input per unit volume - have both been used for scale-up based on geometric similarity. The Davy McKee mixers in the Chingola and Twin Buttes plants were scaled up by use of constant impeller tip speed. In Chingola this proved not entirely satisfactory as stage efficiencies were some 5-10% lower than obtained in the pilot plant. In subsequent scale-up test work for the design of the NCCM mixer, it was found that constant power input per unit volume gave better results. On this basis the large-scale test mixer was designed (see section NCCM mixer). Average stage efficiencies in this mixer differed very little from those obtained in a pilot-scale unit.

Apart from scale-up with respect to mass transfer, entrainment and phase stability must also be considered. If constant power input per unit volume is used as the scale-up criterion for obtaining a particular stage efficiency, it might result in excessive entrainment, although this did not prove the case for the NCCM mixer at Chingola. On the other hand, if constant tip speed is used for scale-up, it should be realized that the power input per unit volume decreases with increasing mixer size to the point at which segregation of the phases occurs. This has been found to occur in a pilot-scale mixer at 0.2 hp/m^3 . The power input per unit volume in the Chingola mixers is close to this critical value; this may contribute to the phase stability problems encountered.

It was recently shown that for a given mixer size but different impeller diameters, the stage efficiencies remain unchanged if the tip speed is kept constant. Organic-in-aqueous entrainments varied and reached a minimum at a tank width:impeller diameter ratio of approximately 3:1.

The following procedure for mixer design and scale-up has thus been proposed [28]:

1. The tip speed for the required stage efficiency is determined in a laboratory mixer.
2. At this selected tip speed the optimum impeller:tank diameter ratio with respect to entrainment is determined in the same vessel under continuous flow conditions.
3. The scale-up from the laboratory mixer to commercial size is carried out by use of geometric similarity and equal power input per unit volume.

Settler Design

Settler area requirements are generally determined from pilot-plant data for given mixing conditions by use of the scale-up criterion of constant flow of dispersed phase per unit settler area. Dispersion band depths are determined for various specific settler flows, which can be conveniently done by changing the settler area with a vertical dam baffle. Important factors to be considered are extractant tenor, diluent type, phase continuity, temperature and suspended solids in the pregnant liquor. As the settling area required for organic continuous dispersions is considerably greater than that for aqueous continuous dispersions, settlers are designed for organic phase continuity, even when several stages operate aqueous continuous, to avoid flooding when phase inversion occurs.

Temperature has a considerable effect on dispersion bands: in the pilot-plant studies in Chingola the dispersion band volume was halved when the temperature increased from 25°C to 35°C. It is thus very important to take seasonal temperature changes into consideration in settler design.

The functional relationship between dispersion band thickness and specific settler flow in the copper-LIX 64N system is generally exponential and can be adequately described by the function:

$$H = k(Q/A)^n$$

where H= dispersion band thickness, Q= dispersion flow rate, A= settler area, K= constant, and N= exponent that varies from 1 to 7. If a high exponent is found, specific settler flows are selected with an ample safety margin to avoid the steep part of the curve and thus flooding of the settler. For a low exponent the selection of the specific flow is less critical. It should be pointed out that for a given extraction process, the exponent may be affected by a number of factors, including size, quantity and type of suspended solids. These suspended solids generally result in more rapid coalescence, although masking of the interface may occur at high concentrations.

Several coalescing aids have been proposed to reduce the required settler area, thereby reducing construction costs and organic inventory costs:

1. Vertical baffles.

Vertical baffles cause an increase in dispersion band depth and reduce the velocity of the dispersion. Thick dispersion bands also tend to reduce aqueous in organic entrainment significantly as compared to thin, wedge-shaped dispersion bands. A settler design incorporating several vertical baffles, each with short horizontal baffles to increase the area available for coalescence [33], has been proposed for the copper solvent extraction plant at Panguna, Papua New Guinea. In this design most of the coalescence takes place in the first one third of the settler, whereas the remainder of the settler serves to reduce entrainment in the separated phases. This settler gave a very marked reduction in aqueous entrainment as compared to an unbaffled settler.

2. Vertical screens.
3. Perforated plates.
4. Vertical parallel rods.
5. Knit-mesh packing.

This consists of interwoven, stainless steel and polypropylene filaments [34]. Coalescence of organic droplets is enhanced by the high-surface-energy, organic wetted polypropylene, whereas coalescence of aqueous droplets is promoted by the low surface energy, aqueous-wetted stainless steel. The presence of both materials ensures enhancement of coalescence regardless of phase continuity.

6. Precoalescence by a packing with Rashig rings [35].
7. Horizontal baffles.

Horizontal or near-horizontal baffles or trays extending over a major part of the settler area divide the incoming dispersion into what can be visualized as a series of superimposed settlers and, therefore, allow a very significant reduction in total settler area required. Examples are the Lurgi multitray settler [36] and the IMI compact settler [37].

These coalescence aids certainly do reduce settler area, but they also complicate crud and scale removal, and as far as is known, they have as yet not been installed on any operating plant.

Settlers installed in copper solvent extraction plants all have a rectangular shape, although there is no obvious reason why circular settlers with a centre feed should not be considered. The latter would, in fact, have the advantage of low linear velocities of the separated phases at the peripheral weirs, thus minimizing entrainment.

The length:width ratio of a settler is determined by the opposing requirements of minimizing the organic inventory and maintaining acceptable entrainment levels. The entrainment levels in the separated phases are a function of the linear velocities in these phases at the discharge weirs. For each phase, a critical linear velocity exists above which entrainment rises sharply until eventually gross flooding occurs as the dispersion band is dragged over the organic weir or under the organic weir into the aqueous weir. Generally, sufficient aqueous depth is allowed to be well below the critical velocity of the clear aqueous, so that only the critical velocity in the organic phase needs to be considered. This critical linear velocity of the organic phase typically is in the region 5-10 cm/s (Fig.6). For a given settler area, the organic inventory becomes proportional to the depth of the clear organic

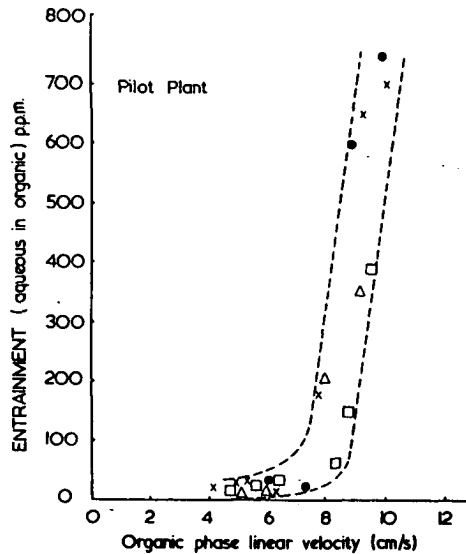


Fig.6. Aqueous entrainment as a function of linear velocity [28].

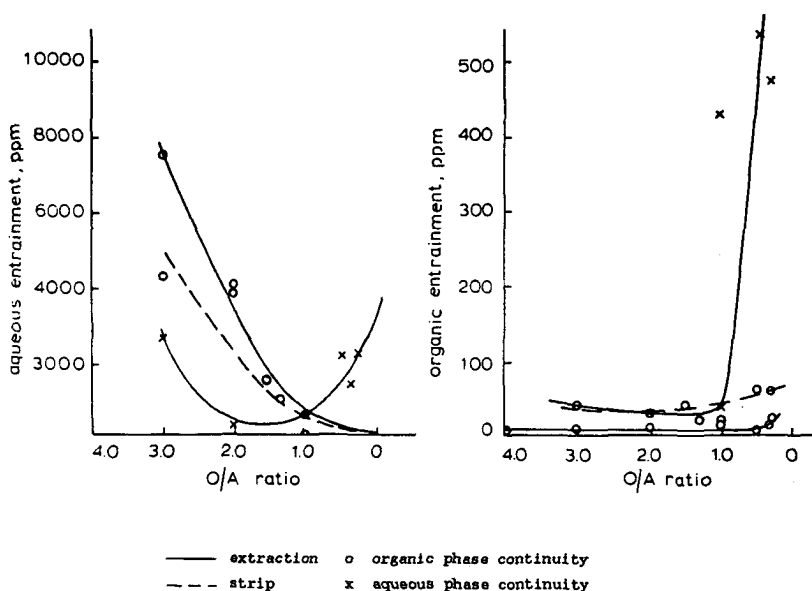


Fig.7. Effect of phase ratio on entrainment [38]

phase. To avoid exceeding the critical linear velocity, the clear organic depth can be decreased only by simultaneously increasing the settler width. The settler width is limited by problems of even distribution of the dispersion from mixer to settler and of maintaining uniform flow within the settler. The latter could be overcome by installing lengthwise flow straighteners. At very shallow organic depths disturbances in the upper surface of the dispersion band could cause a sharp rise in aqueous entrainments.

In most operations the settler length:width ratio is in the region 2-4:1. The first radical change from this aspect ratio was made in the design of the settlers for the Cities Service plant, which have a

length to width ratio of 1:1. For the Chingola Tailings Leach Plant expansion, a settler length:width ratio of 0.93:1 is proposed to reduce organic inventory [28].

Over recent years Davy McKee have developed a combined mixer-settler [39,40], consisting of a large tank with a centrally placed mixer, in which separation of the organic and aqueous phases takes place in the top and bottom sections respectively. The mixer is characterized by a relatively large mixing volume, with low impeller tip speeds; mixer kinetics and mass transfer are not good by comparison with other mixers presently in use for copper solvent extraction, but the "settler" area is reduced by a factor of 8-10. The overall equipment cost and organic inventory are thereby considerably reduced. The combined mixer-settler has found application in the uranium solvent extraction industry; with some modifications its application is likely to be extended to copper solvent extraction, in association with reagents characterised by relatively rapid kinetics.

PROBLEM AREAS IN DESIGN AND OPERATION OF COPPER SOLVENT EXTRACTION PLANTS.

Entrainment

Organic-in-aqueous and aqueous-in-organic entrainment are generated both in the mixer and in the settler. Important factors are:

- Mixing power input

High mixing power input may increase both aqueous and organic entrainment

- Phase ratio

The phase ratio has a marked effect on entrainment [38]. For organic

continuous dispersions, the aqueous entrainment increases considerably at phase ratios higher than approximately $O/A = 1.5-2:1$ in both extraction and stripping (Fig.7). In the extraction circuits of copper solvent extraction plants the phase ratio is generally less than $2:1$. In the stripping circuit high phase ratios are usually applied and thus it is necessary to recycle the aqueous phase to maintain a mixer phase ratio of $1:1$. A further reason for applying aqueous recycle is that at high phase ratios the mass-transfer rate and thus stage efficiencies are reduced, possibly as a result of a decreased rate of coalescence and redispersion of the dispersed phase in the mixer. The organic entrainment appears to be virtually independent of the phase ratio (Fig.7).

For aqueous-phase continuity, the aqueous-in-organic entrainment reaches a minimum at a phase ratio of around $O/A = 1.5:1$, although the exact location of this minimum is not certain. The organic entrainment increases sharply at phase ratios less than $1:1$ (Fig.7).

- Phase continuity

Although a relationship exists between entrainment level and phase continuity, this is not well defined and may be different for particular conditions, as indicated by different operating practice in a number of plants. In the Cities Service plant all mixers operate aqueous continuous except for the last extraction mixer. Here, organic continuity has been found to reduce organic loss in the raffinate. However, less organic in electrolyte entrainment has been observed when operating the second strip mixer aqueous continuous. In the Anamax Twin Buttes plant the first extraction mixer operates aqueous continuous, which reportedly gives lower aqueous entrainment in the loaded organic. In the Cyprus Johnson plant all mixers operate aqueous continuous because of lower aqueous-in-organic entrainment. The Bagdad plant operates with organic phase continuity in the last extraction stage and the second stripping stage to reduce organic entrainment.

Entrainment studies in the Chingola plant showed that the organic entrainment is virtually the same for both phase continuities; stage efficiencies also seem to be independent of phase continuity. Although normal aqueous-in-organic entrainment is low during operation in the aqueous continuous mode, the flotation of dispersion band fragments causes relatively high overall aqueous carry-over. This is generally difficult to quantify with the normal method of aqueous entrainment determination, which uses centrifuge tubes with a calibrated capillary at the lower end to measure the aqueous volume. The volume of these tubes is relatively small. Much larger sample volumes would be required for estimation of the aqueous carry-over due to the dispersion fragments.

- Air entrainment

Entrained air causes a marked increase in the entrainment of organic which is generated in the mixer. It will also enhance the flotation of dispersion fragments in the settler when operating in the aqueous continuous mode. Vortex formation in the mixer should thus be avoided and all weir profiles should be carefully designed to minimize turbulence.

Solids and Crud Handling

Suspended solids in the form of gangue minerals and gypsum precipitated from supersaturated leach liquors accumulate on the settler bottom and in the dispersion band at the coalescing front and are generally referred to as crud. The dispersion band crud contains, when removed, considerable quantities of organic phase that is generally recovered by centrifuging. Removal of interfacial crud should be carried out regularly to prevent build-up and subsequent breakthrough at the weirs.

A crud problem frequently exists in leaching of ground ore or tailings with subsequent solids-liquid separation in thickeners. Dump or in situ

leach operations usually have very low levels of suspended solids in the pregnant liquor.

Prevention of crud formation by an efficient clarification-filtration system is evidently an area to which considerable attention should be devoted. Overflow from the first washing thickener is generally filtered in sand filters, either directly or following an intermediate clarification step, which serves to remove the bulk of the coarser suspended solids and ensures a more uniform feed solids level to the sand filter.

Considerable problems may result from calcium supersaturation of the pregnant liquor, which results in gypsum precipitation in the feed nozzles and in the bed of the sand filter, thus reducing filter capacity. Gypsum scale formation in the pipework of the solvent extraction circuit results in a reduction of flow rates and necessitates expensive descaling campaigns. Calcium supersaturation can be reduced by contacting the pregnant liquor with gypsum seed crystals in a sludge bed clarifier. A critical pH exists below which good clarities cannot be maintained for long periods with a gypsum sludge bed unless portions of the bed are regularly replaced with freshly precipitated gypsum, produced by partially neutralizing some raffinate.

Organic Additives

Flocculants, smoothing agents, and mist suppressants for electrowinning must be carefully tested to ensure compatibility with solvent extraction operations. Cationic flocculants are generally not compatible with LIX 64N in kerosene, but several nonionic and anionic polyacrylamides and guar have been found to be satisfactory. Nonionic polyacrylamide flocculants are currently used in the leaching/CCD circuit of the Chingola Tailings Leach Plant. Both nonionic polyacrylamide and guar are used for inhibition of nodular growth in electrowinning. Satisfactory foaming agents for mist suppression in electrowinning have proved difficult to find since the structural properties that lead to a

lowering of the air-water interfacial tension and foam formation, also lead to low interfacial tension between aqueous and organic phases, with a consequent tendency to formation of stable emulsions. However, a patented reagent has recently been under test at the Inspiration Copper Corporation plant in Arizona with apparently promising results.

Materials of construction

The combination of copper and high acid, together with kerosene, complicates the choice of materials for copper solvent extraction plants. Stainless steel, either free-standing or as a liner for concrete, is the most favoured material for withstanding corrosive attack. Glass-fiber-reinforced plastics have been used for piping. Plasticized PVC has been proposed as a settler lining material, but leaching of the plasticizer by kerosene can occur, and this may affect solvent extraction. Rubber-lined mild steel has been used for construction of tanks and storage vessels. Nitrile rubber must be used as natural rubbers are rapidly attacked by kerosene. Lead lining cannot be used for mixer-settlers as entrained organic droplets cause rapid pitting corrosion.

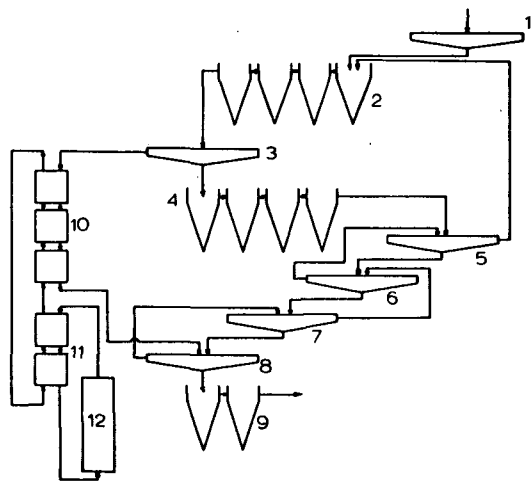
DESCRIPTION OF TYPICAL PLANTS

NCCM Tailings Leach Plant, Chingola, Zambia.

In the Tailings Leach Plant [6] at Chingola (see Fig.8 for flow sheet) the feed material is fine tailings from the concentrator. The material contains a number of acid soluble minerals: malachite, chrysocolla, cupriferous mica, cuprite, azurite and pseudomalachite. Leaching is carried out in a countercurrent two-stage process in pachucas. The secondary leach takes place at relatively high acid strength to achieve maximum copper extraction. Solution from the second-stage leach is contacted with fresh tailings in the primary leach to yield a low-acid pregnant solution for solvent extraction. Solids-liquid separation is

Item	Extraction	Strip
Mixer width (m)	5.9	4.0
depth (m)	3.7	3.2
Mixer impeller diameter (m)	2.7	2.3
Settler width (m)	12.2	12.2
length (m)	36.5	26.2
depth (m)	0.8	0.8
Dist. picket fence1-inlet (m)	13.1	9.1
Dist. picket fence2-inlet (m)	30.5	21.9
Specific settler flow (l/min/m ²)	60	80

Table 2. Dimensions of Tailings Leach Plant mixer-settlers.



- 1 = pre-leach thickener 2 = primary leach (8 pachucas)
- 3 = CCD 1 thickener 4 = secondary leach (4 pachucas)
- 5-8 = CCD2-5 thickeners 9 = neutralisation (4 pachucas)
- 10 = SX extraction 11 = SX stripping
- 12 = tankhouse

Fig.8. NCCM Tailings Leach Plant at Chingola.

carried out in countercurrent wash thickeners in four to five stages, with barren raffinate being used as the wash liquor.

The overflow from the first washing thickener was previously filtered in 11 pressure sand filters. A major difficulty was the precipitation of gypsum in the sand bed, which caused serious reduction in capacity and consequently in overall efficiency of the filter plant. Filtration in pressure sand filters has now been abandoned. Pending construction of an alternative clarification plant, the CCD1 overflow is now being clarified in one of the wash thickeners. The solids content of the pregnant liquor to solvent extraction frequently exceeds 200 ppm; thus crud build-up is extremely rapid.

Pregnant liquor, generally containing 3-6 g/l Cu at pH= 1.9-2.0, is treated in four parallel solvent extraction streams. Each stream consists of three extraction and two strip stages and treats approximately $700 \text{ m}^3/\text{hr}$ of pregnant liquor. Three of these streams use a 22 vol% solution of LIX 64N in Escaid 100. The fourth stream uses a 14% solution of the SME 529, also in Escaid 100. Consideration is being given currently to use PT-5050.

Mixer-settlers are made of stainless steel lined concrete. The square box mixers use double-shrouded pump-mix turbines with backswept blades. The top of the mixer has a full-width horizontal baffle to prevent vortex formation and short circuiting. The mixer discharges through a 1.7 m outlet in the vortex baffle, concentric with the centre shaft, by way of a flared launder through a full-width entry slot into the settler at the level of the dispersion band. Each settler is fitted with two picket fence baffles. Important dimensions of the mixer-settler units are given in Table 2.

Phase ratios (O/A) are 1:1 in extraction and 4:1 in strip, with aqueous phase recycle around each mixer-settler unit on the strip side, to give a 1:1 phase ratio in the mixers. Because of reasons outlined in previous sections, it has proved impossible to operate the mixers in any

but the aqueous continuous mode. Extraction stage efficiencies of 85-90% and stripping stage efficiencies of 75-85% are generally achieved, yielding raffinates of 0.4-0.5 g/l Cu. However, a major problem with this plant is the variable nature of the feed material, giving rise to pregnant liquors with copper contents varying from 3 to 6 g/l. At the upper end of this range, extraction efficiencies naturally fall off because of approach to maximum loading capacity of the extractant and the generation of excess acid from the extraction reaction.

Crud formation results in excessive organic loss, estimated at 170 ppm based on overall raffinate flow. Crud is removed from both extraction and strip stages several times per year by dumping into ground sumps and is then separated in pusher centrifuges. The high rate of crud formation was not foreseen at the design stage, and future plants of this type will probably include more advanced technical crud removal and handling facilities.

The electrowinning circuit is operated at an average current density of 320 A/m^2 ; it may be noted that current densities of up to 450 A/m^2 were found practical in pilot-scale and plant test work. This is a considerable increase over most electrowinning operations and is made feasible by the improved electrolyte purity resulting from solvent extraction. Initial problems with filtration led to carry-over of fine solids that adversely affected cathode quality. Problems with entrainment of organic in electrolyte, causing a loose powdery deposit at the top edge of the cathode, were also encountered. Subsequent operation has shown that high quality cathodes can be produced at the exceptionally high current densities in use at Chingola.

Cities Service Company, Miami, Arizona.

This relatively new plant [32] was commissioned in 1976. Pregnant liquor for solvent extraction is generated by percolating acid solution through an oxidized and weathered cap overlying a mined-out copper sulfide orebody. Copper in the oxidized cap occurs mainly as chrysocolla, wad,

Company and Location	Commenced	Type of Feed	Rate of Production Tons/Year	Pregnant Aqueous Feed			Extraction Agent	Diluent	Number of Streams	Flow per Stream, m ³ /hr	Number of Stages		Phase Ratio (O/A)		Temperature of Solvent Extraction °C
				Flow Rate, m ³ /hr	g/liter Cu	pH					Extraction	Strip	Extraction	Strip	
Ranchers' Exploration Bluebird Mine, Arizona	1968	Heap leach liquor, sulfate	7,500	460	1.8-2.3	1.8-1.9	12% LIX64N	Nap 470B	1	460	3	2	1.15:1	3:1	25-30
Cyprus Bagdad Copper Co. Bagdad, Arizona	1970	Heap leach liquor, sulfate	7,000	550	1.4-1.6	2.0-2.3	8% LIX64N	Chevron, Nap 470B	4	140	4	3	1:1	20:1	16-25
Nchanga Consolidated Copper Mines, Chingola, Zambia	1974	Agitation leach liquor, sulfate	80,000	3200	3-4	2.0	24% LIX64N 14% SME529	Escald 100	4	800	3	2	1:1	4.5:1	30-35
Arbiter Plant Anaconda Co., Anaconda, Montana	1974	Ammonia leach liquor from sulfide concentrate	36,000	84	28-33	180 g/liter NH ₃	32% LIX64N	Nap 470B	1	84	2 + 1 wash	2	-	-	35-40
Anamax Mining Co., Twin Buttes, Arizona	1975	Agitation leach liquor, sulfate	33,000	1400	2.9	1.9	12% LIX64N	Chevron Kerosene	2	700	4	2	1.2:1	12:1	23°C minimum
Capital Wire and Cable, Casa Grande, Arizona	1970	Ammonia leach liquor from scrap copper	2,500	11.5	30	3g/liter NH ₃	20% LIX64N	-	1	11.5	1 + 1 wash	2	6:1	3:1	-
Cyprus Johnson Copper Co., Johnson Camp, Arizona	1975	Heap leach liquor, sulfate	5,000	570	1.3-1.4	2.1	6% LIX64N	Nap 470B	5	120	3	2	1:1	20:1	10-25
Cities Service Co., Miami, Arizona	1976	<i>In situ</i> leach liquor, sulfate	5,500	680	1.0	1.0 g/liter H ₂ SO ₄	6.2% LIX64N	Nap 470B	2	340	3	2	1:1	-	22-26
Cerro Verde, Minero Peru, Arequipa, Peru	1977	Heap leach liquor, sulfate	33,000	1400	5	1.5-1.8	30% LIX64N	-	4	385	3	2	1:1	-	15
Inspiration Consolidated Copper Company, Arizona	1979	Heap leach liquor, sulfate	26,000	908.4	1.4	4.0 g/liter H ₂ SO ₄	7% Acorga P5300	Chevron ion-exchange solvent	1	908.4	2	2	1.1:1	10:1	19

Table 3. Details of copper solvent extraction plants commissioned up to 1979.

Company and Location	Fire-Fighting Facilities	Materials of Construction			Mixer Type	Mixers			Settlers			Specific Settler Flow, liter/m ² min	Crud-Handling Facilities
		Mixer-Settlers	Pipes	Tanks		Residence Time, min	Depth, m	Width, m	Length, m	Width, m	Depth, m		
Ranchers Exploration Bluebird Mine, Arizona	Water posts	Stainless steel and fiberglass-lined concrete	FRP	FRP and RFP-lined steel	Circular tanks, turbine mixer	2	—	—	—	—	—	80	Filtered in plate/frame
Cyprus Bagdad Copper Co., Bagdad, Arizona	Foam sprinklers in settlers	Stainless steel supported by mild steel	PVC- and PVC-lined steel	PVC-lined steel or concrete	Holmes-Narver pump-mix	2	—	1.2 diameter	19.8	4.3	1.14	80	Centrifuge
Nchanga Consolidated Copper Mines, Chingola, Zambia	Foam sprinklers in settlers	Stainless steel lined concrete	PVC-lined FRP	Rubber-, FRP-lined mild steel	Davy McKee pump-mix	extr. 3 strip 3	3.7 3.2	5.9 4.0	36.5 26.2	12.2 12.2	0.76 0.76	60/80	Centrifuge
Arbiter Plant Anaconda Co., Anaconda, Montana	—	304L stainless steel	Stainless steel and PVC	Stainless steel	Davy McKee pump-mix	2.5	—	—	—	—	—	70	—
Anamax Mining Co., Twin Buttes, Arizona	Water sprinklers in settlers	Stainless steel	Stainless steel, PVC in tank-house	Rubber-lined steel, stainless steel	Davy McKee pump-mix	3.5	3.7	4.6	E1, E2: 51 E3, E4: 45.6 S: 37.3	13.7	—	60	Centrifuge
Capital Wire and Cable, Casa Grande, Arizona	—	—	—	—	—	—	—	—	—	—	—	—	—
Cyprus Johnson Copper Co., Johnson Camp, Arizona	Water sprinklers in settlers	Fiber-reinforced plastic	Fiber-reinforced plastic	Fiber-reinforced plastic	Holmes-Narver, pump-mix	3	—	—	—	—	—	80	Centrifuge
Cities Service Co., Miami, Arizona	Water posts	Stainless-steel-lined concrete	Stainless steel	Stainless steel	Holmes-Narver, low profile	3 except 1st stage strip, which has 6	1.0	—	15.2	11.9	—	75	Centrifuge
Cerro Verde, Minero Peru, Arequipa, Peru	Heat-activated sprinklers in settlers	Stainless steel	FRP and stainless steel	Plastic-lined concrete, stainless steel	Wright Engineers design, cylindrical tank	3	3.6	3.25 diameter	21.3	9.1	—	53	—
Inspiration Consolidated Copper Company, Arizona	Automatic foam system to mixers, settlers, and pipe trenches, actuated by fusible link detectors	316L stainless steel	Stainless steel or high-density polyethylene	Mainly 316L stainless steel	Two-stage mixers, pump-mixer followed by a radial flow mixer	2 in first compartment, 1 in second	3.3	3.6	25	17	1.21	61	Movable hand-held suction pump to storage and then to Delaval centrifuge

Table 3. (Continued).

and cupriferous mica, with smaller amounts of sulfide copper. In addition to the normal acid leaching of the oxide copper minerals, bacterial leaching of the sulfide is taking place. It is notable that this is unaffected by traces of solvent extraction reagents. As the acid solution percolates through the orebody, the acid content becomes neutralized and the copper content builds up. The pregnant liquor contains 1.0 g/l Cu, about 0.5 g/l H_2SO_4 , and very low suspended solids, generally less than 25 ppm, and thus no filtration is required.

Pregnant liquor is treated in two parallel solvent extraction streams, where it is contacted with 6% LIX 64N in kerosene. The plant features the Holmes-Narver low-profile mixer with an effective liquor depth of about 1 m. Each separate compartment is now provided with a turbine. The first strip mixer has six compartments, giving a total residence time of 6 min. All other mixers have three compartments, giving a total residence time of 3 min. Linear velocity in the settlers has been reduced by making them almost square in shape. This coupled with the low rate of crud formation and the effective distribution of the feed into the settler by means of a picket fence baffle at the settler feed end has reduced the organic losses to about 30 ppm based on raffinate flow. Crud is removed through a pipe near the organic weir and separated in a centrifuge.

Stripping of the loaded organic is carried out with spent electrolyte containing 30-33 g/l Cu and 150 g/l H_2SO_4 at a phase ratio (O/A) of approximately 2:1. A phase ratio of 1:1 is achieved in individual stages by internal recirculation of aqueous.

The absence of solids and of organic entrainment in the advance electrolyte permits production of high-quality cathode in electrowinning at the relatively high current density of $270 A/m^2$.

Further details on this plant and other operating copper solvent extraction plants are given in Tables 3 and 4.

Company and Location	Commenced	Type of Feed	Rate of Production, Tons/Year	Pregnant Aqueous Feed				Extraction Agent	Diluent	Number of Streams	Flow per Stream, m ³ /hr	Number of Stages	
				Flow Rate m ³ /hr	g/liter Cu	pH						Extraction	Strip
Duval Corp., Battle Mountain	1979	Heap leach liquor sulfate	4,000	400	1.2	2.0	7% LIX64N	Chevron		1	400	3	2
Kennecott Corp., Ray Mine, Arizona	1980	Vat leach liquor sulfate	38,000	1400	3.5	1.8	ACORGA P5100	Escaid 200 Kermac		2	700	2	2
Sociedad Minora Pudahuel, Lo Aguirre, Chile	1980	Tailings leach liquor sulfate	15,000	—	5.0	1.9	30% LIX64N	—		—	—	2	2
CIA Minera de Cananea, Sonora, Mexico	1980	Heap leach liquor sulfate	15,000	900	2.5	1.9	ACORGA P5100	Chevron		1	450	2	2
Minero Peru, Cerro De Pasco, Peru	1980	Mine water liquor sulfate	6,000	—	1.0	1.5	ACORGA P5100	—		—	—	3	2
Noranda Lakeshore Mine, Arizona	1981	Vat leach liquor sulfate	25,000	454	6-7	1.6	ACORGA P5100	Chevron		1	454	3	2
Cities Service Co., Pinto Valley, Arizona	1981	Dump leach liquor sulfate	3,500	1400	0.35	2.2	1.7% LIX622	Chevron		2	700	2	1

Table 4. Details of copper solvent extraction plants commissioned in 1979-1981.

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2.7. DETERMINATION OF THE SEPARATION EFFICIENCY IN DENSE MEDIUM SEPARATION OF POROUS MATERIALS USING MAGNETIC TRACERS

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INTRODUCTION

In 1962, Visman reported the use of density tracers to monitor the performance of water-only cyclones in coal preparation [1]. Tracers were later used to assess the efficiency of dense medium cyclones in the South African diamond industry. Foreman and Amundson [2] report the use of magnetic tracers in a 1 inch cyclone used for pyrite removal from coal.

The statistical aspects of using tracers in dense medium separation were discussed by Napier-Munn [3] and by Davis et al [4]. They showed that rather large numbers of tracers were required to obtain sufficient accuracy in a Tromp curve. For example for a density of 3.1 g/cm^3 , a partition number of 10% and a precision of 1%, a total of 2435 tracers would have to be added. As 5 - 10 density points would be required to determine a Tromp curve and the derived E_p value, the total number of tracers would be very high. An additional requirement is that the tracer dimensions should correspond to the average grain size of the material being processed. For fine dense medium separation in dynamic separators the tracer size and the required number of tracers would be such as to make the manual recovery of the normally used non-magnetic tracers from the product streams impractical. Yet the use of tracers has distinct advantages over the traditional heavy liquid analysis, which requires large samples to be processed in order to ensure sample representativeness and therefore can be very laborious and is thus costly to perform on a routine basis. In the case of porous material,

absorption of the heavy liquid by the particles may cause errors in the Tromp curve. The latter phenomenon occurred during exploratory testwork on oil shale from the Tarfaya deposit in Morocco. It was observed that shale fragments which initially floated in mixtures of tetrabromoethane and toluene started to sink after some time due to absorption of the heavy liquids. In view of this it was decided to employ the tracer method during piloting of the dense medium separation for upgrading the oil shale prior to oil extraction. Considering the statistical aspects mentioned above it was realised that automatic recovery of the tracers would be necessary. The use of magnetic tracers would make this possible.

TARFAYA OIL SHALE

In 1981 Shell Prospecting B.V. and the Moroccan state oil company Onarep entered into a joint venture to explore and evaluate the Tarfaya oil shale deposit. This deposit is situated in the eastern part of Morocco along the Atlantic coast, south of Agadir and on the same latitude as the Canary Islands. It extends over an area of about 170 000 km². The kerogen actually occurs in a chalk, but it is referred to as oil shale following colloquial usage. The oil shale often shows a distinct banding of dark (kerogen-rich) and light (kerogen-poor) components (Fig.1), varying in thickness from 50 to 2500 mm. The kerogen-rich layers frequently show a fine structure of lighter and darker laminae, which vary in thickness from 0.2 to 1.5 mm. These laminae are composed of dark wavy kerogen platelets and light carbonate pellets, foraminifera and a carbonate matrix. As Leine [5] reported, borehole logs showed a good correlation between the bulk density and the kerogen content of the rock. The log can, however, only discriminate over an interval of about 10 cm and therefore displays a moving 10 cm average density. It is thus unable to indicate the potential for upgrading due to the laminations shown in Fig.1. The porosity of kerogen-rich material is as high as 40% but decreases with decreasing kerogen content to 20% due to the filling of pores with calcite and to recrystallisation.

PROCESSING OF OIL SHALE

The kerogen is converted to oil in retorts at high temperature. For the retorting process it is necessary to crush, grind and dry the shale. Billiton Research was asked to investigate the possible process routes and to make recommendations. Since the shale was of comparatively low grade, with high probable retorting costs and relatively low mining costs, the potential of upgrading the shale was also examined.

In view of the density differences and the distinct banding of the oil shale dense medium separation was considered as a possible means for upgrading. By crushing the shale to less than 20 mm the majority of the resulting fragments would contain predominantly material from either the light, higher density bands or the darker, low density bands.

Preliminary laboratory heavy liquid tests on borehole samples had shown promising results. However, the previously mentioned absorption of heavy liquid by the shale particles and the variability in results on different samples led to the decision to test dense medium separation at pilot plant scale.

MAGNETIC TRACERS

Initially various attempts were made to manufacture tracers by casting mixtures of powdered magnetite in a cold setting resin; the method used by Foreman and Amundson [2]. Difficulties were encountered with segregation of the magnetite but these could be overcome by rotating the moulds around a horizontal axis during the hardening process.

Entrainment of air during the casting caused significant variation in the densities of tracers within a particular batch and the manufacturing procedure was rather labour intensive. In view of this the possibility of extruding mixtures of magnetite or ferrosilicon and polypropylene was explored. Extrusion tests were done at the Shell laboratory in Amsterdam. It appeared that with magnetite tracers of the required

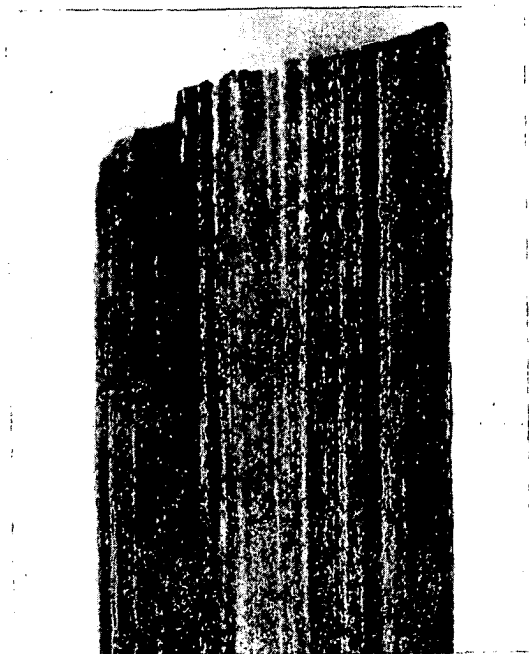


Fig.1. Texture of the Tarfaya oil shale.

Av.tracer density (g/cm^3) and 95% conf. limits	No. of tracers measured
1.610 $\pm$ 0.008	10
1.667 $\pm$ 0.011	10
1.682 $\pm$ 0.010	20
1.688 $\pm$ 0.007	20
1.694 $\pm$ 0.011	10
1.720 $\pm$ 0.010	10
1.752 $\pm$ 0.006	20
1.757 $\pm$ 0.005	20
1.791 $\pm$ 0.005	40
1.795 $\pm$ 0.004	89
1.818 $\pm$ 0.004	40
1.826 $\pm$ 0.005	40
1.865 $\pm$ 0.009	20
1.900 $\pm$ 0.011	10
1.966 $\pm$ 0.007	10

Table 1. Tracer densities.

maximum density (2.1 g/cm^3) could not be produced due to a restriction on the volume percentage of magnetite for sufficient cohesiveness. Ferrosilicon, however, proved satisfactory. The mixture of ferrosilicon and polypropylene was fed to the extruder, in which it was heated to about 350°C and extruded as a 3 mm diameter rod. After quenching in water the rod was broken up into 6 mm long fragments. These appeared to have considerable axial porosity. For further densification the fragments were recycled and the procedure repeated. Fifteen different tracer batches were produced covering the density range of $1.61\text{--}1.97 \text{ g/cm}^3$. The use of ferrosilicon as a filler resulted in the production of black tracers, so tracers of a particular density batch were given a distinctive colour by spraying with paint to allow hand sorting from a mixture of different densities.

From each of the tracer batches a number of tracers were selected and the individual densities measured by a hydrostatic method using a microbalance. The average tracer densities and the 95% confidence levels are given in Table 1.

PILOT SCALE DENSE MEDIUM TESTWORK

For the pilot scale testwork on the Tarfaya oil shale a choice had to be made between a cyclone, a Dyna Whirlpool and a Triflo separator. It was initially considered that less abrasion of the soft shale particles and thus less slimes generation might occur in the latter two separator types as the feed is introduced along the air core, whereas in a cyclone it is introduced along the wall. Further abrasion could occur in the cyclone feed pump. As a 9 inch Dyna Whirlpool was available at the time in the pilot plant at Billiton Research it was decided to use this separator for the testwork.

After crushing to -15 mm and washing, the oil shale was stored in two feed bunkers. The material was fed with a variable speed belt feeder to the Dyna Whirlpool. The sinks and float streams gravitated onto an Allis

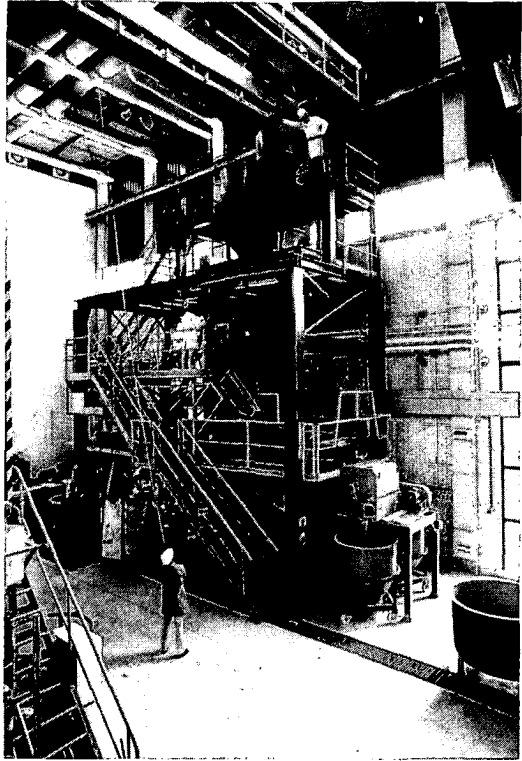


Fig.2. Heavy medium pilot plant.

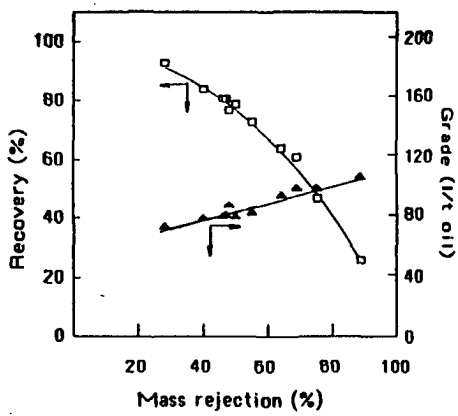


Fig.3. Grade and recovery relationships.

Chalmers vibrating drainage/washing screen. As shown in Fig.2 a Sala dry, low intensity drum magnetic separator at the discharge end of the vibrating screen recovered the magnetic tracers from the product streams. Magnetite with an 80% passing size of 30 μm was employed as the medium. The medium density in the primary circuit was controlled with a gamma ray densitometer and the volumetric flow rate of the feed to the separator was measured with a Doppler flowmeter. Medium from the dilute washings was regenerated with a single stage, wet magnetic drum separator.

Most of the pilot scale testwork was done on a shale sample with an average oil yield of 56 l/t. The relationships between recovery, grade and mass rejection are shown in Fig.3. A mass rejection of 40% was obtained at a loss of 20% of the kerogen and a floats grade of 80 l/t oil. As about 40% of the feed weight lay in the range ± 0.1 of the separating density, it was important to establish whether the separation was limited by the shale characteristics or by shortcomings of the process. An accurately determined Tromp curve was therefore essential and thus tracers were used.

About 1500 tracers of each of the 15 density batches were added together to the feed to the Dyna Whirlpool. The total tracer recovery was 99.3%. The distribution percentages to the sinks are given in Table 2 together with the 90% confidence limits determined from the graphs provided by Napier-Munn [3]. A modified hyperbolic tangent function [6] was fitted to the data using non-linear regression and the resulting expression is:

$$R = 100\{0.37 + 0.076X + 0.49 \tanh(55.58(X - 1.81))\}$$

where: R = distribution to sinks (%)

X = density (g/cm^3)

This function is shown in Fig.4 together with the experimental points. From the fitted expression the E_p value was calculated to be 0.01.

Tracer density g/cm^3	Distribution to sinks (%)		
	Lower 90% conf. limit	Mean	Upper 90% conf. limit
1.610	0.07	0.24	0.58
1.667	0.38	0.68	1.14
1.688	0.48	0.82	1.32
1.682	0.16	0.38	0.78
1.694	0.12	0.31	0.68
1.720	0.23	0.49	0.92
1.752	1.51	2.11	2.86
1.757	1.07	1.58	2.27
1.791	14.88	16.48	18.08
1.795	15.08	16.68	18.28
1.818	68.31	70.31	72.31
1.826	89.00	90.30	91.60
1.865	98.74	99.24	99.58
1.900	99.23	99.63	99.86
1.966	99.48	99.81	99.97

Table 2. Distribution percentages of tracers to the sinks product.

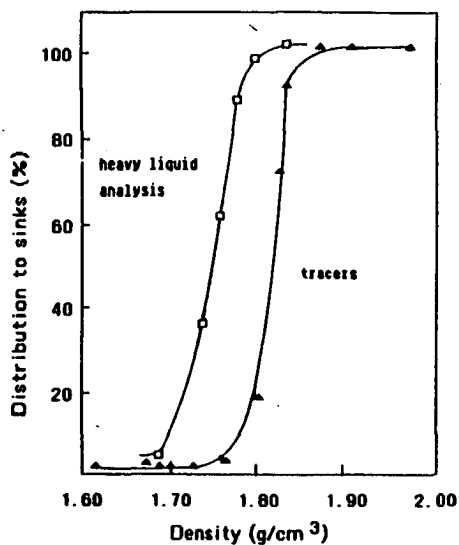


Fig.4. Tromp curves.

For comparison heavy liquid analysis using mixtures of tetrabromoethane and toluene were conducted on the separator products from the same test run. The resulting Tromp curve is shown in Fig.4 and is clearly displaced to lower densities as compared with that determined by the tracer method. The observed absorption of heavy liquid could explain this shift as for any particular density this would result in a higher distribution percentage to the sinks product.

In the present case the tracers were all added at the same time mainly to limit the error introduced by any unsteadiness in the operating conditions and to reduce the duration of this particular experiment during the pilot run, but this has the disadvantage that large numbers of tracers have to be hand sorted afterwards. However, some accuracy could be sacrificed by decreasing the number of tracers per density value and also the total number of density values can be reduced once the position of the Tromp curve is roughly known from previous experiments. Alternatively one could add each tracer batch separately and merely weigh the fractions recovered from the process streams directly after recovery. This would be preferable if the method were to be used on a routine basis in continuous operation.

CONCLUSIONS

The Tromp curve demonstrated that the Dyna Whirlpool operated efficiently and therefore the overall separation was limited by the liberation characteristics of the shale.

For porous materials the tracer method gives more accurate distribution data and thus E_p values. The recovery of magnetic tracers is very efficient. For larger operations simple plate separators could possibly be used instead of drum separators, although on line detection of tracers would probably be the most attractive if a high detection efficiency can be achieved.

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2.8. IMPROVED SELECTIVITY IN HIGH INTENSITY MAGNETIC SEPARATION OF MOUNT PLEASANT WOLFRAMITE FLOTATION CONCENTRATE

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Unpublished research work carried out at Billiton Research B.V., Arnhem.

INTRODUCTION

High intensity high gradient magnetic separation (HGMS) has been applied at the Mount Pleasant tungsten mine in New Brunswick, Canada to remove the arsenic minerals arsenopyrite (FeAsS) and löllingite (FeAs_2) from wolframite ($(\text{Fe,Mn})\text{WO}_4$) flotation concentrate. At times problems were encountered in achieving the required selectivity and to meet the specifications for the final tungsten concentrate. Moreover, the envisaged introduction of a third desliming stage prior to tungsten flotation to reduce the slimes losses might have enhanced these selectivity problems as the amount of very fine wolframite in the flotation concentrate, and thus in the feed to the magnetic separator, would be increased. To recover this very fine wolframite the separator conditions might have to be adjusted, for example by increasing the magnetic field strength, which could also result in enhanced capture of the arsenic minerals. In view of this, testwork was initiated at Billiton Research in Arnhem to study the selectivity problem and to explore possible methods to improve selectivity.

PLANT DESCRIPTION

The Mount Pleasant Tungsten mine is situated approximately 50 km north of St. George in Charlotte County, New Brunswick, Canada and was operated during the period 1982-1985 when forced to close due to the very low tungsten prices. The ore contains typically 0.35% WO_3 , 0.14% Mo and

0.65% As. Wolframite and molybdenite are the main ore minerals. Quartz is the predominant gangue mineral. Feldspar, topaz, fluorite, micas, clays, arsenopyrite, löllingite, chalcopyrite, galena, sphalerite, bismuth minerals and cassiterite occur in minor to trace amounts.

The ore, which was mined by conventional underground methods, was broken in a jaw crusher and then transported by belts along inclines to the surface and stockpiled. Two further crushing stages reduced the ore to -16 mm. The crushed ore was then ground in a two-stage pebble mill circuit to 80% passing 74 μm to liberate the ore minerals. The sulfide minerals molybdenite, chalcopyrite, galena and sphalerite were recovered by bulk flotation, followed by separation of the molybdenite from the other sulfides in multi-stage cleaning. The cleaner tailings, which contained predominantly arsenopyrite and löllingite with some wolframite, were combined with the rougher flotation tailings and formed the feed to tungsten flotation. These sulfide flotation tailings were first deslimed in a two-stage (later three-stage) cyclone operation to remove the -10 μm fraction, which has a deleterious effect on wolframite flotation. Wolframite was then floated with styrene phosphonic acid as the collector at a pH=2.5, using sodium fluosilicate as the gangue depressant. The final wolframite flotation concentrate contained considerable amounts of arsenopyrite and löllingite, which also float easily. To separate the wolframite from these two arsenic minerals high intensity high gradient magnetic separation was used. Prior to magnetic separation the flotation concentrate was first leached with sulfuric acid to dissolve any siderite (FeCO_3), which is also paramagnetic with a somewhat higher magnetic susceptibility than that of wolframite. The leach residue formed the feed to the magnetic separation and contained typically 30% WO_3 and 16% As. A Sala high intensity, high gradient caroussel separator with two magnet heads was used. The separation took place in four stages: in the rougher stage the bulk of the wolframite was recovered. The nonmagnetic product was then scavenged for any remaining wolframite at a higher field strength, at which also significant quantities of arsenopyrite and löllingite were pulled. The low grade scavenger concentrate was recycled to the feed and the rougher

magnetic concentrate was cleaned twice. All these operations were done with a single machine, which was operated either in a rougher/cleaner mode or in a scavenger mode. A rather complicated dewatering and storage system for the intermediate products was required. The cleaned wolframite magnetics were finally leached with ferric sulfate to remove any of the remaining löllingite. Arsenopyrite appeared not to be affected by this treatment and carried through to the final tungsten concentrate.

SCOPE OF WORK

In considering the possible effects of the introduction of a third desliming stage prior to flotation the question arose how efficient the very fine wolframite could be recovered in the magnetic separation stage. This information was generated from a series of tests in a laboratory high intensity, high gradient magnetic separator on an artificial mixture of wolframite and quartz with about the same particle size distribution as that of the plant flotation concentrate (at that time no plant samples were available). This was later followed by laboratory testwork on a sample of flotation concentrate from the plant to improve the selectivity between the wolframite and the two arsenic minerals.

EXPERIMENTAL

Description of the laboratory test circuit

The magnetic separation testwork was done in a Sala 10-15-20 laboratory, canister type separator. The magnet consists of a water-cooled solenoid surrounded by a massive steel shell to return the magnetic flux. The cylindrical space in the solenoid has a diameter of 10 cm and accommodates the canister filled with ferromagnetic matrix elements. The power rating of the magnet is 125 kW. The current is fed via a main

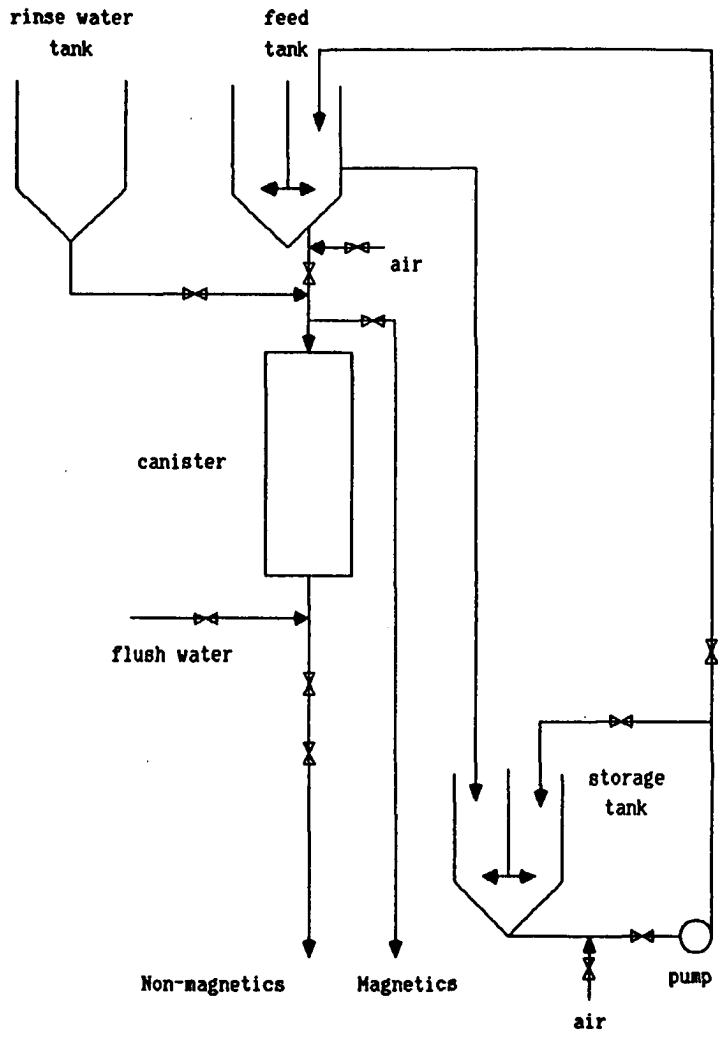


Fig.1. Flowsheet of the HGMS test circuit.

breaker to an autotransformer, which has eight tap settings to provide various output voltages. The output current is rectified and supplied to the magnet.

Magnetic field strengths were measured with an axial Hall probe manufactured by the Institut Dr. Förster GmbH and Co., Germany. The highest possible field strength in the Sala laboratory separator was 1670 kA/m, which corresponds to a magnetic induction of 2.1 T.

For the rougher separation tests the flowsheet in Fig.1 was used. The feed material is pumped from a storage tank to a steady head tank to provide a constant flow through the magnetic separator. Overflow from the steady head tank gravitates back into the storage tank. A considerable amount of testwork was done to minimize segregation in the

Size fraction μm	Mass %	Grade, %		Distribution, %	
		As	WO ₃	As	WO ₃
-315 +200	0.56	35.0	1.0	1.3	0.0
-200 +160	0.98	25.0	1.1	1.6	0.0
-160 +125	2.09	21.8	2.5	2.9	0.1
-125 +100	3.46	20.9	8.6	4.7	0.7
-100 + 63	16.03	14.8	36.4	15.3	14.7
- 63 + 32	28.73	13.6	47.7	25.1	34.6
- 32 + 20	19.58	17.0	44.9	21.4	22.1
- 20 + 8	21.31	17.1	44.6	23.4	23.9
- 8	7.26	9.1	21.2	4.3	3.9
Feed	100.00	15.5	39.7	100.0	100.0

Table 1. Distribution of tungsten and arsenic in the size fractions of the Mount Pleasant plant sample.

steady head tank. The heavy mineral wolframite (s.g. 7.3 g/cm^3) in particular is problematic in this respect. Good results were obtained with a pitched-bladed impeller and an excentric bottom outlet. To prevent settling out of material onto the valve in the bottom outlet after a test had been completed, the outlet opening was closed off by a rubber stopper.

For the magnetic separation testwork a 38 mm diameter canister was used. The matrix in most tests consisted of expanded metal sheets, with a coarse or fine mesh (the rhomb-shaped openings have dimensions of 1.5x3.5 mm and 1x2 mm respectively, the nominal characteristic element diameter was taken as 0.2 mm in both cases). The individual sheets were separated by wire spacers with a diameter of 0.5 mm. In one occasion stainless steel wool was used as the matrix. Matrix magnetisations at different field strengths were determined with a vibrating sample magnetometer at the University of Nijmegen, ensuring that the matrix orientation was the same as that in the magnetic separator.

After feeding the canister for a pre-determined time to give the required matrix loading (mass of feed material/mass of matrix), the canister was rinsed with water to displace residual non-captured material from the canister with the magnet field still on. The magnet was then switched off and the magnetic product flushed out of the canister in upwards direction.

For tests which included cleaning stages the above described system could not be used due to the high solids inventory and the limited amount of sample available. In this case a pre-determined amount of feed material was slurried up in a small stirred tank and allowed to gravitate through the canister. The height of this tank above the canister was sufficient to maintain the desired pulp velocity in the canister during a feed cycle.

Sample characterisation

For the initial testwork related to the recovery of fine wolframite an artificial mixture of wolframite and quartz was used. The wolframite was a concentrate from dry high intensity magnetic separation at the Hollandse Metallurgische Industrie Billiton B.V. in Arnhem. It was ground to 80% -38 μm and mixed with fine quartz (80% -68 μm) to give a nominal feed grade of 10% WO_3 . The magnetic mass susceptibility of this wolframite was determined with a vibrating sample magnetometer and gave a value of $492 \times 10^{-9} \text{ m}^3/\text{kg}$, corresponding to a volume susceptibility of 3420×10^{-6} (SI).

Mineralogical analysis of the sample of the feed to magnetic separation in the Mount Pleasant plant showed that the ratio of arsenopyrite:löllingite was 3:1. The size analysis and the distribution percentages of tungsten and arsenic in the size fractions are given in Table 1. Preferential concentration of wolframite occurred in the fine fractions due to its good cleavage. As a result the coarsest size fractions consisted predominantly of arsenic minerals: the combined +125 μm fraction contained 24.7% As and only 2.1% WO_3 , the corresponding distribution percentages being 5.8% As and 0.1% WO_3 . A considerable rejection of arsenic could therefore already be achieved by screening of the feed.

For the determination of the magnetic susceptibilities of the Mount Pleasant wolframite, arsenopyrite and löllingite a considerable amount of effort was devoted in obtaining sufficiently pure samples. Wolframite was separated from a plant final concentrate. Gangue minerals were first rejected by heavy liquid separation on a -100+40 μm size fraction, using tetrabromoethane (s.g. 2.69 g/cm^3) and methylene iodide (s.g. 3.15 g/cm^3). The heavy fraction was then further purified using a Frantz isodynamic magnetic separator. The magnetic field strength in this separator was varied over a wide range and the mass of magnetics determined and plotted against magnet current, giving an S-shaped curve. The nonmagnetics at high field strength and the magnetics at low field

strength were then discarded, the total weight being about 10% of the original sample. The bulk of the wolframite was contained in the remaining sample. Mineralogical analysis of this purified wolframite concentrate showed an impurity level of only 3.2%. The impurities were mainly gangue minerals with susceptibilities similar to that of the wolframite and these would therefore not affect the final susceptibility determination. The magnetic mass susceptibility of this wolframite was $477.5 \times 10^{-9} \text{ m}^3/\text{kg}$, corresponding to a volume susceptibility of $3490 \times 10^{-6} \text{ (SI)}$.

The two arsenic minerals arsenopyrite and löllingite frequently occur together in the feed to the magnetic separation stage in the Mount Pleasant plant, be it in varying proportions. These two minerals are difficult, if not impossible, to separate and therefore a search was made for samples, which contained either one of these minerals. One of the final magnetic concentrates from Mount Pleasant used in a previous investigation contained virtually only löllingite in association with the wolframite. To separate the löllingite from this sample the bulk of the wolframite was first removed from the $+60 \mu\text{m}$ fraction using a high intensity disc magnetic separator. The gangue minerals were then rejected using heavy liquid separation and finally the remainder of the wolframite was removed with the Frantz magnetic separator. The löllingite concentrate contained 3.2% impurity minerals, of which cassiterite was the most abundant. Determination of the magnetic mass susceptibility of this löllingite gave a value of $5.5 \times 10^{-9} \text{ m}^3/\text{kg}$, corresponding to a volume susceptibility of $41 \times 10^{-6} \text{ (SI)}$. As a comparison a löllingite sample from Center Stafford, New Hampshire, U.S.A. gave a value of $32 \times 10^{-6} \text{ (SI)}$. Arsenopyrite was obtained from a drillcore sample which contained no löllingite. Gangue minerals were again removed by heavy liquids. Minerals with higher susceptibility than that of the arsenopyrite were removed with the Frantz separator. The arsenopyrite concentrate contained 4.2% impurity minerals, being mainly gangue. The mass susceptibility of the arsenopyrite was $3.0 \times 10^{-9} \text{ m}^3/\text{kg}$, corresponding to a volume susceptibility of $18 \times 10^{-6} \text{ (SI)}$. Comparative determinations of arsenopyrite samples from Zacatecas, Mexico and

Panasqueira, Portugal gave values of 29×10^{-6} (SI) and 25×10^{-6} (SI). All these samples were very carefully purified prior to determination of the magnetic susceptibility. In this respect it should be noted that considerable care has to be exercised with published literature data, if no information on the purity of the samples is given.

RECOVERY OF FINE WOLFRAMITE

The magnetic force F_m on a particle with a volume V in an inhomogeneous magnetic field is given by:

$$F_m = V\mu_0(K_p - K_1)|H|\text{grad}|H| \quad (1)$$

where μ_0 is the magnetic permeability of the vacuum (N/A^2), K_p and K_1 are the volume magnetic susceptibilities of the particle and medium (-), and H is the magnetic field strength (A/m).

In the Sala separator the background field (generated by a solenoid and thus essentially homogeneous) is distorted by the insertion of a ferromagnetic matrix, which consists of sheets of expanded metal. High field gradients are generated near the matrix elements. These gradients in combination with a high background field strength can provide sufficiently large magnetic forces on small paramagnetic mineral particles for separation to take place. In addition to the magnetic force, the fluid drag force, the inertial force and the gravity force should be considered.

The capture of a paramagnetic mineral particle on a cylindrical matrix wire has been modelled by Watson [1]. Consider the so-called longitudinal orientation, in which the matrix wire is perpendicular to the directions of the field strength and flow direction, which themselves are mutually parallel. The magnetic potential (ϕ) of the

matrix wire can be determined from the Laplace equation in cylindrical coordinates [2]:

$$\phi = C_1 r \cdot \cos\theta + (C_2/r) \cos\theta \quad (2)$$

At infinite distance from the wire the second term is zero and thus the constant C_1 should equal the background field strength H_0 . The potential outside the wire (ϕ_0) is then:

$$\phi_0 = -H_0 r \cdot \cos\theta + (C_2/r) \cos\theta \quad (3a)$$

Inside the wire the potential at the origin (ϕ_1) should have a finite value and therefore the constant C_2 should be zero.

$$\phi_1 = -H_1 r \cdot \cos\theta \quad (3b)$$

where H_1 is the magnetic field strength inside the wire, at the origin. The constant C_2 can be evaluated by the continuity equations of the tangential component of the magnetic field strength and the radial component of the magnetic induction at the surface of the wire, making use of equations 3a and 3b. The magnetisation M (T) of the wire should be taken into account. Evaluation of these equations, setting r equal to the wire radius a leads to:

$$C_2 = \frac{H_0 a^2 (\mu_0 - \mu_1) + Ma^2}{(\mu_0 + \mu_1)} \quad (4)$$

where μ_1 is the magnetic permeability of the fluid.

Inserting C_2 into equation (3a), assuming $\mu_0 = \mu_1$ and taking the gradient gives the field strength:

$$H_r = H_0 \cos\theta + (Ma^2/2\mu_0 r^2) \cos\theta \quad (5)$$

$$H_\theta = -H_0 \sin\theta + (Ma^2/2\mu_0 r^2) \sin\theta \quad (6)$$

Using equations (1), (5) and (6) the magnetic force on a particle can be calculated:

$$F_r = -V(K_p - K_l)Ma^2(Ma^2/2\mu_o r^2 + H_o \cos 2\theta)/r^3 \quad (7)$$

$$F_\theta = -V(K_p - K_l)Ma^2 H_o \sin 2\theta / r^3 \quad (8)$$

For a wolframite particle (radius R and volume susceptibility 3420×10^{-6} (SI)) on the X-axis in contact with the cylindrical matrix wire (longitudinal orientation) the magnetic force becomes:

$$F_m = -(4/3)\pi R^3 (3420 \cdot 10^{-6}) Ma^2 (Ma^2/2\mu_o (a+R)^2 + H_o) / (a+R)^3 \quad (9)$$

For a wolframite particle with a diameter of $15 \mu m$ the magnitude of the magnetic force is plotted against the ratio of wire radius and particle radius (a/R) in Fig.2. The magnetic force reaches a maximum at an a/R ratio of 2.3:1. As can be inferred from equation (9) the location of this maximum is dependent on the field strength, the magnetisation of the matrix and on the particle diameter. In actual operations a distribution of particle sizes occurs and for a particular matrix with uniform characteristic diameter of the elements not all particles therefore experience the maximum force. Moreover the field strength, and the matrix magnetisation below saturation, may be varied in operating practice. Optimum conditions for all particles will thus not be achieved. From the above it follows that proper selection of the matrix is quite important. In cases with a very large range in particle sizes either a graded matrix, composed of elements with different characteristic diameters or size classification followed by separate treatment can be considered.

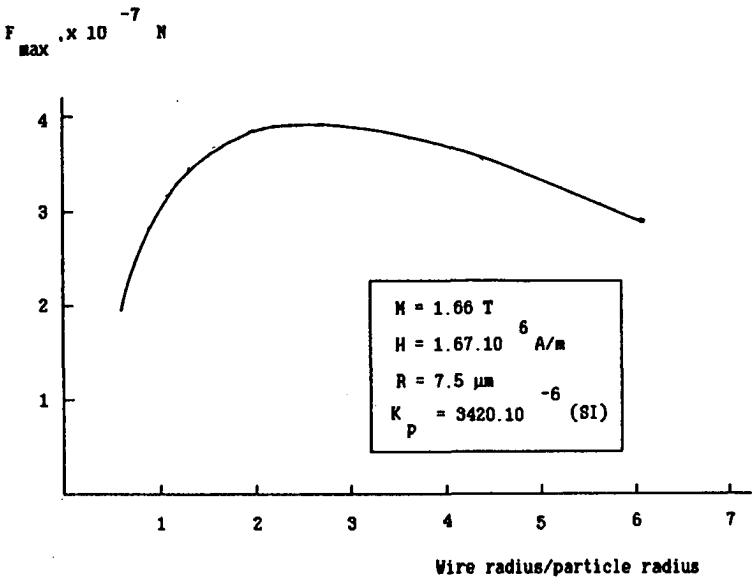


Fig.2. Magnetic force as a function of wire radius.

For small particles the gravity forces and inertial forces can be neglected. The force on the particle is then the difference between the magnetic force (F_m) and the fluid drag force (F_d).

$$F = F_m - F_d$$

For the fluid drag force the Stokes equation is used: $F_d = 6\pi\eta RV$, where V is the fluid velocity and η the viscosity. The distribution of fluid velocity (V) around the cylindrical matrix wire is evaluated in a similar manner as above for the magnetic potential. The fluid potential for an incompressible, frictionless fluid is given by equation 3a with H_0 replaced by V_0 . The constant C_2 is evaluated from the constraint that the radial velocity should be zero at the wire surface. Substitution of C_2 in the potential equation and differentiation gives the radial and

azimuthal velocity components for evaluation of the drag force on a particle at a given location. From the above force equation the particle trajectory can then be determined:

$$\frac{1}{r_a} \frac{dr_a}{d\theta} = \frac{(1 - 1/r_a^2) \cos\theta - (V_m/V_o)(K/r_a^5 + \cos 2\theta/r_a^3)}{-1(1 + 1/r_a^2) \sin\theta - (V_m/V_o)(\sin 2\theta/r_a^3)} \quad (10)$$

where:

$$\begin{aligned} r_a &= r/a \quad (-) \\ V_m &= 2(K_m - K_1)MH_o^2/9\eta a \quad (\text{m/s}) \quad (11) \\ K &= M/2\mu_o H_o \quad (-) \\ V_o &= \text{fluid velocity at } r = \infty \quad (\text{m/s}) \end{aligned}$$

The quantity V_m - the so-called magnetic velocity - is of considerable importance in HGMS and appears in virtually all developed models. It incorporates a variety of terms which relate to the magnetic field, to properties of the mineral particles, medium and matrix, and has the overall dimension of velocity, hence the terminology. The ratio V_m/V_o gives an indication of the effectiveness of particle capture. According to Gerber and Birss [3] a V_m/V_o ratio > 1 indicates that effective loading occurs. To establish a possible correlation with V_m/V_o which could be useful for performance estimation, experiments were done in the Sala laboratory separator using the artificial mixture of wolframite and quartz. Different values of V_m/V_o were obtained by varying the field strength in the range 50-1670 kA/m and the feed velocity from 50-309 mm/s. The tungsten recoveries are plotted against V_m/V_o in Fig.3. There appears to be a definite correlation between recovery and V_m/V_o . It can be seen that a good recovery is indeed obtained when V_m/V_o is around 1. Below a V_m/V_o value of 1 the recovery decreases very sharply.

The trajectory differential equation (10) can be solved numerically using the fourth order Runge-Kutta method. A computer program (CAPRAD) was written to calculate these trajectories. Several of such calculated trajectories are shown in Fig.4 for a 10 μm wolframite particle with

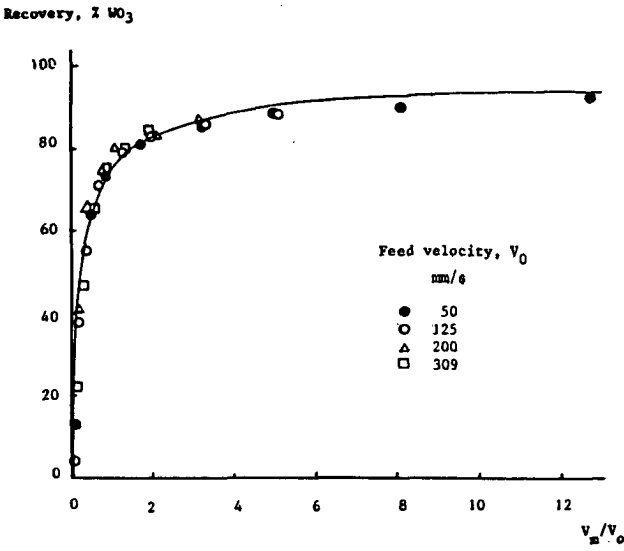
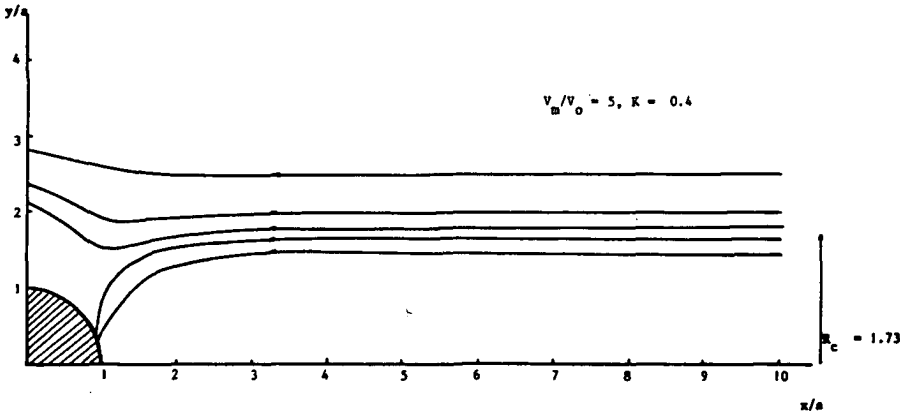


Fig.3. Correlation between tungsten recovery and V_m/V_o .



R_c = capture radius (m) $K = M/(2\mu_o H)$
 a_c = wire radius (m)
 V = magnetic velocity (m/s) where: M = magnetisation (T)
 V_o^m = fluid velocity (m/s) μ_o = magnetic permeability of vacuum (N/A)
 x, y = coordinates H = field strength (A/m)

Fig.4. Particle trajectories.

$V_m/V_o = 5$, starting at different distances from the horizontal axis which is parallel to the fluid flow. Two of these trajectories result in magnetic capture, whereas the others correspond to a non-capture situation. From this it can be inferred that there is a critical y-coordinate (y_c) above which the particle is swept over the wire and below which capture occurs. The dimensionless ratio y_c/a is referred to as the capture radius (R_c). The computer program CAPRAD also evaluates this capture radius. The starting coordinates are specified for a given V_m/V_o ratio and K-value, and the trajectory is calculated. If capture occurs the y-coordinate is increased by a specified amount until a coordinate is reached at which no capture occurs. The coordinate increment is then reduced and the procedure repeated until the difference between the successive y-coordinates corresponding to capture and non-capture is less than a specified value. This y-coordinate is then the capture radius. For a 10 μm wolframite particle the capture radius is 1.8 at a field strength of 1670 kA/m. Based on the above capture model Watson [1] gave the particle recovery (R_p) in a canister-type separator as:

$$R_p = 1 - \exp(-2FR_c L/\pi a) \quad (12)$$

where L is the effective canister length and F is the matrix volume fraction in the canister. For a canister filled with a fine expanded steel matrix (nominal element diameter of 0.2 mm) to a total effective depth of 12 cm the calculated filling factor F is 0.162. At a field strength of 1670 kA/m the capture radius R_c of a 10 μm wolframite particle is 1.8. The term within brackets in equation (12) is then -148 and thus the recovery should be close to 100%. The actual recovery of such fine wolframite is substantially lower. Experimental determinations of the recovery of wolframite by size fraction were carried out in a series of tests on the artificial mixture with quartz using three different matrices. At a field strength of 1670 kA/m recoveries of -8 μm wolframite for a coarse expanded metal matrix, a fine expanded metal matrix and steelwool were 60%, 78% and 90% respectively. This demonstrates the importance of the matrix element dimensions. Although

the steelwool gave the highest recovery the obtained magnetics grades were considerably lower than those obtained with the expanded metal matrices, due to physical entrainment of quartz and this makes it less attractive for application at Mount Pleasant, where high selectivity is of greatest importance. From these tests it was concluded that the expanded metal would be adequate for the recovery of the additional amount of very fine wolframite produced in a third pre-flotation desliming stage.

The overprediction of the recovery by equation (12) has also been mentioned by Gerber and Birss [3]. It seems that good predictions are only obtained on monodisperse feed materials at very low matrix loading values. Under the conditions normally used in HGMS a deposit actually builds up on the matrix elements. Competition exists between the magnetic forces and the fluid drag forces acting on the mineral particles on the surface of such a deposit. As the deposit grows and the particles are deposited further away from the centre of the matrix element, the magnetic force decreases and eventually becomes smaller than the drag force so that the particle cannot be retained on the deposit. This was recognized by Luborsky and Drummond [4] and by Nasset and Finch [5] who developed static build-up models. More recently Liu and Oak [6] developed a build-up model which takes into account the particle size distribution of the feed. However, they apparently have assumed uniform loading of the canister, which is not correct. Furthermore uncertainty exists whether magnetics build-up occurs only on the upstream side of a matrix element or also on the downstream side. This apparently is related to the feed flowrate. If this is sufficiently high a build-up may in fact occur on the downstream side only. The exact mechanism of the particle build-up on the downstream side is not yet known. In view of these uncertainties it was decided not to use modelling techniques in this project, but to employ the empirical correlations between recovery and V_m/V_o in determining the conditions for improved selectivity as detailed in the following section.

SELECTIVITY BETWEEN WOLFRAMITE AND ARSENOPYRITE/LÖLLINGITE

General

In considering the selectivity issue it was initially assumed that the recovery- V_m/V_o correlation might be valid also for a mixture of minerals, i.e. in this case for a wolframite-arsenopyrite/löllingite mixture and that the recovery would correspond to the capture probability. Equal capture probability of wolframite and arsenopyrite particles, for example corresponding to a recovery of 80%, would require equal V_m/V_o values. From the definition of magnetic velocity in equation (11) it follows that, for given separation conditions:

$$\frac{D_{\text{arsenopyrite}}}{D_{\text{wolframite}}} = \frac{(K_{\text{wolframite}})^{0.5}}{(K_{\text{arsenopyrite}})^{0.5}} \quad (15)$$

where D is the particle diameter and K the volume susceptibility. Substituting the susceptibility values for the two minerals - wolframite: 3490×10^{-6} (SI), arsenopyrite: 29×10^{-6} (SI) - in equation (15) gives a diameter ratio of 11. This means that if the magnetic separator is set to recover wolframite particles of $10 \mu\text{m}$ it will also recover arsenopyrite grains of $110 \mu\text{m}$ with the same probability. For löllingite the diameter ratio is 9. This illustrates the selectivity problem for two minerals with considerable differences in magnetic susceptibility but with a relatively wide size distribution. In view of this split size treatment of the feed to magnetic separation stage in Mount Pleasant was considered as a possible way to improve selectivity. The conditions for minimizing competitive capture could then be determined for each of the two size fractions separately. As the purchase of a second magnetic separator at Mount Pleasant was under consideration at the time, separate treatment of the coarse and fine fractions of the feed would indeed be possible. A decision was therefore made to test the split-size concept in the laboratory using a plant sample of feed to the magnetic separation.

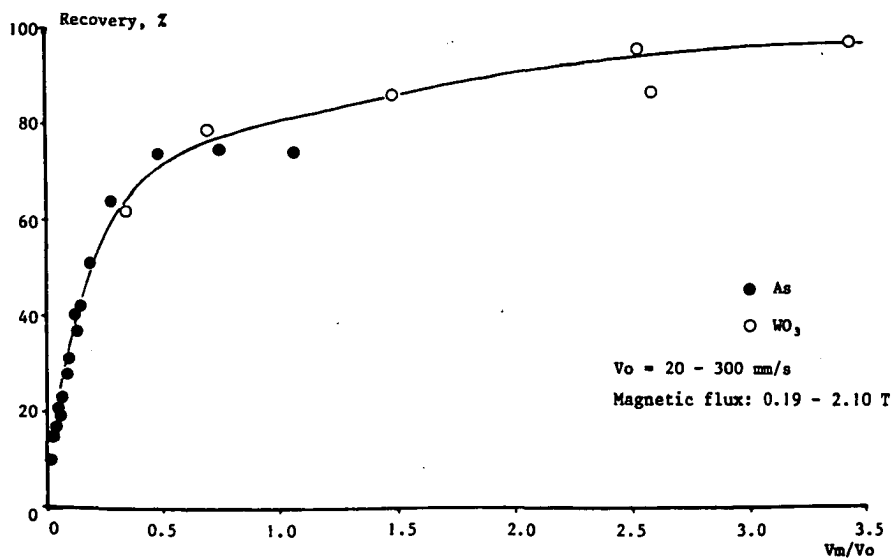


Fig.5. Correlation between tungsten/arsenic recovery from Mt. Pleasant material and V_m/V_0 based on average particle sizes.

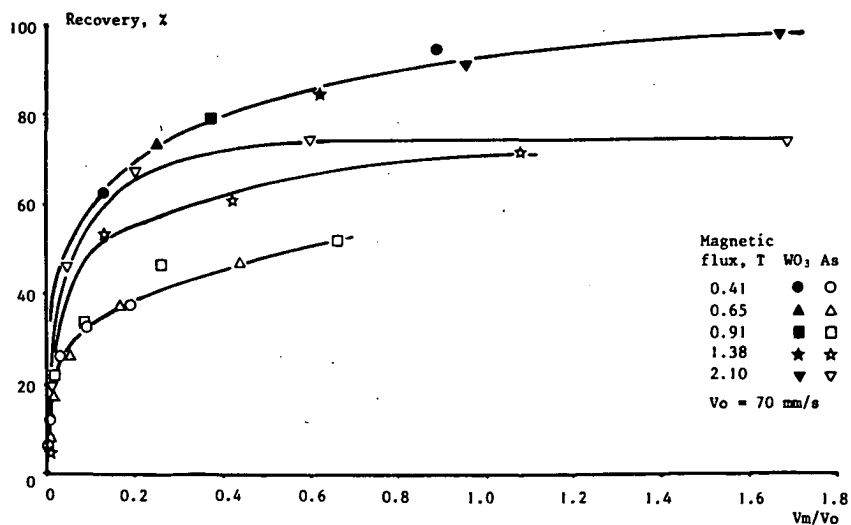


Fig.6. Correlation between tungsten/arsenic recovery from Mt. Pleasant material and V_m/V_0 based on different particle sizes.

2. Determination of the separation size.

In order to determine the particle size at which the feed sample should be classified the correlation between the recovery and V_m/V_o should be established on the plant sample. Initially this was done by conducting tests, in which the field strength was varied from 325 kA/m to 1670 kA/m and the feed velocity from 50 mm/s to 300 mm/s. The V_m values were initially calculated using the average particle size of the feed. For the arsenic minerals the weighted average susceptibility was used (24×10^{-6} SI). The resulting curve is shown in Fig.5. The correlation again appears to be good. Both the wolframite and arsenic points fall on one curve, which is similar in shape as compared to that previously established for the wolframite-quartz mixture (Fig.3). However, so far the V_m/V_o ratio had been varied by changing the feed velocity and field strength (and thus the matrix magnetisation), but not the particle size which is a term in V_m . Therefore it was decided to conduct a second series of separation tests, in which particle size analyses were done on the separation products obtained. Fig.6, generated from tests done at a feed velocity of 70 mm/s, shows that the wolframite data points still fall on one curve, but for arsenic different recovery- V_m/V_o curves appear for different field strengths. This is related to the difference in loading capacity of the canister for wolframite and the arsenic minerals and will be discussed in a subsequent section (capture profiles and selectivity). It should be said here that the relationship between capture probability and V_m/V_o is still valid, but that capture probability and recovery cannot always be equated. The split-size concept is based on capture probabilities and thus on the V_m/V_o values for the mineral components. For the determination of the separation size the outer envelope of the set of curves in Fig.6 should be used as the proper correlation between capture probability and V_m/V_o for both the wolframite and the arsenic minerals.

In the following calculations the feed velocity in the production unit is used, i.e. 70 mm/s. Assume now a size split corresponding to a particle radius of R_{ct} . It is further assumed that wolframite particles

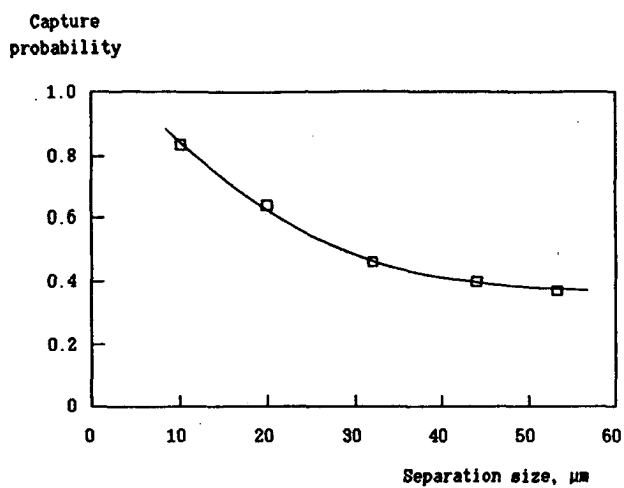


Fig. 7. Capture probability of coarse arsenopyrite (80 μm) as a function of separation size.

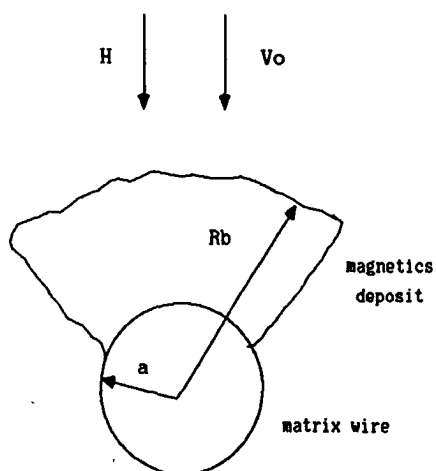


Fig. 8. Magnetics build-up on a matrix wire.

with a diameter of $5\text{ }\mu\text{m}$ are to be recovered with a reasonably high capture probability, say 0.8. This would then set the separation conditions for the fines fraction of a classified feed or for an untreated feed. From the established correlation (Fig.6) a corresponding V_m/V_o value of 0.4 can be derived. The required product of matrix magnetisation and field strength (MH_o) can now be calculated using equation (11):

$$\frac{2MH_o(3490 \times 10^{-6})(2.5 \times 10^{-6})^2}{9(1 \times 10^{-3})(0.2 \times 10^{-3})(70 \times 10^{-3})} = 0.4$$

This gives $MH_o = 1.16 \times 10^6\text{ N/m}^2$, which is closest to tap setting 6 on the laboratory separator, for which $MH_o = 1.0823 \times 10^6\text{ N/m}^2$. Using this value V_m/V_o is recalculated for the $5\text{ }\mu\text{m}$ wolframite particle and this corresponds to a capture probability of 0.79 (Fig.6). For the coarse fraction the smallest wolframite particles (radius also R_{ct}) should be captured with a high probability, say 0.95, corresponding to a V_m/V_o value of 1.25. Equation (11) is again applied:

$$\frac{2MH_o(3490 \times 10^{-6})(R_{ct})^2}{9(1 \times 10^{-3})(0.2 \times 10^{-3})(70 \times 10^{-3})} = 1.25$$

The product MH_o can now be calculated for the different R_{ct} values and for each combination the V_m/V_o values are calculated for coarse arsenic mineral particles, here taken as $80\text{ }\mu\text{m}$ in diameter. The corresponding arsenic mineral capture probabilities can then be determined from Fig.6 and are plotted in Fig.7. It can be seen that the capture probability of the coarse arsenic mineral particles starts to increase more rapidly if the separation size is lower than about $30\text{ }\mu\text{m}$. The nearest available screen size, $32\text{ }\mu\text{m}$, was used as the separation size for the experimental work.

Feed material	Product	Mass %	Grade, %		Distribution, %	
			WO ₃	As	WO ₃	As
+32 μ m	2nd cleaner mags	53.6	68.2	1.6	98.3	4.9
	2nd cleaner nonmags	2.0	5.6	42.8	0.3	4.9
	1st cleaner nonmags	5.8	3.2	40.9	0.5	13.6
	rougher nonmags	38.6	0.8	34.7	0.9	76.6
	feed	100.0	37.2	17.4	100.0	100.0
-32 μ m	2nd cleaner mags	49.0	69.0	0.3	86.1	0.9
	2nd cleaner nonmags	3.2	44.3	10.8	3.6	1.9
	1st cleaner nonmags	6.3	27.7	25.0	4.4	8.6
	rougher nonmags	41.5	5.5	39.0	5.9	88.6
	feed	100.0	39.3	18.3	100.0	100.0
combined feed	2nd cleaner mags	51.4	68.6	1.0	92.3	2.9
	2nd cleaner nonmags	2.6	28.8	23.6	2.0	3.4
	1st cleaner nonmags	6.0	15.5	32.9	2.4	11.2
	rougher nonmags	40.0	3.1	36.9	3.3	82.5
	feed	100.0	38.2	17.9	100.0	100.0
unscreened	2nd cleaner mags	53.1	66.5	2.2	90.9	6.7
	2nd cleaner nonmags	3.4	26.8	23.3	2.3	4.6
	1st cleaner nonmags	7.0	18.3	29.8	3.3	12.1
	rougher nonmags	36.5	3.7	36.3	3.5	76.6
	feed	100.0	38.8	17.3	100.0	100.0

Table 2. Magnetic separation test results on screened and unscreened feed samples.

Separation tests

HGMS tests were done on the $+32\ \mu\text{m}$ and $-32\ \mu\text{m}$ fractions of the plant sample, using different field strengths. Comparative tests were conducted on unscreened feed. Each test consisted of a rougher stage, followed by two cleaner stages as in plant operations. The feed velocity in all tests was 70 mm/s. Both coarse and fine expanded matrices were tested and matrix loadings of 1 and 0.5 were used. The best combination of conditions for the coarse and fine fractions is given in Table 2 and the combined performance is compared with that on unscreened feed. With a sized feed and selecting the optimum conditions a final concentrate with 1% As could be produced from this sample. The combined rougher recovery of wolframite was 97%. From unscreened feed, for the same wolframite rougher recovery, a cleaner concentrate with 2% As was produced, which was considered unacceptable in plant operations.

Capture profiles and selectivity

The divergence of the recovery- V_m/V_o curves for arsenic, mentioned in section 2 is related to the capacity of the matrix in the canister for mineral particles with a specific V_m/V_o . This concept, which has been derived from the determination of capture profiles inside the canister, is fundamental to the understanding of HGMS separation performance. As mentioned before, particles of a given diameter and magnetic susceptibility can build up only to a maximum distance from the matrix element, determined by an equilibrium between the magnetic and fluid drag forces. For a cylindrical matrix wire (radius a) in longitudinal orientation (Fig.8) the radius of the build up (r_b) is a function of V_m/V_o and the azimuthal angle [6]:

$$r_b = a(2V_m/V_o - \cos\theta)^{2/3} \quad (17)$$

Consider first a system with a single paramagnetic mineral, for example

wolframite-quartz. For wolframite particles of a particular size the cross-sectional area of the build-up can be calculated using equation (17). The total potential volume for capture is then equal to this area times the total length of the matrix elements in the canister. However particles of the same mineral, which are coarser in size, also compete for this potential capture volume. In an actual separation the matrix elements in the section nearest to the feed end of the canister will first build up until maximum loading, which is determined by the diameter of the coarsest wolframite particle. Following this zone there is a transition region in which maximum loading has not yet been achieved. The shape of this transition region will depend on the particle size distribution of the wolframite in the feed. This zone is followed by a zone of low loading. This capture profile moves through the canister if feeding is continued and eventually emerges at the other end, similar to a breakthrough curve in an ion exchange column. The situation is further complicated when a second paramagnetic material is present e.g. arsenopyrite. Each particle size of the arsenopyrite and wolframite will have its own potential capture profile, and competitive capture of these two minerals occurs wherever their potential capture volumes overlap. As the susceptibility of the arsenopyrite is considerably lower than that of wolframite the build-up radii are much smaller than those for wolframite particles of the same size and therefore the capacity is limited and breakthrough will occur quickly. It is evident from the foregoing that the capture profiles are quite important. The problem is to determine such profiles in situ as the canister cannot be taken out of the magnetic field. The author has designed a cryogenic canister (Fig.9) in which the complete build-up inside the canister is immobilised by freezing, while in the magnetic field, using liquid nitrogen which is fed into an annular space when a separation test has been completed. After the contents of the canister have been completely frozen, the magnet is switched off. The frozen contents are removed from the canister and sectioned for analysis. Capture profiles for wolframite and arsenopyrite, determined with the cryogenic canister, are shown in Fig.10. It is evident that breakthrough

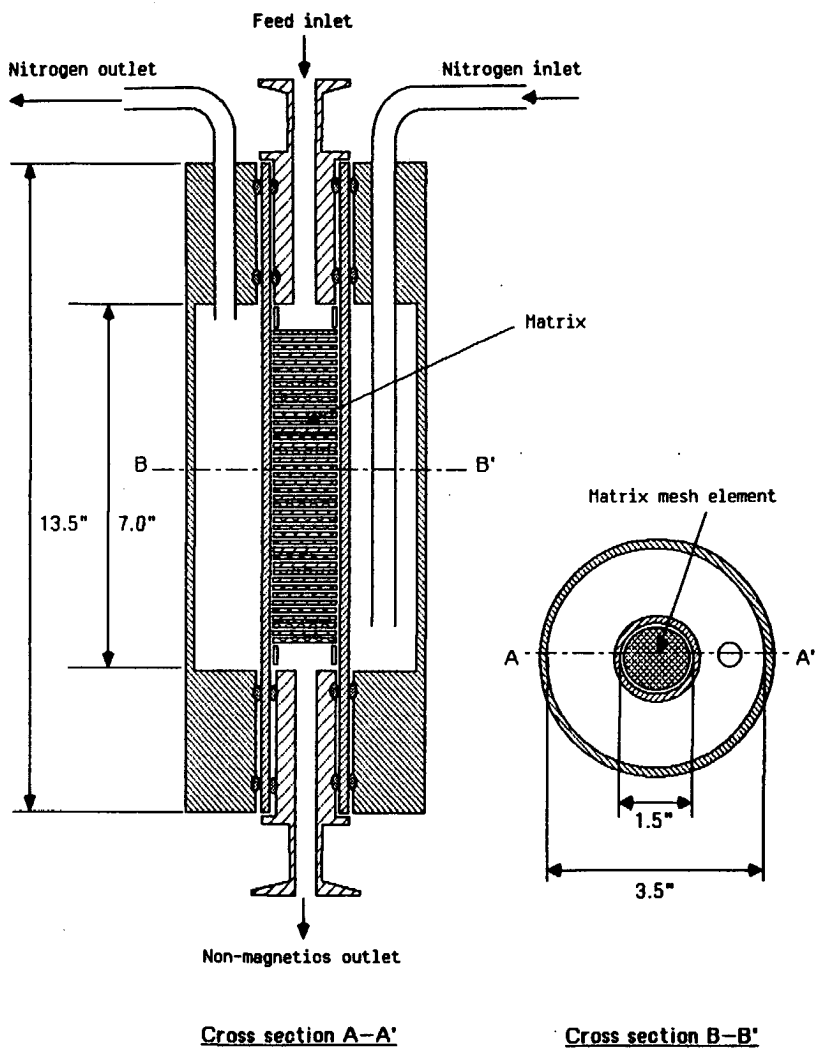


Fig.9. Schematic drawing of the cryogenic canister.

Specific
build-up,
g/g.matrix

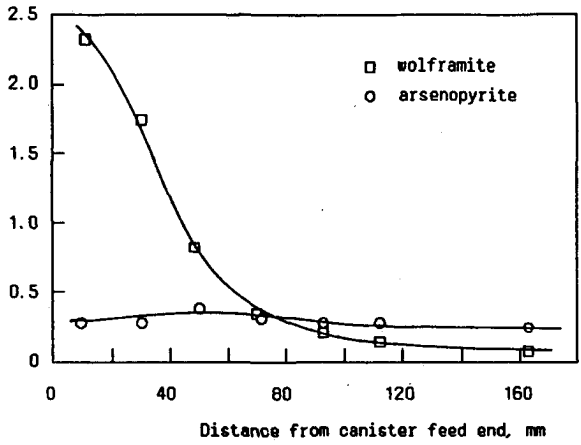


Fig.10. Capture profiles for wolframite and arsenopyrite.

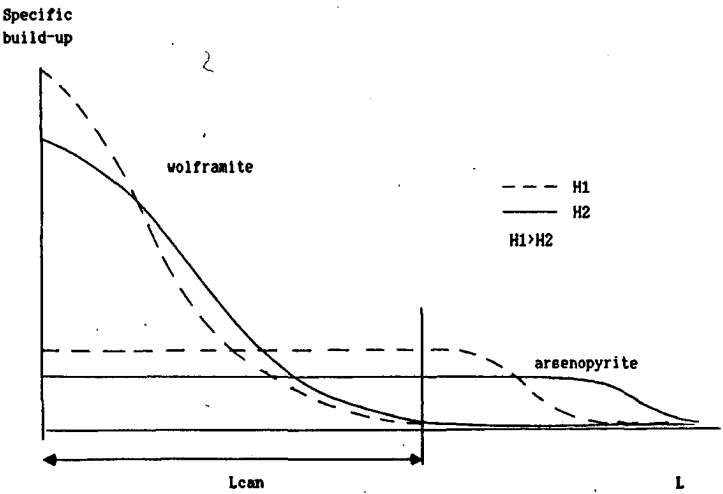


Fig.11. Potential capture profiles for different magnetic field strengths.

of the arsenopyrite has occurred as the capture profile shows almost uniform loading.

Consider now the potential capture profiles for wolframite and arsenopyrite which would be obtained if a very long canister was used (Fig.11). Superimpose an actual canister length (Fig.11). The wolframite profile is almost entirely contained inside the actual canister (i.e. high recovery, say > 90%) as is desirable in actual separation practice. The arsenopyrite profile has "broken through". The recovery of arsenopyrite is equal to the area under the capture profile inside the canister, divided by the total area under the potential arsenopyrite capture profile. If the field strength is now increased and the same amount of material is fed to the canister the wolframite profile is still contained almost completely inside the canister and is merely compressed due to the higher loading capacity per unit length of matrix wire. The maximum radius of the arsenopyrite build-up also increases and this means that now a much greater proportion of the potential capture profile can be accommodated inside the canister, causing a significant increase in arsenopyrite recovery. This is the reason that the recovery- V_m/V_o curves for arsenopyrite in Fig.6 diverge and extend to higher recoveries as the magnetic field strength is increased. If the canister would be very long the recovery- V_m/V_o curve for arsenopyrite would coincide with that for wolframite, and only then could one replace the recovery figures by actual capture probabilities for a canister with low loading.

The split-size treatment concept was based on magnetic equivalence of wolframite and arsenic mineral particles and this actually relates to capture probabilities and not to capacity aspects. However capacity effects should have an effect on arsenopyrite recovery and therefore on selectivity. From the consideration of potential capture profiles (Fig.11) it is now also evident why a reduction of the arsenic content becomes increasingly more difficult during cleaning (the reduction from 2% As to 1% As is not easy as this testwork has shown). During cleaning one should take care that much of the potential wolframite capture

profile actually remains inside the canister to maintain high recoveries. As the amount of arsenopyrite in the feed to subsequent cleaning stages is reduced more of the potential capture profile will also be inside the canister and thus less arsenic rejection occurs.

CONCLUSIONS

Split-size treatment of the feed to the Mount Pleasant magnetic separation stage would give improved selectivity. The recently gained insight into the separation mechanism based on capture profiles shows the importance of good process control in each of the separation stages. In particular excessive canister length for a given feed loading should be avoided as this would be utilised to capture the arsenopyrite and löllingite. Thus the the amount of feed to the separator (matrix loading) should be carefully controlled in each of the separation stages.

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SUMMARY

In an introductory section the importance of mineralogy in process research is indicated by a number of examples of applications in mineral dressing, hydrometallurgy, pyrometallurgy and in the processing of gold ores, which currently receive considerable attention. Subsequently more specific research in various areas of mineral processing is described, of which the details are contained in a series of published articles, supplemented by recent research.

The first subject is the treatment of oxide copper ores in various deposits on the Zambian Copperbelt. The general mineralogy of the Copperbelt ores is described in the first article. Aspects of the flotation of oxide copper minerals at the Rokana mine are then discussed and special mention is made of the copper phosphate mineral libethenite, which floats with difficulty and occurs locally in relatively high concentrations in the orebodies. The unusual occurrence of this mineral at Rokana is detailed in the second article. Near the town of Chingola large ore reserves occur, in which the majority of the copper is contained in a micaceous mineral. Detailed mineralogical and metallurgical work has been conducted with the objective of developing a viable treatment route for these refractory ores. The mineralogical study showed that the copper is contained in the intersilicate layer of an interstratified phlogopite-14 Å component. The data indicates that the copper is coordinated to hydroxyl groups. However, in this intersilicate layer probably also hydrated cations occur, forming a so-called intergradient structure. The evaluation of the mode of occurrence of the copper in the mica structure has provided a good insight into the leaching characteristics of these ores. Based on the metallurgical testwork a conceptual flowsheet has been developed, comprising leaching, solvent extraction and electrowinning. Details are contained in two published articles.

The next topic is the design of mixer-settlers for the expansion of the Chingola tailings leach solvent extraction plant for future processing

of these micaceous ores. A full-scale mixer prototype was designed and commissioned in one of the four process streams at Chingola. This mixer has a dispersion throughput of $1400 \text{ m}^3/\text{hr}$ and is still in use. The mixer design specifically aimed at improving the extraction stage efficiency and the stability against phase inversion. Both objectives were achieved. Using constant power input as the scale-up criterion instead of constant impeller tip speed, the stage efficiency was increased from 88% (existing mixer) to 95% in the newly designed mixer. Organic phase continuity could be maintained at organic:aqueous phase ratios down to 0.7:1, which was impossible with the existing mixers. For the settler design the scale-up criterion of constant specific flow was confirmed by testwork in the pilot plant and in the existing large settlers using a dam baffle. It was proposed to use a deeper settler in the plant expansion. Details of the mixer-settler design were published. More general aspects of copper solvent extraction, such as reagents and the interaction with the leaching and electrowinning operations are discussed in a separate publication.

Also the spatial distribution of a valuable component in a deposit can be utilized in processing. A possible application of this is the upgrading of Tarfaya oil shale (Maroc), in which a banded sediment structure occurs. The subsequent bands differ in kerogen content and thus also in bulk density, so that dense medium separation could be feasible. Pilot-scale dense medium testwork was conducted using a Dyna Whirlpool separator. The determination of the separation efficiency by means of conventional heavy liquid analysis on the separation products from the pilot plant gave problems due to the porosity of the shale. In view of this it was decided to use a tracer method. To achieve sufficient accuracy large quantities of tracers had to be added to the separator feed. The recovery of the commercially available tracers would be a major problem. Therefore magnetic tracers were developed, which were recovered from the process streams by a low intensity magnetic separator. The tracer recovery was 99.3%. From the resulting Tromp curve an E_p value of 0.01 was determined, confirming the high efficiency of the dynamic dense medium separator.

The final subject is high intensity magnetic separation. The importance of magnetic characterisation of the minerals is indicated and the possible utilisation of special magnetic properties is briefly discussed. Recent research work in high intensity magnetic separation to improve selectivity between wolframite and arsenopyrite at the Mount Pleasant tungsten mine in Canada is described. Using correlations, based on modelling of the capture process of weakly magnetic mineral particles on a ferromagnetic matrix, the concept of separate treatment of the coarse and fine size fractions in the feed to the magnetic separation stage was developed. The experimental work indicated a possible reduction in arsenic content from 2% to 1% in the final tungsten concentrate. The capture process and thus the selectivity can be studied in more detail by determining the capture profiles in the canister. Such determinations have been carried out for the first time using a cryogenic technique. This has provided a unique insight into the selectivity problem.

SAMENVATTING

In een inleidend gedeelte wordt het belang van de mineralogie in proces research en ontwikkeling aangegeven door een aantal toepassingen in de mineraalscheiding, de hydrometallurgie, de pyrometallurgie en de verwerking van goudertsen, die nu sterk in de belangstelling staan. Daarna wordt specifiek onderzoek in verschillende gebieden van de ertsverwerkende industrie besproken, waarvan details vervat zijn in een aantal gepubliceerde artikelen aangevuld met recent onderzoek.

Als eerste de verwerking van oxidische koperertsen van verschillende voorkomens in de Zambiaanse Copperbelt. De algemene eerstmineralogie van dit gebied is beschreven in het eerste artikel. De flotatie van oxidische kopermineralen in ertsen van de Rokana mijn wordt dan besproken. Het moeilijk floteerbare mineraal libetheniet komt in deze ertsen plaatselijk vrij veel voor en in een ongewone diversiteit van vormen, die in een tweede artikel zijn beschreven. Nabij de stad Chingola komen grote ertsreserves voor waarin een koperhoudend mica-achtig mineraal de belangrijkste component is. Het koper komt voor in de intersilikaatlaag van een geïnterstratificeerde phlogopiet-14 Å component. Het blijkt dat het koper gebonden is aan hydroxylgroepen. In de koperhoudende structuurlaag komen ook gehydrateerde kationen voor en dus wordt waarschijnlijk een intergradientstructuur gevormd. De wijze van voorkomen van het koper in deze mineraalstructuur heeft in belangrijke mate bijgedragen tot een beter begrip van het looggedrag van deze ertsen. Gebaseerd op het metallurgisch onderzoek is een processchema ontwikkeld, waarin logging, solvent extractie en electrowinning de opeenvolgende bewerkingen zijn.

Het volgende onderwerp betreft het ontwerpen van nieuwe mixer-settlers voor de uitbreiding van de Chingola tailings leach plant, waarin eventueel in de toekomst ook de mica-houdende ertsen verwerkt zouden worden. Een prototype mixer werd ontworpen en geïnstalleerd in een van de vier processtromen in het Chingola circuit. Deze mixer heeft een doorzet van $1400 \text{ m}^3/\text{uur}$ en is nog steeds in gebruik. Het ontwerp was

speciaal gericht om de extractie efficiency en de stabiliteit tegen fase inversie te verbeteren. Beide doelstellingen zijn bereikt. Voor de opschaling werd het criterium constant vermogen per volume eenheid gehanteerd, in plaats van constante roerder omtreksnelheid. Dit resulteerde in een verhoging in extractie efficiency van 88% in de bestaande mixer tot 95% in het nieuwe ontwerp. Organische fase continuïteit kon in stand gehouden worden zelfs bij een organische:waterige fase verhouding van 0.7:1, wat bij het bestaande mixertype niet mogelijk was. De details van het mixer-settler onderzoek en de ontwerp principes zijn gepubliceerd. Meer algemene aspecten van de koper solvent extractie, zoals reagentia en de interactie met de loog en electrolyse circuits worden besproken in een afzonderlijke publikatie.

Ook van de ruimtelijke verdeling van een waardevolle component in een afzetting kan gebruik gemaakt worden in de procesvoering. Een mogelijke toepassing is de opwerking van Tarfaya olieschalie (Marokko), waarin het kerogeen voorkomt in een gelaagde sedimentstructuur. De opeenvolgende banden bevatten verschillende hoeveelheden kerogeen en variëren dus ook in dichtheid, waardoor zware mediumscheiding mogelijkheden biedt. Onderzoek werd verricht in een pilot-scale zwaar medium circuit met een Dyna Whirlpool scheider. De bepaling van de scheidingsefficiency door middel van de gebruikelijke zware vloeistofanalyse op de scheidingsprodukten gaf problemen door de porositeit van de schalie. Daarom werd besloten een tracer methode toe te passen. Om voldoende hoge nauwkeurigheid te bereiken moesten grote hoeveelheden tracers aan de voeding naar de scheider toegevoegd worden. Het terugwinnen van de commercieel beschikbare tracers zou grote problemen veroorzaken. Als oplossing werden magnetische tracers ontwikkeld die door een lage intensiteit magneetscheider uit de processtromen konden worden afgescheiden. Het terugwinningspercentage van de tracers bedroeg 99.3%. Van de resulterende Tromp efficiency curve werd een E_p waarde van 0.01 bepaald, die de hoge efficientie van de dynamische scheider bevestigt.

Het laatste onderwerp betreft de hoge intensiteit magneetscheiding. Het belang van een goede magnetische karakterisatie van mineralen is

aangegeven en mogelijke gebruikmaking van bijzondere magnetische eigenschappen wordt besproken. Recent onderzoek naar het verbeteren van de selectiviteit in de hoge intensiteit magneetscheiding van wolframiet en arsenopyriet in het verwerkingsbedrijf van de Mount Pleasant wolfraammijn in Canada is gedetailleerd. Door correlaties, gebaseerd op het modelleren van het invangproces van zwak magnetische mineralen op een ferromagnetische matrix, is het concept ontstaan van de gescheiden behandeling van de grove en fijne fractie van de voeding naar de magneetscheiding. Het experimenteel werk toonde aan dat een verlaging van het arseen percentage van 2% tot 1% in het uiteindelijke wolframconcentraat bereikt kon worden en dit zou zeker mogelijkheden bieden voor toepassing in het bedrijf. Het invangproces en dus de selectiviteit zouden verder bestudeerd kunnen worden door bepaling van de invangprofielen in de scheidingsruimte. Deze bepalingen zijn nu voor het eerst uitgevoerd door middel van een cryogene techniek. Hierdoor is een uniek inzicht in de selectiviteitsproblematiek verkregen.

DANKWOORD

Ik zou graag een ieder willen bedanken die direct of indirect tot het totstandkomen van dit proefschrift heeft bijgedragen. Vele stimulerende discussies heb ik mogen voeren met voormalige collega's van Nchanga Consolidated Copper Mines in Zambia, in het bijzonder Ruben Orjans, en met medewerkers in Billiton Research in Arnhem. Mijn dank gaat ook uit naar degenen die technische assistentie verleend hebben, vooral in de pilot plant te Chingola, Zambia, maar ook in Billiton Research en dan met name Johny Kruse, Frank van der Meer en Ad Rijkers.

Tenslotte dank ik jou, Tiny, voor het begrip en de steun die je gegeven heb gedurende al die jaren, maar vooral tijdens de recente periode toen ik iedere avond laat thuis kwam en je ook vele weekenden alleen met de kinderen moest doorbrengen.

CURRICULUM VITAE

De auteur werd op 25 april 1942 te Rotterdam geboren.

Na de lagere school vervolgde ik mijn opleiding aan het Johannes Calvin lyceum te Rotterdam waar ik in 1960 eindexamen HBS-B deed. Daarna studeerde ik mijnbouwkunde aan de Technische Hogeschool te Delft en koos de studierichting ertstechnologie. Tijdens de laatste jaren van mijn studie heb ik als assistent ertsmikroskopie gewerkt. In 1968 behaalde ik het ingenieursdiploma.

In 1969 begon ik mijn loopbaan in de mijnbouwindustrie als industrieel mineraloog op het Research and Development Department van Nchanga Consolidated Copper Mines te Kitwe, Zambia. In 1972 ging ik over naar de afdeling mineral dressing en werkte ondermeer aan de flotatie van oxidische koperertsen en speciaal de koperhoudende micas. In 1976 werd ik benoemd tot project leader en later tot chieft research metallurgist in de afdeling hydrometallurgy. Ik had hier de leiding over het solvent extractiewerk dat zowel in het laboratorium als in de pilot plant in Chingola werd uitgevoerd, speciaal gericht op het ontwerpen van mixer-settlers en het testen van nieuwe reagentia.

In 1980 keerde ik terug naar Nederland en kwam in dienst bij Billiton Research in Arnhem in de afdeling ertsscheiding. Hier heb ik mij gespecialiseerd op het gebied van de hoge intensiteit magneetscheiding. Daarnaast heb ik mij onder andere bezig gehouden met de zwaartekrachtscheiding van fijnkorrelige mineralen en met zware mediumscheiding.

Notes on joint authorship.

For the papers with joint authorship the contribution of the author is indicated below.

C.W. Notebaart and B.W. Vink. - Ore Minerals of the Zambian Copperbelt.

The first author (CWN) has written the paper. He also discovered and studied the rare sulfide minerals which had not been found previously on the Zambian Copperbelt. In addition CWN conducted extensive ore microscopical work on the associations of the various minerals which have been summarized in the paper. These were supplemented by literature data and contributions from the second author (BWV) on mines which belonged to a different mining company.

S.P. Korowski and C.W. Notebaart. - Libethenite from the Rokana Mine, Zambia

The second author (CWN) wrote the paper. The field observations and material collection were jointly carried out by the two authors.

J.F.C. Fischer and C.W. Notebaart. - Metallurgical treatment of Chingola cupriferous mica ores.

The two authors contributed equally to the actual text of the paper. The second author (CWN) coordinated orebody sample evaluation, conducted all mineralogical work and was involved in part of the leaching testwork. He also conducted the flotation testwork and solvent extraction evaluations.

J.R. Orjans, C.W. Notebaart, J.C. Godfrey, C.Hanson, M.J. Slater. - The design of mixer-settlers for the Zambian copper industry.

The first two authors were from Research and Development of NCCM Ltd, Zambia and the last three from Bradford University, England. The essential design concepts were developed in NCCM, where also all pilot plant work and actual scale-up work was conducted. The contribution of Bradford University was limited to some small-scale support work after the mixer-settler design work had been completed. The design concepts were jointly developed by the first two authors (JRO and CWN). The second author (CWN) designed and supervised all pilot plant work with the exception of the mixer scale-up from laboratory to pilot plant and the evaluation of some of the coalescence aids. The design of the mixer prototype was done by the second author (CWN). He also conducted the settler scale-up work (pilot plant-full scale) and performed the design calculations for the mixer-settlers for the tailings leach plant extension. The actual text of the paper was written jointly by the first two authors.

J.F.C. Fisher and C.W. Notebaart. - Commercial processes for copper.

The second author (CWN) wrote the paper, with the exception of part of the introduction, and accumulated the data on reagents, other mixer designs and SX operations. A substantial part of this paper is based on the mixer-settler design reported in the preceding paper, which was largely carried out by the second author. He also conducted the plant testwork with the full scale prototype NCCM mixer which by that time had been commissioned. Much of the additional information on operational aspects of SX plants (phase stability, entrainment, crud) was based on observations by the second author.

C.W. Notebaart, F.P. van der Meer and R.D.B. Wilkinson. - Determination of the separation efficiency in dense medium separation of porous materials using magnetic tracers.

The first author (CWN) wrote the paper, developed the concept of the magnetic tracers, designed and supervised the pilot plant testwork on the Tarfaya oil shale. In addition he evaluated tracer statistics and developed the computer program to determine the Tromp curve.