A mineralogical investigation of refractory gold ores and their beneficiation, with special reference to arsenical ores

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SYNOPSIS

A mineralogical investigation of the main causes of refractoriness of some metallurgically complex gold ores in South Africa is reported. It is shown that this refractoriness is related to the presence of submicroscopic gold, carbonaceous material, pyrrhotite, and base-metal sulphides. Gold ores can be classified according to their content of these components.

Electron-microprobe analysis shows that gold occurs in arsenopyrite and pyrite, the gold contents of which can be up to 2700 g/t. The gold and arsenic contents of these minerals are closely correlated. Furthermore, within zoned arsenopyrite grains, the concentration of gold closely follows that of arsenic.

Mössbauer spectroscopy carried out on samples of concentrate from the Barberton area indicates that the submicroscopic gold within the sulphides is in a non-metallic form.

The mineralogical examination of beneficiation products is important, since it sheds light on some fundamental aspects of the behaviour of the ore and gangue components during milling and flotation. Such basic information will lead ultimately to a better understanding of the problems in the beneficiation of these ores. Investigations have shown that the overmilling of the auriferous arsenopyrite and the disseminated nature of the sulphide mineralization are the main problems during beneficiation.

SAMEVATTING

Daar word verslag gedoen oor 'n mineralogiese ondersoek van die hoofoorsake van die ekstraksievastheid van sommige metallurgies komplekse goudertse in Suid-Afrika. Daar word getoon dat hierdie ekstraksievastheid verband hou met die aanwesigheid van submikroskopiese goud, koolstofhoudende materiaal, pirrotiet en onedelmetaalsulfiede. Goudertse kan volgens hul inhoud van hierdie bestanddele geklassifiseer word.

'n Elektronmikrosonde-ondersoek het getoon dat goud voorkom in arsenopiriet en piriet waarvan die goudinhoud tot 2700 g/t kan wees. Daar is 'n nou verband tussen die goud- en arseeninhoud van hierdie minerale. Daar is ook 'n nou korrelasie tussen die goud- en arseenkonsentrasie in gesoneerde arsenopirietkorrels.

Mössbauer-spektroskopie wat op konsentraatmonsters afkomstig van die Barberton-gebied uitgevoer is, het getoon dat die submikroskopiese goud in die sulfiede in 'n nie-metaalvorm is.

Die mineralogiese ondersoek van veredelingsprodukte is belangrik aangesien dit lig werp op fundamentele aspekte van die gedrag van die erts en aarsteenbestanddele tydens maling en flottasie. Sodanige basiese inligting sal uiteindelik lei tot 'n beter begrip van die probleme in verband met die veredeling van hierdie ertse. Ondersoeke het getoon dat die oormaling van die goudhoudende arsenopiriet en die gedissemineerde aard van die sulfiedmineralisasie die vernaamste probleme tydens veredeling is.

Introduction

The term *refractory* as applied to gold ores indicates that they are not totally amenable to conventional cyanidation, mainly because no practicable amount of grinding can expose the fine particles of gold to the solvent action of the cyanide, or because the ore contains minerals that are detrimental to the cyanidation process[1].

South Africa has a variety of mineralogically complex, refractory gold ores, each of which has distinctive mineralogical characteristics and presents unique problems during metallurgical processing. The most abundant of these ores are arsenical and, for this reason, specific reference is made in this paper to the beneficiation of pyrite–arsenopyrite ores.

Attempts are made here, through detailed mineralogical studies of the ore minerals and the metallurgical beneficiation products, to acquire a much better understanding of these gold ores, and how they will behave during metallurgical processing.

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Mineralogical Causes of Refractoriness

The metallurgical problems related to the treatment of refractory gold ores are directly related to the mode of occurrence of the gold in these ores, and to the minerals they contain.

Refractory gold ores commonly contain free gold, submicroscopic gold, carbonaceous material, base metals, and pyrrhotite. The occurrence of these four components can be conveniently depicted in a conceptual tetrahedron[2] (Fig. 1) in which they represent end-members.

A typical ore always contains free gold plus at least one other component. A free-milling gold ore such as gold from the Witwatersrand that gives gold extractions of up to 95 per cent would be plotted towards the free-gold apex of the tetrahedron, whereas ores with a refractory component (e.g. those from Fairview) giving gold extractions of only about 35 per cent would be plotted towards the submicroscopic-gold apex. Some information on other major refractory gold ores in South Africa appears in Table I.

The most significant component of refractory gold in arsenical gold ores is submicroscopic gold. Investigations by means of transmission electron microscopy[3] (TEM), which does not reveal the presence of any discrete grains
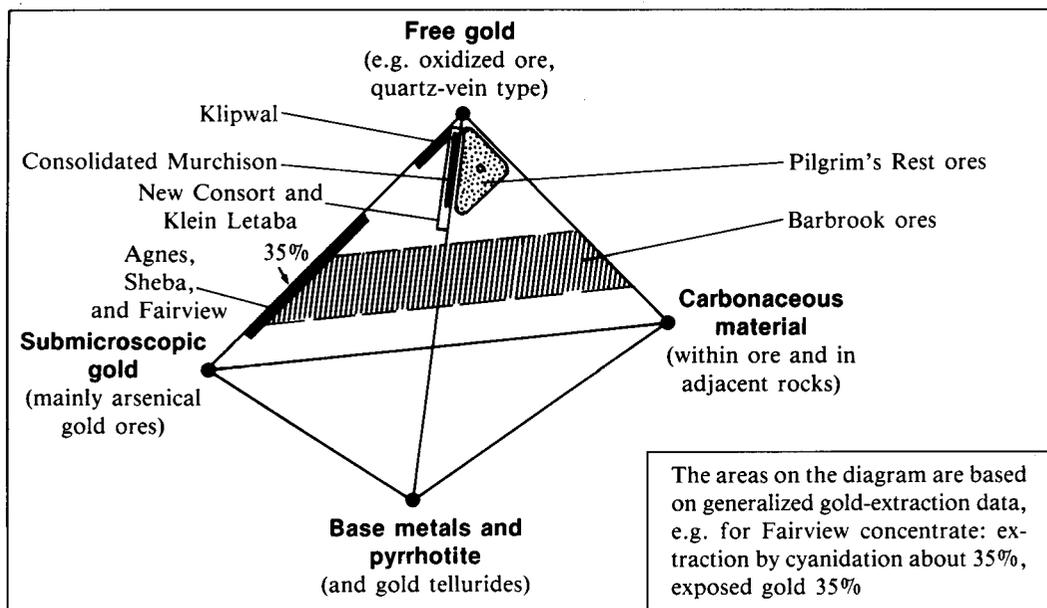
Fig. 1—Diagrammatic representation of the causes of refractoriness in gold ores in South Africa. The top corner represents free-milling gold that is easily recoverable, and the three bottom corners are the main types of components that lead to refractoriness with gold ores

TABLE I

IMPORTANT REFRACTORY GOLD ORES IN SOUTH AFRICA

Stratigraphy	Source	Main mineralogical causes of refractoriness	Special metallurgical process
Archaean greenstone belts	Barberton Mountainland	Submicroscopic gold Pyrrhotite Carbonaceous material Base-metal sulphides Gold tellurides (rarely)	Roasting of sulphide concentrate Bacterial leaching
	Murchison Range	Antimony sulphides Trace amounts of aurostibnite	Roasting; pressure cyanidation of stibnite concentrate
	Sutherland Range	Pyrrhotite Trace amounts of aurostibnite	Milling; cyanidation at controlled pH, dissolved oxygen, and cyanide concentration
Pongola Sequence	Klipwal Mine	Fine gold within sulphides	Fine milling ($\approx$ 80% <75 um)
Transvaal Sequence	Pilgrim's Rest	Base-metal sulphides and oxides (mainly Cu with lesser amounts of Bi) Carbonaceous material	Milling; cyanidation at controlled pH, dissolved oxygen, and cyanide concentration; size classification to remove fine carbon from slimes fractions

of gold, together with Mössbauer spectroscopy[4], indicate that the gold is chemically bound within the sulphides in a non-metallic form. The latter technique, applied to refractory gold ores from the Barberton areas, appears to be a very useful diagnostic tool by which the contents of metallic and non-metallic (refractory) gold can be quantified, and the results obtained correlated with those of the cyanidation tests on samples of arsenopyrite-rich concentrates.

The isomer shift of the non-metallic gold in a sample of Agnes concentrate, which contained arsenic-rich pyrite and only trace amounts of arsenopyrite, appeared to be comparable with that of gold in arsenopyrite-rich samples. This could indicate that the gold is somehow chemically bonded to arsenic in both pyrite and arsenopyrite; however, further work needs to be carried out to fully verify such interpretations.

The presence of submicroscopic gold was further substantiated by investigations with the electron microprobe. These results revealed that the concentrations of sub-microscopic gold in the sulphides from the Fairview Mine were highly erratic, and the maximum concentrations of submicroscopic gold found in arsenopyrite and pyrite were 2700 and 488 g/t respectively.

A more detailed microprobe examination of an individual grain of arsenopyrite from the Sheba Mine (Fig. 2) showed that the gold is apparently associated mainly with the arsenic-rich zones.

Smaller amounts of gold are associated with the central region of the grain, which contains lower amounts of arsenic. Also, a positive correlation is found within pyrite grains between the arsenic and the gold contents. This relationship in both sulphides may indicate that gold atoms readily replace arsenic or, possibly, iron atoms in the sulphide lattice; alternatively, gold may be substituted in suitable interstitial atomic sites. Because of the relatively high concentrations of submicroscopic gold in the sulphides from refractory gold ores, the sulphides in these ores need to be totally broken down by roasting, or by bacterial or pressure leaching, to expose and release the

Gold trace

2000 to 2500 μg/g
1500 to 2000 μg/g
1000 to 1500 μg/g
500 to 1000 μg/g
0 to 500 μg/g

Arsenic trace

44,01 to 45,00%
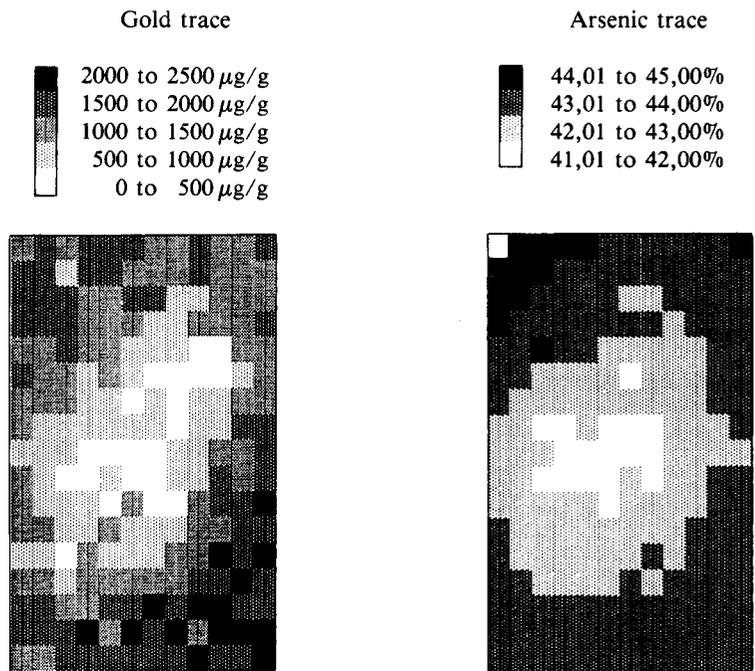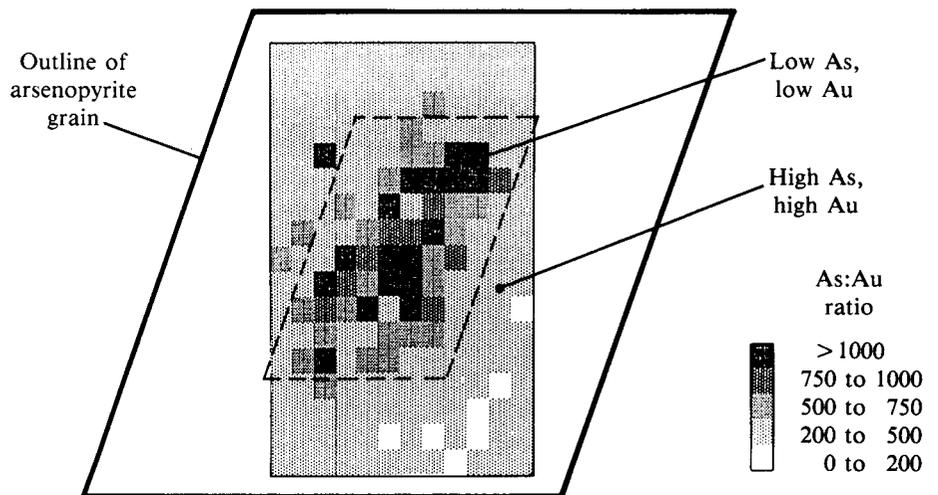43,01 to 44,00%
42,01 to 43,00%
41,01 to 42,00%

Fig. 2—Electron-microprobe analysis of gold and arsenic distribution within an individual arsenopyrite grain from the Sheba Mine. A region of low As and Au situated within the grain is illustrated relative to the morphology of the grain (stippled line)

Outline of arsenopyrite grain

Low As, low Au

High As, high Au

As:Au ratio

> 1000
750 to 1000
500 to 750
200 to 500
0 to 200

lattice-bound gold.

The distribution of gold in these sulphides has important implications for models of sulphide breakdown, since the more arsenic-rich varieties of sulphide are likely to break down at a faster rate than the low-arsenic pyrite and arsenopyrite[5]. This may lead to selective sulphide breakdown and the preferential release of the enclosed gold from an unstable, crystallographically distorted lattice with bonds that are weakened by the incorporation of large incompatible atoms.

In the producing mines of the Barberton Mountainland, carbon is present along microshear planes, within micaceous minerals, and in layers of relatively coarse particles of carbon (larger than 20 μm), as shown in Fig. 3. This carbon is not in an 'active' form, and its X-ray-diffraction pattern is commonly diffuse, indicating it to be graphite but with the carbon atoms in a highly disordered state.

The carbon that is disseminated more evenly throughout the ore and is found along micaceous cleavage planes

Fig. 3—Band of coarse carbon particles (grey) from the Sheba Mine. This crystalline variety does not adsorb gold from the leach liquor. (Oil immersion)

(Fig. 4) is in an active form, and its crystalline structure is very poor. This form of carbon is suspected of having the ability to adsorb gold from the leach liquor, but it is not known whether this ability is due to the larger surface area of the carbon particles or to a surface chemical property of the carbon itself. The problems associated with active carbon are conventionally overcome by roasting, by 'blinding' of the carbon with used motor oil, or by using carbon-in-leach (CIL) or, possibly, special resins.
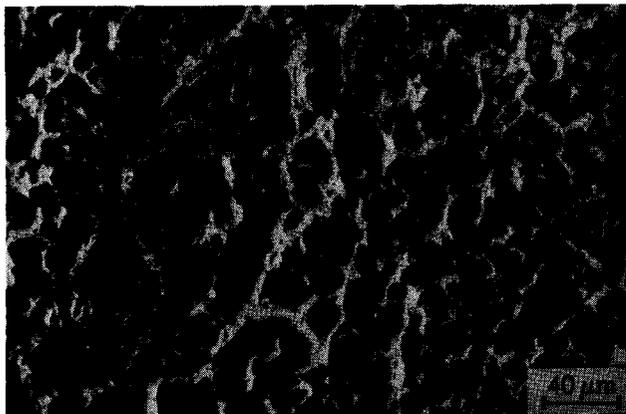

Fig. 4—Finely disseminated carbon from the Barbrook Mine. The interstitial carbon (grey) absorbs gold from the leach liquor, and is often amorphous in character. (Oil immersion)

Pyrrhotite and base-metal sulphides such as chalcopyrite and covellite are cyanicides, and can consume both oxygen and cyanide during cyanidation, thus giving rise to problems in the extraction of the gold. In South Africa, copper sulphides and antimony-bearing minerals are the base-metal minerals that are most commonly encountered during metallurgical processing. The effects of these components can be minimized by roasting, pressure cyanidation, or conventional leaching with low concentrations of cyanide and careful control of pH, aeration, and additions of lime. Lead nitrate can also be used to stabilize the pyrrhorite in some of the ores, e.g. those from the New Consort and Fumani Mines[6,7].

Thermal Remobilization

A suggestion by Boyle[8], which relates to the genesis of arsenical gold ores, is worthy of mention here because of its applicability to the Archaean gold ores of South Africa. Boyle suggested that, in arsenical ores formed at elevated temperature, gold may be incorporated into the lattice of pyrite or arsenopyrite, largely in solid solution, or as atomic layers on the growing crystal faces of the sulphide minerals. When these minerals have cooled, the gold in the structure distorts the sulphide lattice and, consequently, there is a rise in the strain energy of the system.

In South African ores, submicroscopic gold is accommodated mainly within arsenopyrite, owing to its suitable atomic spacing, crystal chemistry, and closure temperature with respect to gold. When such sulphides are subjected to a later thermal event, the submicroscopic gold may then migrate to sites of lower potential such as fractures, grain boundaries, and other micro- and macrostructural sites; the strain energy of the system is thus reduced. This movement of gold may be enhanced by temperature gradients and the movement of geothermal fluids within the sulphide system. Sulphide minerals may

also be re-organized into a new, thermodynamically stable assemblage that is characterized by the presence of pyrrhotite. The arsenopyrite changes from an n-type to a p-type sulphide after it has been remobilized and reconstituted[9]. Pyrite under a similar set of thermal conditions may also undergo an n-type to a p-type change. Such variation in the characteristics of the sulphides may account for their variable rates of breakdown during oxidative leaching.

It would therefore appear that so-called refractory gold ores may be transformed into free-milling ores in which the majority of the gold occurs as discrete particles rather than as submicroscopic gold. In such ores, which characteristically contain mainly pyrrhotite and arsenopyrite, the presence of high concentrations of pyrrhotite and, possibly, coarse gold is the main factor that could cause problems in extraction.

During the thermal remobilization of arsenical ores, the enclosed carbon may be mobilized, recrystallized, or even depleted, whereas ores that have not been subjected to thermal remobilization still have a strong gold–arsenic association, and may contain submicroscopic gold, finely disseminated active carbon, and low concentrations of pyrrhotite. Discrete grains of gold may also be present, predominantly within those pyrite grains in which the gold could not be favourably incorporated into the lattice. This discrete gold–pyrite association is commonly found in the arsenical ores of the Barberton Mountainland.

Although gold grains are also to be found in lesser amounts in arsenopyrite and pyrrhotite, other incompatible elements, such as copper, bismuth, zinc, lead, and antimony also crystallize as discrete phases, and may be texturally associated with gold.

Reactivated ores occur at the Klein Letaba Mine, which is situated in greenstone terrain[10], of a relatively high metamorphic grade, and at the New Consort Mine, which is located in a thermally disturbed area adjacent to a granite pluton[11]. The textural relations indicate that the pyrite and arsenopyrite were dissociated to pyrrhotite. The gold grains in these ores are commonly found in fractures and cracks, and on grain boundaries, and are more often associated with pyrrhotite. During the partial roasting of auriferous arsenopyrite, similar mineralogical changes occur, the submicroscopic gold coalescing to form discrete blebs within the pyrrhotite (Fig. 5).

This phenomenon, which was first reported by Bürg[12] in 1930, can provide diagnostic confirmation of the existence of this mode of occurrence of gold within sulphides.

The Beneficiation Circuit at Fairview

The gold-containing pyrite–arsenopyrite ore of the Fairview Mine normally has a sulphide content of 3 to 4 per cent (less than 0,1 per cent pyrrhotite), and contains minimal amounts of coarse gold. Beneficiation therefore consists of milling and flotation (Fig. 6) followed by roasting of the flotation concentrate in a two-stage horizontal-hearth Edwards' roaster. The calcine is then milled and cyanided, and gold extractions of around 95 per cent are obtained. A bacterial-leaching plant, which will enable increasing tonnages of sulphide concentrate to be treated has recently been brought into operation.

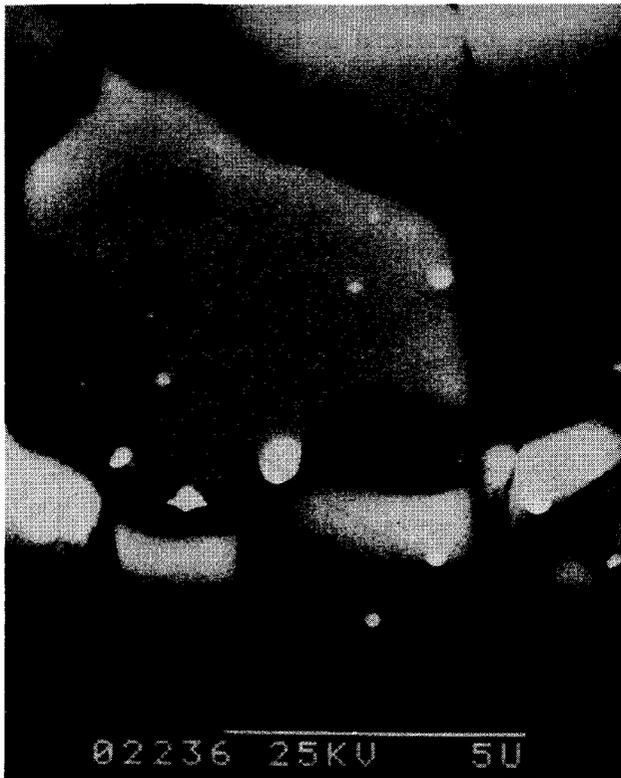In the other mines in the area, the ores contain large

Fig. 5—Scanning-electron photomicrograph of coalesced gold particles (white) in porous pyrrhotite after partial roasting. The gold collects into discrete particles (usually <0,5 μm) during the development of porosity resulting from the escape of the weakly held arsenic or sulphur atoms from the sulphide grains

amounts of coarse gold and sulphide grains. In addition to flotation, extensive use is therefore made of gravity separation in attempts to remove these coarse components in the early stages of treatment, since they may cause problems during extraction.

The distribution of the mineral components in the circuit was determined by the analysis of composite samples that were taken at points throughout the plant; the samples were sized, chemically analysed for sulphur and arsenic, and examined by optical microscopy and X-ray diffraction. The arsenic and sulphur contents of the arsenopyrite and pyrite were determined with an electron microprobe, and were used in the calculation of the arsenopyrite and pyrite concentrations in the size fractions of the products (Table II).

TABLE II
AVERAGE ARSENIC AND SULPHUR GRADES OF SULPHIDE GRAINS FROM ELECTRON-MICROPROBE ANALYSES

Mineral	S %	As %
Arsenopyrite	21,9	43,5
Pyrite	53,9	<0,5*

*Maximum 2 per cent

Comminution

Although milling at increased fineness of grind selectively liberates the fine disseminated sulphides, it also increases the amount of ultrafine gangue, which is readily entrained in the froth and is detrimental to flotation. During milling of the ore, the arsenopyrite is more sub-
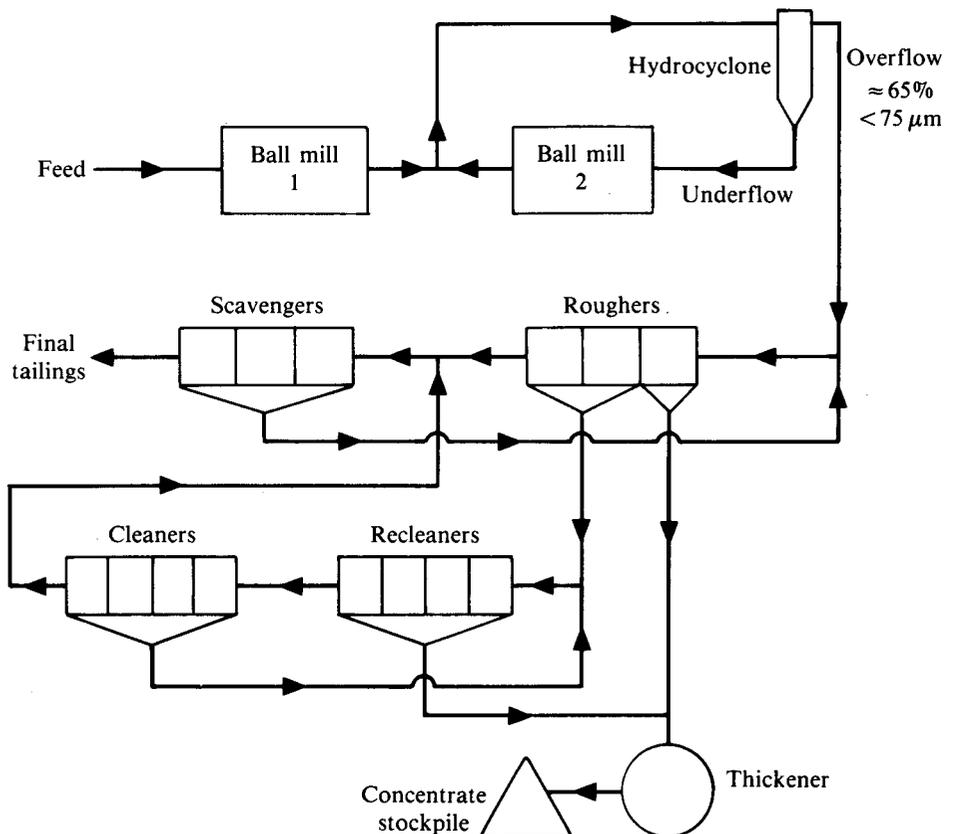

Fig. 6—The simplified beneficiation circuit at the Fairview Mine

ject to overgrinding than the pyrite, and a higher percentage of the arsenopyrite reports to the fraction smaller than 25 μm. As Fig. 7 shows, 47,7 per cent of the arsenopyrite, compared with 20,9 per cent of the pyrite, reports to this fraction of the Fairview flotation feed.
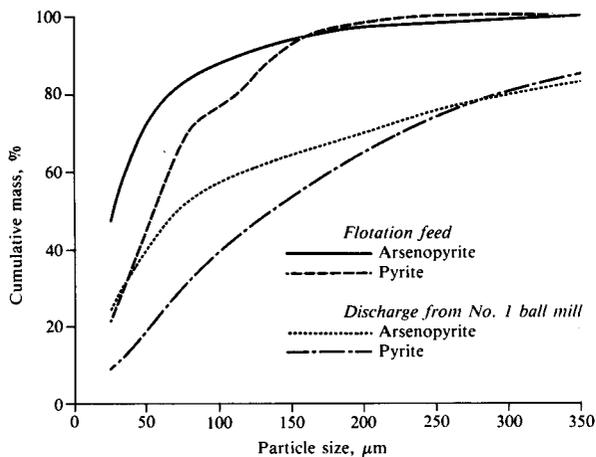

Fig. 7—Distribution of arsenopyrite and pyrite In the products of the milling circuit at Fairview. The arsenopyrite Is always found to be significantly finer than the pyrite In the beneficiation products

This preferential concentration occurs because of the original grain size of the arsenopyrite (usually smaller than 150 μm) in the ore, and because arsenopyrite is marginally less hard and more brittle than pyrite. The latter is harder and more resistant to attrition and fracture, and usually occurs in the uncrushed ore as coarse particles smaller than 2 mm. During milling, these factors lead to the production of relatively coarse, well-liberated particles of pyrite, which are more easily recovered by flotation than the finer particles of arsenopyrite.

This selective breakage of arsenopyrite during milling is also reflected in the ratio of arsenopyrite to pyrite and in the ratio of free to locked sulphide in the various size fractions of the comminuted ore. In the size fractions smaller than 150 μm, the extent of liberation and the relative amount of arsenopyrite increase with decreasing particle size. This is most pronounced in the fraction smaller than 25 μm. In the fractions larger than 150 μm, the extent of liberation tends to be reduced, and pyrite becomes the more dominant sulphide component. In the coarser fractions (larger than 1 mm), the ratio of arsenopyrite to pyrite is eventually from 0,4 to 0,5, which is that of the original ore. This is due to the nature of the mineralization, the sulphides being evenly disseminated throughout the ore. This variation in the degree of liberation of the sulphide particles is ultimately reflected in the response to flotation of the fractions smaller than 25 μm, between 25 and 150 μm, and larger than 150 μm.

A positive relationship was observed between the arsenic and the gold contents of all the Fairview beneficiation products that were examined in the present work. Fig. 8 shows that this positive correlation is more clearly evident for the cyanided, cyclosized products of the sulphide concentrate, i.e. the 8, 12, 17, 24, and 30 μm fractions, from which all the particulate gold had been removed. The 'limiting line' in Fig. 8 represents the limit

to which discrete gold particles can be released and removed by milling and cyanidation. (Such a situation occurs only when the carbon is not in an active form; otherwise, non-linearity would result.) The gold components that remain consist of fine particulate gold and submicroscopic gold, mainly within arsenopyrite. This gold constitutes refractory gold that cannot be liberated significantly by finer grinding.
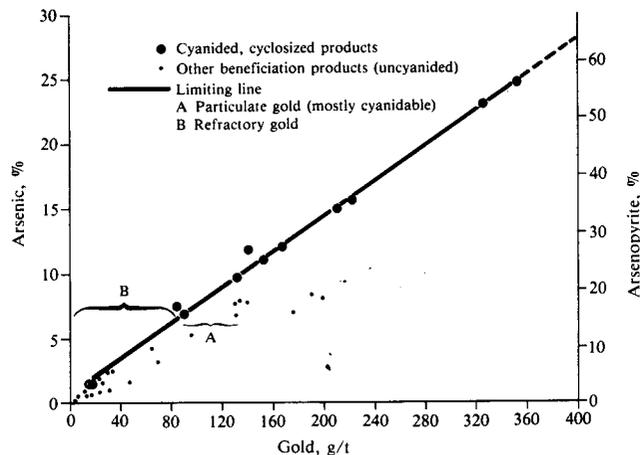

Fig. 8—Gold and arsenic contents of the beneficiation products of Fairview. This shows the positive relationship between gold and arsenic in the samples, and the relationship between the particulate gold and refractory gold components

The amount of refractory gold present can be roughly calculated from the arsenic content and by consideration of the gradient of the limiting line. The concentration of particulate gold in the samples can also be roughly calculated from the gold content of the sample and from the arsenic–gold relationship. Such particulate gold is normally mostly free, only small amounts being locked up within sulphides. The free particles are platy in form as a result of smearing and flattening during milling, and are floated and recovered mainly in the first rougher cell.

Flotation of Gangue

The behaviour of the gangue components in the flotation circuit can be conveniently monitored by the use of X-ray diffraction and comparison of the peak intensities and peak ratios. Allowances are made for the effects of X-ray absorption when high concentrations of sulphide are present (e.g. in the rougher concentrate), and for peak-broadening effects when samples of fine grain size (e.g. cleaner tailings) are analysed.

Some of the Archaean gold ores contain carbonaceous and graphitic material. This material is soft and flaky, and is easily broken down during milling. During flotation, the carbon floats readily owing to its fine grain size, natural hydrophobicity, platy nature, and low density. Some flotation concentrates from the Barberton Mountainland have carbon contents of up to 5 per cent. However, at the Fairview Mine, the carbon contents of the concentrates are usually lower than 1 per cent. High concentrations of carbon can influence the roasting behaviour of the concentrates, as can excessive concentrations of carbonates. Both of these components can dilute the oxygen within the roaster with carbon dioxide, which may form on heating, and may inhibit oxidation of the sul-

phide.

Flotation of Sulphides

On plants that roast auriferous sulphide concentrates, it is imperative to ensure that the concentrate contains sufficient sulphur (15 to 20 per cent) to burn autogenously, i.e. without the input of external energy[13]. Sulphur grades higher than 20 per cent can be attained, but often only at the expense of the sulphide and gold recoveries, mainly because increased amounts of auriferous arseno-pyrite report to the final tailings as free and composite particles.

Examination of a wide spectrum of sized products from the Fairview Mine revealed that the material can be conveniently classified into three size fractions, viz smaller than 25 μm, between 25 and 150 μm, and larger than 150 μm (Fig. 9). Each of these fractions has its own characteristic flotation behaviour.
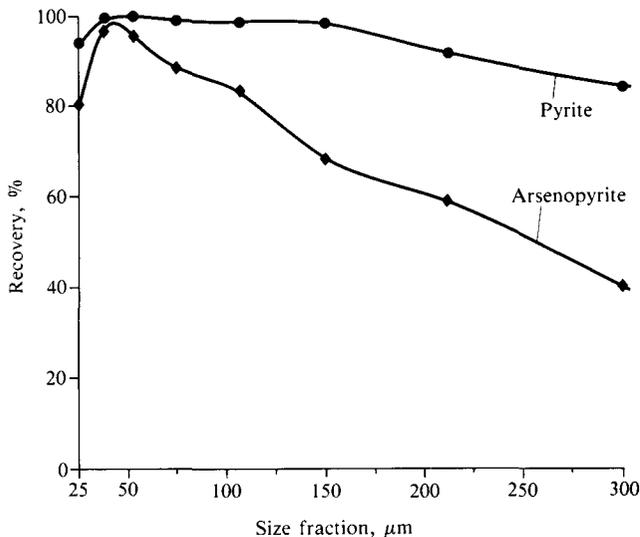

Fig. 9—Recovery of the sulphides in the different size fractions in the flotation circuit at Fairview. This shows the reduced recoveries in the coarse (> 150 μm) and fine (< 25 μm) fractions

The fraction smaller than 25 μm can become entrained in the froth during flotation, and recovery of the sulphides is marginally lower. Also, a large proportion of fine gangue material dilutes the sulphide in the concentrate fraction smaller than 25 μm. In the fraction between 25 and 150 μm, most of the sulphides are well liberated and float readily. However, a liberated particle of sulphide may fail to float readily because its surface is contaminated, or because it is surrounded by a monatomic layer or rim of oxidized material (Fig. 10), which may reduce its adhesion to the bubble. The size fraction larger than 150 μm has a poor response to flotation, mainly because of its increased content of composite sulphide particles.

When the recovery of the sulphides in the circuit is compared, it is found that the recovery of pyrite by flotation tends to be 1,1 to 1,8 times higher than that of arsenopyrite. The difference in the recovery of these two minerals is due not only to the difference in the surface chemical properties of the particle but, as mentioned earlier, to the difference in their overall size distribution and liberation resulting mainly from the variation in the
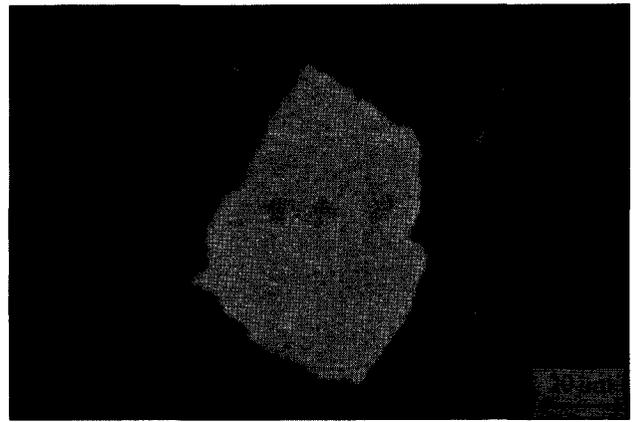

Fig. 10—Rim of iron oxide round a grain of arsenopyrite. This may inhibit the recovery of the grain by flotation. (In air)

original size of the sulphide grains.

Final Tailings

In the final tailings, the concentrations of arsenopyrite and pyrrhotite are both higher than that of pyrite (which floats more readily). In the fraction between 25 and 150 μm, the ratio of free to locked particles of pyrrhotite tends to be higher than that of arsenopyrite or pyrite. This indicates a poor response to flotation, and hence a low recovery of pyrrhotite.

The exposed gold that may be recovered in the final tailings by subsequent cyanidation is in the form of composite gold–gangue particles (Fig. 11), and that in the fraction smaller than 25 μm is mainly in the form of small gold platelets. The remainder of the gold consists of submicroscopic particles associated mainly with arsenopyrite, which occurs as disseminations (Fig. 12) or as grains rimmed with iron oxide (Fig. 10). Lesser amounts of gold are present as discrete particles trapped in gangue.
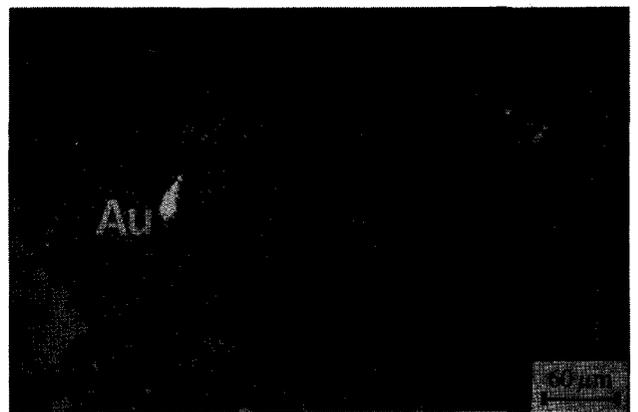

Fig. 11—A particle of gold (Au) attached to gangue in a coarse size fraction of the tailing that was not recovered during flotation

The size distribution and grades of the final tailings indicate that the final tailings smaller than 25 μm contain high percentages of gold and arsenopyrite. The gold grades of the different size fractions in the final tailings are relatively constant, which indicates that the gold is very finely disseminated throughout the particles.

Conclusion

Mineralogical studies have to some extent identified the