



The effect of underground mine water on performance of the Mufulira flotation process

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Synopsis

The experience of Mufulira concentrator, of the Zambia Consolidated Copper Mines Limited, with underground mine drainage water, which is used in milling operations is discussed. It is shown that the underground mine water has a deleterious effect on flotation performance. The adverse effect of the underground water was successfully negated by adding lime into the primary ball mills and increasing the pH of the slurry, from a 'natural' pH of 8 to the flotation pH of 10.5. Traditionally, the pH modifier, quicklime, had been added downstream of the milling. Changing the lime addition point further reduced lime consumption by 50%,—a key issue as lime accounted for over 60% of the Mufulira flotation reagent costs.

The nature of the effect of the underground water at Mufulira, particularly the sensitivity of the flotation to the pH at which the milling was conducted, characterized galvanic interaction. A large-scale plant situation is presented in which the desired electro-chemical response in the flotation was achieved, by a deliberate manipulation of the milling environment. The experience provides practical testimony of a more fundamental role for the milling process, other than the mere physical preparation, i.e. size reduction and liberation, of mineral particles prior to flotation.

Introduction

The Zambia Consolidated Copper Mines Limited (ZCCM)* operates an underground copper mine, at its Mufulira Division,* in the Copperbelt Province of Zambia. Run of mine ore is delivered to the concentrator through three main shafts, at a headgrade of 2% total copper (T/Cu). Bornite and chalcocite are the major copper minerals, occurring in the ratio 1.4:1, respectively. The sulphide minerals are finely disseminated and grinding to 55% minus 75 microns is required before flotation. The concentrator has a design capacity to mill 20 000 tonnes of ore per day.

As part of a ZCCM corporate strategy to improve the quality of concentrates major circuit modifications were undertaken in the

*Now Mufulira Division of Mopani Copper Mines PLC, following privatization of the mining assets of the government owned Zambia Consolidated Copper Mines Ltd

first half of 1990, which resulted in significant improvement in performance of the flotation process. After the recommissioning of a once 'mothballed' regrind circuit, to liberate middlings in the cleaner tailings stream, coupled with the installation of column flotation cells, to clean rougher concentrates, Mufulira concentrator performance improved to world class standards in 1990, as shown below.

Copper recoveries were increased from 93% to 96% and the quality of concentrate improved from 18% insolubles (gangue) to 7% insolubles. The ambition in the early 1990s was to increase recovery further to 97%, without sacrificing the quality of concentrate being produced. The issue then was whether the effort to recover the extra copper was economically justified, in terms of the actual cost of further innovation and circuit modifications in the concentrator, or whether the high recovery should be lowered somewhat and the focus placed on producing even lower than 7% insol in the concentrate, for more favourable economies in the subsequent smelting process.

The success brought about by the modifications noted above were well established when suddenly, without apparent disturbance or change in the circuit parameters, i.e. mineralogy, grind, pH, reagent addition etc, flotation performance began to fluctuate drastically. In the space of one week copper recoveries went from 95+% to a 50-year low of 89% and back to 95+% again. The insolubles in concentrate went from 7% to 12–18% and back again.

A few months later the same recovery drop phenomenon occurred again. During the first occurrence of the low recovery, a change in mill water composition had been noted. The second and a third low recovery occurrence also coincided with a change in mill water

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composition and it was this that led to the realization that mill water was a key operational variable in the Mufulira context.

Mufulira concentrator obtains its mill water largely from recycled tailings thickener overflow, which is mixed with make-up water pumped from the underground mine water drainage system. Due to operational problems at the tailings thickeners a much higher than normal proportion of underground make-up water was used in the mill during the low recovery periods. Laboratory tests were to further confirm the deleterious effect of too much underground water in the mill water.

In this paper, plant data is presented on the unprecedented problem with mill water at Mufulira. The discovery of the deleterious influence of underground water on the flotation process, the underlying electrochemical phenomena and how this problem was solved are discussed. In order to fully appreciate the significance of the underground water problem a brief discussion is given of the key circuit modifications which preceded the uncovering of the water problem at Mufulira.

Historical background

Mufulira Mine is a large underground operation, supported by an equally large surface metallurgical infrastructure. The metallurgical complex comprises a concentrator, smelter and a refinery. The smelter and refinery have annual design capacities to produce 200 000 tonnes of 99.8% new anode copper and 300 000 tonnes of 99.99% cathode copper, respectively. Extra capacities in the metallurgical finishing plants are taken up by toll treatment of concentrates and anodes, respectively.

The concentrator was brought into production in 1933, at an initial throughput of 495 tonnes of ore milled per day. Milling practice has gradually developed over the years and production peaked in the 1960s and 1970s, when throughput was increased to 20 000 tonnes per day. The plant has a design capacity to treat 600 000 tonnes of ore per month. However, due to depletion of ore reserves, certain plant equipment has recently been decommissioned and as such current production capacity has dropped to 300 000 tonnes per month.

The initial mine production was drawn from shafts at the east of the concentrator until the mid-1960s when an entirely independent new shaft system, supplying fresh production, was commissioned, about a kilometre west of the plant. Mufulira Division has since then been operating virtually two separate ore sources, *Mufulira East* and *Mufulira West*, respectively. The ore arising from the two sources is treated separately in the concentrator, starting from the two separately located crushing plants to the independent east and west flotation sections, respectively. The final concentrate is, however, mixed and dewatered in a single plant, as is the case with the disposal of the final tailings.

When mine production increased in the mid-1950s the concentrator capacity was expanded by extending the ball mill aisle and increasing the number of small mill units, as was typical of that time. This was the era before the present day large *SAG/FAG mill*. As a result, Mufulira concentrator has ended up with one of the longest ball mill aisles in the

world, with its parallel 'chain' of twenty-eight small 9 ft × 8 ft Hardinge conical ball mills, (6 of the small mills have since been replaced by two 14 ft × 18 ft Vecor mills).

The flotation circuit has fared slightly better than the milling plant in keeping abreast with technology. The small 45 ft Agitair cells of the 1950s were all replaced by 300 cubic feet Wemco cells in the 1970s. Further, column cells were installed in the early 1990s to clean rougher concentrates, which has had a positive and significant impact on the quality of final concentrate produced.

Mineralogy

Mufulira ore consists mainly of bornite and chalcopyrite, as disseminated particles in a fine grained and highly siliceous rock. The ore also contains very minor amounts of chalcocite, malachite, covellite, chrysocolla and occasionally some native copper.

The country rock around Mufulira Mine is relatively competent and has not been significantly disturbed geologically. The orebody has, as a result, not suffered much notable oxidation or secondary leaching and virtually all the copper exists as pure sulphide. The trace oxide mineral content normally contributes as low as only 0.01% copper, in absolute terms, to the total copper head grade of 2%. Mufulira ore further contains no deleterious substances of practical consequence in the beneficiation process. As would therefore be expected, the ore responds quite favourably and is, in fact, one of the most amenable to flotation on the Zambian Copperbelt.

The two respective ores at the east and west exhibit some fairly notable differences, particularly in the host rock. East ore is generally richer in copper than the west and occurs in a host rock which is typically sericitic quartzite with some carbonaceous greywacke facies. It is thought that the more reducing medium at the east was relatively more favourable to copper precipitation. The Mufulira west host rock is ordinary quartzite with some feldspar and has virtually no greywacke. The west ore has higher levels of pyrite and chalcopyrite while the bornite content is relatively richer at the east. Mufulira ore is generally quite hard as it contains 75% to 85% silica. The high silica content of the ore makes good fluxing medium, which is prepared in the tertiary stage of the West crushing plant, for the smelter.

Flotation practice

The Mufulira concentrator flowsheet is shown in Figure 1. The flotation circuit is typically a simple and basic sulphide *Rougher-Cleaner-Scavenger* design, which suits the uncomplicated mineralization of the ore being treated. Figure 1 depicts the geographical setting of the plant and clearly shows how the two ores, from the east and the west respectively, are separately treated in the concentrator. The crushing plants are located far apart, at the east and west respectively, while both the milling and flotation plants are under one roof. The two flotation sections are very similar and 'sit' like mirror images, set parallel to each other as they are. The 28 ball mills share a common and long aisle running from east to west. The first twelve mills feed the east while the last sixteen feed the west flotation section. The separate

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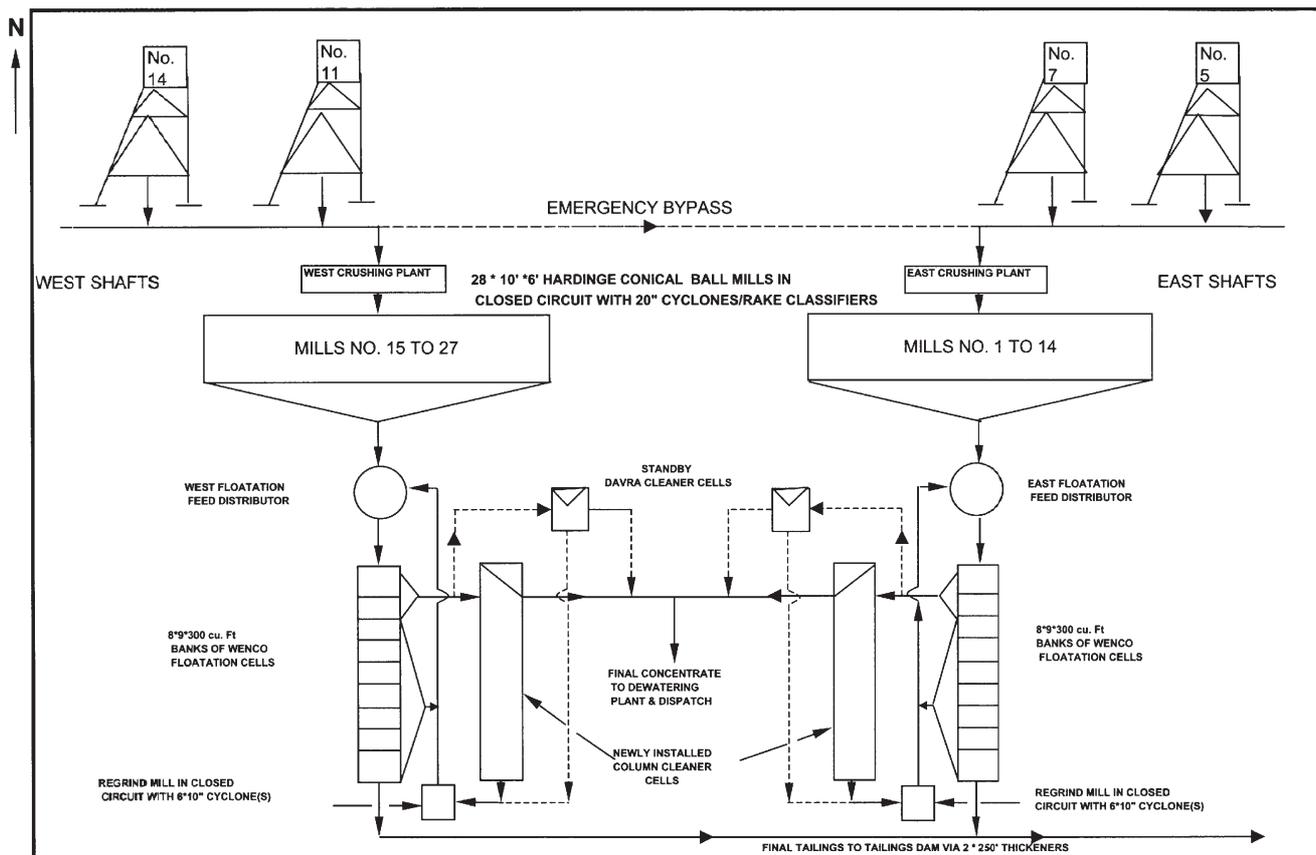


Figure 1—Mufulira concentrator material flow circuit

processing of the east and west ores was key to the diagnosis of flotation problems in general, e.g.:

- Problems affecting only one section would tend to be mineralogical in nature and are easily associated with the ore source, whilst
- Problems affecting the entire flotation plant would tend to have common cause, such as the nature of reagents. The flotation reagents are prepared at one central point, in common mixing tanks, and the same batches of reagents are used for the east and west, respectively, without discrimination.

In terms of the key flotation variables the two ores are floated under virtually similar conditions and these include the *grind, flotation slurry densities, reagent concentration and dosage* (see Table I). The flotation pH is, however, slightly different. East ore responds better at a higher pH of 10.5 while the west ore is best floated at a pH of 9.5 (Table I). The reason for this difference is not precisely known but this is likely attributable to the slight mineralogical variation in the host rock and the bornite to chalcopyrite ratios—these being the key notable variances in the two ores. Experience has shown that chalcopyrite floats in slightly less alkaline conditions than bornite. Further, a slightly higher dosage of collector is used at the east section than the west, which presumably compensates for the marginally higher head grade of the ore from the east.

The old circuit: high circulating load in flotation

In spite of being fairly uncomplicated, the Mufulira flotation

Table I

Flotation reagent addition and consumption at Mufulira

Reagent	Function	Addition point	Average (g/t), East	Consumption, West
(a) Before 1990 flotation circuit modification				
D14	Frother	Rougher Scavengers	1 3	1 3
Sodium ISO-propyl Xanthate and potassium amyl Xanthate as alternate scavenger collector at high headgrade	Collector	Roughers Scavengers	20 35	15 30
Quicktime	pH modifier	Roughers (Flotation* Feed slurry)	1300 (pH=10.5)	900 (pH-9.5)
(b) After 1990 circuit modifications				
D14	Frother	Rougher Scavengers	10 12	10 12
Sodium ISO-propyl Xanthate and potassium amyl Xanthate as alternate scavenger collector at high headgrade	Collector	Roughers Scavengers	20 35	15 30
Quicklime	pH modifier	Roughers (Flotation* Feed slurry)	1300 (pH=10.5)	900 (pH-9.5)

*N.B. Lime addition point was later moved from the flotation feed slurry to downstream of Primary milling, to increase the entire grinding pH, which forms the subject of this paper

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circuit had in the past a very peculiar and 'deep rooted' operational difficulty, associated with an uncontrollable and high circulating load of locked middlings. The circulating load was caused mainly by the very poor efficiencies in the regrind and cleaner circuits, respectively. The tailings from the cleaning circuit were previously recycled directly to the head of flotation, without prior regrinding, while the scavenger concentrate stream was retreated, in a not so effective regrind circuit and then recycled to the head. As a result locked particles tended to accumulate to an unknown extent in the recycle streams, causing a basic instability in the flotation circuit. Figures 2(a) and (b) show the old and new flotation circuits respectively.

The lack of selectivity and low recoveries in the cleaning circuit was mainly due to a technological limitation of the type of cells, being used at the time to clean the rougher concentrates. The cleaner cells were not effective enough to selectively produce a sufficiently clean concentrate at acceptable recoveries. The deficiency in the regrind circuit was found to be due, on the other hand, to inappropriate unit design—installation in addition to bad operational practice. The regrind mills were operated in closed circuit with 26 inch cyclones, which proved to be too big for the very fine cut required in that duty. Further, used mill balls, rejects from the primary ball mills, were, as a practice, re-used as grinding media in the regrind ball mills. The reject balls were not only too big (+50 mm) for the regrind job but also tended to badly deform, as they wore down, to the correct top up size of less than 30 mm diameter, rendering them ineffective media for the very fine regrinding action required.

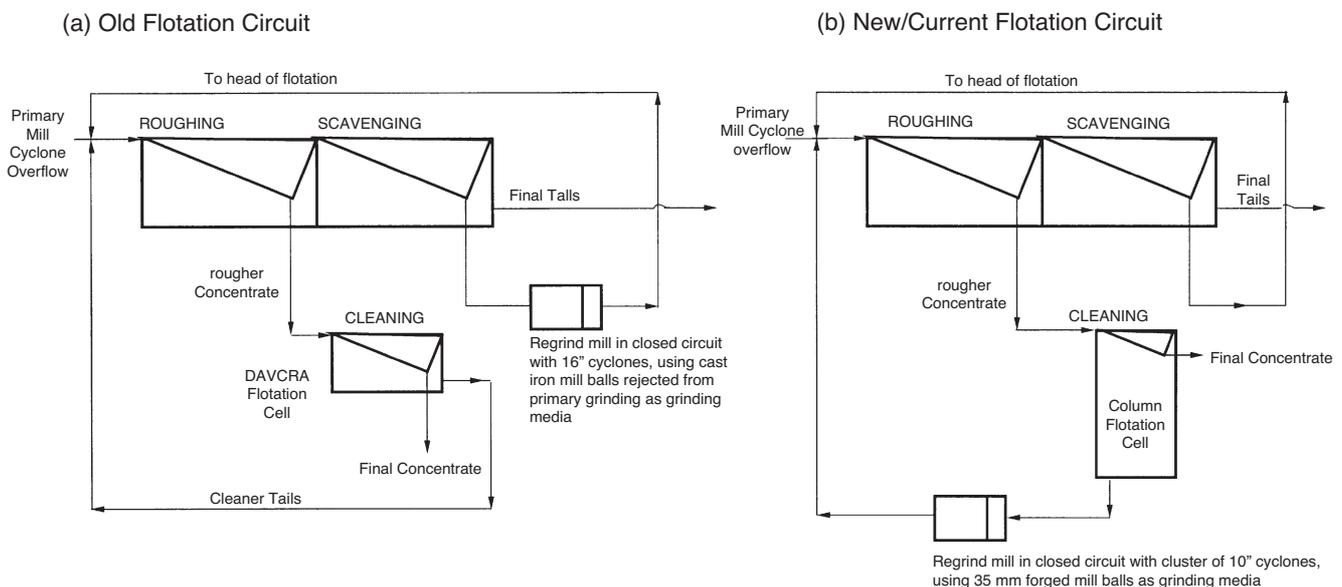
The new circuit

A renewed effort to improve performance of the Mufulira flotation circuit was embarked on towards the end of the 1980s and Figure 3 shows the stepwise improvement which resulted from this initiative. The deficiencies of the old flotation circuit were by this time very well known and it was abundantly clear that the abnormally high circulating load

needed to be drastically reduced, in order to achieve lasting improvement. With this view in mind the metallurgical development work discussed in Figure 3 was undertaken, the result of which has had what is arguably the most dramatic beneficial impact on the performance of Mufulira concentrator.

The new flotation circuit brought with it a large change in the consumption pattern of frother, further illustrating the degree to which the circulating load affected the old circuit. The consumption of frother increased immediately to 22 grammes per tonne of ore treated in the new circuit, from 4 grammes per tonne in the old circuit, representing an increase of 450%. The consumption of the rest of the other flotation reagents remained relatively unchanged, as can be seen in Tables I(a) and I (b). The sharp increase in the consumption of frother was directly related to the reduction of the circulating load.

The old circulating load was estimated at 500% of the total mass of fresh feed to the flotation circuit which in fact turned out to be the same order of magnitude as the increase in the consumption of frother in the new circuit, at 450% as discussed above. The excessive volume of recirculating material in the old circuit carried with it large quantities of residual frother. The reduction of the volume of this circulating load drastically reduced the residual frother returning to the head of flotation, which directly and immediately necessitated a corresponding increase in the dosage of fresh frother. Residual frother, which typically resides in the aqueous phase of recycle slurries can be highly reactive and in fact has a critical influence on the frothing characteristics of many a flotation circuit. Residual collector, in contrast, is carried in proportion with mineralized particles in the internal recycle streams and is generally unavailable to react or suitably influence the collection of particles in the fresh feed to flotation. The reduction of the circulating load had for this reason virtually no impact on collector utilization.



Figures 2 (a) and (b)—Mufulira flotation circuits—old and current

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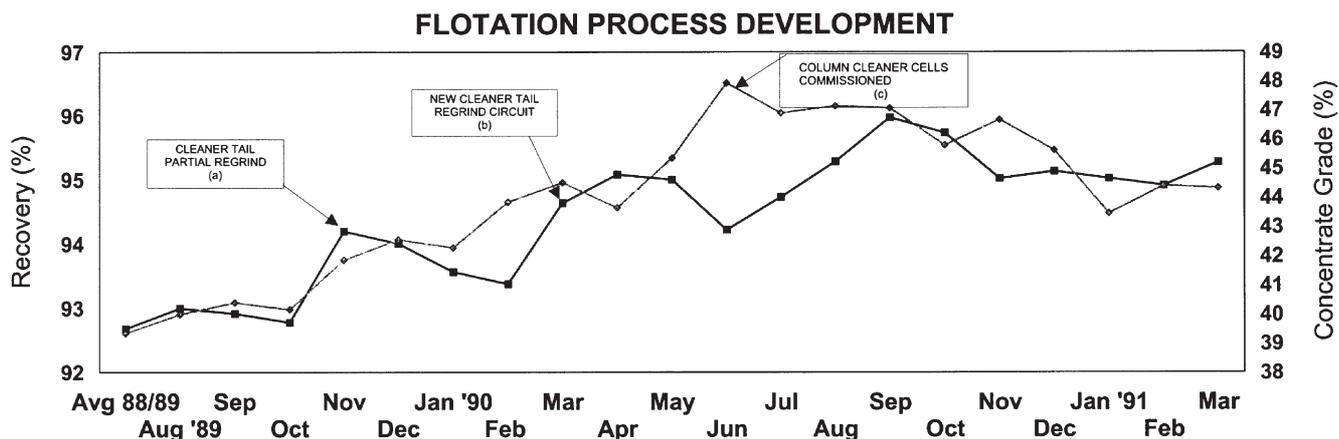


Figure 3—Stepwise flotation performance improvement brought about by innovative process development work implemented in the period between 1989–1990

(a) 'Partial regrinding' of cleaner tailings—The stream carrying tailings from the cleaning circuit was diverted from the head of flotation to a few primary ball mills, where this slurry was now mixed and milled with fresh ore. This practice was locally termed «partial regrinding»-a colloquial differentiation with conventional regrind practice. The effect on flotation was immediate. Flotation recovery improved from below 93% to just over 94%. The improvement was attributed to a reduction in the circulating load, resulting in more stable flotation control. The primary mill cyclones had the effect of building up a concentration of the relatively dense locked middling particles, within the mill circuit, which were subsequently liberated by a 'semi-autogenous' grinding action. The primary mill circuit further acted as an effective 'surge-barrier,' enabling more steady feed to flotation

(b) The new regrind circuit—A decision to rehabilitate the old regrind circuit had been made long before the successful trials with the 'partial regrinding' above. The old regrind circuit had in fact been decommissioned in 1987. Taking full cognisance of the design failures of the old installation the regrind circuit was recommissioned with a new 'Face'. The new mills were now charged with 35 mm forged steel balls and operated in closed circuit with clusters of 250 mm (10 inch) cyclones. Further, the new regrind circuit was now employed to regrind cleaner tailings rather than scavenger concentrate. An earlier analysis of the recycle streams has shown that the tailings from the cleaner cells contained a much higher proportion of locked particles and was richer in middlings content. This new regrind circuit was a total success. The circulating load was reduced even further, to manageable levels. The flotation recovery improved to well over 95% whilst the gangue in the final concentrate was reduced from plus 18% to 12% insols.

(c) Column cells—In line with a pressing requirement to improve the quality of concentrate in ZCCM two column flotation cells were installed at Mufulira and commissioned in May 1990 to clean the east and west rougher concentrates, respectively, in place of the Davcr cells. The columns proved themselves immediately and produced remarkably high quality concentrate, which contained less than 7% 'insols' compared to 12–18% before. The relatively high recovery and more efficient cleaning action of the columns virtually eliminated the circulating load to Mufulira

A new major problem in flotation

Trouble-free and stable flotation operations presented a new and exciting challenge to the metallurgical team at Mufulira. There was evidently more time now and a greater zeal to improve plant performance even further—a departure from the previous pre-occupation with reacting to all too frequent process problems, which were more often than not associated with the inherent instability in the circuit. The plant was at the height of this innovative mode when an entirely unfamiliar problem was experienced. The new problem was experienced in the plant on three separate occasions and these three experiences are discussed below as cases I, II and III respectively.

Case 1: November/December 1990

Figure 4(a) shows a sudden sharp drop in the total plant recovery and concentrate grade, which persisted for five days, from 29 November 1990 to 03 December 1990. The recovery dropped from a normal average of 95.5% to 91% on the first day and gradually further down to 89% by the fifth day. On the sixth day, performance suddenly normalized but 'unfortunately' before whatever was happening could be metallurgically understood. It was nevertheless noted that the problem in flotation had coincided with the failure of one of the two tailings thickeners, a situation which upset the normal water balance, causing an abnormal increase in the proportion of the underground mill make-up water.

Figures 4(c) and 4(e) show similar data as above but for

the east and west flotation sections, respectively. The two sections though operationally independent of each other were uncannily affected simultaneously and in exactly the same manner. The east flotation circuit was notably more severely affected. The recovery at the east dropped to 90% on the first day, and further, to 87% by the fifth day, while the lowest recovery at the west was relatively higher at 91%. The concentrate grade at the east dropped from 46% total copper (T/Cu) to 42% T/Cu and at the west from 48% T/Cu to only 46% T/Cu. In absolute terms the total plant recovery dropped by 6.5% to which the east and west flotation sections contributed 8.5% and 4.5%, respectively, albeit negatively.

Figures 4(b), (d) and (f) show further the extent to which flotation performance deteriorated, in this case in terms of the actual loss of copper to the tailings and the increased levels of gangue in the concentrate; for the entire plant, the east and west flotation sections, respectively. The tailings losses sharply increased to above 0.2% T/Cu, from the normal operating range of 0.08% to 0.10% T/Cu—an increase of more than 100% for both sections of the flotation plant, respectively. The gangue in concentrate increased by similar magnitude, from about 6% insolubles to as high as 12% insolubles and 9% insolubles, at the east and west respectively.

Case II: February 1991

Two months after the experience discussed in Case I above, early in February 1991, the other of the two tailings thickeners, No. 2, developed a serious fault which required a

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CASE I



Figures 4(a-f)—Showing the effect of underground water on the Mufulira flotation process, from 28th November to 3rd December 1990, resulting from the failure of No. 1 tailings thickness in the night shift of 28th November. Figures (a), (c) and (e) show recoveries and concentrate grades while Figures (b), (d) and (f) show actual copper losses to the tailings and the level of gangue (Insol) in concentrate; for the entire flotation plant, East and West flotation sections, respectively. Comparison of graphs (c)–(f) respectively, clearly shows how the East circuit was more severely affected than the West

major shutdown of this unit. At this stage an appreciation of the effect of upsetting the mill water balance had been developed and in fact, performance in the flotation circuit drastically deteriorated immediately the thickener was taken off range.

Figure 5(a) shows the drop in the total plant recovery which resulted from the outage of No. 2 thickener and the consequent excessive use of the make-up underground water, from 4th to 10th December. Figures 5(c) and (e) show the respective effect on the two separate flotation sections. It is notable that the east flotation circuit was affected more than the west, as was the case in the earlier experience. The reason for this is not well understood. It is worthy of note, however, that bornite, which is more predominant at the east, does not generally float as well and as easily as chalcopyrite, a mineral relatively more abundant at the west. The eastern ore has traditionally always been more sensitive to pH and responds to flotation at higher pH 10.5 compared to 9.5 for the western ore.

It is further evident that the impact on flotation, resulting from the failure of No. 2 thickener was not as severe as the earlier experience when No. 1 thickener failed. This was explained by the fact that No. 1 thickener contributes more recycle overflow water than No. 2. The thickener No. 2, by design, discharges a part of its overflow as effluent, therefore, requiring relatively less underground make-up water to supplement the outage of this particular thickener.

Figures 5(b), (d) and (f) illustrate further the negative effect on flotation performance, in terms of the loss of copper to the tailings and the level of gangue in concentrate; for the entire plant, the east and west flotation circuits respectively.

Case III: February/March 1991

The structure of the two tailings thickeners at Mufulira, which by now had been in operation for a very long time, had become weak over time and were, as a result, failing to take the full design load. Unstable flotation performance was experienced in the period immediately following the second failure, (Case II above), and this again culminated in a total loss of control, similar in nature to the two cases above.

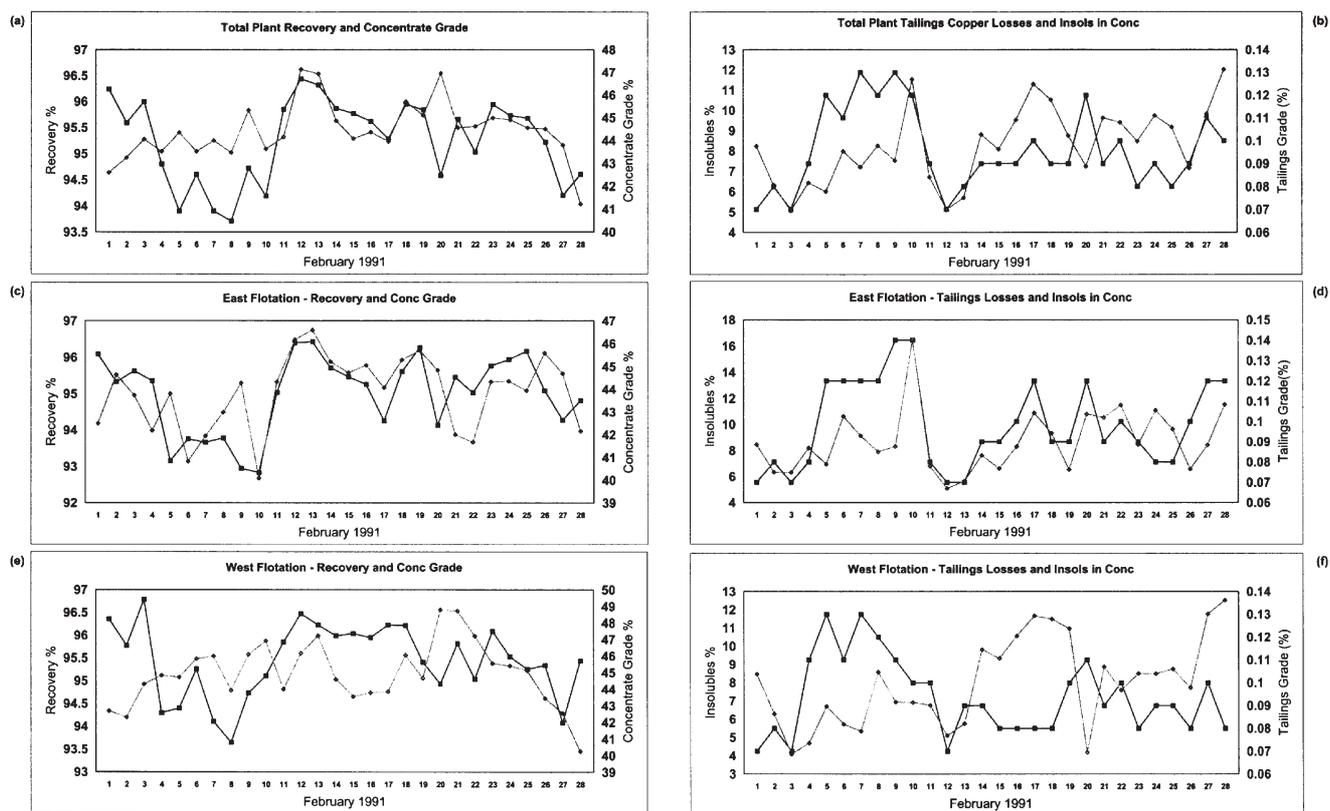
This third experience was very alarming because a permanent solution was now required. The structural weaknesses of the thickeners necessitated operating low underflow densities, therefore, compelling the usage of a higher proportion of underground make-up water for the mill than was traditionally the practice. Figures 6(a) to (e) show the extent of the decline in flotation performance, which directly resulted from having to operate the two tailings thickeners at low underflow densities.

Observable physical characteristics

Accompanying the poor performance was a very notable change in the physical characteristics of the entire flotation circuit in all the three cases reported above. The nature of the

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CASE II



Figures 5 (a-f)—Showing the second experience of the effect of underground water which was caused by failure of No. 2 tailings thickener on 3rd February 1991. As was experienced earlier in November 1990, Figures 4 (a-f), the East section was notably more affected. Comparison of graphs (c)-(d) and (e)-(f) respectively, clearly shows this. All the graphs above further show unstable flotation performance up to the end of February, even after recommissioning of No. 2 tailings thickener on the 10th. This was due to operating the structurally weak thickeners at low underflow densities

froth sharply changed, from the typically heavily laden and very rich polyhedral bubbles to a light and excessively voluminous froth, of apparently stable tiny spherical bubbles evidently depleted of minerals. Frothing became abnormally fast; causing continuous overflow of launders and concentrate sumps. In the rougher section, only a very thin layer of the froth was mineralized whilst the froth bed beneath was notably barren and whitish. The froth in the scavenger section was unmistakably whitish and starved.

The observable physical change in the flotation circuit was critical to initial diagnosis of the problem and it was metallurgically helpful that this strange phenomenon was associated with a particularly drastic change in the nature of the froth. The excessive frothing was characteristic of too much lime in the circuit, under normal Mufulira flotation conditions, while the stable tiny bubbles typified contamination by oil spillages. These two phenomena were quite easily discounted by adjusting lime dosage and suspending retreatment of process spillages, actions which failed to normalize operations.

The froth 'rush', particularly the sharp change in the nature of the bubbles, had from the onset implied that deleterious interfacial chemical activity, akin to contamination by surfactants, might be at the root of the problem. This consequently led to associating the problem with water. As soon as water was an issue, the obvious became

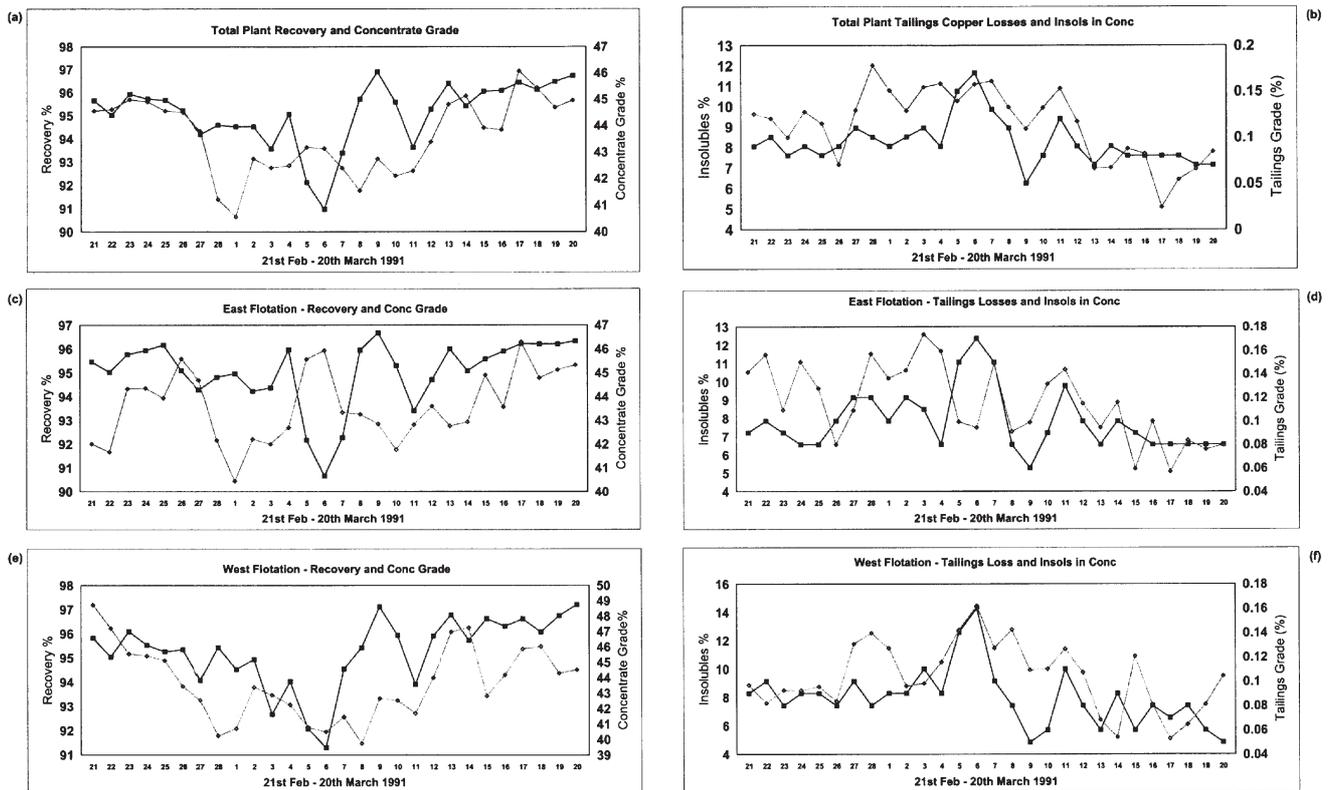
immediately apparent—that the breakdown of one of the two tailings thickeners, which had coincided with the problem in the flotation process, had affected the mill water composition. The thickener breakdown had drastically reduced the proportion of recycle water in the mill water. To make up the water balance a higher proportion of underground water was used, particularly during the five days when No. 1 tailings thickener was down (Case I). By the time water was becoming an issue, however, the broken down thickener was being recommissioned. It was nonetheless compellingly evident that the problem in the flotation circuit disappeared, immediately the normal mill water balance was restored, when the broken down thickener was put back on range.

Mill water balance

Figure 7 shows the water source and the mill water balance for Mufulira concentrator. The make-up water is drawn from the underground mine water drainage system and this traditionally contributed 40% of the mill water. Mill return water from the two tailings thickeners is recycled and mixed with the underground water to account for the remaining 60%. Recycled concentrate thickener overflow water accounts for less than 1%. As can be seen from Figure 7, either of the two thickeners can, by design, be easily bypassed and unthickened tailings pumped directly to the slimes dam, together with thickened tailings underflow from the thickener

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CASE III



Figures 6(a-f)—Show the third experience of the effect of underground water, occurring within one month of the second case. From 10th February flotation performance was erratic, due to high recycle process water loss to the tailings thickener underflow, culminating in total loss of control on 28th February. Addition of lime to the mills on 7th March and grinding at alkaline pH improved performance. All the graphs above (a-f), clearly show the adverse effect of grinding at natural pH on 11th March, when the lime addition into the primary ball mills was deliberately stopped and added downstream of milling as per previous tradition

on range. This practice drastically reduces the ratio of recycle in the mill water and this shortfall is complemented by increasing the volume of underground water. Prolonged pumping of unthickened tailings was, however, undesirable as this adversely affected proper maintenance and construction of the tailings dam.

Solution for the problem

The initial suspicion that disproportionate use of underground water was causing serious problems in flotation raised more questions than answers. In the long life of Mufulira concentrator the tailings thickeners had failed countless times but without recording the type of problem now being experienced. The situation was compounded further by an initial difficulty in determining precisely how and why the water was suddenly affecting the flotation.

Some of the trouble-shooting measures taken to combat what was perceived as a water problem included adding reagents and surface-active substances such as sodium silicate to the primary mills, in an attempt to influence the chemical condition of the slurry being fed to flotation. Everything else failed except lime, which seemed to normalize flotation performance when it was added into the mills at the east section. This effort was, however, belated and its positive impact was not conclusive, as it had coincided with the recommission of the tailings thickener,

which normalized the entire flotation circuit, during the first experience in Case I.

Encouraged by the response of the east circuit when lime was added into the grinding mills, as opposed to the traditional adjustment of the flotation feed pH, laboratory tests were carried out to verify both the effect of underground water and the milling pH, respectively, on the flotation response.

Table II shows the average results of several flotation tests carried out to verify the effect of underground water. As can be seen the underground water achieved lower recovery, by 2.6% and 3.9% at 92.9%, than potable tap water and mill return water, in which 96.9% and 97.40%, respectively, was achieved. However, adding lime into the laboratory mill and raising the grinding pH resulted in similar flotation results for the three types of water tested. These flotation results for the first time clearly showed that grinding at alkaline pH of 10.5 neutralized/negated all other phenomena to achieve similar flotation performance, regardless of the type of water used in the grinding/flotation trials. It was of particular significance that the underground water recovery improved from 92.9% to 97.2% due to the mere addition of lime and adjustment of the laboratory mill pH. All the flotation tests were conducted at a pH of 10.5. The difference being that in one case the pulp was ground at a natural pH of 8 and lime then added to the flotation cell to adjust the pH to 10.5, while in the other case the lime was added to the mill in which the

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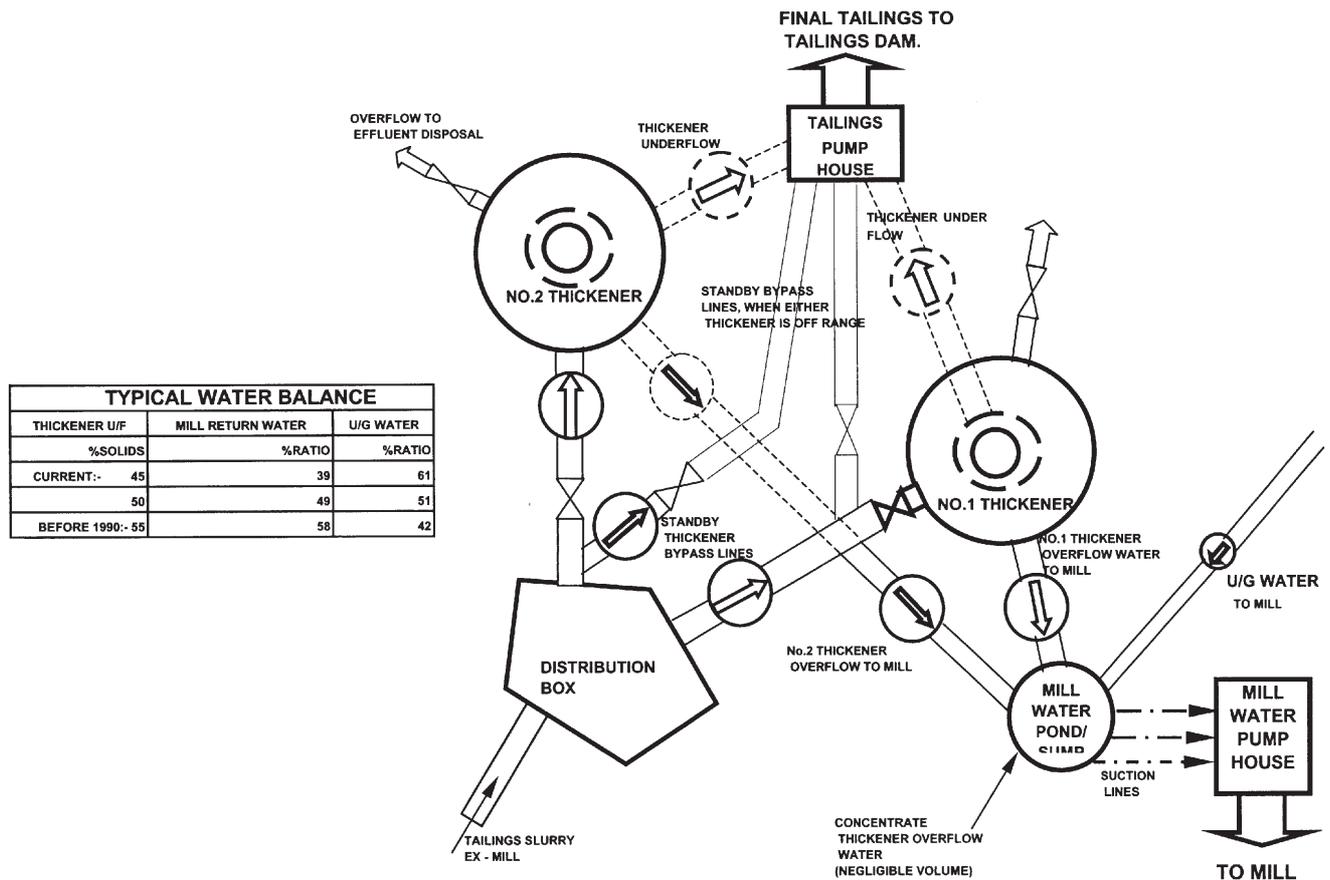


Figure 7—Mufulira concentrator mill water balance: No. 1 tailings thickener contributes more return water to the mill than No. 2 thickener because of the proximity of the former to the mill pond and pump house. The long canal, which is partially below the surface, for overflow water from No. 2 tailings thickener restricts flow. As a result No. 2 thickener overflow is largely discharged to the environment as effluent. The impact of the failure of No. 1 thickener, therefore, results in higher underground water requirements, causing more severe flotation problems

Table II
Laboratory flotation test results

	Lime added to flotation cell (grinding pH=natural (8))		Lime added to mill (grinding pH=10.5)	
	Recoveries %	Insols %	Recoveries %	Insols %
Mill return water	96.80	18.1	97.40	19.7
Lab. tap water	95.50	19.5	96.90	16.9
Underground water	92.9	19.3	97.20	17.8

pH was adjusted to 10.5. The mill return water achieved slightly higher results in all the laboratory tests, most probably due to residual reagents, as this water is recycled from the process tailings thickener.

By the time the third experience was occurring, Case III, the solution to the problem had been virtually established. The addition of lime, which was traditionally downstream of the primary mills, was therefore transferred to the mill return water sump and the grinding pH in the entire primary milling increased from 8 to 10.5. The graphs in Figures 6(a) to (e) show the improvement achieved by changing the mode of adding lime—from a point downstream of milling to upstream of the primary balls, effectively increasing the grinding pH. Mufulira ore has always been floated at alkaline

pH of 9.5 to 10.5 and lime has since inception in the 1930s been used to modify the pH. The traditional practice had been to mill at a natural pH and then adjust the pH of the feed to flotation, using lime. The change in the practice, to adding lime upstream of the primary mills and grinding 'at the alkaline pH', was instituted in March 1990 as a measure to combat the deleterious effect of underground water.

Ten years later to this day the lime continues to be added to the mill return water pond and grinding is conducted at the flotation pH. This is how a series of unprecedented flotation crises culminated in a solution which has permanently changed milling and flotation practice at Mufulira.

General observations

For all its neatness in terms of low impurity content and the consequent high amenability to flotation, Mufulira ore has traditionally had an inherently high sensitivity to flotation pH, therefore, requiring very strict control of lime dosage. Further, for a simple and straightforward rougher-cleaner-scavenger circuit, the concentrator has relatively high processing costs mainly due to a high lime usage, which at its peak accounted for more than 60% of the entire reagent costs. The change of lime addition practice from the head of flotation into the primary milling achieved the immediate indirect beneficial effect of drastically reducing the usage of

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lime, from 1.2 to 0.7 kg/tonne of ore milled, as highlighted in Figure 8. The benefit of reducing lime consumption was attributable to the relatively better conditioning which the violent mill environment accorded. Figure 8 also shows the sharp drop in mill throughput starting in March 1990, which was due to declining production at the mine. The extent of the structural weaknesses of the two tailings thickeners was such that both of these relatively large units were maintained on range in spite of the declining throughput. At peak production nearly 20 000 tonnes of tailings was thickened but the two units were now reduced to handling a mere 10 000 tonnes. The need to operate the thickeners at low underflow densities compelled a much higher usage of make-up underground water in the mill.

It has been shown in this report, Figure 3, how Mufulira concentrator transformed its flotation circuit to achieve unprecedented levels of performance. The commission of an efficient regrind circuit and replacement of Davcr cells with the more selective column cells combined to stabilize the flotation process by significantly reducing the level of recirculating middlings. The old circuit, prior to the improvements facilitated in the innovations discussed above, must have been so unstable and the influence of the recirculating load in flotation so dominant as to render the influence of underground water undetectable in the past. It is significant that no sooner had the flotation circuit re-engineering process been completed, with the commission of the column cells in June 1990, than the influence of underground water experienced, hardly 6 months later, in November. The tailings thickeners had failed before and excessive

underground water must have been used under the old circuit without noticing the effect in the flotation process.

As it is widely known, numerous factors are at play in flotation but normally a single major variable will tend to be dominant at any given time. In Mufulira's case, the old circuit had the circulating load as its major problem and its elimination 'bequeathed' underground water to the new circuit. Water is very rarely a variable in mineral dressing operations. It is for this reason that its adverse effect at Mufulira was not immediately understood.

Standard laboratory tests, carried out initially, as part of the trouble-shooting activity, failed to detect the source of the problem mainly because of the use of fresh ball mill feed. These samples were ground in the laboratory using potable water. The flotation tests conducted, therefore, showed normal response while the plant continued to experience abnormal losses. These investigations, as is generally the case, were directed at detecting a problem with either the ore or the reagents. Serious lessons were learnt about the importance of designing laboratory tests that simulate practical plant conditions more precisely:

- Because flotation tests were conducted on ball mill feed samples which had been repulped and reconstituted in the laboratory, as was the tradition, these flotation tests failed to detect the effect of underground water as was being experienced in the plant
- If the flotation tests had been performed on the ball mill cyclone overflow slurry feeding flotation, the flotation results would have shown poor response. However, this alone would have been insufficient

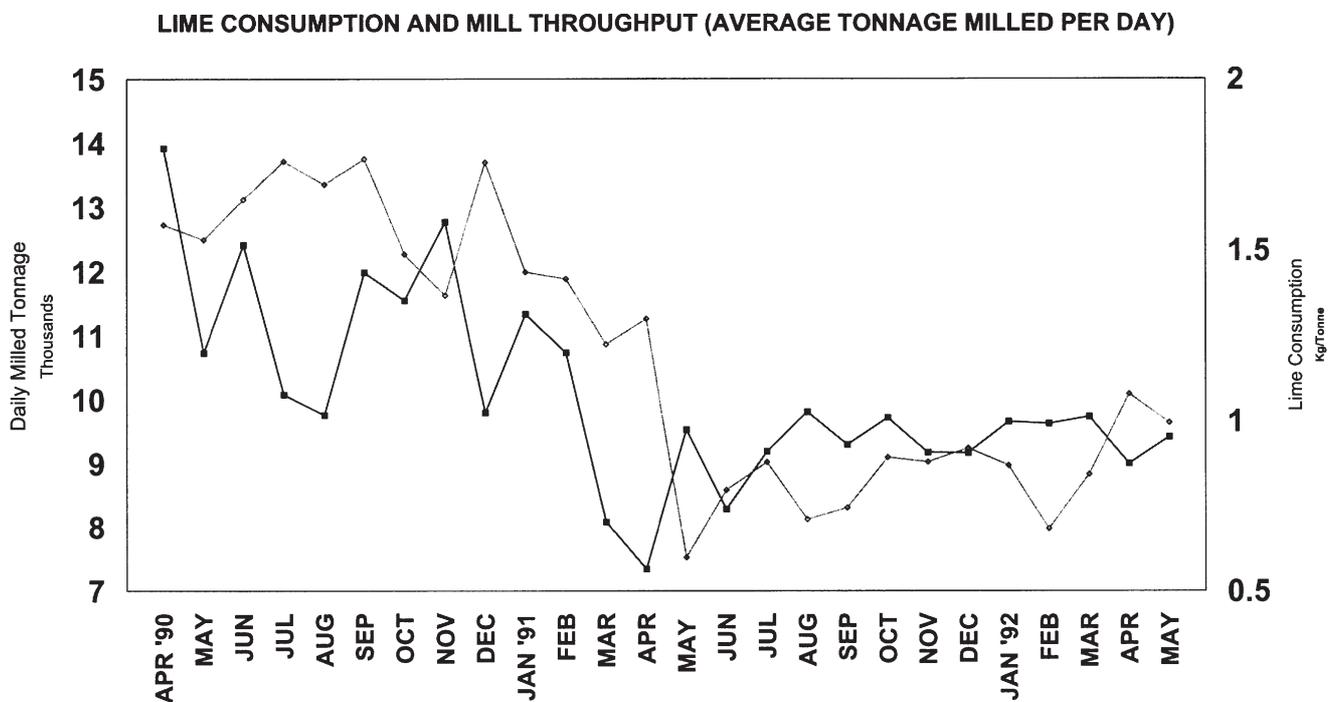


Figure 8—Lime consumption and mill throughput (average tonnage of ore milled per day). The addition of lime into the primary mills on the 10th of March 1990 immediately reduced lime consumption from 1.2 kg per tonne of ore milled in February to 0.70 kg per tonne for the month of March and further down to 0.05 kg per tonne in April 1990. This was attributed to more effective conditioning in the violent mill environment. A sharp decline in the mill throughput adversely affected lime consumption in May and subsequent months. Throughput declined to levels lower than the minimum required to effectively control lime dosage. The lime handling facility which was designed to control dosage at plant throughput of 20 000 tonnes per day proved to be ineffective at the current low throughput which had dropped to less than 10 000 tonnes per day. Figure 8 nevertheless shows remarkable reduction in the consumption of lime after March 1990

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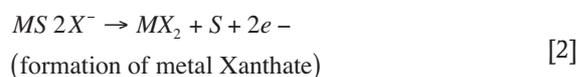
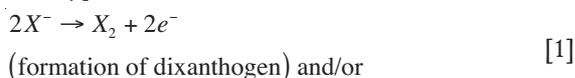
evidence of the effect of underground water as the potential effect of other deleterious substances such as residual reagents, organics and cations, particularly in the mill recycle water, would have needed to be explained.

Fundamental explanation

Electrochemical theory of flotation—background

Selective flotation of minerals is normally achieved using collectors. The fundamental process in flotation is the interaction of a collector with the mineral surface. This process renders the mineral surface hydrophobic and so enables the mineral to be held at the air–water interface. The reaction between collector and sulphide minerals in particular is now widely believed to be electrochemical in nature, involving the transfer of electrons between the solid (sulphide mineral) and liquid (water) phase.^{1–4} *The exact mechanism involved in flotation reagent–mineral reaction has been a subject of active controversy among researchers, for several decades, particularly in the earlier years. However, the electrochemical approach, first proposed by Salamy and Nixon^{5,6} has gained wider support in recent years.* The electrochemical theory of flotation describes an anodic (oxidation) reaction between mineral and collector and a rebalancing of charge through the reduction of dissolved oxygen in the water.

Some typical anodic reactions are:



The common cathodic reaction is:



Where;

MS = Sulphide mineral and
 X^- = Xanthate

Each charge transfer reaction corresponds to a definite electrochemical potential E related to the Gibbs free energy change of the process:

$$G = -zFE$$

where F is the Faraday Constant and z the number of electrons transferred per unit mole.

The above Equations indicate that the two criteria for reaction between collector and sulphide minerals are:

- ▶ The mineral must be conducting or semi-conducting to permit flow of electrons from the site of reactions [1] and [2] to that of [3]
- ▶ Dissolved oxygen must be present to act as the electron accepting element (reaction [3]).

An anodic reaction can take place at a mineral surface, if a potential exists, at which both this process and the cathodic reduction of oxygen proceed at finite and equal rates. Such a potential is called a mixed potential^{1,2,7}. (Mixed potential: solution potential and galvanic potential.)

The solid phases which can give rise to a galvanic potential are metals and semi-conductors^{8,9}. It should be noted that the solids need not touch; the ions in the solution may transport the electrons from one solid to the next by entering into oxidation/reduction reactions at the solid surfaces. Sulphide minerals have in the past few decades been established to be semi-conductors by several researchers, who have used them in electrochemical cells^{1,3,8,9,7}. Ahn and Gebhardt¹⁰ mounted chalcopyrite and grinding media electrodes in epoxy resin and established electrical contact by attaching conductive wire to the back of the electrodes. They were able to measure rest potentials against a standard calomel electrode. The galvanic interaction between chalcopyrite and grinding media was measured by coupling the two electrodes and measuring the resulting combination potential and galvanic current using an EG & G Princeton applied research model 173 potential meter and model 379 digital coulometer, respectively. They performed all the electrochemical measurements in well-stirred electrolyte.

S.A. Allison *et al.*⁹ arranged the rest potentials of various sulphide minerals in an electrochemical activity order of a kind, in a study to determine the products of reaction between various sulphide minerals and aqueous xanthate solutions. Table III⁹ shows the rest potentials of the mineral electrodes after 10 minutes in a $6.24 \times 10^{-4}M$ solution of potassium ethyl xanthate having a pH value of 7. This work further correlated the reaction products with electrode rest potentials. S.A. Allison *et al.*⁹ determined that all minerals on which dixanthogen is formed, as the principal product of reaction, have rest potentials in excess of the equilibrium potential of the dixanthogen/xanthate couple and those on which the metal xanthate is formed have potentials below this value, as shown in Table III.

Among all the sulphide minerals, pyrite has the highest rest potential (Table III). This mineral may therefore be regarded as the least active or the most cathodic. Electrons flow from a less cathodic mineral to a more cathodic one^{8,9}. Pyrite thus acts as an electron acceptor. The less cathodic mineral loses electrons and, for example, the sulphide is oxidized to sulphur. The electrons drawn by pyrite (or the more cathodic mineral) ultimately transfer to oxygen present in water, forming OH⁻ ions^{1,2,9}.

Table III
Rest potentials and products of interaction of ethyl xanthate with sulphide minerals

Mineral	Rest potential	Product
Pyrite	0.22	X ₂
Arsenopyrite	0.22	X ₂
Pyrrhotite	0.21	X ₂
Molybdenite	0.16	X ₂
Chalcopyrite	0.14	X ₂
Covellite	0.05	X ₂ (MX)
Chalcocite	0.06	NPI
Bornite	0.06	MX
Gallna	0.06	MX
Cinnabar	-0.05	NPI
Stibnite	-0.13	NPI
Sphalerite	-0.15	NPI

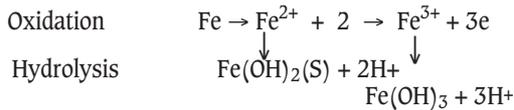
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Electrochemical aspects of grinding and its effect on flotation

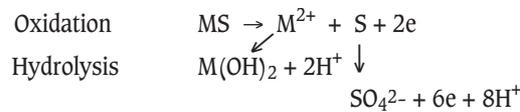
During grinding, particularly in an iron/steel mill, intimate galvanic contact among sulphide minerals and between sulphides and iron/steel grinding media takes place. Redox reactions thus take place at the surfaces of the materials in contact, and given below, are some of the reactions that have been suggested^{10,12-17}.

Some typical anodic (oxidation) reactions are:

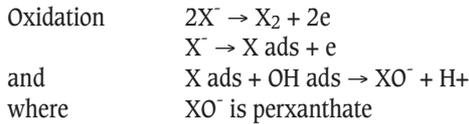
(i) Iron or steel media



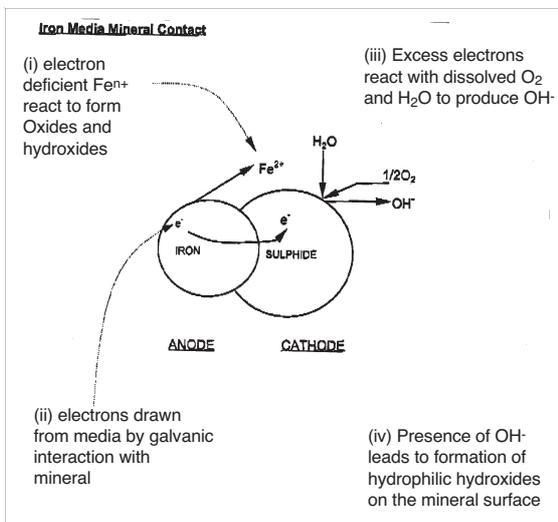
(ii) Sulphide minerals



(iii) Xanthate collectors



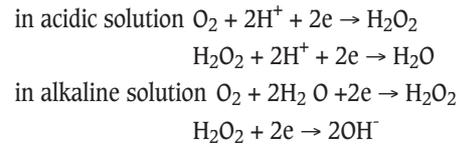
Some typical cathodic (reduction) reactions are:



Source: S R Rao et. Al. 1992⁽¹⁰⁾

Figure 9a—Model of galvanic interaction inside grinding mill. When a sulphide mineral is ground in an iron/steel mill with iron or steel as grinding media a galvanic cell will be formed. The iron medium then acts as an anode and sulphide mineral as a cathode. Iron is galvanically oxidised while oxygen reduction takes place on the surface of the sulphides. Consumption of oxygen (O₂) by iron media results in a strong reducing environment which may bias the sulphide to prevent the absorption and oxidation of Xanthate. Electrochemical measurement by several workers has indicated that if metallic iron was kept in galvanic contact with a sulphide mineral, the potential is observed to be lowered. Such lowering of potential shows that the sulphide mineral becomes more cathodic, that is, reducing in character. At the same time, the surface of sulphide particles will be covered by oxide layers. Sulphide minerals ground in this manner usually display poor response to flotation. However, a high concentration of OH⁻ or starvation of oxygen inside the ground mill environment hinders galvanic interaction, as was achieved at Mufulira when the grinding PH was increased

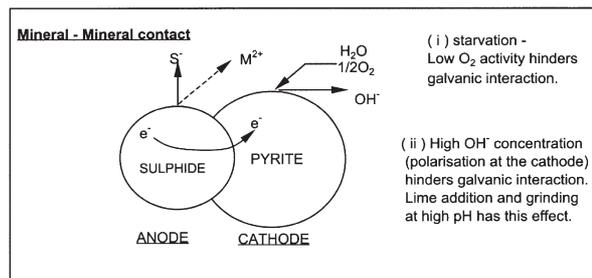
(iv) Oxygen



(v) Copper ions (activator) $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$

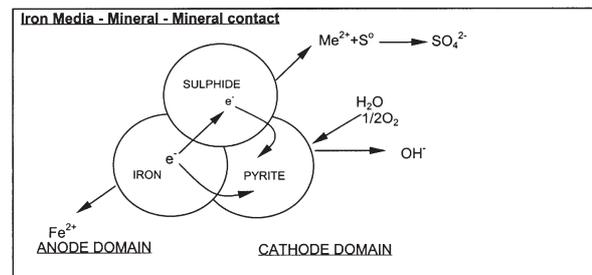
(vi) Other noble metal action $\text{M}^{2+} + 2e^- \rightarrow \text{M}$

The actual reactions depend strongly on the materials which are in contact with their polarization behaviour, the ratio of the surface areas as well as the solution compositions^{10,15}. The iron medium in this case acts as an anode and sulphide mineral as a cathode. Therefore, iron media is galvanically oxidized (reaction (i)) while oxygen reduction takes place on the sulphide surfaces (reaction (iv))^{10,13-15}. The consumption of oxygen by iron media results in a strong reducing environment which may bias the sulphide to prevent the absorption and oxidation of xanthate in the subsequent flotation process^{10,13,15}. At the same time, the surfaces of the sulphide particles will tend to be covered by oxide layers, causing poor flotation response with



Source: S R Rao et. Al. 1992⁽¹⁰⁾

Figure 9b—Model of galvanic interactions inside grinding mills. When two sulphides with large differences in their rest potential are in contact or ground in a mill, the sulphide with lower rest potential (e.g. galena) will act as an anode and the one with higher rest potential (e.g. pyrite) as cathode. The sulphide mineral with the lower rest potential is oxidized, initially to elemental sulphur and finally to sulphur oxyanions and sulphate if over-oxidation takes place. This sulphide will exhibit good flotation response due to the formation of elemental sulphur on its surface and more importantly the basis of the surface towards an oxidizing state, which favours the absorption and oxidation of xanthates. On the other hand, oxygen reduction takes place on the nobler sulphide (usually pyrite). Its surfaces then show quite small affinity to xanthate due to the bias of the surface to a reducing state



Source: S R Rao et. Al. 1992⁽¹⁰⁾

Figure 9c—Model of galvanic interactions inside grinding mills. For a multiple mineral/iron (media) grinding system, the galvanic reactions are much more complex than the two component systems. However, the substance with the lowest rest potential must in principle be an anode and the mineral with the highest rest potential should act as a cathode

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xanthate¹⁸⁻²⁰. One way of hindering galvanic interaction is therefore to increase the concentration of OH ions, (raising the grinding pH)^{10,14,15}. The other is to lower the activity of oxygen in water, thus depriving the system of the ultimate electron acceptor^{10,13-15}. The decrease in galvanic interaction rate is further explainable on the basis of high cathodic Tafel constants^{21,22} (polarization at the cathodic site), indicating that the reaction is highly diffusion controlled. Figures 9(a), (b) and (c) show schematic representations of the now widely accepted models of galvanic interactions among minerals and grinding media discussed above¹².

Ahn and Gebhardt¹⁰ compared the combination potentials and galvanic current for the chalcopyrite: High carbon steel coupled electrode pairs, at varying pH of 7.5, 9.3 and 11.0. They determined that current was lowest at pH 11 and increased with decreasing pH. At pH 11.0 the combination potentials were more positive and galvanic current was lower; i.e. the extent of galvanic interaction was reduced. The effect of high pH on galvanic current was consistent with their measurements of the individual polarizations, which had indicated that high carbon steel was readily passivated in pH 11.0 solution. In the same work and in an effort to establish a link with the above fundamental results flotation tests conducted by Ahn and Gebhardt showed chalcopyrite recovery increasing as grinding solution pH increased, consistent with the electrochemical measurements¹⁰.

Galvanic interaction between grinding media and chalcopyrite decreased as solution pH increased and the higher chalcopyrite recovery was a result of less galvanic interaction during grinding in higher pH solution. At lower pH values galvanic interaction produces dissolution of iron from the grinding media, which acts as the anode, while the chalcopyrite surface acts as the cathode and is reduced¹⁰.

Electrochemical explanation for the effect of water at Mufulira

Table IV shows water analyses for laboratory tap water, underground water and the thickener overflow (mill recycle) water and further includes the laboratory flotation recoveries achieved by the three respective water types, after grinding at natural pH, without adding lime during grinding. Of the differences between the three water types, in respect of the elements analysed, the flotation recoveries are clearly most sensitive to pH.

The underground water which has the lowest pH, achieved poorer flotation results than the laboratory tap water and the mill return water respectively. The latter, which is at the highest pH achieved the highest recovery, notwith-

standing the possible effect of residual reagents.

The mine water at Mufulira is pumped at virtually neutral pH (7) from the underground operations. This water has traditionally been mixed with tailings thickener overflow water to achieve a mixed mill water pH of between 8.5 and 9.5. Milling at Mufulira has therefore traditionally been carried out at pulp pH of 8.5 to 9.5, which was sufficiently alkaline to prevent deleterious galvanic interaction inside the grinding mills. The increase in the proportion of underground water in the mill return water in 1990 had the net effect of reducing the pH at which milling was now being conducted, which immediately adversely affected flotation performance, as was experienced.

The relatively low milling pH caused immediate problems in the floatation process, due to enhanced galvanic interaction between the sulphide minerals and the cast iron grinding media. The consumption of oxygen resulting from galvanic interaction between the anodic grinding media and the sulphide copper minerals created a strong reducing environment in the slurry fed to the subsequent floatation process, adversely affecting proper absorption and oxidation of xanthate. Further, the surfaces of the sulphide particles which will tend to be cathodic became prone to covering by hydrolytic oxide layers, causing poor flotation response with xanthate.

Summary

The experience of Mufulira with the underground water can, therefore, be summarized as follows:

- The mill process water is composed of tailings thickener overflow recycle water which is mixed with underground mining water, before it is used for milling and flotation operations
- The traditional ratios of mill water prior to 1990 were 40% of underground water and 60% of mill recycle-tailings thickener overflow
- A change in concentrator operating practice, in part caused by a sudden and unplanned decline in the mine throughput, resulted in the ratio of underground water increasing to 60% of the mill process water at the expense of recycle water, later in 1989 and early 1990
- The underground water has a pH of 7.5 whereas the recycle thickener overflow is at a higher pH, which is in excess of 10.5
- The increase in the proportion of underground water in 1990 reduced the pH in the primary grinding mill environment, from the traditional range of 8.5 to 9.5 to less than 8.5, which enhanced galvanic interaction and adversely affected the floatation

Table IV

Water analysis

Water source	Cu (ppm)	Fe (ppm)	Zn (ppm)	Pb (ppm)	Mg (ppm)	Ca (ppm)	Total hardness (ppm)	pH	SO 4 ²⁻	Redox potential MV	Flotation performance recoveries (%)
Underground water	0.02	0.70	0.10	0.30	104	268	9.36	7.50	755	+120	92.90
Mill return water	1.60	1.10	0.10	0.50	36	653	1692	10.50	1363	-2654	96.80
Lab. tap water	<0.10	0.60	0.10	0.20	-	113	1062	8.90	-	-	95.50
Underground water	3.18	0.70	0.10	0.23	-32	189.6667	1356	10.37	1971	+121	97.67

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- ▶ The addition of lime and raising the pH of the slurry inside the grinding mills negated the deleterious effect of underground water by directly increasing the concentration of Hydroxyl (OH⁻) ions
- ▶ The effect of the underground water was never experienced before 1990 due to highly inefficient flotation operations, in which recycling middlings in the circuit had an overriding impact on the process. Unprecedented innovations improved the Mufulira flotation recoveries from 92% to over 96% in 1990, largely by improving the efficiency of regrinding and selectivity in the cleaning circuit. It was only after eliminating the overriding negative effect of the recirculating load that the impact of underground water became apparent in the flotation process.

Conclusions

- ▶ The underground mine water has a deleterious effect on performance of the Mufulira flotation process.
- ▶ The effect of the underground water was successfully negated by adding lime and raising the pH of the environment inside the primary grinding mills
- ▶ The underground water affects flotation performance because of its relatively low pH of about 7, which enhances deleterious electrochemical activity. The nature of the effect of the underground water and the sensitivity of the Mufulira flotation process to the pH inside the grinding mill environment characterizes galvanic interaction
- ▶ The consumption of quicklime was reduced by as much as 50% when the lime was added ahead of the primary ball mills compared to the previous practice of adding lime downstream of the milling process, to the flotation feed.
- ▶ The experience of Mufulira with underground water testifies that the effectiveness of sulphide mineral separation by flotation can be greatly improved by effecting proper electrochemical conditions in the grinding mill environment.

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References

1. WOODS, R. 'Electrochemistry of sulphide minerals' *Proceedings Aust. Institute Min. Met.* no. 241, March 1972, pp. 53-61.
2. WOODS, R. 'Electrochemistry of Sulphide Flotation'. *Flotation*, M.C. Fuerstenau, Ed, *AIME*, 1976, New York, pp. 298-333.
3. CHANDER, S. 'Electrochemistry of Sulphide Mineral Flotation'. *Minerals and Metallurgical Processing*, Aug. 1988, pp.104-114.
4. CHANDER, S. 'Electrochemistry of Sulphide Flotation: Growth Characteristics of Surface Coatings and their Properties, with special reference to Chalcopyrite and Pyrite'. *Int. J. Min. Proc.*, 33, (1991) pp.121-134.
5. SALAMY, S.G. and NIXON, J.C. 'Reaction Between a Mercury Surface and Some Flotation Reagents. An Electrochemical Study'. *Aust J Chem.*, vol. 1 May 1954, pp.146-156.
6. SALAMY, S.G. and NIXON, J.C. 'The Application of Electrochemical Methods to Flotation Research', Recent Developments in Mineral Dressing, *Institute of Mining and Metallurgy*, 1953, pp. 503-516.
7. RAO, S.R., LABONTE, G., and FINCH, J.A. 'Electrochemistry in the Plant' *Innovations in Flotation Technology*, Kluwer Academic Publishers, Eds P. Mavros and K.A. Matis, Netherlands, 1992, pp. 57-100.
8. GOOLD, L.A. 'The Reaction of Sulphide Minerals with thiol Compounds', National Institute for Metallurgy, RSA, Report No. 1439, 2 June 1972.
9. ALLISON, S.A., GOOLD, L.A., NICOL, M.J., and GRANVILLE, A. 'A Determination of the Products of Reaction Between Various Sulphide Minerals and Aqueous Xanthate Solution, and a Correlation of the Products with Electrode Rest Potentials', *Metallurgical Transactions*, vol. 3, 1972, pp. 2613-2618.
10. AHN, J.H. and GEBHARDT, J.E. 'Effect of Grinding Media—Chalcopyrite Interaction on the Self Induced Flotation of Chalcopyrite'. *Int. Journal of Mineral Processing*, 33 (1991), pp. 243-262.
11. SATO, M. 'Oxidation of Sulphide Ore Bodies, II. Oxidation mechanisms of Sulphide Minerals at 25 degrees Celcius.' *Economic Geology*, vol. 55, 1960, pp. 1202-1231.
12. MARTIN, C.J. *et al.* 'Review of the Effect of Grinding Media on Flotation of Sulphide Minerals', *Minerals Engineering*, vol. 4, no. 2, pp. 121-132.
13. YELLOJI RAO, M.K. and NATARAJAN, K.A. 'Factors Influencing Ball Wear and Flotation With Respect to Ore Grinding', *Mineral Processing and Extractive Metallurgy Review*, 1991, vol. 7, pp. 137-173.
14. GUY, P.J. and TRAHAR, W.J. 'The Influence of Grinding and Flotation Environments on the Laboratory Flotation of Galena' *International Journal of Mineral Processing*, 12, 1984, pp. 15-38.
15. ERIC FORSBERG, K.S. 'Influence of Grinding Method on Complex Sulphide Ore Flotation: a Pilot Plant Study'. *Int. Journal of Mineral Proc.*, 38, 1993, pp. 157-175.
16. ADAM, and IWASAKI, I. 'Pyrotite Grinding Media Interactions and its Effect on Floatability at Different Applied Potentials', *Minerals and Met Proc.*, May 1984, p. 81.
17. KOCABAG, D. and SMITH, M.R. 'The Effect of Grinding Media and Galvanic Interactions Upon the Flotation of Sulphide Minerals,' A.D. Zunkel, R. S. Borman, A.E. Morris and R.J. Wesley (Ed.) *Complex Sulphide*, the Met Society, 1982, p. 55.
18. XIANG HUAI WANG and YEN XIE. 'The Effect of Grinding Media and Environment on the Surface Properties and Flotation Behaviour of Sulphide Mineral' *Mineral Proc and Extractive Metallurgical Review*, 1990 vol. 7, pp. 49-79.
19. HODGSON, M. and AGAR, G.E. 'Electrochemical Investigations into the Flotation Chemistry of Pentlandite and Pyrrhotite: Process water and Xanthate Interactions' *Canadian Metallurgical Quarterly*, vol. 28, no. 2, 1989, pp. 189-1989.
20. LUI, A.W. and HOEY, G.R. 'Corrosive and Erosive Wear of Metals in Mineral Slurries', *Canadian Metallurgical Quarterly* vol. 12, no. 2, 1973, pp. 185-190.
21. PARKER, R.H. 'An Introduction to Chemical Metallurgy', Pergamon Press, 2nd Ed., Oxford, 1983, pp. 205, 342.
22. MOORE, J.J. 'Chemical Metallurgy', Butterworths, London, 1981, p. 316. ◆