Differential flotation of copper-zinc at Prieska Copper Mines (Pty) Limited: a preliminary report

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SYNOPSIS

Over a period of three years, since samples first became available, laboratory and pilot plant experiments have been conducted to develop a method of treatment to recover copper and zinc in saleable grades of concentrates from the Prieska complex sulphide orebody. These experiments have been based on adaptations of principles investigated by research workers and applied to similar ore types throughout the world. The differential flotation process finally worked out involves a comparatively coarse grind, flotation of the copper at near-neutral pH with the use of a zinc-cyanide sphalerite depressant, followed by flotation of the reactivated sphalerite. This procedure has had such success that the construction of a full-scale plant is proceeding with confidence that the small-scale operations will be duplicated or improved upon. It is to be expected that the large plant will follow the pattern of almost every flotation plant that has been built in that modifications to the circuitry and reagent systems will be made as experience is gained.

SINOPSIS

Oor 'n periode van drie jaar, vanaf monsters beskikbaar gemaak was, was laboratorium en gids aanleg eksperimente uitgeoer om 'n metode van bewerking te ontwikkel vir die herwinning van koper en sink in konsentrete van verkoopbare grade, afkomstig van die Prieska saamgestelde sulfide ertsiggaam. Die eksperimente was gebaseer op aanpassings van prinsipe geondersoek deur navorsers en aangewend op soortge- lyke tipie etse por die hele wêreld. Die differensiaal flotasie proses is uiteindelik uitgeoer, omvat 'n vergelykende grootte vergruising, flotasie van die koper by 'n amper neutrale pH met die gebruik van 'n sink-siande sfaleriet neerdrukker, gevolg deur flotasie van die her-opgewekte sink. Hierdie prosedure was so suksesvol dat met die konstruksie van 'n vol-kaal aanleg voortgegaan word met vertroue dat die klein-kaal prosesse geduplikasie of verbeter kan word. Dit is te wagto dat die volle aanleg die patroon sal volg van die gewone flotasie aanlegte wat al opgerig is in dat veranderings aan die vloeil en reagens sisteem gemaak sal word soos ondervinding opgebou word.

INTRODUCTION

The copper and zinc-bearing sulphide orebody of Prieska Copper Mines (Pty) Limited is situated at 29°58'S, 22°17'E on the farm Vogelstruisbult No. 104 which is 60 kilometres south-west of the town of Prieska in the Cape Province.

The deposit lies on one flank of an anticline on the contact between a succession of quartz-biotite schist footwall rocks and a heterogeneous assemblage of quartz-biotite schists, amphibolites, epidiorites and meta-quartzites on the hanging wall side. It takes the form of a steeply dipping tabular mass that averages 1 400 x 10 metres in dimension and continues to a depth of at least 900 metres. Below the leached zone, which extends to a depth of approximately 85 metres, it occurs as a texturally-zoned massive body composed mainly of pyrite, chalcopyrite and sphalerite with minor quantities of arsenopyrite, pyrrhotite, galena, magnetite and neodigenite and with a gangue content varying from about twenty to forty-five percent by volume. The commonest gangue minerals are quartz, muscovite, hydromuscovite, biotite, sericite, calcite, chlorite, antigorite, serpentine, iddingsite, talc, cordierite, tremolite, garnet and sillimanite. Diamond drilling, which was commenced in August 1968, has established that the orebody contains 47 million metric tons assaying 1.74% copper, 3.87% zinc, some 30% of pyrite and approximately 8 g/t Ag and 0.4 g/t Au.

Metallurgical testwork to investigate separation of the sulphide minerals by flotation on a laboratory scale was started in February 1969 on borehole core samples and a pilot plant on the mine was commissioned in April 1970 when ore became available from a prospect shaft sunk to a depth of 105 metres.

This paper traces the progress of the experimentation to date, not in chronological order, but rather against a backdrop of findings of research workers and experience on ores of a similar nature in other parts of the world. Various lines of investigation were followed simultaneously in the Anglovaal Laboratory, in the pilot plant and in a number of laboratories in this country and overseas. Not all the testwork will be described nor are details given of individual tests.

The successful outcome of these investigations culminated in the decision to erect a full-scale plant which is at present being built and is planned to go on stream in January 1973 at a milling rate of 1,365 million metric tons per annum, with a final milling rate of 2,73 million metric tons per annum to be achieved in the second half of 1974.

GENERAL CONSIDERATIONS

The Prieska mineralisation belongs to that class of massive polymetallic sulphide orebodies in which pyrite is the predominant sulphide. Its lead content is, however, lower than that of many of the similar ore types elsewhere. The separation of the individual metals from these complex bodies by differential flotation has always been one of the most difficult problems which the metallurgist has had to solve. In many cases, satisfactory separation has not been possible and the mineral processor has had to leave a partially-solved problem to the
smelter or the hydrometallurgist to complete the separation.

A striking feature of the ores is their varying response to identical treatment and a survey of the literature relating to plants in North and South America, Europe, Australia, Japan, Africa and Russia, reveals many different flowsheets and the use of a number of flotation reagents in various combinations and permutations. Generally the minerals are floated in the normal sequence of their response to the soluble sulphide collectors, i.e. chalcopyrite, activated sphalerite and then pyrite, although there are exceptions to this order of removal, notably in Japan and Zaire. The laboratory investigations and pilot plant testwork were devoted to the usual order of differential flotation. Since their flotation characteristics are so similar, separation of the sulphides cannot be achieved without the use of depressants; there are, however, no universally-used selective depressants — each ore is different. In Tennessee at one plant the copper, zinc, pyrite and pyrrhotite are removed from the gangue in a bulk concentrate which is then selectively floated, while in Russia in a number of plants, the copper and zinc are lifted away from the pyrite and gangue, to be separated by differential flotation. A variation of this latter method was tested on Prielska ore in the laboratories of the National Institute for Metallurgy and in the pilot plant. In view of their overriding importance, depressants, their mode of action as presently understood, their usage in flotation generally and the testwork devoted to them, claim most of the attention in this report.

Among the factors accounting for the numerous methods of treatment are the variations in the mineralogy and textures of the ore minerals which affect their activity and floatability; the metallurgical problems and the diversity of techniques used to solve them are geologic in origin. Geometric structures such as intergrowths or inclusions may complicate the separation in respect to the degree of grinding, of the total ore or of intermediate products, necessary to effect economic liberation. Iron-bearing sphalerite may be slow-floating or even non-floating in an environment designed to depress iron sulphides and the choice of reagents may be dictated by the presence of secondary minerals or soluble heavy metal ions which pre-activate some of the minerals. Variations in the extent of oxidation and surface activation, the relative percentages of the ore minerals and the nature and quantity of gangue materials have a profound bearing on the type and quantities of reagents used. Two valuable attempts at correlating the variations in the complexity of the ores with their methods of treatment were made at the International Mineral Dressing Congress in Stockholm in 1957.

MINERALOGY

Early in the investigation, a mineralogical examination of a number of samples of the orebody was carried out by the Geological Division of the National Institute for Metallurgy, making use of a petrological microscope and X-ray diffraction analysis, to describe the textures and modes of occurrence of the various minerals.

The examination revealed that the interrelationships between the ore minerals vary considerably within the orebody. The variations in mineral assemblages and textures of the ore minerals are as follows:

The pyrite occurs as:

a) massive pyrite in large grains greater than 1 cm in diameter, of various degrees of crystallinity and containing pyrrhotite, chalcopyrite and sphalerite;

b) sugary pyrite comprising smaller grains less than 1 cm diameter with varying amounts of gangue, chalcopyrite, sphalerite, arsenopyrite and pyrrhotite. The copper and zinc mineralisation is more intense than it is in the massive pyrite;

c) lamellae of pyrite pseudomorphs after pyrrhotite protruding from boundaries of primary grains into gangue minerals and, rarely, arsenopyrite;

d) subgraphic intergrowths of pyrite with sphalerite and, very occasionally, magnemite.

No problems are anticipated in liberating the pyrite of the first three types, but the subgraphic intergrowths may involve problems in separating sphalerite from the pyrite.

The chalcopyrite comprises:

a) large veins associated with gangue minerals and inclusions of mottled coarse sphalerite, graphically intergrown sphalerite and chalcopyrite;

b) smaller veins associated with pyrite and sphalerite replacing and making up the groundmass between pyrite grains. They are either monomineralic or associated with sphalerite (0.2–2 mm diameter) as granular intergrowths or include atole-like pyrite grains (10 μm to a few mm diameter). The liberation of the small atole-like inclusions of the pyrite may present difficulties;

c) veinlets and droplets of chalcopyrite occurring inside the gangue minerals and also together with sphalerite as stringers between the leaves of micaeous gangue minerals.

The sphalerite occurs as:

a) first generation sphalerite making up the groundmass between euhedral pyrite grains and as sub-graphic intergrowths with pyrite and as veinlets and stringers inside gangue;

b) second generation sphalerite in granular intergrowths with chalcopyrite and pyrrhotite;

c) third generation sphalerite which crystallized in the presence of, but later than, chalcopyrite. On cooling copper and iron exsolved as chalcopyrite, pyrrhotite and pyrite inclusions of grain sizes from less than 5 μm to a few mm. Liberation to free the sphalerite from these inclusions is impossible.

Subsequent x-ray diffraction analysis in another laboratory has shown that a small percentage of the sphalerite is iron-bearing and, while not falling into the category of marmatite, a variety containing up to 10 percent Fe S has been identified.

The degree of grinding necessary to achieve economic liberation will be determined by the relative percentages of the 'free-milling' minerals and those such as the subgraphic pyrite-sphalerite intergrowths and the inclusions of pyrite in chalcopyrite and of chalcopyrite, pyrrhotite and pyrite in third generation sphalerite.
THE METALLURGICAL OBJECTIVE

The marketing agreements into which the company has entered demand a fairly complete separation of the metal sulphides. The specifications generally require a copper concentrate containing not more than 8 percent zinc and a zinc concentrate with not more than 3 percent copper. Misplaced zinc does not earn any revenue while copper contained in the zinc concentrate is paid for at an appreciably lower than normal copper price. The aim, therefore, is to achieve better than specification limits for both the products. There are also penalties for other impurities in the concentrates, particularly as regards bismuth, antimony and arsenic. Gold and silver are paid for above certain minimum levels in either concentrate while some of the cadmium in the zinc concentrate is also paid for. It is not intended, at this stage, to recover pyrite which will, therefore, form part of the tailings.

To obtain ninety percent copper recovery in a concentrate analysing 24 percent copper and not more than 6 percent zinc from head values of 1,74 percent Cu and 3,87 percent Zn, it is necessary that the zinc rejection be at least 89.9 percent. Considering the copper float as a two-component separation, these recoveries and grades reduce to a mineral separation efficiency of 79.9 percent or a Baudin selectivity index of 8.9. Mineral separation efficiency as a single figure criterion to characterise separation has proved useful in analysing operations. Attainment of the high performance required is a difficult task bearing in mind that the chalcopyrite and sphalerite have not only to be separated from one another, but also from a gangue high and variable in pyrite, a sulphide which displays similar flotation behaviour and which reacts with the reagents used to effect separation. The required separation efficiency is naturally a function of the relative percentages of copper and zinc in the feed as illustrated in Fig (1) which defines the metallurgy required for a concentrate grade of 24 percent Cu and 6 percent Zn from varying head values. Obviously at any given copper/zinc ratio in the feed a greater copper recovery results in a relaxing of the required zinc rejection to satisfy the copper concentrate grade specifications. Similarly the smaller the copper/zinc ratio in the feed, the greater the zinc rejection and efficiency demands.

Besides the economic inducement of a high copper recovery per se, a high copper extraction is imperative to ensure that the zinc concentrate does not exceed the specified copper content, since testwork has shown that a fraction of the copper remaining in the copper flotation tails is floated into the zinc concentrate. As shown in Fig (2), with the average feed grade to the mill of 1,74 percent Cu, 3,87 percent Zn, a ninety percent recovery of the copper necessitates a minimum recovery of 67 percent of the zinc to obtain a concentrate grade of 50 percent Zn and not more than 2 percent Cu on the assumption that sixty percent of the copper rejected from the copper float reports with the zinc; an eighty-eight percentage copper recovery requires a minimum of 79 percent recovery of the zinc for the same grade of concentrate to be obtained, while a ninety-two percent recovery of copper requires only 54 percent zinc recovery. At higher copper/zinc ratios in the feed, higher copper recoveries are of course obligatory while lower ratios allow a lower copper recovery. A successful zinc float is thus largely dependent upon the success of the preceding copper float.

![Diagram](image)

Fig. 1—Zinc rejection and efficiency required for copper concentrate grade of 24%, Cu, 6% Zn

![Diagram](image)

Fig. 2—Minimum zinc recovery requirements for grade of 50% Zn, 2% Cu conc., assuming 60% of Cu in copper float tails is floated with zinc

The difficulty experienced throughout the world in attaining good copper-zinc separation is summed up in...
a Russian comment: 'A characteristic feature of many copper-zinc concentrating plants is the ability to produce copper-free zinc concentrates containing 50-55 percent zinc (or even more), but zinc extraction into the concentrate is relatively low. For example, about 30 percent of the copper-zinc plants in the U.S.A. produce zinc concentrates with a zinc extraction of less than 50 percent; only 10 percent achieve an extraction of 80 percent or more. The low level of zinc extraction into the zinc concentrate is due principally to losses in the copper concentrate'.

TESTWORK IN THE ANGLOVAAL LABORATORY AND THE PRIESKA PILOT PLANT

Laboratory testwork started in February, 1969 on samples of cores from the first sixteen boreholes which intersected the orebody at depths between 60 and 280 metres. These became available at regular intervals and testing was carried out on individual core samples as well as on composites. When completion of the prospect shaft enabled the pilot plant to begin operating in April, 1970, laboratory research continued in parallel with pilot plant testwork on ore drawn from development on the 105 metre level. Testing has continued as ore has become available from deeper levels with the opening up of the orebody through another shaft and a declined roadway.

Short descriptions of laboratory flotation procedures and of the pilot plant are provided in the appendices.

DIFFERENTIAL FLOTATION USING ALKALI DEPRESSION

As shown by Wark & Cox, each collector-sulphide mineral combination has a critical pH value below which the mineral will float and above which flotation is impossible. The value varies with the concentration of the collector and to a lesser extent with temperature.

In an early series of bench-scale tests, an attempt was made to achieve separation by taking advantage of the different critical pH values exhibited by the different sulphides. In the copper stage of the float, lime was added to the mill to control the pH in preference to soda ash because of the known fact that calcium ions have an inhibiting effect on pyrite flotation independently of the hydroxyl ion. Grinding to 65 percent -200 mesh a number of sulphur-bearing collectors were tested and it was found that the optimum pH value was 10.5 when using isopropyl ethylthionocarbamate as collector at a concentration of 0.005 g.p.l. Excellent separation of the pyrite was achieved with good recoveries of copper (90 percent recovery of copper with 97 percent rejection of the pyrite), but the zinc rejection was found to be inversely proportional to the copper recovery. By increasing collector strength, either in concentration or quality, it was possible to obtain well over ninety percent of both metals in a bulk concentrate not too heavily contaminated with pyrite. It was obvious that none of the collectors was sufficiently selective for chalcopyrite over sphalerite when used as the only depressant. Separation was also found to be affected by the copper:zinc ratio in the feed. In addition, results on fresh samples of individual cores were much better than those obtained from composite samples which were crushed and allowed to stand for a while before grinding and testing. In a Canadian laboratory using lime and zinc sulphate in the mill, grinding to 97 percent -200 mesh and using mercaptobenzothiazol as collector at pH 9.5, 80 percent separation was achieved on a borehole core sample assaying 2.29 percent Cu, 3.43 percent Zn and only 63 percent from a bulk, weathered sample assaying 1.06 percent Cu, 3.42 percent Zn. It was concluded from all these tests that oxidation had a deleterious effect on the separation. These conclusions were confirmed when the pilot plant went on line for the first time, following the same technique of alkaline depression. Difficulties were experienced in maintaining the knife-edge reagent control necessary to avoid over-promotion of the zinc or over-depression of the copper, difficulties which were accentuated by variations in the head and tail sulphides vis-a-vis lead and copper sulphides. It has been commonly used in lead-zinc separation since it has no depressant action on galena.

In studies extending over many years, Gaudin and his co-workers have provided the chemical reasons for the cyanide depression of sphalerite. They showed that the sulphide minerals pure sphalerite is one of the most difficult to float, being completely non-flatable with ethyl xanthate and sparingly so with the more powerful collectors, and that its practical flotation is possible only because of activation by salts of the metals, silver, copper, cadmium, lead and mercury, whose sulphides are less water-soluble than is zinc sulphide. In particular, they demonstrated that sphalerite acquires from copper-bearing solutions a coating of cupric sulphide, Cu S, which readily absorbs collectors and is easily floated with ethyl xanthate.

\[ Zn + Cu^{+} + Cu S + Zn^{++} \]

(i)

The role of cyanide in zinc depression is to dissolve the copper sulphide coating to form the soluble undissociated cupro-cyanide ion \( Cu(CN)_{2} \), whereby the floatability of the copper-activated sphalerite is reduced to the normal low response of the pure mineral.

\[ Cu^{+} + 3CN^{-} \rightarrow Cu(CN)_{2} + \frac{1}{2} (CN)_{2}^{-} \]

(ii)
The cyanide’s function as a depressant for zinc is essentially that of deactivation. No adsorption of cyanide or copper-cyanide complex takes place on the sphalerite surface, and cyanide does not inhibit unactivated sphalerite which can be floated to some extent with amyl xanthate or amyl mercaptan.

The failure of the ‘weaker’ short chain sulphydryl collectors such as ethyl xanthate and diethyldithiocarbamate to induce flotation of non-activated sphalerite has been interpreted by Steininger and others as being due to their high degree of ionisation. Ionised collectors have difficulty in displacing the hydroxyl groups absorbed on the sphalerite surface whereas with collectors having a low degree of ionisation the non-ionised collector molecules are able to react with and replace the surface absorbed hydroxyl groups. At low pH collector adsorption decreases because of the lower number of hydroxylated zinc surface sites; at high pH ionisation of the collectors is more complete and flotation of pure sphalerite would be poor unless the high alkalinity results in increased activation of the sphalerite surface.

The use of zinc sulphate in combination with cyanide as a sphalerite depressant formed part of the original Sheridan-GrisswoId patent. Zinc sulphate by itself does not de-activate copper-activated sphalerite unless present in large excess; it does not prevent activation in the presence of CuSO\(_4\) and in copper-zinc separation is normally used only in conjunction with cyanide. Practice varies widely, the ratio of zinc sulphate to sodium cyanide equivalent used varying from nil to about three. The combination is particularly favoured to reduce cyanide dissolution of gold and silver when these are present in quantity.

Gaudin, Fuerstenau and Mao have shown that de-activation is the combined result of the mass action and common ion effect of the zinc sulphate in supplying zinc ions to replace copper ions in the sphalerite surface and the complexing action of the cyanide on the replaced copper ions. Zinc salts speed up the cyanide de-activation and render it more complete by driving reaction (i) to the left:

\[
K = \frac{(Zn^{++})}{(Cu^{++})} \approx 10^{11} \quad \text{and} \quad K = \frac{(Zn^{++})}{(Cu^{++})} \approx 10^{23}
\]

define the ratios of the concentrations of zinc and copper ions in solution which prevent or permit activation of the sphalerite. Because CuS is so much less soluble than ZnS (0.3 mg per litre against 7 mg per litre), a sequestering agent such as cyanide is necessary to complex the copper ion into a more stable form than the zinc ion and thus control K to a value greater than 10\(^{20}\) (since most of the copper in solutions containing cyanide is reduced to the cuprous state the higher concentration ratio must be established). The use of zinc sulphate without cyanide, often with the addition of soda ash to reduce the concentration of Pb\(^{++}\), is common in lead-zinc separation practice, the Zine Corporation and New Broken Hill Cons. Limited plants on the Broken Hill field and the Bunker Hill & Sullivan plant, Idaho, being examples. Fuerstenau & Metzger have shown that activation of sphalerite by lead may be prevented with an addition of zinc sulphate such that the ratio \((Zn^{++})/(Pb^{++})\) in solution exceeds approximately 10\(^{6}\). In this case the presence of cyanide is unnecessary because of the relative closeness of the solubilities of ZnS and PbS.

Russian workers using radioactive tracer techniques have confirmed that CN\(^{-}\) adsorption on the sphalerite surface is negligible and is of minor importance in depression. They further confirmed the greater effectiveness and more stable depression obtained with K\(_2\)Zn(CN)\(_4\) compared to KCN and showed that this is due to the formation of zinc ion film, adsorbed presumably as hydroxide, which obstructs xanthate adsorption. They also suggested that Zn\(^{++}\) depresses activated as well as unactivated sphalerite if zinc hydroxide or basic zinc carbonate is precipitated on the surface; soda ash combined with zinc sulphate could be the source of the protecting film.

Unfortunately from the point of view of chalcopyrite—sphalerite separation cyanide is also a depressant for all the sulphide minerals except galena, having the effect of reducing the degree of alkalinity necessary for depression. As shown by Wark & Cox at any given pH the amount of cyanide necessary to depress pyrite is much less than that required for chalcopyrite depression, so that separation of these two minerals is relatively easily accomplished. The mechanism of cyanide depression of the copper and iron sulphides has not been studied as completely as sphalerite de-activation and it is not as fully understood. In the case of pyrite, Gaudin suggested that its action may be similar to that pertaining to sphalerite de-activation, i.e. a solvent action on films of copper sulphide (covellite and chalcocite). Eliglani and Fuerstenau postulate that cyanide depression of pyrite is due to the formation of surface ferric-ferrocyanide Fe\(_4\)(Fe(CN)\(_6\))\(_3\), the collector species responsible for pyrite flotation being the dixanthogen and not the xanthate ion when using xanthate as the collector. Plante & Sutherland suggest that chalcopyrite flotation is enhanced by auto-activation of the surface by cupric ions, formed as a result of the superficial oxidation of the mineral; it is well known that chalcopyrite flotation is improved with aeration. The depressing effect of cyanide and zinc sulphate on this mineral may, therefore, be partly explained by the same solvent and complexing action. Mitrofanov states that CN\(^{-}\) ion is adsorbed by chalcopyrite and displaces ethyl xanthate from the surface. Whatever the phenomena involved in depression of the various sulphide minerals, it has been established that it is the portion of the cyanide which is present as the cyanide anion which is of significance, whether the cyanide is complexed with zinc sulphate or with metal ions derived from the pulp. The concentration of the cyanide ion in solution is a function of pH, the dissociation of NaCN being nearly seventy times as great at pH 9.0 as it is at 7.0. Hence the efficacy of the added cyanide both in de-activating sphalerite and in depressing other sulphide minerals should be greater at high pH values. High alkalities thus result in a saving in the added cyanide but, as was confirmed in the testwork, not necessarily in greater selectivity. To obtain selectivity, control
of collector, cyanide and alkali concentrations would have to be very close.

**DEPRESSION WITH SODIUM SULPHIDE**

Part of the function of sodium sulphide in zinc depression is that of precipitating activating ions such as copper and lead, similarly to the function of soda ash; in this rôle it serves to prevent activation rather than to act as a de-activator and the correct place for its addition is early in the circuit as a supplement to zinc sulphate. Sodium sulphide, of course, is well known as a sulphidiser of oxidized minerals with oxygen-bearing anions such as malachite and chrysocolla, but it finds no application as such in the Prieska flotation. As the salt of hydrogen sulphide and caustic soda, sodium sulphide hydrolyses and dissociates to form hydrosulphide ions (\(SH^-\)) and sulphide ions (\(S^2-\)), the degree of dissociation being determined by the pH of the pulp. As shown by Sutherland & Wark\(^{18}\) from the data of Wark & Cox\(^{23}\), it is the hydrosulphide ion which is the effective depressant, its adsorption by all the sulphide minerals inhibiting collector adsorption. They showed that the relationship between pH value and the concentration of Na\(_2\)S necessary to prevent flotation of chalcopyrite with ethyl xanthate implies a critical hydrosulphide ion concentration above which flotation is not possible. This concentration is in the order of 0.30 mg per litre, considerably less than the critical cyanide concentration. From the same data of Wark & Cox, it can be calculated that the critical concentration for activated sphalerite is 0.27 mg per litre. Control of the addition of sodium sulphide to permit separation of the minerals in the absence of deactivation of the sphalerite would, therefore, be exceedingly difficult, particularly as the dissociation products are so readily oxidised. The \(SH^-\) ion appears to have some power in displacing adsorbed collectors and sodium sulphide is extensively used in Russia for desorbing collectors from bulk concentrates\(^{20,21}\). (In the same way it has been shown\(^{22}\) that alkali dissolves xanthate attached to chalcopyrite and sphalerite and that this removal results in a faster specific flotation rate for the fine particles.)

**DEPRESSION WITH SODIUM SULPHITE**

In the presence of oxygen the dissociated sulphide ion from sodium sulphide forms sulphite, thiosulphate and sulphate ions. Sodium sulphite, bisulphite and hyposulphite, the hydrolysis products of sodium sulphide, are reducing agents which have been used for pyrite and sphalerite depression as replacements of cyanide or in conjunction with it since they reportedly depress chalcopyrite less strongly than does cyanide. A full understanding of the phenomena responsible for depression with these reagents is lacking, but it is more than likely that they are related to their reducing properties. The first reported use of sulphite for pyrite and sphalerite depression was that at the Midvale, Utah, lead-zinc mill in 1919, before the advent of cyanide. Sutherland & Wark\(^{18}\) have reported that in the presence of 3-5 p.p.m. of copper ions, sodium sulphite with ethyl xanthate at pH 7.0-8.0 depresses galena and pyrite, but allows chalcopyrite to float normally; this fact had been taken advantage of at Lake George Mines, N.S.W. The Department of Mineral Engineering, University of Utah\(^{29}\) obtained a seventy percent improvement in copper rougher concentrate grade at the same recovery from a chalcopyrite-pyrite ore using sodium sulphite in place of cyanide. Approximately five times more sulphite than cyanide was found necessary to depress the pyrite adequately. They explained the depressant action as being due to the prevention of the formation of dixanthogen which they accept as being the collector species responsible for pyrite flotation; the adsorption of the reductant on the surface prevents the adsorption of oxygen which oxidises the xanthate. Broken Hill South used sodium sulphite intermittently for partially oxidised lead-zinc ore together with sodium cyanide and zinc sulphate, the action of the combination being explained as the cleaning of the mineral surfaces and removal of coatings by the sulphite, thus permitting the collector and cyanide-zinc sulphate depressant to act effectively. Today the use of cyanide has been discontinued. At the Rosebery copper-lead-zinc mill of the Electrolytic Zinc Company of Australasia, sodium sulphite is produced by burning sulphur under pressure and passing the SO\(_2\) into a packed tower irrigated with soda ash solution. After adjusting the pulp in the grinding circuit to pH 9.5 with soda ash, the flotation feed is conditioned with the sodium sulphite solution, care being taken to avoid the entrainment of air. Flotation of the copper-lead is carried out at pH 8.2. It is considered that the sodium sulphite controls the adsorption of oxygen at the mineral surfaces or the removal of such adsorbed oxygen. Cu-Zn separation efficiency is 61 percent from a head value of 0.60 percent Cu, 17.75 percent Zn. At Lake Dufault, Quebec, sodium sulphite is added together with lime, frother and collector to the grinding circuit, sometimes with soda ash replacing lime to precipitate dissolved salts introduced into the circuit through make-up water. Unit cells after the mill provide stage flotation of chalcopyrite, some seventy to eighty percent of the copper being recovered in the unit cell concentrate. Overall separation efficiency of 76.9 percent is obtained from a head value of 1.70 percent Cu, 1.36 percent Zn. At Idarado, Colorado, a bulk copper-lead concentrate is lifted from sphalerite and pyrite at pH 9.8 using sodium sulphite, zinc sulphate, a proprietary zinc oxide—calcium cyanide compound and lime in the grinding circuit. Collector is stage-added to the rougher cells. A copper-zinc separation efficiency of 85.55 percent is obtained from a head value of 0.99 percent Cu, 4.14 percent Zn. At Cobar Mine Limited, N.S.W., sodium sulphite at pH 9.5 is used to depress pyrite, pyrrhotite and small quantities of sphalerite from chalcopyrite. Copper recovery is 91.4 percent. In the central concentrators of the Boliden Company of Sweden, when treating complex Pb-Cu-Zn ores with high pyrite contents, soda ash is used to pH 9.0 with additions of zinc sulphate and sodium-hydrosulphite to the roughers. Some pyrite is floated at this pH, but its retention in the lead concentrate is acceptable. At the Santander Mine in Peru, a lead-copper concentrate is floated away from zinc using soda ash in the rod mill
to pH 8.1, zinc sulphate, sodium bisulphate and collector in the secondary mills and lime to pH 9.0 in the cleaners. A 45.5 percent efficiency of copper-zinc separation is obtained from a head assay of 0.38 percent Cu, 15.14 percent Zn. Sodium bisulphite appears to be the most favoured zinc depressant in nearly all the South American plants.

**DEPRESSION WITH SULPHUR DIOXIDE**

Sulphur dioxide as a depressant for sphalerite goes back to its use by Bradford in 1913 in lead-zinc separation at Broken Hill. It has been extensively used in Australia and the U.S.A., and in recent years, due to its availability in concentrated liquid form, has been finding increased application in Canada and the U.S.A. With the present concern with environmental pollution, it is likely to find even more application in the future. As a reducing agent, its action is possibly similar to that of the salts of sulphurous acid and the lack of understanding of the method of action of these depressants applies to sulphur dioxide as well. It is considered that besides acting as an iron and zinc depressant, it has the added advantage of having some activating properties for copper minerals by cleaning the surfaces of oxidation tarnish.

At Lake George Mines, N.S.W., sulphurous acid is used to float chalcopyrite preferentially before galena, sphalerite and pyrite, the acid being added to the primary mill for maximum conditioning time, to the conditioner ahead of copper flotation and to the final cleaner. Flotation is carried out at pH 6.5 with starvation amounts of collectors. The acid does not depress the galena so that selectivity between these minerals is obtained by careful collector additions. At Buchans, Newfoundland, sulphur dioxide is used to depress sphalerite from chalcopyrite and galena. Collectors and zinc sulphate are added at the primary mill, the final mill pulp passing through a sulphur dioxide absorption tower before being floated at pH 6.2. Additional collector and zinc sulphate are fed to the conditioner ahead of flotation and sodium cyanide and zinc sulphate are added to the cleaners. The action of the SO₂ is said to be obscure; other acidic and reducing reagents have been tried without success. At the low pH used, the cyanide does not inhibit chalcopyrite flotation, reportedly because of the high pyrite content. The Kestall (Kidd Creek) concentrator of the Texas Gulf Sulphur Company floats chalcopyrite at a pH of 6.5 maintained by lime additions in the presence of SO₂ as a sphalerite and pyrite depressant. An interesting use of sulphur dioxide is that at the two concentrators of the Brunswick Mining & Smelting Corporation, New Brunswick, where pyrite and pyrrhotite are floated from a zinc concentrate in the one case and from a bulk Cu-Pb-Zn concentrate in the other. Flotation is at pH 5.0-5.3 in pulps heated to 170°F with steam. Sulphur dioxide is also used at the London Mill of the Tennessee Copper Company at Copperhill, Tenn. to depress sphalerite from pyrrhotite at pH 5.0.

**FLOTATION OF ZINC**

Copper sulphate is used universally for the activation or re-activation of sphalerite, often with lime as an alkaliinity modifier, since it has the ability to activate sphalerite in preference to pyrite or pyrrhotite in the presence of calcium, cyanide and oxygen. Its use goes back to the days of acid flotation circuits when L. Bradford first applied it at Broken Hill, Australia, in 1913, and to its adventitious discovery at the Mascot Mill, Tennessee, in 1914, when bronze impellers supplied the copper. Under the cyanide-free and acid conditions of that time, the pyrite was not depressed and copper sulphate did not come into extensive use until the adoption of alkaline circuits.

In an alkaline pulp, the copper sulphate is not present as such, but is converted to copper hydroxide or basic carbonate precipitates. These precipitates have solubilities in water of 6.5 and 2.6 p.p.m. respectively which are sufficient for the concentration of copper ions in equilibrium with the precipitates to react with sulphides in the ore to form copper sulphide films. In the case of sphalerite, the displaced zinc passes into solution as the soluble zinc sulphate or hydrate. The activation of the sphalerite is thus identical to the unwanted activation which takes place prior to copper flotation. De-activation with cyanide or sulphite has no permanent effect on the surface of the sphalerite and depression disappears on the addition of sufficient copper sulphate. The greater activating effect of copper sulphate for sphalerite in preference to pyrite is explained by Ralston 24 as being due to the fact that the iron that is displaced from the pyrite surface by the copper cannot pass into solution in an alkaline pulp because of the low solubility of ferric hydroxide at high pH, the film of copper sulphide being contaminated by ferric hydroxide precipitate (he explains the greater activation of sphalerite over chalcopyrite on the same grounds). Bushell 25, 26 is of the opinion that the formation of an insoluble ferric hydroxide film which prevents the copper ion from displacing the iron applies to pyrrhotite, but in the case of pyrite the mechanism is due to the thermodynamic driving force for the adsorption of copper ions by sphalerite being much greater than that by pyrite. Whatever the mechanism as long as unflotted sphalerite remains in the pulp, copper activation of pyrite is negligible.

The ability to re-activate sphalerite after de-activation with cyanide forms the basis for the procedure commonly followed in the sequential flotation of copper and zinc. Practice is fairly standard, the main variation being in the degree of alkalinity necessary to depress the pyrite and, if present, pyrrhotite. Not all of the copper which is not floated in the copper circuit will necessarily float in the zinc circuit since CuSO₄ activation for sphalerite is greater than that for chalcopyrite.

With the above background information available, as soon as it became apparent that alkalinity control in itself was not a satisfactory method of treatment, testing of the alternative procedures was begun in various laboratories and in the pilot plant. Most of the work has been concentrated on cyanide depression which remains the basis of the treatment still favoured and being followed today. The other reagents have nevertheless received their fair share of attention and the work devoted to them will first be briefly described.
TESTWORK USING SODIUM SULPHIDE

A number of tests were carried out in the Anglovaal Laboratory in which sodium sulphide, zinc sulphate and lime were added to the mill. Grinds varied from 60 percent to 90 percent — 200 mesh and flotation was carried out at pH values ranging from 9.5 to 11.3. Efficiencies varied from 67 percent to 71 percent from feed values of 0.47-0.58 Cu:Zn ratios. Replacing the zinc sulphate with ferrous sulphate gave virtually the same results. Pilot plant tests duplicated these results. A test in a Japanese laboratory using slightly more sodium sulphide at pH 12.5 and a grind of 94 percent — 200 mesh resulted in a 49.8 percent efficiency from a head value of 1.59 percent Cu, 2.40 percent Zn. Collector used in all cases was di-thiophosphate. It thus does not appear that sodium sulphide is sufficiently selective in its depressing effects to permit differential flotation of the chalcopyrite and sphalerite and no further test work is contemplated.

TESTWORK USING SODIUM SULPHITE

No laboratory work to test sodium sulphite as a depressant was carried out, but pilot plant runs were made with additions of sodium cyanide, sodium sulphite and sodium carbonate to the primary mill. Mereaptobenzothiazol was used as a collector at pH 8.5 and zinc sulphate and additional cyanide were added to the copper cleaning stage. Grinding to 75-80 percent — 200 mesh, efficiencies ranging from 47-70 percent were obtained from feed ratios of 1.09-0.82 Cu:Zn. A series of tests was then carried out in the pilot plant without cyanide additions and with additions of sodium sulphite up to 2 000 g/t; virtually no differentiation was achieved and further testing was abandoned in favour of investigating the related reagent, sulphur dioxide.

TESTWORK USING SULPHUR DIOXIDE

Bench scale batch tests to evaluate sulphur dioxide-zinc sulphate depression of sphalerite and pyrite were first carried out in a Swedish laboratory on samples of diamond drill cores. Grinding was carried out at pH 7.1 in the presence of sulphur dioxide dissolved in water (the ‘natural pH’ of the sample being 8.0). Zinc sulphate and collector added to the conditioner reduced the pH to 6.5 which rose to 7.0-7.1 as flotation proceeded. Results were found to be strongly separation efficiencies of 12.5 percent, 47.6 percent and 50.3 percent being obtained at grinds of 73 percent, 92 percent and 98 percent — 200 mesh respectively from head values of 1.60 percent Cu and 1.52 percent Zn. Investigations in a Japanese laboratory disclosed that grinding to 94 percent — 325 mesh and consumption of very high quantities of H2SO4 at pH 5.4 (15.7 kg/ton) were necessary to achieve reasonably separation. In spite of the not very encouraging indications, pilot plant runs were made to investigate the process more fully. Bottled sulphur dioxide was added to the grinding circuit through a pipe protruding through the vortex finder into the low pressure zone of the cyclone in closed circuit with the secondary mill. In this way the SO2 was distributed to the secondary mill, to the final pulp feeding the mill thickener and through the return water to the primary mill. The large volume of the thickener resulted in slow response to gas additions unless the sulphur dioxide was added to the thickener as well. To eliminate this disadvantage the thickener was taken out of circuit and the cyclone overflow was fed to the copper conditioner via a storage agitator. Extra additions of SO2 were made to the conditioner together with ZnSO4 and collector. Flotation was carried out at pH 6.5 and the grind held at 90 percent — 200 mesh. Flotation was not successful in that good depression of the zinc was once again only obtainable at the expense of a lower copper recovery, achieved by reducing collector addition. Further tests, this time in the Anglovaal Laboratory, led to a procedure involving a combined SO2-zinc sulphate-cyanide combination. Grinding a sample of deep level borehole core to 65 percent — 200 mesh at pH 8.0 with additions of Zn(CN)2, sodium cyanide and collector to the mill, SO2 was introduced into the conditioner and flotation carried out at pH 6.5. Although copper recovery was somewhat on the low side, very effective zinc depression was achieved and a separation efficiency of 79.8 percent obtained from a head value of 1.59 percent Cu, 8.13 percent Zn. This good separation was bettered using the same technique on a composite sample of development ore for which an 86.8 percent efficiency was obtained from head values of 2.27 percent Cu, 4.71 percent Zn. This latter result, however, was only slightly superior to that achieved in a parallel test using sulphuric acid to adjust the pH to the same value. The difficulties of absorbing large volumes of sulphur dioxide at low concentration into large volumes of pulp in a full-scale plant discouraged further test work when it was demonstrated that sulphuric acid could be substituted without great loss of efficiency. However, valuable information had been gathered which can be summed up as follows:

(i) On the Prieksa ore the sulphur dioxide-zinc sulphate combination is not an effective depressant for zinc nor an activator of copper. It is more effective, but not acceptably so, at extremely fine grinds. It is very efficient as a pyrite depressant at pH 6.5.

(ii) The efficiency is vastly improved if cyanide is used in conjunction with the SO2 and zinc sulphate. This combination does not require adding the gas to the grinding circuit. The critical dependence upon fine grinding when cyanide is not used does not apply and good results are obtainable at 65 percent — 200 mesh.

(iii) Sulphuric acid appears to be as effective as sulphur dioxide when cyanide forms part of the reagent combination. The basic function of these reagents when used in conjunction with cyanide is, therefore, suggested as being that of pH modification.

TESTWORK USING THE CYANIDE-ZINC SULPHATE COMBINATION

First attempts at the use of cyanide involved adjusting the alkalinity of the pulp in the grinding circuit
to pH 10.0-11.0 with lime, followed by the addition of small quantities of sodium cyanide and zinc sulphate to the cleaning stage of the copper flotation. Improvement over alkali depression was hardly noticeable, but the first indications of some success came when the depressants were added earlier in the circuit, viz., to the conditioners ahead of the roughing stage. The two reagents were mixed together in stoichiometric quantities to form the compound Zn(CN)₂; it was considered that the limited solubility of this precipitate (9 p.p.m. in water) would impart greater tolerance of the chalcopyrite to excessive additions of cyanide. Further improvement resulted from moving the cyanide addition yet further back in the flowsheet, the addition being made together with lime to the primary mill to pH values ranging from 9.0-10.0; zinc sulphate continued to be fed at the conditioner. In spite of the more encouraging results, the separation was still unsatisfactory in that it was far too dependent upon definite reagent control. Nevertheless the slight improvement following the addition of the cyanide to the mill supplied valuable data which could be interpreted in either one or both of two ways:

(i) Pre-activated sphalerite requires a longer contact time with the cyanide for de-activation. Gaudin has shown that cyanide deactivation is extremely slow if the copper ion has penetrated into the sphalerite lattice to any depth.

(ii) Solubilising of copper takes place in the mill and the resultant activation of the sphalerite is inhibited by introducing the cyanide at the same time (at this stage of the investigation the deleterious effect of high alkalinity in increasing sphalerite activation was not appreciated).

Confirmation of the beneficial effect of zinc sulphate in assisting cyanide de-activation by accelerating the displacement of the copper from the sphalerite, came when the zinc sulphate was added together with the cyanide to the ore feed to the primary mill. These two reagents were again added as the compound Zn(CN)₂, lime being added to the mill to pH 10.0. Separation immediately improved and fairly reasonable recoveries and concentrate grades were obtained from a high sulphide feed. Table I summarises a typical run in this period during which xanthates and dithio-phosphate were tested as collectors. The results were consistent as long as the ore remained constant in quality, but they were very sensitive to variations in feed grade.

Excellent separation was finally achieved when lime additions to the mill were discontinued and grinding was carried out at the natural pH of the ore. A number of laboratory tests were then carried out to confirm this finding and to investigate the effect of reduced pH; one of this series is illustrated graphically in Figure (3). In these tests, grinding was carried out at the natural pH (7.4) except in the case when it was raised to 8.7 by the addition of lime. Constant additions of Zn(CN)₂ were made to the mill and flotation was carried out at the different pH values obtained by varying acid additions to the conditioner. As seen from the graph, separation improves steadily with decreasing pH until a value of 6.0 is reached where pyrite is strongly floated, using sodium isopropyl xanthate as collector. Microscopic examination has shown that it is the extremely fine sphalerite which is the more readily activated and floated with the copper and the coarser fraction of the chalcopyrite which is the slowest floating. Both of these hindrances to good separation are reduced with lowering pH.

Improvement resulting from grinding in the absence of lime can be attributed to:

(i) The deleterious effect of lime in encouraging activation of the sphalerite. Plante & Sutherland have demonstrated that in grinding chalcopyrite soluble oxidation products are greater at high pH, particularly with lime as the alkali, or

(ii) The effect of alkalinity on the efficacy of the cyanide-zinc sulphate depressant.

Improved flotation of the chalcopyrite at low pH may be due simply to the greater collecting power of xanthates at these values, but in the complex pulp climate existing it is probable that this is an over-simplification and that other factors play a part. The fact that it is in the flotation of the coarser particles of chalcopyrite that improvement results from decreased pH suggested that the acid may also perform as a dispersant in preventing over-floculation. That this is not an important factor was proved in tests which showed that

### Table I

**Pilot plant copper float: Depressant and lime added to primary mill**

<table>
<thead>
<tr>
<th></th>
<th>% Wt</th>
<th>Analyses %</th>
<th>Distribution %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Zn</td>
<td>Cu</td>
</tr>
<tr>
<td>Flotation Feed</td>
<td>160,0</td>
<td>2,60</td>
<td>1,70</td>
</tr>
<tr>
<td>Copper Recleaner Concentrate</td>
<td>8,1</td>
<td>3,77</td>
<td>3,77</td>
</tr>
<tr>
<td>Copper Scavenger Tails</td>
<td>91,9</td>
<td>0,36</td>
<td>1,42</td>
</tr>
</tbody>
</table>

Reagent Additions:
- To Rod Mill: NaCN (647 g/t), ZnSO₄·7H₂O (1987 g/t), CaO (600 g/t)
- To Conditioner: Dithiophosphate (31,2 g/t), Frother (28,0 g/t)

pH of Float: 9,8
Grind: 93,4% 200 mesh
Dispersing agents such as tetrasodium pyrophosphate and sodium silicate had no beneficial effect on copper recovery. The main effect of lowering pH must be a reduction in the cyanide-ion concentration and consequent reduction of the depressing action upon chalcopyrite. A theory may be formulated from Gaudin's and the Russians' findings that cyanide ion depresses chalcopyrite, but not unactivated (or de-activated) sphalerite which is depressed by the zinc ion, whether present as hydroxide or basic carbonate. Once the cyanide has performed its functions of de-activating the sphalerite and of depressing the pyrite it has served its purpose and any excess would have a detrimental effect on the flotation of the chalcopyrite. Free cyanide ion owes its presence to excess cyanide added and to the dissociation of the zinc cyanide complexes which are fairly stable but far less so than the cuprocyanides. At low pH values, any soluble sulphide present would precipitate copper and zinc from solution forming H,CN. in the process. Cyanide from all these sources is largely undissociated at low pH and, therefore, harmless. At the usual pulp dilution at pH 7.0 for every 100 g/t NaCN added, the concentration of CN ion is 0.12 p.p.m.; at pH 9.0 the concentration would be 8 p.p.m. Low pH, therefore, has the same effect of locking the cyanide ion as has the limited solubility of the Zn(CN)₂ complex which also dissociates to a lesser extent at low alkalinitities. Research is now being conducted into the possibilities of using the specific ion cyanide electrode as an aid to control.

Improvement in sphalerite depression probably lies in the apparently anomalous fact, first detected by Wark & Sutherland, that in the presence of cyanide and carbonate ions, copper-activated sphalerite could be depressed at neutral pH and floated at high pH, an 'island' of non-contact obtaining between pH 6.7 for intermediate cyanide additions. Figure (4) is a reproduction of their graphs showing the relationship between

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Fig. 3—Effect of pH on separation
Feed value 2.73% Cu, 2.73% Zn
Na₂P₂O₇ 28 g/t
NaCN 550 g/t
ZnSO₄·7H₂O 1 700 g/t
H₂SO₄ & Ca(OH)₂, Variable
cyanide concentration and critical pH values for contact on sphalerite, chalcopyrite and pyrite. They attributed the lack of contact inside the island to xanthate deficiency due to the precipitation of copper xanthate in the presence of excess copper ions\(^{18}\). Steininger\(^{27}\) disagrees with this interpretation and offers the explanation that depression in this range is due to the formation of hydroxylated basic copper–collector complexes. He showed further that even in the absence of sodium carbonate, flotation of both sphalerite and pyrite in the presence of \(\text{CuSO}_4\) abruptly changes from good flotation to almost complete depression as the pH approaches neutrality. At high or low pH values where good flotation obtains copper reacts with xanthate to form cupric xanthate which is unstable and decomposes into cuprous xanthate and dixanthogen. Near neutral pH, however, basic copper xanthate complexes are formed and these contribute to the depression of sphalerite and pyrite in this region.

As far as is known very few practical applications of these findings have been made. It may well be that fear of \(H\text{CN}\) generation has contributed to hesitation in the joint use of sulphuric acid and cyanide; at least one plant\(^{28}\), in a slightly different application, viz., that of floating sphalerite from pyrite, making use of optimum \(\text{CuSO}_4: \text{NaCN}\) ratios at low pH, was discouraged from lowering the pH below 7.5 because of this fear, in spite of laboratory work indicating improvement at still lower values. Mount Isa, in lifting lead from zinc, using \(\text{SO}_3\), cyanide and zinc sulphate, controls the pH to 7.3 with lime. It was considered that with adequate precautions no danger should arise from lowering the pH to the neutral point and possibly below this figure. Experience has been gained in the industry with similar conditions which have been accepted in pyrite flotation and uranium leaching after gold dissolution. Accordingly test runs were made in the pilot plant following the above procedure. Table II illustrates a typical test and gives details of the reagent combinations used. This is the system currently being employed in the pilot plant and which is being incorporated in the full-scale plant. A typical analysis of the copper concentrate being produced is shown in Table III.

### ZINC FLOTATION TESTWORK

A pilot plant investigation of the factors affecting zinc flotation was delayed until reasonably good and consistent copper flotation had been obtained. When this aim had been achieved, pilot plant flotation of the zinc was commenced following conventional methods as adapted in the laboratory.

### TABLE II

<table>
<thead>
<tr>
<th>Flotation Feed</th>
<th>Copper Releaner Concentrate</th>
<th>Copper Scavenger Tails</th>
</tr>
</thead>
<tbody>
<tr>
<td>100,0</td>
<td>6.3</td>
<td>93.7</td>
</tr>
<tr>
<td>(% \text{Wt})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analyses (%)</th>
<th>Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu})</td>
<td>(\text{Zn})</td>
</tr>
<tr>
<td>2.60</td>
<td>1.43</td>
</tr>
<tr>
<td>29.20</td>
<td>2.82</td>
</tr>
<tr>
<td>6.18</td>
<td>1.34</td>
</tr>
<tr>
<td>8.3</td>
<td>87.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagent Additions:</th>
<th>To Rod Mill:</th>
<th>To Conditioners:</th>
<th>pH of Copper Float:</th>
<th>Grind:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{NaCN})</td>
<td>(\text{ZnSO}_4\cdot7\text{H}_2\text{O})</td>
<td>(7.1)</td>
<td>(66.9%) 200 mesh</td>
</tr>
<tr>
<td></td>
<td>(226 \text{ g/l})</td>
<td>(889 \text{ g/l})</td>
<td>(722 \text{ g/l})</td>
<td>(30.1 \text{ g/l})</td>
</tr>
</tbody>
</table>

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In the direct differential flotation procedure which is being followed, the zinc flotation step consists essentially in lifting sphalerite from pyrite and gangue minerals. A 50 percent grade of zinc concentrate would analyse 25 percent pyrite, assuming that all the diluent is pyrite. To obtain this grade at 80-90 percent recovery from average zinc head values, at least 92 percent rejection of the pyrite is necessary from a feed containing 20 percent FeS₂ and 95 percent if it contains 30 percent.

The standard method of copper sulphate activation of the sphalerite, after its depression with cyanide in the copper flotation stage, varies from plant to plant mainly in respect to the quantities of copper sulphate used, the number of cleaning stages, the pH in each of the roughing and cleaning stages and the nature of the collector. These then were the main variables which the laboratory examined.

In practice, pH values are usually controlled between 8.2 and 11.5, the lower ranges being used for marmattic sphalerite, increased alkalinitites being common in the cleaning stages. Fig. (4) shows that sphalerite-pyrite separation is theoretically possible at all pH values between 7.0 and 11.8 in the presence of copper sulphate, but that the practical range is limited by the degree of oxidation of the minerals and the quantity of cyanide present. At the lower pH values, ferrous salts remain soluble and these assist in the depression of the pyrite.

With regard to the quantity of copper sulphate used, for activation to be effective, free copper ions must be present; in the presence of cyanide at such a concentration that three cyanide ions are present for each copper atom (equation ii), free copper ions are incapable of existence and the sphalerite would not be activated.

Copper consumption, therefore, besides being dependent upon the zinc content, is largely a function of the residual cyanide ion concentration of the copper flotation tailings. The cupro-cyanide complex carried through from the copper float is stable and takes no part in the re-activation of the sphalerite unless it is caused to dissociate. Soluble sulphur increases CuSO₄ consumption by precipitating copper sulphide in competition with the desired sphalerite-copper reaction, particularly at low pH values, and for this reason sodium sulphide, although a good depressant of pyrite, is not used in the zinc float. Since the copper sulphate activation is faster at low pH, it is normally added ahead of the lime and also ahead of the collector addition. Over-conditioning has to be avoided because of the danger of abrading away the film of Cu₈S₈.

In the early laboratory testwork when lime was the sole depressant used in the copper-zinc separation, copper sulphate activation of the sphalerite at an addition rate of 135-180 g/t CuSO₄·5H₂O proved to be adequate for collection with isopropyl ethylthionocarbonate. The lime carried through from the copper stage was highly effective in depressing the pyrite, the zinc float being conducted at pH values varying between 8.8 and 11.8. In tests on seventeen samples, zinc recoveries from the copper tailings varied from 83.3 percent to 97.7 percent with an average of 92.2 percent and the pyrite rejected varied from 88.6 percent to 97.7 percent with an average of 95 percent. The average separation efficiency of 87.2 percent was completely acceptable, but naturally overall zinc recoveries were poor because of losses in the copper concentrate.

In the second series of laboratory tests with the adoption, at high pH values, of the cyanide-zinc sulphate reagent to effect better copper-zinc separation, the residual cyanide carried forward to the zinc float increased the requirement of CuSO₄·5H₂O additions to 500 g/t, in accordance with the above comments regarding Cu:CN ratios necessary for activation. Over the same pH range as used in the previous series, the zinc recovery suffered a 7.3 percent decrease to 84.9 percent with the efficiency of pyrite depression remaining unimpaired. The overall recovery of the zinc into the zinc concentrate averaged 67.8 percent but was very erratic, again mainly due to losses of zinc into the copper concentrate.

The third phase of the laboratory investigation of zinc recovery was that which followed naturally from the adoption of the low pH, zinc cyanide method of copper-zinc separation. With this method there are three possibilities in regard to the pH of zinc flotation:

(i) Raising of the pH by the addition of lime. This is the more conventional approach which is successfully used in most sphalerite-pyrite separations since it is accepted that alkalinity reduces the floatability of pure pyrite and its activation by copper salts.

(ii) Acceptance of the low pH to which the copper tailings settle. Zinc recovery from a zinc-pyrite ore with a high soluble salt content is being carried out at pH 7.5 at one plant (28) where copper sulphate

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**TABLE III**

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis of typical Copper concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper: Cu</td>
<td>26.28 %</td>
</tr>
<tr>
<td>Zinc: Zn</td>
<td>4.08 %</td>
</tr>
<tr>
<td>Aluminium as: Al₂O₃</td>
<td>0.35 %</td>
</tr>
<tr>
<td>Antimony: Sb</td>
<td>0.007 %</td>
</tr>
<tr>
<td>Arsenic: As</td>
<td>0.0009 %</td>
</tr>
<tr>
<td>Bismuth: Bi</td>
<td>0.015 %</td>
</tr>
<tr>
<td>Cadmium: Cd</td>
<td>N.D.</td>
</tr>
<tr>
<td>Calcium as: CaO</td>
<td>0.56 %</td>
</tr>
<tr>
<td>Chlorine: Cl</td>
<td>0.024 %</td>
</tr>
<tr>
<td>Chromium: Cr</td>
<td>0.005 %</td>
</tr>
<tr>
<td>Cobalt: Co</td>
<td>0.004 %</td>
</tr>
<tr>
<td>Fluorine: F</td>
<td>0.009 %</td>
</tr>
<tr>
<td>Germanium: Ge</td>
<td>N.D.</td>
</tr>
<tr>
<td>Indium: In</td>
<td>N.D.</td>
</tr>
<tr>
<td>Iron: Fe</td>
<td>28.00 %</td>
</tr>
<tr>
<td>Lead: Pb</td>
<td>0.40 %</td>
</tr>
<tr>
<td>Magnesium as: MgO</td>
<td>0.52 %</td>
</tr>
<tr>
<td>Manganese: Mn</td>
<td>0.050 %</td>
</tr>
<tr>
<td>Mercury: Hg</td>
<td>0.003 %</td>
</tr>
<tr>
<td>Nickel: Ni</td>
<td>0.002 %</td>
</tr>
<tr>
<td>Potassium: K</td>
<td>N.D.</td>
</tr>
<tr>
<td>Selenium: Se</td>
<td>0.008 %</td>
</tr>
<tr>
<td>Silicon as: SiO₂</td>
<td>2.73 %</td>
</tr>
<tr>
<td>Sodium: Na</td>
<td>N.D.</td>
</tr>
<tr>
<td>Sulphur: S</td>
<td>30.70 %</td>
</tr>
<tr>
<td>Tellurium: Te</td>
<td>0.005 %</td>
</tr>
<tr>
<td>Tin: Sn</td>
<td>N.D.</td>
</tr>
<tr>
<td>Gold: Au</td>
<td>2.8 g/t</td>
</tr>
<tr>
<td>Silver: Ag</td>
<td>57.0 g/t</td>
</tr>
</tbody>
</table>

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and cyanide additions are made in such proportions as to ensure the presence of free copper ions. 

(iii) Lowering the pH still further by additions of sulphuric acid. The plant mentioned in (ii) above, in laboratory testing, found that lowering the pH to below the neutral point improved separation. 

Results of testwork on the alternatives are as yet inconclusive, but it appears that there is little to choose between the first two methods. The third method has not been fully tested. In laboratory tests using method (i), at pH 11.1, zinc recoveries from the copper tailings averaged 94.1 percent with 400 g/t CuSO₄·5H₂O, overall recovery averaging 83.4 percent. Operating at pH 7.8 (method (ii)) with 50 g/t NaCN and 250 g/t CuSO₄·5H₂O additions, zinc recoveries from the copper tailings averaged 93.7 percent with overall recoveries averaging 81.0 percent. Dependent upon the final choice of method is the possible recycling of tailings water to the circuit, including milling, and the effect of the contained reagents on the copper-zine separation. This is being investigated on the pilot plant. 

Although laboratory and pilot plant investigations are continuing, it is apparent that either of the two methods tested is successful in achieving satisfactory separation of the zinc and pyrite. Locked cycle laboratory testing has shown that two cleaning stages are sufficient to obtain satisfactory grades and this has been confirmed in the pilot plant. A typical analysis of the zinc concentrate being produced on the pilot plant is shown in Table IV.

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis of typical Zinc concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper: Cu</td>
<td>1.16</td>
</tr>
<tr>
<td>Zinc: Zn</td>
<td>50.37</td>
</tr>
<tr>
<td>Aluminium as: Al₂O₃</td>
<td>0.22</td>
</tr>
<tr>
<td>Antimony: Sb</td>
<td>0.01</td>
</tr>
<tr>
<td>Arsenic: As</td>
<td>0.0005</td>
</tr>
<tr>
<td>Bismuth: Bi</td>
<td>0.012</td>
</tr>
<tr>
<td>Cadmium: Cd</td>
<td>0.11</td>
</tr>
<tr>
<td>Calcium as: CaO</td>
<td>0.14</td>
</tr>
<tr>
<td>Chlorine: Cl</td>
<td>0.036</td>
</tr>
<tr>
<td>Chromium: Cr</td>
<td>N.D.</td>
</tr>
<tr>
<td>Cobalt: Co</td>
<td>0.002</td>
</tr>
<tr>
<td>Fluorine: F</td>
<td>0.011</td>
</tr>
<tr>
<td>Germanium: Ge</td>
<td>0.001</td>
</tr>
<tr>
<td>Indium: In</td>
<td>0.0005</td>
</tr>
<tr>
<td>Iron: Fe</td>
<td>10.56</td>
</tr>
<tr>
<td>Lead: Pb</td>
<td>0.043</td>
</tr>
<tr>
<td>Magnesium as: MgO</td>
<td>0.25</td>
</tr>
<tr>
<td>Manganese: Mn</td>
<td>0.36</td>
</tr>
<tr>
<td>Mercury: Hg</td>
<td>0.005</td>
</tr>
<tr>
<td>Nickel: Ni</td>
<td>0.002</td>
</tr>
<tr>
<td>Potassium: K</td>
<td>0.02</td>
</tr>
<tr>
<td>Selenium: Se</td>
<td>0.007</td>
</tr>
<tr>
<td>Silicon as: SiO₂</td>
<td>1.32</td>
</tr>
<tr>
<td>Sodium: Na</td>
<td>0.09</td>
</tr>
<tr>
<td>Sulphur: S</td>
<td>31.72</td>
</tr>
<tr>
<td>Tellurium: Te</td>
<td>0.004</td>
</tr>
<tr>
<td>Tin: Sn</td>
<td>0.005</td>
</tr>
<tr>
<td>Gold: Au</td>
<td>1.4 g/tn</td>
</tr>
<tr>
<td>Silver: Ag</td>
<td>19.4 g/tn</td>
</tr>
</tbody>
</table>

FINENESS OF GRIND

Numerous laboratory tests have been performed throughout the testwork period to evaluate the effect of fineness of grind on the metallurgy obtained with each of the reagent combinations being tested. From the microscopic evidence it is apparent that complete liberation of the minerals would not be attained unless the ore were milled to 5 microns, which is clearly impracticable. Invariably it was found that with the less successful depressants finer grinds improved copper-zinc separation. In the case of sulphur dioxide for instance, well over 90 percent — 200 mesh is necessary to obtain a separation efficiency of 50 percent from 1:1 copper-zine feed values. With the more effective zinc cyanide depressant a fine grind is not nearly so necessary and a laboratory batch grind to 65 percent — 200 mesh has proved adequate to reduce the quantity of locked particles sufficiently to permit the recovery of commercial grades of concentrate. Reregrinding of middling particles does not result in a significant increase in recoveries or grades. In the closed circuit grinding of a complex ore containing gangue and high percentages of pyrite and valuable sulphides, the size distributions of the individual minerals are influenced by the comparative densities as well as by their friabilities. In the pilot plant operating with a circulating load ratio of five, cyclonesizier and infra-sizer tests showed that the cumulative percentage passing any designated size is 5 percent greater for the sphalerite and 9 percent greater for the chalcopyrite than it is for the pyrite in spite of the greater density of the latter mineral. In laboratory batch milling the differential is even greater, due to the greater hardiness of the pyrite.

No attempts were made in the laboratory to simulate closed circuit grinding, the effect of fineness on the flotation being more accurately assessed in the pilot plant. It was found that overgrinding gives rise to high tailings losses of the sphalerite and that an overall grind of 65 percent — 200 mesh was the optimum from this point of view. Sharp classification is consequently very necessary, but it is difficult to achieve, particularly in a small scale operation. It is confidently expected that in the large plant in which the size of cyclones in closed circuit with the mills can be more conveniently matched with the throughput, the classification efficiencies will be higher than in the pilot plant.

COLLECTORS

Although the emphasis in the testwork has been on finding the best means of selectively depressing the sphalerite and the collectors used have merely been mentioned in passing in the above discussion, it is realised that collectors and depressants cannot be divorced from one another. Considerable attention has, therefore, also been paid to testing out various collectors and the conclusions are briefly summarised below. 

In the copper float, weak collectors such as ethyl xanthate or dithiophosphate are theoretically the most selective, but it has been found that even at the low pH values finally settled upon they are not powerful enough to prevent excessive copper tailings losses. Amyl and butyl xanthates on the other hand proved to be too potent to avoid over-dosage; at any given pH value, higher cyanide additions are necessary with these to obtain the same depression of the sphalerite as with ethyl xanthate. The collector offering the best economy
in usage has proved to be isopropyl xanthate. Isopropyl ethylidenecarbamate, while effective, is costly.

In the zinc float, although it has been reported that isopropyl ethylidenecarbamate is more specific than xanthate for sphalerite in the presence of pyrite and is more effective at low pH values, no great advantages were found with this reagent and the economics favour the use of ethyl xanthate.

In the copper float, particularly, selectivity is improved by staging the collector addition, starvation quantities being added at each stage to avoid exceeding threshold concentrations. Experiments are being conducted on the pilot plant on blends of the various collectors, but conclusions have not yet been drawn.

BULK FLOTATION METHOD

The Ore Dressing Division of the N.I.M. adopted a somewhat different approach to the conventional sequential flotation of copper and zinc from the pyrite and gange which was being investigated by the Anglovaal and overseas laboratories. The method developed involves the depression of the pyrite and gange at a coarse grind from the copper and copper-activated zinc which are removed in a combined bulk concentrate which is then subjected to differential flotation after a regrinding and sphalerite de-activation step.

Among the features which combined to make this alternative method appear attractive are the following:

(i) The pyrite is relatively easily separated from the copper and zinc compared to the difficult copper-zinc separation which could conceivably be more easily controlled in the absence of the voluminous and varying quantities of pyrite.

(ii) The preliminary tests showed that the chalcopyrite and the sphalerite are liberated from the pyrite at very coarse grinds (50 percent – 200 mesh) and that over 93 percent of both the copper and zinc can be recovered in the bulk concentrate with very slight pyrite contamination. It was considered that the elimination of fine grinding of the total ore would effect a considerable saving in capital and operating costs of grinding and thickening equipment. Since it has subsequently been shown that fine grinding is also not necessary for direct differential flotation, this apparent advantage does not really apply. Had fine grinding of locked copper-zinc particles been shown to be necessary, this could have been confined to one or other of various middling products, analagous to the grinding of the bulk concentrate.

(iii) De-activation of the sphalerite without excessive depression of the copper is the key to success of the operation, whether carried out by the selective or bulk flotation procedures. The depth to which copper atoms replace zinc and occupy sites within the sphalerite lattice, resulting in activation, is a function of time and de-activation, or the removal of the copper, is a corresponding function of time. Any de-activating step which is successful in removing the copper from sphalerite which has been in contact with copper-bearing solution for any length of time would be more than adequate to remove that placed on the surface by design. The bulk flotation technique takes advantage of any activation which may take place in the ore-in-situ, in the mine, the mill or the flotation cells, and it was considered that it has the merit over differential flotation of limiting to a small volume the equipment necessary for a possible lengthy de-activation. Variations in the degree of pre-activation are not critical since complete de-activation can conveniently be provided for in the absence of pyrite.

The laboratory method as finally evolved at the N.I.M. is as follows: The ore is milled to 60 percent – 200 mesh at natural pH in the presence of NaCN. Bulk flotation is carried out with additions of lime to pH 11.0, copper sulphate and, as collectors added stage-wise, ethyl and amyl xanthates. The bulk concentrate is filtered, diluted and conditioned with NaCN for 30 minutes, refiltered and ground to 85 percent – 200 mesh in the presence of NaCN and Na2SO3. The regrind concentrate is conditioned for 15 minutes and then for a further 1.5 minutes with Na2SO3 before floating the copper with ethyl xanthate. The copper float tailings are then floated for zinc in the conventional manner using CuSO4, lime to pH 11.0 and ethyl xanthate added stage-wise. The above standard procedure, using fixed quantities of reagents and flotation times, was applied to all the samples available. Without any recycling of the zinc tailings, copper-zinc separation efficiencies varied from 57.4 percent-77.1 percent (average 65.8 percent) from head Cu:Zn ratios varying from 0.46:1 to 1.77:1 (average 1.22:1). Average copper recovery was 82.8 percent and zinc recovery 67.3 percent. In a test on a sample in which the Cu:Zn ratio was 0.46:1 recycling of the zinc tailings resulted in an 88.6 percent Cu recovery and 79.4 per cent Zn recovery at a separation efficiency of 72.9 per cent. It should be noted that these results reflect the roughing operations only. In a few further tests to simulate plant conditions, it was shown that thickening of the bulk concentrate to a liquid-solid ratio of 0.65:1 could replace the filtration step, the extra dilution being carried forward to the de-activation stage without any harm, but the recycling of the filtrate after the de-activation adversely affected the copper recovery; this filtrate would have to be discarded.

During the course of the investigations a few puzzling problems emerged, which sound a note of warning to all those engaged in correlations of laboratory procedures and plant practice. Before the standard technique described above had been developed, the second filtration stage had not been included in the flow sheet, the bulk concentrate being filtered once before being regrind in the presence of cyanide and sulphite. Attempts to duplicate the results at the Anglovaal Laboratory were unsuccessful until it was discovered that the type of mill used had a profound bearing on the quantity of collector carried forward to the differential float. After testing in rod, ball and pebble mills with stainless steel rods, carbon steel rods, ball bearings, porcelain balls and ore pebbles in cast iron, stainless steel and porcelain shells, it was found that the method worked satisfactorily provided the collector addition was optimised for each type of mill. In the case of pebble milling, sufficient
residual xanthate remained attached to the mineral particles as to make it unnecessary to supply further collector to the copper float and in some cases excessive xanthate resulted in the contamination of the copper concentrate with excessive xanthate. No precise explanation of the phenomenon can be advanced but it appears likely that xanthate consumption is a function of the amount of fine 'nascent' iron abraded into the pulp. Rey & Formanek²⁰ and Fahlstrom²¹ have reported similar problems in laboratory flotation experiments. With the incorporation into the flowsheet of the second filtration stage, the type of milling employed no longer had an influence and the standard procedure was found to be applicable on all samples in any type of mill. One further disclosure, significant as corroboration of the conclusion drawn in the differential flotation experiments at the Anglovaal Laboratory, was the fact that better copper-zinc separation obtained at close-to-neutral pH.

Encouraged by the laboratory results, the pilot plant was converted to the bulk flotation flowsheet to check the operation on a continuous basis and larger scale. At the time this was done the two-step de-activation procedure had not been developed and the pilot plant operation was successful only in so far as the removal of a bulk concentrate containing 93 percent of both copper and zinc with 95 percent rejection of the pyrite presented no difficulties. Grinding was 55-60 percent - 200 mesh. A second attempt was made after the success of the modification to the process had been demonstrated in the laboratory. A fair amount of improvisation was necessary and the operation of the plant presented difficulties as insufficient equipment was available, the plant having been designed before a bulk process had been envisaged. In spite of the difficulties, a total of two weeks was spent in investigating the process, of which one week was occupied with relatively unoxidized ore with an average feed value of 1.71 percent Cu, 2.48 percent Zn (Cu:Zn ratio 0.69). Copper recovery was 84.9 percent at a grade of 26.80 percent Cu, 5.64 percent Zn and the zinc recovery 74.0 percent at a grade of 49.54 percent Zn, 1.59 percent Cu. Copper-zinc separation efficiency was 74.1 percent with 10.85 percent of the zinc being recovered in the copper concentrate. By this time, the low pH copper-zinc separation process had been developed and in a series of comparative tests on ore from the same source the differential float procedure gave a copper recovery of 89.4 percent at a grade of 25.75 percent Cu, 3.61 percent Zn and a zinc recovery of 81.2 percent at a grade of 50.6 percent Zn, 1.30 percent Cu. From a head value of 1.56 percent Cu, 2.95 percent Zn (Cu:Zn ratio 0.53), the separation efficiency was 83.7 percent with 5.68 percent of the zinc floating with the copper. The decision was, therefore, made to continue testing with the direct differential procedure and with continued success with this method, it has been decided to design the final plant on this basis. The bulk flotation process lost a lot of its attraction when it was shown that the low pH zinc-cyanide process was effective at coarse grinds in de-activating pre-activated sphalerite in the presence of pyrite. Nevertheless the neatness of the method commends its application to ores in which the sphalerite is so strongly pre-activated that the normal short de-activating period obtained in conditioning ahead of copper float is insufficient. In applications such as these, it is suggested that the method could well be simplified to effect a saving in reagents; the use of large quantities of cyanide in the initial grinding could possibly be replaced with alkali depression of the pyrite using carbamate as the collector in place of xanthate. During the period of testing alkali depression at the Anglovaal Laboratory, high extractions of the valuable sulphides into a combined concentrate could be made in this manner without the use of cyanide to depress the pyrite or copper sulphate to activate the sphalerite; the beneficial effect, in this case, of alkali activation of the sphalerite in the presence of chalcopyrite has already been dealt with. In this modification of the bulk process, there is no danger of depressing chalcopyrite due to over-additions of cyanide which is consumed by the copper sulphate, and the subsequent de-activating step could possibly be carried out with smaller quantities of zinc sulphate and cyanide in what would amount to a cleaning operation.

ACKNOWLEDGEMENTS

My acknowledgements are due to Mr A. C. Langton, Technical Director, Anglo-Transvaal Consolidated Investment Company, Limited, for permission to present this paper and to Dr D. I. Legge, Consulting Metallurgist, for his guidance and encouragement throughout the programme. I also wish to express my thanks to Mr W. H. Pittie, Chief Chemist of the Anglovaal Laboratory, who was in charge of the Laboratory investigations and to Mr K. Doig and Mr L. von Blottnitz who were successively in charge of the pilot plant operation.

REFERENCES

APPENDIX I
LABORATORY FLOTATION

Sample preparation
The entire sample, which is normally delivered in sealed drums, is crushed to -10 mesh, spread on the mixing floor and mixed by coning. A representative sample for analysis is taken by quartering. The balance of the sample is stored in sealed drums.

Milling
Cast iron balls 14 em long x 22 cm diameter, loaded with 5 kgs of ball bearings ranging from 12-40 mm rotate at 76 r.p.m. on rollers. The sample for grinding weighs 1 kg and is diluted with 800 ml water. Eighteen minutes grinding time is required for 65 percent -200 mesh and forty minutes for 80 percent -200 mesh.

To avoid over-conditioning, reagents which are to be added to the grinding stage are added five minutes before the end of the grinding period.

Flotation
Flotation tests are carried out in a Wemco laboratory machine of 2 300 ml capacity or in a Denver Sub-A laboratory machine, model D-2 of 8 litre capacity, both fitted with variable speed drives. In the latter machine, roughing is carried out at 21 percent solids with a load of 2 kg of dry solids. A model D-1 machine, with three tanks of 4.2 and 1 litre capacity, is used for cleaning and recleaning of the rougher concentrate at 10 percent solids. Flotation tests are either:
a) single open cycle consisting of roughing, cleaning and recleaning stages, the three tailings being weighed and analysed, or
b) simulated continuous closed circuit operation of six cycles in which the cleaner and reclaimer tailings produced from the rougher concentrate of the first cycle are added to the rougher and cleaner steps of the second cycle and so on up to six cycles. The reclaimer concentrate and rougher tails of each cycle and the cleaner and reclaimer tailings of the last cycle are dried, weighed and analysed.

Filtration and drying
Are carried out on Buchner funnels or compressed air filters, followed by drying at 110°C on a hot-plate or in a slow-drying oven.

APPENDIX II
THE PILOT PLANT

The pilot plant was designed for a nominal 4 tons per hour feed rate when grinding to 90 percent -200 mesh. In addition to conveyor belts, water tanks and pumps the main equipment comprises:

- 15 ton run-of-mine ore bin
- 10" x 20" jaw crusher
- 4" x 6" double deck vibrating screen
- 2' x 6' double deck vibrating screen
- 2' 6" diameter by 15' long rod mill
- 4' 6" diameter by 14' long ball mill
- 18" diameter by 10' long thickener
- 25" diameter by 10' long thickener
- 18" and 12" cyclones in series
- 500 cu ft conditioner
- 25 cu ft roughing cells
- 10 cu ft cleaning and/or reconditioning cells
- 20 sq ft disc filter
- 40 sq ft disc filter
- 24 sq ft pan filter

Equipment was also installed for pyrite recovery from the zinc tailings, but once it had been established that the recovery presented no problems, this section was withdrawn from the circuit.

For maximum flexibility pumps were installed for all intermediate circuit flows, gravity flows being used as seldom as possible. Reagent feeding is by means of positive displacement metering pumps and cup-and-disk feeders. All sampling is by hand.

A control laboratory adjoins the pilot plant and is provided with an atomic absorption spectrometer, pyknometer, laboratory flotation machines and facilities for sizing and chemical analyses.

Initially, before housing had been provided for sufficient operators, the plant was run during daylight only. For test purposes this was satisfactory, provided the circuit was allowed to reach stability before samples
were taken. When sufficient employee accommodation had been provided, the plant was operated around the clock for six days per week. Continuous operation allowed better assessments to be made of the effect of slight and gradual changes in reagent additions, and highlighted more clearly the effect on flotation of variations in the quality of the ore since at the present stage of mining operations it is difficult to obtain a homogeneous feed for prolonged periods. Continuous operation has also made possible the sale of concentrates, the revenue from which partly pays for the cost of the operation.

Laboratory and pilot plant testing have been complementary to one another and together have supplied information which has been valuable in avoiding possibly costly mistakes in the design of the large plant. For example, certain discrepancies in results from bench scale and pilot plant operation led to investigations which showed the importance of factors such as conditioning time and temperature on the separation.

Discussion

Dr. T. Groenewald and P. J. Lloyd

Mr de Kok has presented data (Fig. 3) showing that in the region pH 8.8-6.4 the Cu-Zn separation efficiency improves significantly with decreasing pH. Other studies (Fig. 4) indicated that the region of improved separation may extend as far as pH 5.8 for unoxidised material and pH 6.1 for oxidised material. As the author mentions ‘fear of HCN generation has contributed to hesitation in the joint use of sulphuric acid and cyanide’. We wish to present data which suggest that at low cyanide concentrations, pH values as low as 4 may be used without fear. This is contrary to many feelings about cyanide solutions, because it is always felt that the undissociated HCN, which is virtually the sole form of cyanide present below pH 7.3, should distribute readily between air and the solution. We were surprised to find, after an extensive search, that there was no record of this distribution in the scientific literature, and accordingly measured the amount of HCN released from both acidic and alkaline solutions.

The equilibrium concentrations of HCN gas over various cyanide solutions at different pH levels are shown in the table below.

<table>
<thead>
<tr>
<th>[KCN] M</th>
<th>NaCN g/1</th>
<th>pH</th>
<th>HCN gas in air (% v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5.00</td>
<td>4</td>
<td>0.001</td>
</tr>
<tr>
<td>0.1</td>
<td>5.00</td>
<td>7</td>
<td>0.06</td>
</tr>
<tr>
<td>0.1</td>
<td>5.00</td>
<td>10</td>
<td>0.24</td>
</tr>
<tr>
<td>0.01</td>
<td>0.50</td>
<td>4</td>
<td>0.34</td>
</tr>
<tr>
<td>0.01</td>
<td>0.50</td>
<td>7</td>
<td>0.26</td>
</tr>
<tr>
<td>0.001</td>
<td>0.05</td>
<td>4</td>
<td>0.018</td>
</tr>
</tbody>
</table>

The results show that the concentration of HCN gas in the air is:
(i) roughly proportional to the concentration of cyanide in solution (at a given pH level);
(ii) dependent upon the pH of the solution, being far lower when the solution is strongly alkaline;
(iii) does not increase markedly when the pH decreases from a value of 7 to a value of 4;
(iv) will reach levels in excess of the maximum allowable concentration (0.001% by volume) over all aqueous solutions containing significant (>0.01 g NaCN/l) cyanide concentrations at pH values below pH 10, if allowed to build up to equilibrium.

As Mr de Kok has demonstrated, it is possible to design for safe operation using solutions which would generate highly dangerous concentrations of HCN if equilibrium were to be attained. The added risk of reducing the pH levels further, to the region of pH 4 or above, appears on the data presently available to be negligible.

Mr. W. A. Gilbert

One of the most important findings in Mr de Kok’s excellent and informative paper is to my mind that the development of an optimum reagent schedule resulted in a significantly coarser grind: 65 percent minus 200 mesh versus 90 percent minus 200 mesh for a non-optimum reagent schedule. This must surely play an important part in the overall economics.

It was interesting to note the part played by pH in the efficient separation of chalcopyrite from sphalerite. Some years ago I was associated with the original laboratory testwork on a complex lead zinc sulphide ore (Rosh Pinah) which had sufficient copper sulphide minerals present to make the separation of the copper-lead minerals from sphalerite a tricky and difficult business.

I noted then that the classical sphalerite depressants such as sodium carbonate and sodium sulphite appeared to enhance the floatability of sphalerite, as did sodium cyanide if used in excess. In fact sodium alkalinity appeared to be harmful.

We found that the important variables in the selective flotation of galena and copper minerals were fineness of grind, amount and point of addition of sodium cyanide, pH control with either calcium hydroxide or sulphur dioxide or sulphuric acid and addition of zinc sulphate to the cleaner and recleaner cells.

Under these conditions lead concentrates assaying from 58-72 percent lead (depending on the ore types of which there were five) and 3-6 percent zinc were obtained. The head samples varied from 0.5 to 1.5 percent lead and 7 to 8.5 percent zinc. Copper in the head samples varied from trace to 2 percent.

The effect of cyanide was unusual: excess cyanide appeared in certain instances to promote the flotation of sphalerite and close control of cyanide addition had to be exercised.

Our best results were obtained at pH 8.0. It is very probable from Mr de Kok’s paper that we would have achieved still better results if we had lowered the pH further, say 7.0. But such was our rooted fear of cyanide in near acid pH that we never did.

Sphalerite flotation was fairly normal but with a few oddities when treating one ore type with a predominately dolomitic gangue. Here we found that sodium sulphite had a pronounced and beneficial effect on zinc concentrate grade. Calcium hydroxide also improved grade and appeared to be most effective when added to the conditioner ahead of the rougher cells. Copper sulphate if used in excess had a marked and deleterious effect on sphalerite recovery.

It appears generally that these complex ores all have their tricks and individual quirks and these have to be understood and resolved before satisfactory metallurgy can be achieved.