Antimony in South Africa

by D.R. DAVIS*, D.B. PATERSON†, and D.H.C. GRIFFITHS‡

SYNOPSIS
Consolidated Murchison Limited is the only primary producer of antimony in South Africa, producing approximately 18 percent of the total world production. This paper gives a technical review of the history, occurrence, mining, and metallurgy of antimony at Consolidated Murchison. World antimony markets are also discussed, together with the end-uses.

SAMEVATTING
Consolidated Murchison Limited is die enigste primêre produsent van antimoon in Suid-Afrika en produseer nagenoeg 18 persent van die wêreld se totale produksie. Die referaat gee 'n tegnieke oorsig van die geskiedenis, voorkoms, ontginning en metallurgie van antimoon by Consolidated Murchison. Wêreld antimoon markte en die eindgebruik van dit word ook bespreek.

Mine Development and Geological Setting
The Murchison Range is one of several Archaean greenstone belts found in the Kaapvaal Craton of Southern Africa. The belt lies in the Lowveld of the north-eastern Transvaal, and can be traced from the Transvaal Drakensberg escarpment in the west to the Lebombo Mountains in the east. The belt itself is 140 km long and 10 km wide (Fig. 1), striking east-northeast, and comprises a sequence of metamorphosed volcanic and sedimentary rocks that are similar in many ways to other greenstone belts in South Africa, e.g. that at Barberton.

In 1870, two prospectors, Button and Sutherland, reported having found gold in this belt. However, it was only later, in 1886, that a gold rush started, and this was followed soon afterwards by the declaration of this area as a public digging by the Zuid-Afrikaansche Republiek, and the laying out of the township of Leydsdorp.

The gold ores were found to be refractory at depth, and only a few of the original mines were still operating by 1928. During the First World War antimony, in the form of cobs of stibnite, was first produced for export from the United Jack Mine, but production ceased shortly after the termination of hostilities. However, in 1928 exploitation of antimony as a byproduct of gold was considered to be worthwhile, and there was a revival of interest in the area. In 1934, the Consolidated Murchison (Transvaal) Gold Fields & Development Company was formed in conjunction with Anglovaal Consolidated Investment Company Limited (now Anglovaal Limited), with a view to prospecting and exploiting the more extensive mineralization along the Antimony Line east of Leydsdorp.

Many types of mineralization are present in the Murchison belt, including antimony, gold, mercury, copper, zinc, tungsten, titaniferous magnetite, and emeralds. Only three of these commodities—antimony (with gold as a byproduct), gold (ex dumps), and emeralds—are currently being exploited.

Consolidated Murchison is the only primary producer of antimony in South Africa, and produces approximate-
ly 18 per cent of the total world production, making it the biggest single antimony mine in the world. The mill at Consolidated Murchison is supplied with ore from a variety of shafts. Currently only two shafts, Athens and Alpha, are actively in production, but two additional shafts (Monarch and Beta) are being deepened and equipped.

History of Antimony
Stibnite (Sb₂S₃) is the primary source of antimony, an element that can be described as a universal metal because of its wide range of chemical and metallurgical uses. The chemical symbol for antimony, Sb, is derived from the Latin stibium. Stibnite has been known in China for approximately 5000 years, and the ancient Egyptians used it as a powder in ophthalmology and as a cosmetic eyeshadow². Owing to its poor mechanical properties, antimony metal is not used directly but in numerous alloys, primarily with lead and tin. Medieval alchemists knew how to extract the metal, and to apply it in the separation of gold and silver as described in the works of Philippus Paracelsus (1526 and 1541), Georg Agricola (1621), and others.

During the Second World War and the Korean War, the consumption of antimony for its more traditional uses such as a lead hardener and in ammunition remained high. In later years, however, the use of the metal has decreased, although antimony trioxide has found an important market as a flame retardant in the plastics industry. Antimony trioxide was first widely used in flame-retardant compounds for tenting material, canvas, and paints during the Korean War, but the world demand for this commodity was low until 1972-1973, when flame-retarding legislation was widely enforced for the first time³.

Geology
The Antimony Line, which hosts all the known major occurrences of antimony in the Murchison Greenstone Belt in the eastern Transvaal is approximately 50 km long¹, and occurs within the Weigel Formation⁴, a heterogeneous unit of quartzite, quartz mica schist, mafic and ultramafic schist, iron formation, and carbonate-bearing rocks (Fig. 2). The Antimony Line itself consists largely of a resistant core of siliceous carbonate rocks surrounded by a less-resistant envelope of talcose and chloritic schists. Where the carbonate host is well developed as thick plugs or nodes, economic antimony mineralization may be present (Fig. 3).

Geochemical analysis of the quartz–carbonate host rocks reveals high concentrations of SiO₂, FeO, MgO, and Al₂O₃ with a low CaO-to-MgO ratio⁵. Alteration, as indicated by the highly variable grades of many of the alkali and alkaline-earth elements, has taken place, with the gross addition of CO₂ and the removal of H₂O. It has been suggested that the quartz–carbonate host rocks were originally magnesium-rich basalts or, more particularly, peridotitic komatites.

The quartz–carbonate rocks contain magnesite, dolomite, and quartz, with minor chlorite, fuchsite, talc, and sulphides. The chromium-rich mica fuchsite imparts a bright-green colour and, where locally developed with the other micaceous minerals, outlines a gross foliation to the quartz–carbonate.

The contact with the surrounding talcose rocks is sharp, especially where the quartz–carbonate bodies are boudinaged. However, where the host rocks are schistose and good cleavage is developed, the contact may be gradational, with the contact zone generally conformable with the cleavage.

The Murchison Belt has undergone a variety of deformational events in its complex structural history. The most important regional structural feature is the foliation, which strikes east–northeast and is characterized by pervasive cleavage and schistosity. The Antimony Line is more recently thought to be a zone of heterogeneous strain and locally intense shear, with folding having taken place around a steep east–northeast axis⁶–⁸. Additional cross-folds and associated axial planar cleavage, heterogeneous shear deformation, lesser kink bands, and chevron folds may all have been actively important in the localization of the economic mineralization⁹–¹². Strike-slip faulting has taken place but is not thought to have been a major mineralization process⁶. The strike of the schistosity sub-parallel the strike of the Barberton and Pietersburg greenstone belts. The original lithological bedding, banding, and the more subtle features such as way-up structures have to a large extent been completely overprinted and obliterated by the schistosity.

Geochronological studies of the belt are somewhat ambiguous, the dating of the mineralized assemblages by the Pb–Pb isochron method⁹ giving an age of 3020 Ma. This age is interpreted as a possible minimum age of emplacement for the greenstone belt and a maximum age of emplacement for the mineralization itself. Although the younger felsic intrusive rocks have been dated accurately, the exact timing of their emplacement with respect to the structural history of the belt is uncertain. An age of 3020 Ma indicates that the rocks of the Murchison Greenstone Belt are some of the oldest rocks in the world.

Mineralization and Mineralogy
The Antimony Line is mineralized economically in both gold and antimony, and is currently mined at various localities along a strike of some 12 km. The sulphide mineralization along the Antimony Line is dominated by the antimony sulphide stibnite (Sb₂S₃), which forms the bulk of the economic mineralization. Minor arsenopyrite (Fe₃AsS₃), berthierite (Fe₅Sb₅S₈), and a variety of lesser known iron, nickel, copper, lead, and antimony sulphides are also present (Table 1).

Stibnite is found as disseminations (grain size up to 0.3 mm) throughout the host quartz–carbonate, with local reconcentrations along the cleavage planes of the gangue minerals¹¹. More commonly, the stibnite forms discrete veins as remobilized networks with varying amounts of quartz and coarse-grained carbonate.

Gold is economically a highly important byproduct and occurs as coarse visible gold, as finer disseminations, or in close association as sub-microscopic intergrowths within the sulphides. Additional gold is also found associated with the arsenopyrite horizons, which form discrete lenses at or near the antimony mineralization.

Zoning is a common feature on both macroscopic and microscopic scale, the stibnite being richest at the core.
of the orebody and the iron-rich antimony minerals (e.g. berthierite) being more prevalent towards the margins. On the microscopic scale, berthierite is often seen to rim stibnite grains, especially in semi-closed sub-systems such as spur reefs into the unmineralized enclosing wall rocks. The gangue consists mainly of quartz, dolomitic carbonate, chlorite, and talcose material.

**Genesis**

Up to now there has been no agreement on the genesis of the antimony and gold mineralization in the Murchison Greenstone Belt, and the number of genetic theories is almost equal to the number of investigators. Essentially, they fall into two categories: epigenetic or syngenetic.

The various theories of ore genesis seem to have a cyclical popularity, the epigenetic theories being supported during the 1960s and 1970s. Essentially, epigenesis requires the orebody to be developed as a discrete mineralization phase after the initial deposition of the rock layers.

In the late 1970s a syngenetic origin was favoured since it explained certain aspects of the deformation fabric observed in the antimony mineralization. The syngenetic model assumes that the mineralization took place at the same time as the enclosing rocks, and thus any subsequent deformation of the enclosing rocks would also have deformed the mineralization. Envisaged in the syngenetic model is a submarine volcanic exhalative source with its associated hot-springs actively pouring out solutions rich in gold, arsenic, antimony, mercury, bismuth, and sulphur from the volcanic vent.

However, any attempts at determining the origin of the mineralization are severely hampered by the almost total destruction of the original banding or bedding by a variety of deformation events, and the subsequent remobilization and recrystallization of the mineralized horizons.

In an attempt to rationalize conflicting observations and views, recent workers in the 1980s proposed a
TABLE I
MINERALS OBSERVED IN THE MURCHISON GREENSTONE BELT

<table>
<thead>
<tr>
<th>Type of mineral</th>
<th>Name of mineral</th>
<th>Chemical composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony-bearing minerals</td>
<td>Stibnite</td>
<td>Sb₂S₃</td>
</tr>
<tr>
<td></td>
<td>Berthierite</td>
<td>FeSb₂S₄ (FeS, Sb₂S₃)</td>
</tr>
<tr>
<td></td>
<td>Gudmundite</td>
<td>Fe₃Sb</td>
</tr>
<tr>
<td></td>
<td>Native antimony</td>
<td>Sb</td>
</tr>
<tr>
<td></td>
<td>Cervantite</td>
<td>Sb₂O₄</td>
</tr>
<tr>
<td></td>
<td>Valentinite</td>
<td>Sb₂O₃</td>
</tr>
<tr>
<td></td>
<td>Senarmontite</td>
<td>Sb₂O₂</td>
</tr>
<tr>
<td></td>
<td>Breilautpite</td>
<td>NiSb</td>
</tr>
<tr>
<td></td>
<td>Aurostibite</td>
<td>AuSb</td>
</tr>
<tr>
<td></td>
<td>Gersdorffite</td>
<td>Cu₃Sb</td>
</tr>
<tr>
<td></td>
<td>Jamesonite</td>
<td>Pb₂FeSb₂S₄</td>
</tr>
<tr>
<td></td>
<td>Kerensite</td>
<td>Sb₂S₀</td>
</tr>
<tr>
<td></td>
<td>Livingstoneite</td>
<td>HgSb₂S₇</td>
</tr>
<tr>
<td></td>
<td>Ullmannite</td>
<td>NiSbS</td>
</tr>
<tr>
<td>Arsenic-bearing minerals</td>
<td>Arsenopyrite</td>
<td>Fe₃As</td>
</tr>
<tr>
<td></td>
<td>Gersdorffite</td>
<td>(Fe,Ni,Cu)₂AsS</td>
</tr>
<tr>
<td></td>
<td>Enargite</td>
<td>Cu₃AsS₄</td>
</tr>
<tr>
<td></td>
<td>Coryrite</td>
<td>Ni₃Sb₃AsS₄</td>
</tr>
<tr>
<td>Other sulphide minerals</td>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
</tr>
<tr>
<td></td>
<td>Pyrite</td>
<td>FeS</td>
</tr>
<tr>
<td></td>
<td>Pentlandite</td>
<td>(Fe,Ni)₃S₈</td>
</tr>
<tr>
<td></td>
<td>Covellite</td>
<td>CuS</td>
</tr>
<tr>
<td></td>
<td>Pyrrhotite</td>
<td>Fe₇S₈</td>
</tr>
<tr>
<td></td>
<td>Galena</td>
<td>PbS</td>
</tr>
<tr>
<td></td>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
<tr>
<td>Major gangue constituents</td>
<td>Quartz</td>
<td>SiO₂</td>
</tr>
<tr>
<td></td>
<td>Dolomite</td>
<td>Ca₂Mg(CO₃)₂</td>
</tr>
<tr>
<td></td>
<td>Magnesite</td>
<td>MgCO₃</td>
</tr>
<tr>
<td></td>
<td>Muscovite</td>
<td>K₂Al₂Si₃Al₂O₁₀(OH, F)₄</td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td>(Mg₂Al₃Fe₉)(Si₆Al₁O₂₀)(OH)₁₆</td>
</tr>
<tr>
<td></td>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
</tr>
</tbody>
</table>

two-stage model that incorporates an initial syngenetic origin, followed shortly after by an epigenetic concentration of the mineralization during the early phase of deformation.

Development of Reserves

The complex structural and genetic history of the orebodies has resulted in narrow, vertically dipping lensoid bodies that are developed discontinuously along the Antimony Line. Evaluation of this sort of orebody is naturally difficult but is a vitally important task. Orebodies are categorized into three classes as containing possible, probable, and proven reserves, which reflect increasing confidence levels in the block tonnage and grade as more information on the orebody is recorded. The ongoing generation of new ore reserves is an arduous task for a mine as old as Consolidated Murchison but is vital both for the life of the mine and for the future production of antimony.

Possible Reserves

The possible reserves are those delineated by diamond drilling from the surface or underground. The underground drilling is conducted from the various haulage levels 60 m apart, which are positioned some 30 m distant from the mineralized zones. The ore zone is divided into blocks with dimensions of 30 m by 60 m, and the ore intersection values from the boreholes are assigned to the relevant blocks. The block grades are determined from the weighted arithmetic mean of all the values in the block. Tonnage figures are determined by use of the mean width of the block, together with the relative density of the run-of-mine ore, which is 2.94. These values are then transferred to the computer for storage.

Probable Reserves

After a possible reserve block has been determined by diamond drilling, cross-cuts from the haulage are developed through to the ore zone. Raises are put up in the ore zone to the level 60 m above. Sub-level reef drives and cross-cuts from the raise afford additional exposure for sampling to take place. They also afford a physical appreciation of the complex nature of the ore zone such as S-folding, spur reefs, mineral banding, and boudining, which ultimately determine the morphology of the ore and the lines of mining. Where complexities in the orebody are indicated, additional diamond drilling or cross-cutting from the interlevel development is recommended for evaluation purposes.

All development is surveyed, geologically mapped, and sampled, and in this way greater confidence in the continuity, tonnage, and grade of the orebody is attained. These results are then computed, and probable reserve values for both tonnage and grade are determined and are transferred to the computer for storage.

Proven Reserves

When the underground development has progressed for 30 m from the original twin-raise system and a new twin-raise system has been completed in that position, the block is ready for final evaluation. All the information from the sampling and mapping is collected, and cross-sections through the orebody are drawn every 10 m, indicating the ore outline as determined from the information available. Where possible, gross lithological contacts are used as cut-offs for ease of mining and for breaking characteristics. In wide orebodies, grade cut-offs as determined from sampling may be incorporated.

The best shape of mining stopes is then designed and delineated from this information and, by use of the frustum formula, the cross-sections are combined so that the tonnage of the sections can be calculated for the block tonnage. The grades are computed by means of a weighted arithmetic mean. These results are updated on the computer, and the block grade and tonnage are now transferred from the probable to the proven reserve. Lines corresponding to the mining lines as determined by the final evaluation are now physically painted underground where possible in order to assist and control the mining department, which can now go ahead and begin to stope the block.

Pay Limit

Prior to the implementation of the final step of transferring the block of ground from the probable to the proven reserves, the calculated grade of the proven reserves must be above the current pay limit. The payable ore limit is controlled by three factors: the underground recovery factor, the surface-plant recovery factor, and
the current prices of the combined commodities.

As Consolidated Murchison is a two-product mine, the
individual recoveries of both antimony and gold must be
considered separately. All the variables are thus computed
and a pay limit is set quarterly.

**Mining**
The mining method employed at Consolidated Mur-
chison, sub-level open stoping, has been modified to suit
the needs of the orebodies. Levels are cut 60 m apart, with
the haulages positioned 20 to 30 m away from the ver-
tically dipping orebodies. From the haulage, a cross-cut
is developed to the reef, and a twin raise is positioned
on the best mineralized portion of the reef. The twin raise
consists of a travelling way (staggered for additional safety
and equipped with ladders) and an ore pass. Altogether
8 interlevels are cut, with the first interlevel as a coning
level at 6 m elevation above the footwall and the remain-
ing 7 interlevels 6 m apart. Strike drives on all the
interlevels including the footwall are developed simultane-
ously, and cross-cuts are made in a staggered array
30 m apart on each interlevel. A new twin-raise system
30 m along strike from the original twin raise is
developed, and this 30-by-60 m area between these two
twin-raise systems constitutes an ore block (Fig. 4). All
development dirt is transported by wheelbarrow along the
development drives of standard size (2.2 by 1.3 m) and
tipped into the orepass. Once the 30-by-60 m block of
ground has been completely developed and evaluated, the
block of ground is transferred to the proven category and
stoping can commence. Stoping on the original orepass
takes place by the use of conventional atleg-mounted
rock drills for stopes of 4 m width or less, and longhole
machines for wider stopes.

Cones are cut on the first interlevels every 6 m, and a
drawpoint layout is provided by the Survey Department
after consideration of the final orebody shape, width, and
dip, with the drawpoints planned for loader maneuver-
ability and access to each cone, and to allow more than
one drawpoint to be in use at any one time.

For narrow orebodies, slipping-and-ledging takes place,
with upholes drilled from each interlevel, minimizing
where possible on down- and side-holes. In wider ore-
bodies, long-hole machines drill a combination of both
fan holes and up- and down-holes from ledges at every
second interlevel. Every possible use of cross-cuts and
other internal development is made for drilling purposes.
In orebodies wider than 6 m, a drilling drive on either con-

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*Fig. 4—A schematic longitudinal section showing the sub-level open-stopping method*
tact is positioned with fan holes drilled towards one another in order to limit the overbreak potential inherent in drilling with long-hole machines. Faces are carried slightly overhand with an inverted cone shape so as to minimize dilution.

Lennings 215 Rockershovel loaders are used to load the 4 t Gable-type side-discharge hoppers. Goodman 6 t battery locomotives are used to pull the hoppers since they have been found to be more reliable, non-polluting, and cheaper to operate than equivalent diesel-powered locomotives, which are currently being phased out.

Footwall development and drawpoints are mined ahead of the retreating face to ensure that there is no delay in cleaning. The drawpoints in the backstope areas are barricaded off so that any scaling taking place in these areas cannot be drawn.

Concurrently with the stoping, the next 30 m block is developed to ensure that the proven reserves are maintained and that stoping can continue unhindered. Furthermore, the material to equip the initial 30 m block is reclaimed and leap-frogged ahead for use in the ongoing strike drives.

Mining operations are planned so as to allow, where possible, the employment of a 'concentrated' mining technique, the philosophy being that the stoping groups are clustered together on various portions of the orebodies rather than scattered throughout the mine. The advantages of this method are as follows:

1. increased management control,
2. better usage of material,
3. flexibility of mining personnel,
4. increased productivity, and
5. less delay in lag time during the move from one stope to the next.

Ore is transported on 15 kg rails to the ore- and waste-pass systems. The ore is passed through a 30 cm grizzly positioned on each haulage level, and gravitates down through the ore-pass system to the loading box at the shaft bottom, from where it is fed into 4 t or 6 t skips and hoisted to surface. On surface, the ore is transported from the various shafts to the central 2 kt receiving bin at the plant by end-tipping Mercedes Benz trucks.

The shafts work on a three-shift basis, with men and material going down in the morning shift, and hoisting of ore and waste taking place during the other two shifts. A total of approximately 50 kt of rock is hoisted per month.

The underground workings are ventilated by surface fans (downcasting the air in the main shafts) that deliver approximately 120 m³ of air per second per shaft. The upcast air is returned through the second outlet. The average wet-bulb temperatures of the working areas are 27°C, with virgin-rock temperatures in the deepest portions of the mine (1041 m below surface) of approximately 38°C. The relatively low underground temperatures, together with an essentially dry mine, make the underground conditions tolerable.

Reef is mined from the various types of orebodies that occur within the operating shaft complexes at Consolidated Murchison. The styles of mineralization at the various shafts are different, as are the rock chemistry and mineralogy. The flexibility that the system of sublevel open stoping provides is highly suited to the problems encountered underground. Problems, such as the sudden narrowing of wide orebodies, localized structural effects (S-folding) resulting in changes of dip, plunging orebodies, sections of orebodies that become 'unpay', and orebodies that have ill-defined contacts, are frequently encountered. Sub-level open stoping offers additional flexibility with machinery and material, since conventional and long-hole machines can be interchanged. The vertical interlevel distance of 6 m affords high standards of control vis-à-vis long-hole deviation and borehole layouts, which results in greater selectivity and control in the mining of irregularly shaped orebodies.

The disadvantages of sub-level open stoping are that, not only is there a long delay time in the development stage (approximately 12 to 18 months) before stoping commences, with the capital investment of the development high, but the method affords no extra stability to the sidewalls.

In sub-level open stoping, the stope must remain open while the ore is being blasted and drawn. At Consolidated Murchison in long stopes where the horizontal component of stress is high, slabbing can take place. In areas where geological discontinuities have reduced the sidewall tensile strength, or in areas of known poor ground conditions (i.e. sidewall rocks with a low rock-quality designation, e.g. talc and schist), dilution in the form of sidewall scaling can and does take place. This problem is further aggravated by sudden localized changes in the dip of the orebody.

This situation can be minimized by the following:

(a) advancing the stope faces as quickly as possible to ensure that scaling takes place preferentially in backstope areas,
(b) limiting waste development in the sidewall,
(c) leaving rib pillars for sidewall stability, and
(d) closing off drawpoints in backstope areas if it is ascertained that significant scaling has taken place.

All backstope areas are carefully monitored by the use of a laser measuring device to control and measure the degree of scaling.

Of the other mining methods suitable for the narrow vertical orebodies found at Consolidated Murchison (i.e. shrinkage or cut-and-fill), shrinkage is cheaper than sub-level open stoping, and affords sidewall stability, but it is less selective and requires more support of the hanging, especially in wider stopes. Furthermore, full production from the stope can take place only once the entire stope has been blasted. Cut-and-fill is more selective, and offers total sidewall support with negligible scaling but suffers from being costly, has a stop-start production pattern, and can be potentially dangerous in wider stopes where support of the hanging is necessary.

Metallurgical Processes

Consolidated Murchison currently operates three separate plants to produce antimony sulphide concentrates and crude and refined antimony trioxide respectively. Developmental work is currently underway to produce sodium antimonate—Na(Sb(OH)₃)—from low-grade off-specification material. World markets require that these products should conform to certain specifica-
tions with respect to the antimony grade and the level of impurities within the product. Numerous impurities such as arsenic, lead, copper, zinc, iron, nickel, selenium, and mercury, which occur naturally in the orebodies, can markedly affect the properties of the antimony alloys and oxides.

The metallurgical process has been developed to ensure the desired grades: namely, a concentrate containing more than 56 per cent antimony and less than 0.25 per cent arsenic. The crude oxide should not fall below 81 per cent antimony and should have no more than 0.35 per cent arsenic.

Table II gives the typical grades produced at Consolidated Murchison for antimony concentrate and crude oxide.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentrate</th>
<th>Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony, %</td>
<td>58,0</td>
<td>81,0</td>
</tr>
<tr>
<td>Arsenic, %</td>
<td>0,17</td>
<td>0,3</td>
</tr>
<tr>
<td>Lead, %</td>
<td>0,18</td>
<td>0,15</td>
</tr>
<tr>
<td>Nickel, %</td>
<td>0,11</td>
<td>0,01</td>
</tr>
<tr>
<td>Copper, %</td>
<td>0,17</td>
<td>0,02</td>
</tr>
<tr>
<td>Iron, %</td>
<td>1,9</td>
<td>0,03</td>
</tr>
<tr>
<td>Selenium, p.p.m.</td>
<td>3,0</td>
<td>-</td>
</tr>
<tr>
<td>Mercury, p.p.m.</td>
<td>10,0</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur, %</td>
<td>22,3</td>
<td>0,22</td>
</tr>
<tr>
<td>Insoluble matter, %</td>
<td>9,9</td>
<td>1,2</td>
</tr>
</tbody>
</table>

Properties of Antimony

Since the physical and chemical properties of the major forms of antimony are fundamental to an understanding of the metallurgical operations and the subsequent end-uses of antimony, a brief review is given of the important properties of the metal, sulphides, and oxides before details of the processes used in South Africa are discussed. Table III compares the properties of these forms of antimony.

Antimony Metal (Regulus)

Antimony occurs as two allotropes, α being an unstable yellow form and β being a stable metal. The most important physical properties of the metal are that it expands on freezing by 0.95 per cent by volume and that it transmits this property to its alloys. It acts as a hardening agent with lead and tin. The metal is not oxidized by dry or moist air at room temperature, but the molten metal burns in air, with the formation of Sb₂O₃ and to a minor extent Sb₂O₅.

Antimony Sulphides

Stibnite (Sb₂S₃) is the most important source of antimony. However, it is often associated with other antimony minerals that have formed as products of its decomposition. As mentioned previously, it frequently occurs with other sulphide minerals and gold. Refined antimony trisulphide, containing more than 70 per cent antimony, is known as black powder. It is used as a primer in ammunition, in which it acts as a friction element and heat-transfer medium. When ignited, the tri-sulphide generates a dense white smoke, and is also therefore used in smoke markers. Refined antimony pentasulphide is used as a vulcanizing agent in the production of red-rubber compounds.

Antimony Oxides

Antimony trioxide (Sb₂O₃), the most common form of antimony oxide, is produced by oxidation of the metal or sulphide. Two allotropic forms exist, senarmontite being formed above 570°C and valentinite below 570°C. Antimony pentoxide (Sb₂O₅) decomposes at 380°C to form the tetroxide cervantite (Sb₂O₄), which decomposes to the trioxide above 930°C. Oxygen is evolved during the decomposition reactions. The most important chemical property of antimony trioxide is its ability, in combination with a halogen such as chlorine or bromine, to impart flame-retardant properties to paint, plastics, adhesives, textiles, and other flammable materials.

Sodium Antimonate

Sodium antimonate—Na(Sb(OH)₆)—is commonly produced as a byproduct in the Harris process for the refining of lead. Sodium antimonate is an oxidizing agent and is used mainly as a fining agent in the manufacture of specialist glasses (as a decolorizing and degasification agent).

Beneficiation of Ore

The concentrator at Consolidated Murchison uses an integral process for the recovery of both gold and an-
Amalgamation. Bullion sales. Carbonto Rand Refinery. Fig. 5-Agoldsales schematic diagram showing Consolidated Murchison’s processes for the recovery of gold and antimony. Thus, in any discussion of current plant practice, certain aspects of the gold-recovery process must be mentioned. The current plant encompasses crushing, milling, gravity recovery of gold, flotation of antimony and gold, low-alkalinity high-pressure cyanidation of the concentrate for gold recovery, filtration, and drying. The emphasis in the process has changed considerably in the 51 years since the company was formed. This, together with frequent plant expansions, has led to a plant that consists of equipment of varying ages and efficiencies. A schematic diagram of the processes for the recovery of antimony and gold is shown in Fig. 5.

Historical Development of the Process

Details of the early exploitation of the mineral wealth in the Murchison Range have already been given. Viable exploitation of the area’s antimony reserves had its origin with the formation of Consolidated Murchison in 1934. The first plant (the east plant) was designed and erected in 1936 for the treatment of arsenical and antimonial gold ores by flotation. The concentrates were roasted in an Edwards roaster, which had a capacity of 10 t/d, and were then subjected to cyanidation for the recovery of gold.

This venture was not particularly profitable, and research was directed into the exploitation of antimony. In 1940, pilot-plant tests on the flotation of antimony indicated a possible treatment route, and production started with a ten-stamp mill (600 lb stamps) and a few flotation cells.

A larger plant (the west plant) comprising a ball mill and flotation cells was constructed during 1941 and commissioned in May 1942. The process was well-established by late 1942. The east plant (for gold recovery) remained in operation on material of low antimony grade until March 1943, when it was converted to the recovery of antimony while the smaller, west plant was used to treat antimony-free gold ore from a lode of banded ironstone.
In September 1943, the treatment of this orebody in the west plant ceased in favour of antimony-rich ores, and from that time onwards the company's emphasis has been on the recovery of antimony with gold as a byproduct.

Company records from the 1950s indicate that, during the early years, flotation was carried out with sodium isobutyl xanthate as an antimony collector, pine oil as a frother, and lead nitrate as an activator. The activation stage was based on a 1934 patent by the Franco Wyoming Oil Company. During flotation, the pH was controlled with sulphuric acid to ensure an antimony recovery of more than 85 per cent.

Antimony head grades to the plant for the period 1944 to 1970 were between 6 and 12 per cent; during the same period, the arsenic grades were between 0.1 and 0.2 per cent. By the early 1970s, the antimony head grade had dropped to below 5 per cent, while there was no corresponding drop in arsenic grades. As the antimony head grade declined, the ratio of antimony to arsenic became such that a refining of the metallurgical processes was required in order to attain acceptable arsenic levels, i.e., below the 0.25 per cent market requirement for concentrates. Gravity tabling was therefore introduced to remove arsenic from the concentrates. This process was reasonably successful for approximately 2 years (reducing the overall antimony recovery by only 3 to 5 per cent).

With a continuing decline in head grade, tabling was no longer feasible, and the Franco Wyoming float was commissioned in 1972 based on the 1934 patent. In this process, the antimony was floated as previously, carrying with it large amounts of pyrite and arsenopyrite. Copper sulphate and caustic soda were added to the concentrate to modify the pH and produce copper hydroxide, which acted as an activator for pyrite and arsenopyrite while simultaneously inhibiting the flotation of stibnite. A further flotation step in which an arsenical concentrate was removed from the primary antimony concentrate was therefore carried out.

This process proved to be difficult to control, and only 40 to 50 per cent of the concentrates produced were marketable. Furthermore, the ultrafine antimony minerals did not respond well to the copper hydroxide depression, and some 15 to 20 per cent of the recovered antimony reported to the arsenic concentrate. The overall plant recovery of antimony in the final concentrate therefore dropped to below 70 per cent.

The 1934 Franco Wyoming patent indicated that sodium cyanide assisted in the depression of arsenical minerals in the flotation of antimony, and research conducted at the National Institute for Metallurgy (now Mintek) in 1972 indicated that depression by cyanide was a feasible alternative to the Franco Wyoming process. A further decrease in plant efficiencies in response to the declining head grade led to the introduction in October 1978 of the cyanide depression of arsenic as an alternative to the Franco Wyoming differential flotation process.

The high-grade reefs exploited from the Gravelotte and Alpha sections of the Mine prior to 1982 contained large pockets of high-grade mineralization with low arsenic head grades, and it was possible to produce saleable material by the hand cobbing of ore from this section of the Mine. Run-of-mine ore was passed over a 5 cm vibrating screen, and the oversize was washed before going to a sorting belt, where suitable cobbled ore was selected. The antimony grades produced by cobbing varied over the years according to demand, but could rise as high as 70 per cent. The arsenic grades were low—generally below 0.1 per cent. Cobbed ore was still produced by the Chinese and Bolivian antimony suppliers, although the supply of this material from Bolivia is dropping steadily.

A pilot-scale (5 t/d) ammonium polysulphide leaching plant to produce refined stibnite was built in 1976 in an attempt to generate saleable material from the stockpiled, high-arsenic, low-antimony concentrate generated in the Franco Wyoming process. This plant was based on studies by Louw, Gussman, and Edwards but, although the process was feasible on a laboratory scale, it presented a serious health hazard owing to the high levels of hydrogen sulphide gas, and the pilot plant was unable to produce acceptable products. The process was therefore abandoned soon after the pilot plant had been commissioned.

Comminution

The comminution circuit is shown in Fig. 6. The ore received by road from the operational shafts has a maximum particle size of approximately 0.4 m and a typical analysis of 1.8 per cent antimony, 2 g of gold per ton, and 0.2 per cent arsenic. After being weighed, the ore is tipped into a surface reef box at the plant. Initial comminution is effected by means of a conventional dry-crushing and screening operation comprising a vibrating grizzly of 11.5 cm aperture ahead of a primary Telsmith single-toggle jaw crusher, two parallel open-circuit primary screens, and two 1.3 m short-head Symons cone crushers in closed circuit with a further two vibrating screens. All the screens are fitted with 13-by-50 mm polyurethane screen panels. The typical crusher-plant product has a maximum particle size of 13 mm, with a $d_{50}$ size of 11 mm. Crushed ore is stored in three 450 t live-storage silos prior to being transferred to the primary mill-feed silos.

Primary milling occurs in two 2,44-by-3.05 m ball mills and one 1.83-by-3.66 m ball mill. The mills are lined with manganese-steel pocket-type liners, and use 90 mm cast-steel balls as a grinding medium, the steel consumption being approximately 0.7 kg per ton milled. The mill discharge is screened over a 2-by-25 mm slotted polyurethane-decked screen to remove pebbles, which are recycled to the mill feed on a pebble conveyor (Cantwell W80 flexible walls on the edge of the belt and T75 cleats at a 300 mm pitch along the belt's surface).

The typical primary-mill discharge has a particle size of 45 per cent passing 75 μm and a $d_{50}$ size of 400 μm. Laboratory testwork has shown that the energy requirements can vary by up to 36 per cent for a given grind, depending upon the mineral composition of the gangue in the ore being treated.

The screened mill discharge is treated over eight parallel lines of two-in-series, twin-sided, corduroy-covered rotating tables for the recovery of a crude gold gravity concentrate. The refractory nature of the ore makes efficient gravity-based recovery of the gold vital. Although other methods of initial gold concentration such as those using riffle belts and spirals have been evaluated, the
traditional corduroy blankets have proved to be the most efficient primary concentration method for gold.

The tailings from the corduroy tables are classified by hydrocyclone, the underflow of which is reground in two secondary mills prior to being treated through an identical secondary corduroy-concentration step that is operated in closed circuit with the hydrocyclone.

The secondary mills consist of one 1,83-by-3,66 m and one 1,98-by-3,66 m ball mill with white-iron solid-wave liners. The grinding medium is 50 mm drop-forged steel balls, the steel consumption being about 0,6 kg per ton milled.

The cyclone overflow is scavenged over a third set of manual corduroy tables prior to being pumped to flotation. The gold concentrates produced from the three gravity-separation stages are redressed on James tables prior to amalgamation and smelting. The gold recovery by gravity techniques lies in the range 27 to 37 per cent, being highly dependent upon the mineral composition of the ore in the pockets that are exploited at any one time.

A guard cyclone, in operation on the scavenger flotation feed, scalps remaining coarse material out of the flotation circuit and recycles it to the secondary mills. The final grind achieved is about 1 per cent retained at 300 µm and 65 to 75 per cent passing 75 µm. The plant capacity is in the region of 2 kt milled per day, but drops considerably when the harder quartz-rich reefs are mined from the Alpha Shaft.

**Flotation Practice**

The flotation circuit involves roughing, scavenging, cleaning, and recleaning to produce a concentrate with an antimony grade of more than 56 per cent. The recovery of antimony of this grade varies between 80 and 88 per cent, depending upon the head grade and mineralization. Gold is also recovered in the flotation concentrate at grades of between 25 and 40 g/t.

The circuit is shown in Fig. 7 and comprises 4 parallel rougher banks, 4 parallel scavenger banks, 2 cleaner banks, and a reclaimer bank. Each of the rougher and scavenger banks consists of six Denver No. 24 cell-to-cell flotation units, followed by four Wemco No. 56 cells. Each of the cleaner and reclaimer banks comprises six Denver No. 18 cell-to-cell flotation units. Additional flotation capacity in the form of 3 Wemco No. 144 units is currently being evaluated on the scavenger section with a view to complete replacement of the flotation cells with large-capacity units.

Lead nitrate is used as an activator for the antimony flotation, with sodium isobutyl xanthate as a primary collector. Aero promoter 208, a dithiophosphate, acts as a secondary collector for antimony and a promoter for gold flotation. The dithiophosphate has an alcohol base and doubles as a frother, although small amounts of other alcohol-based frothers are used occasionally. Dextrin is used as a gangue depressant since the ore is of a talcose nature. The ore is naturally alkaline owing to the presence
of dolomite as a major gangue constituent. Sulphuric acid is therefore used to control the pH: pH 6.8 to 7.0 in the roughers, pH 6.5 to 6.8 in the scavengers, and pH 6 to 6.5 in the cleaners.

Stibnite (Sb₂S₃), which has an antimony content of 71.68 per cent, is the major source of antimony in the ore, and is floated readily by the reagents in current use. Studies indicate that stibnite losses to the tailings are minor, and occur as a result of either surface oxidation or overgrinding. Some loss may also occur with coarse grinds, particularly with ore from the Alpha Shaft, where finely disseminated stibnite commonly occurs in the matrix of the hard quartz gangue.

Berthierite (Fe₅S₇) and gudmundite (Fe₅S₈), which contain 56.95 and 58.07 per cent antimony respectively, represent the major remaining source of antimony, varying between 10 and 35 per cent of the total. These minerals are relatively slow floating, and contribute most to the recoverable antimony lost to the plant tailings.

Plant and laboratory experience has shown that, at reduced pH, the floatability of berthierite and gudmundite, together with that of the oxide minerals of antimony, is enhanced. The pH of the scavengers is therefore controlled between 6.5 and 6.8. As a result of the lowering of the pH in the scavengers, more arsenic reports to the scavenger concentrate, which is therefore subjected to a regrind for polishing before being returned to the head of the roughers for further arsenic suppression and antimony recovery.

Native antimony and the antimony oxide minerals cerrvantinite, valentinite, and senarmontite are generally minor constituents of the total antimony mineralization. These minerals do not respond easily to flotation.

The presence of other sulphide minerals such as galena and complexes of lead, mercury, and antimony is of limited importance. However, they contribute to the level of impurities in the final flotation concentrate and may make some batches of concentrate undesirable for certain end-users. No effort is being made at present to control these impurities.

At present, the final concentrate grades are routinely controlled on the basis of half-hourly sulphur analyses of the final concentrate. The results obtained are extrapolated to give the antimony grades, and are used in the adjustment of the mass pull from the cleaner circuit (2 to 2.5 per cent). This method is unreliable when the proportion of stibnite to other minerals such as berthierite and pyrite in the plant feed changes markedly. Low antimony grades have resulted periodically from such changes in mineral composition. Furthermore, no rapid estimate of the arsenic grade can be made by this method. The control method is therefore being changed to produce routine antimony and arsenic analyses by X-ray techniques. A typical analysis of the concentrate is given in Table II.

The need to depress arsenic within the flotation circuit adds complexity to the overall flotation process. Arsenopyrite—FeAsS—and gersdorffite—(Fe,Ni,Co)AsS—of which arsenopyrite is the more common, represent the two major arsenic minerals within the ore (in which the arsenic concentrations vary between 0.1 and 0.3 per cent).

Natural depression of arsenopyrite is enhanced at alkaline pH owing to absorption of the hydroxide ion at the positive iron sites in the crystal lattice. Authors differ as to the precise mechanism involved in this depression, but Vreugde has suggested that the depression occurs as a result of the formation of a ferric hydroxide surface layer that does not respond easily to the primary collector reagents. The natural depression is prevented at low pH ranges, thus promoting flotation of the arsenic minerals. It is at these pH values, 6 to 6.8 as previously...
discussed, that the antimony minerals berthierite and gudmundite are also promoted. Sodium cyanide is therefore used to depress the flotation of arsenic minerals.

It has been shown\(^1\) that the depression of arsenopyrite by cyanide is at a maximum at high pH (above 7.8), although some depression is evident at lower pH levels when the concentrations of cyanide are high (above 100 mg/l). It is at these high concentrations of cyanide that the depression of stibnite\(^2\) becomes evident.

Little is known about the flotation characteristics of gersdorffite. Plant trials involving the batch treatment of ores from the various operational shafts showed that the depression of arsenic was most difficult to control with the arsenopyrite-rich ore from the Monarch East Shaft. This indicates that gersdorffite is reasonably well controlled by cyanide additions, while the competing factors previously discussed lead to poorer control of arsenopyrite.

The cyanide addition is split, 50 per cent of the total dosage (50 to 80 p.p.m.) being fed to the rougher feed and the balance being distributed between the feed to the cleaner and that to the recleaner bank. The pH in the cleaner and recleaner bank is controlled between 6 and 6.5 to minimize the depression of stibnite. However, this leads to excessive consumption of cyanide.

Cyanide appears to have a transient effect on the depression of arsenic minerals, and an inverse relationship is evident between the arsenic and antimony grades: as the antimony grade decreases down the flotation bank, so the arsenic grade increases. Fig. 8 shows the effectiveness of cyanide depression on the arsenic minerals.

The use of cyanide as a depressant for arsenic not only tends to inhibit the flotation of stibnite at high concentrations but also leads to the partial dissolution of gold in the flotation circuit (3 to 7 per cent of the total gold input). Scavenger carbon columns have been installed on the various water circuits in the plant in order to recover this gold.

In summary, the current flotation practice represents a series of competing interactions between the various reagents and mineral species aimed at optimizing the recovery of antimony and gold while maintaining acceptable concentrate grades. These interactions are summarized qualitatively in Tables IV and V.

**Leaching, Filtration, and Drying**

Some 30 to 40 per cent of the gold in the plant feed is recovered during flotation with the antimony concentrate, which analyses 25 to 40 g of gold per ton. The concentrate is therefore scavenged over a further set of manual corduroy tables in an attempt to recover any remaining coarse free gold. Thereafter, the concentrate is subjected to a low-alkalinity high-pressure cyanidation
leach in a ‘pipe reactor’ to recover additional gold prior to filtration, drying, and bagging. This leaching process has been described by Muir. Gold is recovered from the pressure-leach liquor as it passes through a series of eight (2,1 by 0,78 m) columns containing activated carbon.

After thickening, the flotation concentrate is filtered on two Oliver 2,44-by-2,44 m drum filters (with a cake moisture content of approximately 14 per cent), and is dried to below 1 per cent moisture in a thermo-venturi drier fired by coal-tar fuel. The dried product is bagged according to customer requirements into either paper bags (40 kg per bag) or bulk bags containing approximately 1,4 t each. The bags are palletized (each pallet containing 36 of the smaller paper units) and formed into ‘reserves’ of 22 or 44 pallets each for marketing. If the ‘reserves’ are marketed as sulphide concentrate overseas, they are railed from the Mine to Durban for containerization and subsequent export. Fig. 9 shows the leaching, filtration, and drying circuit.

Disposal of Tailings

Flotation tailings are thickened in two thickeners of 22,9 m diameter prior to being impounded on the tailings dam. The tailings are cycloned prior to thickening, the cyclone underflow and thickener underflow being recombined for combined treatment.

The tailings are impounded in a complete ring-dyke deposit constructed according to an upstream method. The outer walls of the impoundment are constructed in an unconventional manner, which is a cross between the ‘wet’ method employed in conventional base-metal operations and the ‘semi dry’ method used in most gold mines.

This method involves the erection of a temporary vertical 0,45 m high steel plate, which acts as a mould for initial beach formation. With each successive stage of deposition, a shallow trench is dug 0,45 m in from the current edge of the dam. A series of steel plates 2,4 m long by 0,45 m high are installed vertically in the trench and sealed into position. Slurry is then deposited from the ring-type spigot line against the vertical plates to form a beach. Once this beach has been established, the slurry flow is redirected towards the centre of the impoundment. The backing plates are removed once the beach has dried, and are moved to the next area to be developed. Thus, the outer wall of the dam has a stepped appearance angled at 27 degrees. The impoundment is similar in construction to a conventional ‘wet’ dam in all other respects.

Production of Crude Antimony Trioxide

Antimony sulphide concentrate is the final product produced by Consolidated Murchison but, with the increasing demand for antimony trioxide in the 1970s, a new plant known as the Antimony Products (A.P.) plant was commissioned at the Murchison Mine in 1974 to produce crude antimony trioxide.

Typical crude oxide analyses 81 to 82 per cent antimony, and comprises approximately 97 per cent antimony trioxide, the balance being various deleterious constituents. (Table II gives a typical analysis of the crude oxide.)

Crude oxide is produced by a volatilizing roast of the sulphide concentrate in a rotary kiln according to the reaction

\[ 2 \text{Sb}_2\text{S}_3 + 9 \text{O}_2 \rightarrow 2 \text{Sb}_2\text{O}_3 + 6 \text{SO}_2 + 287 \text{kJ.} \] (1)
Depending upon the grain size, the reaction begins at between 290 and 430°C, and reaches maximum intensity at approximately 500°C. However, the vapour pressure of antimony trioxide is low at these temperatures, and good recoveries are achieved only at 1000 to 1100°C. Since stibnite boils at 857°C, it is likely that the above reaction occurs partly in the gaseous phase. The process is best described in stages: roasting, cooling, bagging, and finally deslagging.

Roasting

The conversion of stibnite to oxide at the A.P. plant is carried out by the Chemetron Process, which is classical in respect to the roasting operation but has unique features embodied in the oxidation and cooling control.

The plant comprises six independent lines, one of which is shown in Fig. 10. Energy for firing the kilns is supplied by a 2 m-diameter Wellman predistillation raw-gas producer, which generates producer gas from coal to supplement the energy generated in the exothermic reaction shown in equation (1). The kilns are 1,82-by-7,62 m rotary kilns lined with super-duty fireclay refractory bricks.

Until recently, stibnite was fed to the kilns in 40 kg paper bags at the rate of approximately 4 bags every 15 minutes. This method was labour-intensive, difficult to control, and costly with regard to packaging materials. A system for feeding the kilns from bulk bags was therefore designed and has recently been commissioned.

The stibnite concentrate is discharged from bulk bags into a hopper before being screened for the removal of agglomerated material. It is then elevated into two primary storage hoppers. From these hoppers, the material is transported to feed hoppers above each kiln by means of a bucket elevator-and-screw conveyor system. From the feed hopper, the material discharges via a rotary valve to a kiln-feed screw conveyor, which is located on a movable trolley. The kiln is fed when the discharge end of the screw feeder is moved into the mouth of the kiln every 1,45 minutes by a hydraulic ram. The feeding sequence is pre-programmed to deliver approximately 450 kg of concentrate per hour. The entire kiln-feeding system from the primary storage hoppers is designed to be fully automatically controlled by a Temptron 9001 programmable controller.

The kilns rotate in a clockwise direction (feed end), and the concentrate is carried under the gas burner by the rotation of the kiln, causing reaction (1) to proceed. Temperatures in the kiln are in the range 1100 to 1200°C. The flow of air through the kilns is maintained by a centrifugal fan (which draws 280 m³/min) situated at the header end of the product baghouse.

Cooling and Bagging

At the discharge end of the kiln is an adjustable quench shroud, which allows cool air to be drawn into the system to join the vapour-laden discharge from the kilns. This shroud is adjusted so as to ensure a high throughput through the kilns while at the same time allowing a rapid drop in kiln exit temperature to below 800°C. Sublimation of the vapour phase occurs mainly at that point, forming fine particles of oxide.
After the quench shroud, the air flows through a series of stainless-steel hairpin cooler pipes in which heat is lost to the atmosphere. These cooling pipes are known as primary and secondary coolers, and the air entering each stage is about 480 to 300°C and 380 to 250°C respectively.

The higher oxides of antimony, primarily $\text{Sb}_2\text{O}_5$, form larger particles in the initial cooling and tend to drop out in the primary coolers. In addition, some bypassing through the kiln may occur, and this coarse, unconverted material may also drop out at this stage. Being impure, dropout from the primary coolers is recycled to the kiln feed.

The oxide tends to form loose powdery formations on the pipes, which are equipped with vibrators to discharge the material. Dropout from the secondary coolers is removed from the hoppers at the base of the cooler by means of a screw conveyor, which feeds the oxide to a pneumatic conveying system. This consists of a positive pressure blower that creates an airstream in transmission piping. The oxide is thus transferred to a product storage hopper.

An adjustable louvre after the secondary cooling pipes allows further air into the main ducts to reduce the final temperature of the stream entering the dust-collection baghouse to below 100°C.

In the product baghouses, the fine antimony trioxide dust is filtered from the airstream on Nomex filter sleeves, which are cleaned cyclically by a reverse-pulse air system. The oxide drops off the bags and is conveyed pneumatically to the final-product storage hopper. The filtered air, which contains sulphur dioxide off-gas, is vented to the atmosphere via a 61 m stack.

The final product is bagged into bulk bags and palletized for export or retreatment to produce fine oxide. A typical analysis of this material is given in Table II.

**Deslagging**

The gangue in the stibnite concentrate, which consists mainly of talc [Mg₃Si₅O₈(OH)₂], dolomite (Ca,MgCO₃), and chlorite (Mg,Fe,Al silicate complex), forms a pastelike slag in the kilns. The build-up of slag within the kilns depends upon the grade of concentrate, but a slag load of 8 to 9 t is reached after a period of 5 to 6 days. At that stage, a so-called 'burndown' cycle begins, the object of this process being to fluidize the slag so as, firstly, to maximize the recovery of any remaining entrained antimony and, secondly, to facilitate the removal of slag from the kilns. The feeding of concentrate to the kilns is stopped and, during the initial stages of the operation, coke is fed into the kilns to reduce any higher oxides of antimony to the metallic antimony form. In addition, the burner fuel is supplemented with diesoline and with oxygen enrichment (when necessary) of the burner air supply. As a result, the kiln temperatures rise to approximately 1300°C, and a fluid slag bed is formed. The antimony content of the slag drops as the antimony is burnt off.

Once the slag can be seen to have ceased fuming, it contains typically less than 12 per cent antimony and the energy input to the kilns is stopped. The molten slag as it cools forms balls up to 20 cm in size. When the kiln temperature has dropped below 550°C, the slag is mov
ed manually from the kiln with long-handled spoons. The recovery of antimony during the process depends on the grade of the feed concentrate. Typical recoveries are in the range 93 to 96 per cent, with roughly 3 per cent of the antimony being lost to the slag. Gold in the concentrate feed to the A.P. plant reports to the slag, which is subsequently treated by milling and flotation to recover the gold as a slag concentrate. This concentrate is then exported for the treatment and recovery of gold.

**Competing Reactions**

Arsenic and other volatile metals follow the same route as the antimony during the oxidation process, and must therefore be controlled during the flotation stage as previously described if saleable oxide grades are to be achieved.

Klin-feed rates, burner positioning, and cooling rates have been found to be important parameters in the process control of the product grade and recovery owing to the reactions that compete with the basic reaction previously outlined. Between 500 and 900°C, higher non-volatile oxides of antimony may be formed, leading to excessive losses to the slag. However, these oxides decompose (Table III) if no excess oxygen is present above 930°C. In addition, antimony sulphide melts at 546°C and tends to form oxysulphides with antimony trioxide. This reaction is favoured with high-grade ores in an air-deficient environment. These oxysulphides may produce a glasy coating on the ore particles that can seriously impair the oxidation reaction. With the current operating parameters, 95 per cent of the oxide is in the form of the cubic mineral senarmonite (Table III), the balance (about 5 per cent) being in the greyish rhombic form of valentine. Incorrect plant practice could lead to a shift in the balance between these forms, with subsequent discoloration of the product.

**Environmental Control**

One of the major problems associated with this type of process (in view of the extremely fine nature of the product) is control of the dust. While antimony chemicals must be considered toxic, antimony trioxide is almost innocuous because of its extremely low solubility in body fluids. An accumulation of dust may show on chest X-rays and is reported as antimony pneumoconiosis, but it is not accompanied by functional disturbance. Symptoms of dermatitis, especially if the oxide is in contact with perspiration, have been recorded. The contaminating elements within the oxide, primarily arsenic, are known to be carcinogenic at high levels.

Continuous efforts have been made to maintain plant hygiene, and the steps taken by management to control this problem in recent years include general refurbishment of the plant and hygiene baghouses over the kiln feed, the installation of a new kiln-feeding system, routine use of medicated soaps, daily washing of all overall, and the use of "air stream helmets" to provide personnel in high-risk areas with filtered air to breath. Plants in the U.S.A. are striving to achieve a target dust threshold limit value (T.L.V.) of 0.5 mg per cubic metre of air. As a result of measures taken at the A.P. plant, atmospheric dust levels in the plant are now approaching this value.

**Production of Refined Antimony Trioxide**

End-users of antimony trioxide require compliance with rigid specifications in regard to the purity of the oxide, grain size, and coloration. The crude oxide produced by the A.P. plant comprises approximately 97 per cent antimony trioxide, the balance being deleterious waste constituents. The crude oxide has a variable off-white colour and a variable particle-size analysis.

Refined antimony trioxide running at 99.5 per cent purity is produced by the refining of the crude oxide under rigidly controlled conditions in order to meet individual consumer specifications with respect to the aforementioned critical parameters. The chemistry of the processes used again depends on the formation of the various oxides as previously described but, owing to the competitive nature of the oxide market, specific details of plant design and the methods of control used are regarded as confidential. Prior to 1982, the majority of crude oxide was exported to Europe and the U.S.A. for refining.

**Production of Antimony Metal**

Although antimony metal is not produced in South Africa, some information on the methods used is given to complete the review.

Antimony metal is commonly produced by the reduction smelting of oxides (crude powdered oxides or oxide ores) with carbon in the form of charcoal, coke breeze, or anthracite fines according to the reactions

\[
Sb_2O_3 + 3C \rightarrow 2Sb + 3CO \\
Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2
\]

Current practice is to carry such reactions out in small blast furnaces, reverberatory furnaces, or short rotary-drum furnaces.

The metal can also be produced by direct smelting of sulphide and mixed antimony ores in blast furnaces according to the reactions

\[
2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6S0_2 \\
2Sb_2S_3 + Sb_2S_3 - 6Sb + 3S0_2 \\
3Sb_2S_3 + 9O_2 \rightarrow 6Sb + 9S0_2
\]

A hydrometallurgical route involving leaching in alkaline hydroxides and sulphides, forming antimonite and sulphantimonites with subsequent electrowinning of antimony metal, has also been used in the U.S.A. In addition, numerous extraction methods for the recovery of the metal from secondary sources have been used.

Further details of the various smelting processes used are given by Werner and other authors.

**Uses of Antimony**

The historical aspects of antimony usages have already been briefly reviewed. At present, antimony usage can be divided into two broad categories: uses in alloys, and uses in the oxide form. Owing to its poor mechanical properties, antimony metal is not used directly but is used in numerous alloys, primarily with lead and tin. The more important of these alloys and oxides are detailed below.

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Antimonial (Hard) Lead

The addition of antimony to lead increases the tensile strength of cold-rolled lead from approximately 16.6 MPa to approximately 32.1 MPa for an 8 per cent antimony alloy. Uses include storage-battery grids (7 to 12 per cent antimony), small-arms ammunition (12 to 15 per cent antimony), and cable sheathings and lead piping (1 to 9 per cent antimony). Lead piping is used in many applications that require acid-resistant pipe coils.

Antimonial lead (1.5 to 3 per cent antimony) is used in the grid plates, straps, and terminals of lead–acid batteries. The addition of antimony to lead improves the fluidity, making the casting of battery grids easier; moreover, the tensile strength is increased, and the thin grids are able to withstand the stresses imposed by the charging and discharging reactions during battery use. There is also an improvement in the electrochemical stability of the lead.

Tin-based Babbitts

Tin-based babbitts consist of either ternary tin–antimony–copper alloys or quaternary tin–antimony–copper–lead alloys containing 4.5 to 14 per cent antimony, and are used for low-load bearings that have good anti-seize properties and corrosion resistance but low fatigue strength.

Lead-based Babbitts

Lead-based babbitts are alloys of antimony, tin, and lead containing 8 to 15 per cent antimony, and may contain 1 to 3 per cent arsenic. They are used for heavy-duty bearings where fatigue resistance is important, e.g., in railways.

Type Metals

Alloys of lead and antimony containing 2.5 to 25 per cent antimony are used in the printing industry. Antimony lowers the casting temperature, increases the hardness, and minimizes the shrinkage during freezing.

Britannia Metal and Pewter

Britannia metal and pewter are alloys consisting primarily of tin with approximately 2 per cent copper and 7 to 20 per cent antimony, and are used in the manufacture of vases, lamps, candlesticks, tea and coffee services, etc. The antimony raises the hardness of the metal and permits a highly polished surface to be obtained.

Solders

Antimony is added to solders to increase the hardness of the tin–lead alloys. The antimony content is typically less than 1 per cent but may be as high as 13 per cent for certain applications. Solders are used in numerous applications such as electrical equipment, the end–and side-seams of cans, car radiators and other plumbing, and as a car-body filler to fill gaps in spot-welded seams.

Semiconductors

Minor amounts of antimony are used as dopants in the manufacture of n-type semiconductors and in the manufacture of Group III–V intermetallic semiconductor materials such as indium, aluminium, and gallium antimonide for the substrates of light-emitting diodes (LED). Other minor alloys include white metal and tin die-casting alloys.

Antimony Trioxide

The uses of this compound can be divided into two broad categories: as flame retardants and non-flame retardants.

When antimony trioxide is in intimate contact with a halogen, it imparts (as previously discussed) flame-retardant properties to various materials. Ineffective on its own, the antimony must be intimately associated with the halogen, which is usually present as a chlorinated alkyd, a polyvinyl chloride resin, or a chlorinated plasticizer. A theory commonly used to explain this phenomenon recognizes that the primary mechanism concerns the generation of antimony trihalide and/or oxyhalide. Antimony halides promote reactions that cause the formation of carbonaceous char, rather than of volatile gases. This char then acts as a heat shield that retards the breakdown of the plastic, thus preventing flammable gases from being released.

As an additive in plastics, antimony trioxide also acts as an opacifier. This is sometimes an undesirable characteristic if one wishes to control the additive levels of colorants. It has been found that, in order to minimize colorant requirements while retaining flame retardancy, the oxide particles should be 2 to 3 μm larger than the grain of standard pigments. Savings of up to 30 per cent in pigments can be achieved if the average grain size is increased from 1 to 3 μm. This fact explains the need for the fine control of particle size during the final refining of the antimony trioxide.

The market for antimony trioxide has expanded rapidly since 1972, and the material is now used as detailed below:

- Polyvinylchloride for conveyor belting in mines, cable coverings, and coated fabrics for wall coverings, furniture, cushion covers, etc.
- High-impact polystyrenes for television backs and domestic electrical appliances, and as housings for electronic equipment (including home computers).
- Polyethylene and polypropylene, which is used primarily for wire sheathing and ducting to carry electrical services in buildings.
- Polyamides and engineering plastics such as nylons for automotive uses, industrial equipment, and electrical moulded parts.
- Unsaturated polyesters for applications such as building panels, automotive parts, and lifeboat hulls.

The major uses of antimony trioxide as a non-flame retardant are as follows:

- In pigments, particularly in the manufacture of chromate pigments.
- As an opacifier for ceramic glazes and as a frit.
- In the refining of lead glass for crystal applications and glass for television tubes. The oxide acts as a refining agent to remove colour and gas bubbles. Sodium antimonate is also used for these purposes.
- As a polymerization catalyst in the manufacture of polyester fibres.
**Other Uses of Antimony Chemicals**

Antimony and antimony salts are used for a number of minor applications, including the following.

- **Medicinal uses.** Antimony compounds have known therapeutic and toxic properties. Organic antimony compounds such as tartar emetic (potassium antimonyl tartrate) and fuadin are used in the treatment of certain tropical diseases such as bilharzia.
- **In certain pesticides.**
- **Ammunition primers, flares, tracer shells, and fireworks (black powder).**
- **Vulcanizing of red-rubber compounds (Sb₂S₃).**
- **Mordants.**
- **As a lubricating agent in the manufacture of disc-brake pads and cutting discs.**

**Effects of Some Impurities on End-uses**

The need to control impurities during the beneficiation stage was discussed previously, the most important effects of these impurities being outlined below².

1. **Arsenic renders alloys brittle and must be controlled below 0.08 per cent in certain storage-battery grids.** It is also suspected of being carcinogenic, and its level must be controlled in materials for export to Europe and the U.S.A.
2. **Lead impairs the colour and lustre in some tin-based alloys.**
3. **Copper affects the properties of various alloys.**
4. **Zinc renders alloys pasty during pouring.**
5. **Iron elevates the fusion point of alloys.**
6. **Nickel is undesirable for the manufacture of battery grids.**
7. **Other transition metals such as selenium and mercury give rise to undesirable tints in antimony trioxide, which is white.**

**World Antimony Market**

The antimony-producing industry is ultimately controlled by the fortunes of the major antimony consumers in the world, namely the automobile, construction, and consumer-durable industries. The market demands and price trends for antimony in recent years have reflected the inherent cyclical nature of these industries, which is compounded by the overproduction of primary producers, particularly of small operators during market upturns, followed by oversupply and severe price discounting during the ensuing market downturns³.

**Antimony Production**⁴

The estimated world reserves of antimony are shown in Fig. 11, which shows that the majority of the world’s reserves occur in Eastern Bloc countries, primarily China. During the period 1975 to 1983, 72 per cent of the world’s antimony supply originated from Western countries, with the balance of only 28 per cent coming from the Eastern Bloc. Four major producing countries accounted for 70 per cent of the world’s supply during the same period: Bolivia, South Africa, China, and the U.S.S.R. The remainder of world production originates from minor antimony industries in the following countries: Canada, Mexico, Peru, U.S.A., Australia, Burma, Malaysia, Thailand, Austria, France, Italy, Spain, Turkey, Yugo-

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1. **Approximately 90 per cent of the primary antimony production is derived from main-product mines, the remainder being a byproduct of various lead-zinc, copper, silver, and gold operations.**
2. **Consolidated Murchison, South Africa’s only antimony producer, is the largest single producing antimony mine in the world. South Africa annually produces between 12 and 14 kt of sulphide concentrates at grades of between 57 and 60 per cent antimony. Bolivia, traditionally the Western World’s largest producer, continues to experience severe production shortfalls due to recent political-economic problems⁵, and is now operating at ap-
TABLE VII
PRODUCTION OF PRIMARY AND SECONDARY ANTIMONY IN THE U.S.A. (IN TONS OF CONTAINED ANTIMONY)

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<tbody>
<tr>
<td>Primary production*</td>
<td>14320</td>
<td>14880</td>
<td>16770</td>
<td>11600</td>
<td>12570</td>
</tr>
<tr>
<td>Secondary production</td>
<td>21910</td>
<td>18050</td>
<td>18010</td>
<td>15060</td>
<td>12700</td>
</tr>
<tr>
<td>Total</td>
<td>36230</td>
<td>32930</td>
<td>34780</td>
<td>26660</td>
<td>25270</td>
</tr>
<tr>
<td>Primary production as a percentage of total production</td>
<td>39.53</td>
<td>45.19</td>
<td>48.22</td>
<td>43.51</td>
<td>49.74</td>
</tr>
</tbody>
</table>

* Mine production plus production from imported concentrates
† Estimated

approximately 35 per cent of its capacity. Large amounts of Chinese material were imported into the U.S.A. in 1984, and China has the potential for massive production increases since approximately 50 per cent of the world's reserves occur in that country.

The secondary production of antimony is significant, as can be seen from Table VII. A major source of secondary antimony in recent years has been the battery industry resulting from the advent of the calcium-lead maintenance-free battery. It is estimated that some 200 kt of secondary antimony must have been recovered from batteries during the past ten years and diverted to other markets. However, the battery industry is again becoming a consumer of primary antimony metal.

Demand for Antimony

World markets for antimony have changed markedly since the early 1970s owing to the advent of maintenance-free batteries and the enforcement of the use of flame retardants. Whereas traditional batteries contained approximately 6 per cent antimony alloys, current batteries produced in the U.S.A. comprise approximately 1.5 per cent antimony alloys, while European batteries contain approximately 3 per cent antimony alloys. Fig. 12 shows the U.S. consumption of primary antimony by metallic and non-metallic end-uses for the period 1960 to 1984, which clearly illustrates the decline in metallic-antimony markets and, conversely, an increased consumption of oxides.

Fig. 12—U.S. consumption of primary antimony by metallic and non-metallic end-uses, 1960–1981
The consumption of antimony chemicals by the Western World, principally in flame retardants, is currently estimated to be about 40 to 55 kt per annum, while other end uses account for 20 to 30 kt per annum.

**Oxide Demand for Antimony**

Table VIII shows the world consumption of antimony oxides. By far the largest use of antimony as a flame retardant is in plastics. Consumption in this area is the fastest-growing, having averaged 7 per cent per annum between 1974 and 1981. It is estimated that the overall demand for antimony oxide in flame-retardant formulations will grow at an annual rate of 3 to 4 per cent. A breakdown of the various end-uses of the oxide in Europe is given in Table IX. Consumption in the plastics industry is further divided by polymer categories in Table X.

<table>
<thead>
<tr>
<th>Market</th>
<th>Annual consumption kt</th>
</tr>
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<tbody>
<tr>
<td>North America</td>
<td>20</td>
</tr>
<tr>
<td>Europe</td>
<td>16</td>
</tr>
<tr>
<td>Far East</td>
<td>8</td>
</tr>
<tr>
<td>U.S.S.R./Eastern Europe</td>
<td>3</td>
</tr>
<tr>
<td>China</td>
<td>2</td>
</tr>
<tr>
<td>Scandinavia</td>
<td>1</td>
</tr>
<tr>
<td>South America</td>
<td>0.7</td>
</tr>
<tr>
<td>Middle East</td>
<td>0.7</td>
</tr>
<tr>
<td>Australia</td>
<td>0.3</td>
</tr>
<tr>
<td>Africa</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Demand for Antimony Metal**

In 1984 the total estimated antimony content in the Western World's stock of batteries was some 100 to 150 kt in a population of 379 million vehicles. Demand in the U.S. battery industry declined, however, from some 13.75 kt of antimony in 1977 to 7.36 kt in 1982, of which only 5 per cent was primary antimony. Opinions regarding the outlook for antimony in storage batteries differ considerably. One group believes that a further decrease in the consumption of primary metal will result from improvements to the calcium–lead battery (which tends to develop problems during very 'deep' discharges). The other school of thought holds that either a low-antimony lead–acid battery or a hybrid type of battery in which the positive grids are made of 1.5 per cent antimonial lead and the negative grids from calcium lead will supersede the current calcium–lead battery. Indications are, however, that the battery industry has once again become a net consumer of primary antimony.

Other metallic applications of antimony have traditionally taken minor amounts of the metal; these, with the exception of the solder market, have shown a general downward trend since 1972.

**Acknowledgements**

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*1 MTU = 10 kg of contained metal.*
References


Engineering awards

On 20th March, 1986, Mr Robin Plumbridge, Chairman and Chief Executive Officer of Gold Fields of South Africa Limited, announced the recipients of the Gold Fields Foundation's National Engineering Awards for 1985. He also announced a restructuring of the awards, which involves substantial increases in prize money from next year, when Gold Fields celebrates its centenary. The first prize will be increased from R5 000 to R10 000, and the second prize will be R5 000, with the remaining five prizes rising to R1 000 each. In addition to the increased value of the individual prizes, awards of R10 000 each will go to the university faculty, and to the department within the faculty, of the recipient of the first prize.

As a rule, each university affiliated to the South African Federation of University Engineering Students (S.A.F.U.E.S.) selects a candidate who in its opinion presented the most outstanding design project in his/her final year. The candidates are assessed on written and oral presentations of their theses by a panel of judges nominated by Gold Fields, and for this year the judges were Professor George Round, visiting Mechanical Engineering Professor from McMaster University, Ontario, Canada; Mr Ron Heydenrych, a Civil Engineer and a Senior Partner in Ove Arup Inc.; Mr Bodo Schmitz, head of the Gold Fields group's Mechanical and Electrical Engineers' Division; and Mr Peter Janisch, General Manager, New Business, Gold Fields.

The 1985 candidates were as follows:

WINNER: Martin Weiss
Thesis: 'Baby Screening Audiometer'
Born 17th October, 1961, in Pretoria, he enrolled at the University of Pretoria for B.Eng. (Electronics) in 1980. He is the only candidate who will join the private sector in the near future.

RUNNER-UP: Robert Mawrey
Thesis: 'Wideband VHF Converter for the Racal RA 1772HF Receiver'
Born 30th April, 1964, in Durban, he started his studies towards a B.Sc. Eng. (Electronics) at the University of Natal in 1982. Having completed that degree at the end of 1985, he is now working towards an M.Sc. Eng. (Electronics) at the same University.

Con-Vivier Venter: Rand Afrikaans University
Ian Lowitt: University of the Witwatersrand
Hubertus Otto-Wilhelm von Petersdorff: University of Stellenbosch
Pieter Erasmus: University of Potchefstroom.

Refractories for continuous casting

The Institute of Ceramics of the Technical University of Aachen, the Refractories Research Institute in Bonn, and the Verein Deutscher Eisenhüttenleute (VDEh) in Düsseldorf are holding the XXIXth International Colloquium on Refractories on 9th and 10th October, 1986, in Aachen (Germany). The theme is 'Refractories for Continuous Casting'. The subject covers all problems arising from the properties of the refractories used in continuous casting—predominantly in the steel industry—and their behaviour in practice.

The presentations will be in German, English, French, or Spanish. Simultaneous translation will be provided in the four languages.

Further details are available from

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Mauerstrasse 5
D-5100 Aachen
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