Chapter 10

Refining of Gold at the Rand Refinery

K.G. Fisher

10.1 Introduction
Since 1921, all gold produced in South Africa has been refined at the Rand Refinery (Adamson, 1972). To give the reader a complete picture of gold refining in South Africa, the historical development and all operations of the refinery are described in detail in this chapter, although some activities cannot strictly be defined as gold refining.

10.2 Historical Development
In the early days of South African gold mining, the crude bullion produced had to be shipped to London for refining. The concept of a local refinery had been considered for several years before the first positive step was taken in 1909, when the Transvaal Chamber of Mines founded the Witwatersrand Co-operative Smelting Works, to treat the gold and silver bearing by-products from reduction works. These by-products required special treatment and were obviously best handled by a central, joint concern under the sponsorship of the Chamber.

Later, in 1917, the South African government proposed the establishment of a local mint and consequently the Pretoria branch of the London Royal Mint was opened in 1922. During the same period the Transvaal Chamber of Mines investigated the possibility of establishing a local gold refinery. The technical aspects were discussed with Sir T.K. Rose, a leading authority on gold metallurgy, and the chlorine refining process was chosen specifically with a view to the rapid and effective treatment of large amounts of bullion. This process had been patented by F.B. Miller, Assayer of the Sydney Mint, in 1867 and used in Australia since 1872 in contrast to the London and continental refineries which were still using the sulphuric acid (parting) process.

On 27 November 1920, Rand Refinery Limited was registered as a private company with initial capital of £50 000, raised from shares limited to gold mining companies that were members of the Transvaal Chamber of Mines. A further £165 000 was borrowed and secured by registered debentures. Following a comprehensive survey, the site at Germiston, 16 kilometres east of Johannesburg, was selected because services and rail facilities were available and its position was the geographical centre of the Witwatersrand gold mining area.

By December 1921, the refinery was completed with a capacity of 12 million troy ounces (373 250 kg) of fine gold per annum. Designed capacity
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Table 10.1. Throughput of the Rand Refinery
(Year ending 30th September).

<table>
<thead>
<tr>
<th>Year</th>
<th>Bullion received (kg)</th>
<th>Fine gold produced (kg)</th>
<th>Fine silver produced (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1922</td>
<td>133 230</td>
<td>110 362</td>
<td>6 710</td>
</tr>
<tr>
<td>1930</td>
<td>381 732</td>
<td>337 230</td>
<td>31 985</td>
</tr>
<tr>
<td>1940</td>
<td>518 982</td>
<td>457 949</td>
<td>39 273</td>
</tr>
<tr>
<td>1950</td>
<td>436 855</td>
<td>380 196</td>
<td>42 191</td>
</tr>
<tr>
<td>1960</td>
<td>745 761</td>
<td>660 675</td>
<td>67 189</td>
</tr>
<tr>
<td>1970</td>
<td>1 149 945</td>
<td>1 007 603</td>
<td>86 100</td>
</tr>
<tr>
<td>1980</td>
<td>806 505</td>
<td>695 189</td>
<td>77 293</td>
</tr>
<tr>
<td>1983</td>
<td>802 529</td>
<td>690 006</td>
<td>80 275</td>
</tr>
<tr>
<td>1984</td>
<td>800 583</td>
<td>678 199</td>
<td>73 459</td>
</tr>
</tbody>
</table>

was reached within ten years and since then the throughput has increased considerably, as Table 10.1 illustrates.

Modifications and improvements were made to cater for this increasing throughput, but by 1965 it had become necessary to undertake a major four-year expansion programme at a cost of R4 million. Electrolytic gold and silver refining facilities were installed and many new concepts were introduced, including large-scale refining (up to 500 kg per furnace), induction furnaces, mechanical handling and modern analytical techniques.

At the same time, the old Witwatersrand Co-operative Smelting Works (by then known as By-Products Limited) located in Johannesburg was also in need of large-scale renovations but, because of site limitations, it was considered more economical to build a new plant elsewhere. A suitable site was available at Rand Refinery, so it was decided to amalgamate the two companies and in 1966 the new by-products treatment plant (smelter) was erected alongside the gold refinery. The interchange of products between refinery and smelter was greatly facilitated and support functions (administration, laboratory, assay office, workshops, etc.) were combined with consequent economies in operation.

In 1969, embryonic facilities were installed for the production of alloy and blanks for the Krugerrand family of coins. Owing to the subsequent success of the coin marketing programme, a purpose-built coin blank complex was erected in 1984 at a cost of R4 million. Thus Rand Refinery Limited has developed into a fully integrated complex capable of refining all South African gold bullion and gold-containing by-products and is the largest establishment of its kind in the world, being responsible for approximately 62% of the free world's production of fine gold.

10.3 Function
Rand Refinery Limited is a subsidiary of the Chamber of Mines and operates on a non-profit making basis for the benefit of member companies, but also services the requirements of non-members. The refinery's principal functions
are to refine bullion and recover precious metals from by-product materials received from member gold mines and to sell the refined gold to the Reserve Bank, which credits the mines accordingly. A subsidiary function is now the production of blanks for the Krugerrand and its sub-denominations.

Depositors are credited with fixed percentages of the gold and silver contents of their deposits, less appropriate treatment charges. These percentages are currently (mid-1986):

<table>
<thead>
<tr>
<th></th>
<th>Bullion:</th>
<th>By-products:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bullion:</td>
<td>99,85%</td>
<td>94,00%</td>
</tr>
<tr>
<td></td>
<td>of the gold</td>
<td>of the silver</td>
</tr>
<tr>
<td>By-products:</td>
<td>97,50%</td>
<td>90,00%</td>
</tr>
<tr>
<td></td>
<td>of the gold</td>
<td>of the silver</td>
</tr>
</tbody>
</table>

Periodically a pro rata distribution of the value of any metallurgical surplus is made to members. A vital feature of the whole operation is that of metallurgical control, whereby each of twelve metallurgical centres is required to compile a monthly balance for gold and silver and to explain any loss or gain.

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**Figure 10.1. Simplified flow sheet of Rand Refinery.**

Not shown for simplicity are:
(a) Transfer of by-products to smelter from GRB and SRB
(b) Transfer and returns of samples to assay and chemical laboratories from all departments

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10.4 Metallurgical Operations

10.4.1 Summary description
The metallurgical operations of Rand Refinery are summarised in Figure 10.1, in which it can be seen that the operations can be considered under the following five headings: Gold Refining Branch (G.R.B.), Silver Refining Branch (S.R.B.), Coin blank production, Smelter, and Assaying and chemical analysis.

10.4.2 Gold Refining Branch
10.4.2.1 Flow sheet
As shown in Figure 10.2, incoming bullion is weighed into the melthouse where it is melted down for sampling purposes and recast into bars suitable for the refining furnaces. When the assay and mass have been agreed with the depositing mine, the bullion is delivered to the refinery, where it is refined to 996,0 parts per thousand purity (fineness 9960) by the chlorine injection technique. Most of the refined bullion is cast into 12.6 kilogram monetary bars and is delivered to the Administration department, for sale to the Reserve Bank. Some crude bullion is contaminated with the platinum group metals.
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osmium and iridium (osmiridium), which are not removed by chlorination and such deposits must be further refined by electrolysis. The product of the electrolytic gold section (fineness 9999) is delivered to the Coin Bank Complex for the manufacture of Krugerrand blanks.

Molten chlorides from the refinery are first de-golded, in the de-golding section, by partial reduction with sodium carbonate, then quenched and transferred to the Silver Refining Branch for subsequent silver recovery.

10.4.2.2 Melting and sampling
The average assay of the crude bullion received from the mine is gold 84%, silver 11% and base metals 5%, although any gold assay over 50% is normally acceptable. A standard shape of tapered bar has been adopted by all mines, especially designed to fit face to face in a melting crucible, giving a maximum bar mass of 31 kg. Bars from a single mine are combined in groups of up to four bars each to make up nominal 125 kg "deposits". Each deposit has its mass determined on a beam balance and checked on a second balance (Figure 10.3), the mass being determined to the nearest gram.

It is considered that the only reliable method of sampling heterogeneous alloys such as crude gold bullion is by taking dip samples from the molten mass. For sampling, therefore, each deposit is melted down in an induction furnace crucible and, after a few minutes at peak temperature, four dip samples for fire assay are taken simultaneously by means of a special carbon-
coated mild steel spoon (Figure 10.4), together with a disc sample for X-ray analysis. The mixing induced in the melt by the induction heating method guarantees the homogeneity necessary for accurate sampling. The samples are despatched via a pneumatic conveyor system to the assay office for gold and silver determination. Assays are done in duplicate in two separate assay offices, each office taking two of the spoon samples.

The bullion is cast out manually into 12.5 kg bars on a 1.6 m diameter casting wheel and the solidified ingots are automatically tipped on to a slatted conveyor which conveys them via a cooling trough to a marking table (Figure 10.5). Each ingot is stamped with its original deposit number and the deposit is reweighed to determine its “mass after melting”. Strict control is exercised over any spillage, and crucibles are cleaned after each melt. The deposit is stored in a strong-room, normally overnight, to await its assay results.

The refinery assay is compared with the depositor’s advised assay and any discrepancy greater than 15 parts per 1000 results in possible re-sampling and re-assaying. Upon agreement of the fine gold content, the deposit loses its identity and is subsequently transferred to the refining section. It is seldom that a genuine discrepancy arises in the assays, but such disagreements are generally due to the presence of platinum group metals which interfere with the assay or of excessive amounts of iron which form a separate phase at normal sampling temperatures.
The six furnaces used in this department are stationary 2 000 Hz induction furnaces, employing clay/graphite crucibles which are lowered into and raised out of the furnace on an hydraulically operated platform. A normal deposit is heated for 20–25 minutes using 70 kW at 1200 V to reach a temperature about 100°C above its melting point of approximately 1050°C. Power generation and the cooling water system are shared with the refining room, described in the following section.

10.4.2.3 Refining
Refining of the gold bullion is carried out in seven 500 kg capacity induction furnaces, using the Miller chlorine injection process, whereby all the base metal impurities are converted to their chlorides and hence separated from the gold either as a fume/gas or liquid slag, according to Table 10.2.

In practice, the iron is removed first as gaseous FeCl, followed by lead and zinc chlorides, also in gaseous form. The reaction is therefore quite vigorous and the chlorine injection rate must be limited to control the turbulence. Only when these three elements have been almost completely removed do the copper and silver start to form their chlorides, which are liquids at the reaction temperature of 1150°C, enabling the injection rate to be increased. As the end point is approached, gold chloride fumes start to form and considerable turbulence again occurs. Figure 10.6 shows how a typical reaction proceeds.
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Table 10.2. Chlorination reaction data.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free energy $\Delta G$ at 1150°C (kCal)</th>
<th>Melting point of chloride (°C)</th>
<th>Boiling point of chloride (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{Au} + 3\text{Cl}_2 \rightarrow 2 \text{AuCl}_3$</td>
<td>Positive</td>
<td>Decom. 254</td>
<td>–</td>
</tr>
<tr>
<td>$2\text{Ag} + \text{Cl}_2 \rightarrow 2 \text{AgCl}$</td>
<td>−33</td>
<td>455</td>
<td>1 550</td>
</tr>
<tr>
<td>$2\text{Cu} + \text{Cl}_2 \rightarrow 2 \text{CuCl}$</td>
<td>−30</td>
<td>430</td>
<td>1 490</td>
</tr>
<tr>
<td>$\text{Fe} + \text{Cl}_2 \rightarrow \text{FeCl}_2$</td>
<td>−48</td>
<td>672</td>
<td>1 026</td>
</tr>
<tr>
<td>$\text{Pb} + \text{Cl}_2 \rightarrow \text{PbCl}_2$</td>
<td>−48</td>
<td>501</td>
<td>950</td>
</tr>
<tr>
<td>$\text{Zn} + \text{Cl}_2 \rightarrow \text{ZnCl}_2$</td>
<td>−69</td>
<td>383</td>
<td>732</td>
</tr>
<tr>
<td>$2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$</td>
<td>N/A</td>
<td>306</td>
<td>315</td>
</tr>
</tbody>
</table>

Each 450 kg furnace charge is made up in the melthouse by selecting from the deposits whose assays have been agreed. The ingots, normally around thirty-six in number, are stacked on a pallet, delivered to the refining room and loaded manually into a preheated furnace. Approximately 3 kg of a borax/silica/salt flux is added to absorb extraneous impurities, protect the crucible and inhibit volatilisation.

In normal operation the charge melts in 45 minutes. Thereafter, two tapered graphite tubes, internal diameter 13 mm, are inserted into the molten bullion and linked to the chlorine distribution system by rubber hoses. As shown in Figure 10.6 and described above, chlorination takes approximately 35 minutes. As the molten chlorides fill the crucible they are bailed off into a preheated 6 litre crucible and delivered to the de-golding section. Further flux is added after bailing and three or four bailing/fluxing operations.

![Typical initial concentrations](image)

**Figure 10.6. Chlorination graph.**
are required, depending on the original bullion quality.

The end point of the refining operation is indicated by the smell of free chlorine in the fume and by the colour of the fume, which begins to turn reddish-brown as gold chloride forms. At this point a disc sample is taken from the metal, through the slag, using a special crucible as shown in Figure 10.7.

The sample is conveyed to the laboratory via a pneumatic conveyor, where it is immediately analysed for silver using an EDX (energy dispersive X-ray) spectrometer. If the silver content is less than 0.35%, the bullion is considered sufficiently refined, then chlorine injection is stopped, the pipes removed, and the residual chlorides bailed off and finally skimmed off after thickening with bone ash.

After heating the refined bullion to 1100°C, the furnace is tilted and the bullion poured into a pre-heated transfer ladle which is conveyed by fork truck to a 1000 kg capacity holding furnace. It is normal to transfer two refined charges to the holding furnace before casting out into bars.

Approximately 14 kg of gold is poured from the holding furnace into a pre-heated crucible from which the metal is poured manually into a mould placed on a platform scale, until an increase of 12.6 kg is indicated (Figure 10.8). A soft reducing gas flame is then directed on to the surface of the bar until the surface is solidified. In this way the bar cools from the bottom upwards and shrinkage cavities are avoided; the flame also polishes the bar surface and drives small particles of refractory dust to the edges.

Five such arrangements of scales and polishing flames are placed in front of the holding furnace and as soon as a bar is solidified, it is tipped out of its mould on to a copper carrier and immersed in a quench tank. The mould is replaced ready for another bar. All moulds are pre-heated and given a mould dressing of diesoline smoke. For every twelve bars poured, a pair of dip samples is taken and sent for fire assay. The cooled bars are removed from the quench tank and stamped with a series of code numbers, the trademark and the name “Rand Refinery Limited”. They are then weighed
twice on separate balances (Figure 10.9) and stacked on pallets to await the assay results.

When the assay results are received, the fineness is stamped on the bars, the bars inspected for surface defects and the finally approved bars are delivered to the Administration department, which handles sales and deliveries to the Reserve Bank.

The acceptable mass range for monetary bars is 12,441.4 to 12,752.4
kg corresponding to a range of 400 to 410 troy ounces and the fineness is a minimum of 995,0 parts per thousand, average 996,5.

Seven identical furnaces are used for refining, these being tilting, 2 000 Hz induction furnaces. Normally, power up to 100 kW at 1 200 V is employed for melting but is reduced for refining. The 500 kg capacity clay-lined clay/graphite crucibles are fixed into position with a castable refractory. Crucible life is normally 21 – 27 heats, depending on the bullion refined; base metals, particularly lead, have a deleterious effect on the lining.

The two holding furnaces are of similar design but are fitted with 1 000 kg unlined crucibles, are rated at 220 kW and employ two coil voltages, i.e. 800 V for holding molten metal and 1 200 V for melting ingots or bars.

The refining, holding and melthouse melting furnaces are all fed with 2 000 Hz power from a central station, consisting of five 350 kW frequency converters, up to four of which operate at any one time. The converters deliver power at 800 V which is transformed to 1 200 V and 600 V. These three voltages are supplied to the furnaces as required via a busbar system. Each furnace is equipped with overload protection, coil voltage control, automatic power correction and power metering. The overall load is balanced between the departments to maintain a steady maximum demand. Constant temperature cooling water is distributed to the furnaces from an ice bank/ammonia compressor system, with provision for emergency flushing with mains water in the event of power failure.
10.4.2.4 De-golding
The de-golding room is an extension of the refining room in which the molten chlorides from the refining operation are freed of contained gold before being delivered to the Silver Refining Branch.

The process comprises the addition of sufficient sodium carbonate to the molten chlorides to precipitate some 4% of the contained silver. The reactions are:

\[
\begin{align*}
2 \text{AgCl} + \text{Na}_2\text{CO}_3 &\rightarrow \text{Ag}_2\text{CO}_3 + 2 \text{NaCl} \\
\text{Ag}_2\text{CO}_3 &\rightarrow \text{Ag}_2\text{O} + \text{CO}_2 \\
2\text{Ag}_2\text{O} &\rightarrow 4\text{Ag} + \text{O}_2
\end{align*}
\]

Gold is present either as mechanically entrained particles or as a result of the dissociation of gold chloride, which is unstable. In either case it is more soluble in the metallic phase and is collected by the myriad fine silver droplets produced by reaction (10.3), and the resulting gold-silver alloy settles to the bottom of the melt.

In practice, the molten chlorides are transferred in a 15 kg crucible from the refining furnaces and poured into the crucible of a gas-fired tilting furnace. A furnace charge of approximately 120 kg is heated to 1100°C, at which temperature the borax silica flux from the refining process floats to the surface of the melt and is used to inhibit the volatilisation of silver chloride. Three additions each of 15 kg of sodium carbonate are required; the reaction is quite vigorous and must be allowed to subside between additions. The reaction is complete after about 10 minutes but the furnace is allowed to stand for a further 10 minutes, after which the viscous slag layer is removed and most of the chlorides are decanted into a pre-heated 250 kg capacity transfer ladle. The remaining chloride plus the gold-silver alloy are poured into a 6 litre crucible and cooled to 800°C, at which temperature the chloride is still fluid and is poured off and returned to the gas furnace. The solidified gold-silver button remaining assays about 25% gold, 72% silver and 3% base metal and is tipped out of the crucible and recycled to the refining furnaces.

The ladle containing the “de-golded” (less than 100 ppm) chlorides is hoisted above a rubber-lined mild steel quenching tank containing 350 litres of water and the chlorides are slowly poured via a funnel into the tank. This granulation process produces a finely divided product ideally suited to the leaching process that follows. The tank and contents are delivered to the silver leaching department (see section 10.4.3.2).

10.4.2.5 Electrolytic gold refining
The electrolytic gold refining section fulfils two purposes in the refinery: firstly it provides the means of producing high purity gold, i.e. 9999 fine as opposed to the 9960 fineness of monetary bars, and secondly it provides the means of removing platinum group metals (P.G.M.s) which cannot be removed by chlorination. In practice these two objectives are combined by selecting deposits high in P.G.M.s for electrolysis (after chlorination) to satisfy the
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demand for high purity gold.

The Miller chlorination process is capable of producing high purity gold, but the inevitable volatilisation of gold chloride at low impurity concentrations necessitates elaborate fume collection arrangements to prevent excessive gold losses. Therefore the Wohlwill electrolysis process is preferred, despite its inherent lock-up of gold (and hence operating capital) in electrodes and electrolyte.

The electrolyte used is acidic gold chloride, which ionises thus:

\[
HAuCl_4 \rightarrow H^+ + AuCl_4^- \quad (10.4)
\]

At the cathode:

\[
AuCl_4^- \rightarrow Au^{3+} + 4Cl^- \quad (10.5)
\]

\[
Au^{3+} + 3e^- \rightarrow Au \quad (10.6)
\]

At the anode:

\[
Au^{3+} \rightarrow 3e^- \rightarrow Au^{3+} \quad (10.7)
\]

\[
Au^{3+} + 4Cl^- \rightarrow AuCl_4^- \quad (10.8)
\]

Also at the anode, some gold dissolves in the monovalent state:

\[
Au - e^- \rightarrow Au^+ \quad (10.9)
\]

\[
Au^+ + 2Cl^- \rightarrow AuCl_2^- \quad (10.10)
\]

Consequently, some gold is precipitated close to the anode as a fine sludge:

\[
AuCl_2^- + H^+ \rightarrow HAuCl_2 \quad (10.11)
\]

and

\[
3HAuCl_2 \rightarrow 2Au^{3+} + 2HCl + HAuCl_4 \quad (10.12)
\]

The formation of monovalent gold is known to occur, since the fine gold precipitated near the anode (equation 10.12) has been found to be of higher purity than the anode; also cathode efficiencies based on trivalent gold (equation 10.6) are often greater than 100% (the electrochemical equivalents of \(Au^+\) and \(Au^{3+}\) are 2.45 and 7.35 grams per ampere-hour, respectively).

This formation of monovalent gold is undesirable because the “disproportionation” reaction (equation 10.12) results in excessive cell cleaning requirements and also because, at the high current densities employed, the deposition of monovalent gold at the cathode produces a rough dendritic deposit. Therefore, considerable investigation work has been carried out on this aspect, resulting in various changes to the operating data previously reported. The present operating data are given in Table 10.3.

Anodes are produced in the refining room, by pouring chlorine-refined gold into vertical moulds. The cathode starters are rolled from specially cast billets of recycled cathode. Fresh electrolyte is made up by dissolution of refined gold in aqua regia.

Copper, zinc, platinum and palladium are the major impurities which are soluble in the electrolyte, and because they do not deposit at the cathode they accumulate until the electrolyte must be discarded. The insoluble impurities, mainly iridium, osmium, ruthenium and silver chloride (the electrolyte is saturated with silver), fall to the bottom of the cell and are removed as a sludge. The sludge is largely metallic gold and is returned to the refining room and refined back to anodes. All anode scrap is recycled, so in this
Table 10.3. Operating data — Electrolytic gold refining.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Au content, g/l</th>
<th>Free HCl content, g/l</th>
<th>Temperature</th>
<th>Circulation</th>
<th>Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical</td>
<td></td>
<td></td>
<td></td>
<td>Natural convection</td>
<td>Immersion element</td>
</tr>
<tr>
<td>Anodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrode current density, A/m²</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Current per cell, A</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Voltage per cell, V</td>
<td>1.0 - 1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrode spacing, mm</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mass, kg</td>
<td></td>
<td>16.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dimensions, mm (L x B x Th)</td>
<td>230 x 280 x 12</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>No. per cell</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Life, hr</td>
<td></td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathodes</td>
<td>Composition of starters</td>
<td>9999 rolled gold</td>
<td>999 fine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dimensions, mm (L x B x Th)</td>
<td>320 x 74 x 0.5</td>
<td>12 (3 rows of 4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>No. per cell</td>
<td></td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Final cathode weight, kg</td>
<td>1.0</td>
<td>999 fine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Final cathode purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cells</td>
<td>Material</td>
<td></td>
<td>Glazed porcelain</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dimensions, mm (L x B x H)</td>
<td>465 x 405 x 250</td>
<td>4 banks of 10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

way the insoluble P.G.M.s accumulate in the circuit until it becomes necessary to treat the sludge for their removal.

All the anodes and cathodes are renewed daily. The cathode deposit exhibits a very open porous structure, so in order to remove entrained electrolyte completely, a thorough washing procedure is necessary, comprising two hot water washes, a sodium thiosulphate wash (to remove silver chloride) and two further hot water washes. The final product is delivered to the refining room where it is melted and cast into bars for delivery to the Coin Blank department or, occasionally, as required, cast into special fine gold bars to be sold for industrial use.

10.4.2.6 Fume recovery and sweep treatment
The nature of the various processes in the Gold Refining Branch and also the Silver Refining Branch (see the following section) dictates that comprehensive ventilation measures be applied to the working areas, particularly the furnaces. Furthermore, because the fumes are very rich in gold and silver, the fume and dust collection equipment must be very efficient. Unfortunately, because of the chlorides and moisture in the gas stream, a fabric filter cannot be used, so in this case electrostatic precipitators were selected.

Fumes from all areas are drawn into a common flue delivering to three separate banks of precipitators. Basically the three units are of similar design, being tube and wire types, with mild steel wires suspended in 3 m long,
250 mm diameter tubes. Wire current is 1 mA at the maximum potential of 50 000 V and the gas velocity through the tubes is 0,8 m/sec. The total volume extracted and treated is 31,3 m³/sec, made up as follows:

- Melthouse = 2,8 m³/sec
- Refining = 14,3 m³/sec
- De-golding = 7,2 m³/sec
- Silver bar casting = 2,3 m³/sec
- Silver anode casting = 4,7 m³/sec
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All fume and dust collected from the precipitators is delivered to the smelter plant, and in this way some 350 kg gold and 1 000 kg silver per annum are recovered.

Spent crucibles, furnace linings, chlorine pipes, borax slags etc. are collected in the “sweep” room where they are crushed, rod milled with the addition of zinc dust to reduce chlorides and passed over a spiral concentrator. The metallics are returned to the refinery, while the fines are sent to the smelter plant as “refinery sweep”.

10.4.3 Silver Refining Branch

10.4.3.1 Flow sheet

As shown in Figure 10.11, the quenched chloride is delivered to the silver leaching department, where the silver is separated from the base metals by a leach/reduction process. The resultant silver sponge is cast into anodes and sent to the electrolytic silver plant for final refining.

Doré bullion received from smelter plant and silver bullion purchased from depositors are also refined electrolytically.

The electrolytic silver crystals are finally melted and cast into silver bars and delivered to the Administration department for sale to commercial dealers and banks. Occasionally, unmelted silver crystals are also sold.

![Figure 10.11. Flow sheet of the Silver Refining Branch (S.R.B.).](image_url)

10.4.3.2 Leaching and reduction

Depending on the bullion refined, crude silver chloride received from the G.R.B. assays within the ranges:

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AgCl  =  48 - 70%
CuCl  =  10 - 30%
PbCl₂ =  1 - 7%
NaCl  =  10 - 20%

The sodium chloride is formed during the de-golding operation and, being highly soluble, is easily removed during leaching, so it is necessary here to describe only the leaching of copper and lead, and the problems of silver chloride solubility.

A detailed flow diagram for the leaching and reduction is given in Figure 10.12, which shows that the main leaching step actually takes place in the

![Diagram](image-url)

Figure 10.12. Flow sheet for the silver leaching and reduction process.

de-golding section during the quenching of the molten chlorides. To the 350 litres of water in the quench tank are added 25 litres of 30% hydrochloric acid and 3 kg sodium chlorate. This causes the insoluble cuprous chloride to be oxidised to the highly soluble cupric chloride, according to the following reaction, which is very rapid:

\[
6\text{CuCl} + \text{NaClO}_3 + 6\text{HCl} \rightarrow 6\text{CuCl}_2 + \text{NaCl} + 3\text{H}_2\text{O} \quad (10.13)
\]

At the same time the sodium chloride in the chlorides is dissolved and this in turn increases the solubility of any unreacted cuprous chloride. Most of the copper is thus leached during the quenching operation. The remaining traces are removed during the subsequent washing operations.

The contents of the quench tank after quenching some 250 kg of molten chlorides are deposited on to a pan filter and the filtrate pumped to waste, via scrap iron cementation tanks.

The solids on the filter (i.e. the leached silver chloride) are given a wash with approximately 100 litres of water at 60°C acidified with hydrochloric acid. The solubility of lead chloride is relatively high under these conditions of low chloride ion concentration and high temperature, but six to ten such washes are required to give a filtrate free of lead and copper (as tested with NH\(_4\)OH).

The solubility of silver chloride increases at high NaCl and HCl concentrations and also with temperature, so although most of the silver dissolved in the effluent is recovered from the cementation tanks, it is advisable to control these conditions carefully.

Traces of gold exist in the crude silver chloride and some is dissolved during the leach process by chlorine which is formed by reaction between the hydrochloric acid and sodium chlorate thus:

\[
6\text{HCl} + \text{NaClO}_3 \rightarrow 3\text{Cl}_2 + \text{NaCl} + 3\text{H}_2\text{O} \quad (10.14)
\]

Any dissolved gold is ultimately precipitated in the cementation tanks.

The next step is the reduction of the silver chloride to metallic silver by zinc dust. The six reaction vessels used are 550 litre rubber-lined conical tanks with a more acutely angled second conical bottom section (Figure 10.13). A tank is first part filled with approximately 100 litres of water, then a charge comprising 250 kg of leached, washed chlorides is added. The charge is agitated by rubber-covered mechanical stirrers and air which is admitted through 25 mm diameter pipes from a manifold below the tank. The stoichiometric amount of zinc required is calculated from the reaction equation, which is:

\[
2\text{AgCl} + \text{Zn} \rightarrow 2\text{Ag} + \text{ZnCl}_2 \quad (10.15)
\]

The zinc dust is added in slurry form over a period of 30 minutes. Care
is needed, since the reaction is very rapid and exothermic. At the end of the reduction period, hydrochloric acid is added to pH 2 to dissolve any surplus zinc and the agitation is stopped. The supernatant liquor is decanted through a valve on the side of the tank, leaving the fine silver behind. Three washes with hot acidified water are given, before discharging the silver sponge on to a pan filter via the bottom discharge valve of the tank. The silver sponge from the pan filter is dried in a centrifuge before being charged to a 300 kg capacity gas-fired tilting furnace, where it is melted and cast into anodes for the electrolytic plant.

10.4.3.3 Electrolytic silver refining
Approximately 5 500 kg of anodes from the silver leaching section plus over 1 000 kg from the smelter are refined per month in the electrolytic silver plant.

The relatively pure leach anodes are refined in vertical (Moebius) cells (Figure 10.14), whilst the smelter anodes with their high gold content are refined in horizontal (Thum) cells (Figure 10.15). In both types of cell, the basic electrochemistry is the same and the operating data are summarised in Table 10.4. The significant difference is the gold content of the anodes and hence the amount of sludge fall-out (gold is insoluble in nitrate solutions).
The theory of silver electro-refining is basically simple by virtue of silver's position in the Electromotive Force Series, silver being more noble (electropositive) than the electrolyte impurities copper, lead, iron, zinc etc. and so is plated preferentially. However, it is necessary to ensure that the electrolyte cannot be depleted of silver ions at the cathode, since copper would then plate out. In the horizontal cells, the convectional flow suffices, but in the vertical cells the electrolyte must be constantly agitated by a circulation pump and the cathode scrapers. Daily analysis ensures that there is sufficient free acid present to dissolve chemically some anode silver and so maintain the silver tenor. Left to itself a slow depletion would result, due to the
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Table 10.4. Operating data — Electrolytic silver refining.

<table>
<thead>
<tr>
<th>Type of cell</th>
<th>Moebius (vertical)</th>
<th>Thum (horizontal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Ag content, g/l</td>
<td>30 - 40</td>
</tr>
<tr>
<td></td>
<td>Cu content, g/l</td>
<td>4 - 70</td>
</tr>
<tr>
<td></td>
<td>Pb content, g/l</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Free HNO₂ content, g/l</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>30°C</td>
</tr>
<tr>
<td></td>
<td>Circulation</td>
<td>Scrapers &amp; pump</td>
</tr>
<tr>
<td>Electrical</td>
<td>Anode current, A/m²</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>Current per cell, V</td>
<td>2,0</td>
</tr>
<tr>
<td></td>
<td>Electrode spacing, mm</td>
<td>55</td>
</tr>
<tr>
<td>Anodes</td>
<td>Composition</td>
<td>99% Ag</td>
</tr>
<tr>
<td></td>
<td>Mass, kg</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Dimensions, mm (L×B×Th)</td>
<td>290 × 220 × 20</td>
</tr>
<tr>
<td></td>
<td>No. per cell</td>
<td>8 (4 rows of 2)</td>
</tr>
<tr>
<td></td>
<td>Life, hours</td>
<td>48</td>
</tr>
<tr>
<td>Cathodes</td>
<td>Material</td>
<td>316 S/S</td>
</tr>
<tr>
<td></td>
<td>Dimensions, mm (L×B)</td>
<td>290 × 480</td>
</tr>
<tr>
<td></td>
<td>No. per cell</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Production, kg/day/cell</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Purity of crystals</td>
<td>99,93 - 99,99%</td>
</tr>
<tr>
<td>Cells</td>
<td>Material</td>
<td>Fibre glass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>coated PVC</td>
</tr>
<tr>
<td></td>
<td>Capacity, litres</td>
<td>300</td>
</tr>
</tbody>
</table>

fact that silver plus impurities dissolve at the anode, whilst only silver deposits at the cathode. Thus it is necessary to maintain a higher free acid level in the horizontal cells where the anodes are less pure.

Apart from copper nitrate which is deliberately added to fresh electrolyte to increase its conductivity, the only electrolyte addition reagent used is tartaric acid, which is added to the horizontal cells to produce harder, denser and larger crystals, although the exact mechanism of this effect is not known.

In the vertical cells, the anodes are suspended in pairs inside an anode bag made of polypropylene, mounted on a PVC frame. The sludge collects in the bottom of the bag and is removed monthly. Anode scrap amounting to less than 15% of the original anode mass is transferred into special cells equipped with anode baskets made of perforated titanium plate, the titanium carrying the current to the residual anode pieces, enabling them to be completely dissolved. The deposit on the cathodes is crystalline and dendritic and is removed by mechanical scrapers. The crystals fall to the bottom of the cell and are removed daily by scraping them up the inclined side of the cell into a stainless steel trolley.

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In the horizontal cells, a stainless steel sheet on the bottom of the cell serves as the cathode; suspended above it is a PVC-framed basket, covered with a polypropylene cloth. The anodes are laid flat on top of the cloth and the electrical connection is made by a 100 mm diameter carbon rod. In this case, the anodes dissolve completely and there is no recycle, but the high sludge fall-out dictates that the cloth must be cleaned off every three to five days. The cathode crystals are scraped off the bottom of the cell daily.

Sludge from both sets of cells is mainly gold and is washed off the bags/cloths with spent electrolyte and filtered in a Buchner filter. Thereafter it is dried, melted and cast into bars which are returned to the gold refinery for chlorine refining.

Fresh electrolyte is made up by dissolving silver crystals in nitric acid and remains in use until the lead level has built up to around 5 grams per litre, at which point it must be discarded. In this case the silver is precipitated with sodium chloride and the copper-bearing liquor is sent to the cementation tanks; the precipitated silver chloride is sent to the leach plant.

Crystals from both types of cell are washed in a centrifuge, first with 1% HNO₃ solution and then with further water washes. The crystals are then melted into standard 34 kg bars, which assay:
Silver = 99.9% minimum
Oxygen = 50 - 70 ppm
Copper = 5 - 15 ppm
Iron = 10 - 15 ppm
Lead = 1 - 2 ppm
Zinc = 1 ppm

The melting furnace is a 2 000 Hz, tilting, induction furnace. Crucible capacity is 342 kg and 1.25 hours are required to melt the charge, using 100 kW at 1 200 V (Figure 10.16).

10.4.4 Coin blank production
10.4.4.1 Historical
Historically, coins have all had a face value given in the currency of the issuing country. However, in 1966 provision was made to issue a South African coin with a face value of one ounce of fine gold. Krugerrands were produced in limited quantities in 1968 and 1969. Towards the end of 1969 the Chamber of Mines of South Africa decided to increase the production of these coins and to sell them internationally. Rand Refinery Limited undertook to produce the gold blanks, and started production in February 1970 at the rate of 2 000 blanks per day. These initial blanks were produced on equipment borrowed from the South African Mint and an old refurbished rolling mill.
During the next 10 years demand for the coins rose and, in order to keep pace, production was increased in stages to 40,000 blanks a day. This was done largely by scaling up the existing processes, but additional equipment such as a locally manufactured rolling mill was purchased.

In 1980 production of three smaller coin denominations containing respectively a half, a quarter and a tenth of an ounce of gold was started. The small size of these coins, particularly the tenth, demanded very close dimensional tolerances in the rolled strip. This meant that for the one-tenth Krugerrand only about 8% of the gold cast into strip finally appeared as coin. To overcome this high scrap recycling problem and to permit production of large quantities of small coins, it was subsequently decided to install modern high precision rolling equipment.

A prerequisite for this type of equipment is that the strip should be as long as possible, and certainly much longer than the starting length of 500 mm that was being produced at the refinery. This meant that a continuous casting machine would also be needed. Additional advantages expected from a continuous casting machine were much higher quality strip and the ability to produce this in a wide range of widths and thicknesses. To accommodate this equipment, a new building was planned for the production of blanks from gold-copper alloy and, in addition, provision was made for the minting of coins at the refinery, should this be required. Construction started in September 1982 and the first production runs took place in October 1983.

The installation of the new plant has considerably improved production efficiencies, particularly for the smaller sized coins. Compared to the old plant, this has enabled more than four times as many tenth Krugerrands to be produced for every kilogram of alloy cast. The casting, rolling and punching operations all produce far less scrap, resulting in improved security. The overall result is that production rates of the smaller sized coins have been increased and the number of staff reduced.

10.4.4.2 Process description

![Flow sheet for the production of coin blanks.](image-url)
The new coin blank production process is summarised in Figure 10.17. To produce the required 22 carat alloy containing 91.67% to 91.72% gold, refined gold from the Gold Refining Branch is weighed and the calculated amount of copper added. The charge is melted in a 3 000 Hz induction crucible furnace and, when molten and well stirred to ensure uniform composition, is sampled and poured directly into a holding furnace. The holding furnace is also a 3 000 Hz induction furnace with a cylindrical crucible. The bottom of the crucible comprises a set of graphite dies between water-cooled copper blocks. These dies, which are the heart of the continuous casting machine, have shaped channels to give the required cross section of alloy strips. Molten metal flows by gravity to fill the channels and the cooling system causes the metal in the channels to set. The solid metal is then withdrawn by a few millimetres, allowing more liquid metal to flow into the die, which in turn sets and is withdrawn. In this way a continuous strip of solid metal is drawn in small steps from the bottom of the holding furnace. The strip is coiled and cut when the mass approaches 600 kg. Continuously cast strip is ideal for coin production as it has a very uniform cross section and virtually no defects.

The coils are weighed and passed to the rolling mill. The mill’s principal features are two coilers which allow the strip to be rolled in one piece, from one coiler to the other, and thickness gauges which automatically adjust the roll gap to maintain consistent thickness of the product (Figure 10.19). Strip thickness is reduced by 20% at each pass through the rolls, so after six to eight passes the strip is reduced from its original 8.0 mm to 2.34 mm for production of Krugerrands, or 0.94 mm for tenth Krugerrands. By keeping the allowable variation in thickness to a minimum, the number of blanks rejected as under- or over-weight is reduced.

The strip, now at the required thickness, is weighed again and taken to the punch section. Here the coils are straightened and fed into a punch which produces four blanks at each stroke. The blanks are tumbled to remove sharp edges and oil, then dried and counted into bags.

Bags of blanks, each containing 500 one-ounce pieces, are delivered to the weighing and final inspection department. Here the blanks are fed one by one into automatic sorting machines. The blanks are weighed to within a milligram on an electronic balance and the mass of each blank is fed into a microcomputer programmed to determine the mass category of the blank. The microcomputer then operates the appropriate gate through which the coin passes into one of seven buckets according to category, and controls the feeding of the next blank into the machine.

The blanks are thus sorted by mass. The first bucket contains blanks which are of an acceptable mass; for Krugerrands this is between 5 and 50 milligrams over the nominal one ounce of gold. The next bucket contains blanks which are either below the minimum mass, or are too heavy for grinding to the correct mass, and are therefore rejected. The remaining buckets contain blanks which vary from 50 to 250 milligrams overweight. These blanks have their edges ground by a set amount to bring the mass down into the "correct" range. The edges are ground and not the faces, in order to avoid
scratches on the faces which might show up on the final coin. A similar procedure is followed for the other denominations.

The ground blanks, together with the coins of acceptable mass from the first bucket, are given a final mass check and a visual inspection of the surface and edges to ensure that they are free of any faults which could mar the finish of the final coin. The blanks are then weighed and counted into bags for despatch to the South African Mint where they are minted.
10.4.5 Smelter

10.4.5.1 Flow sheet
Gold mines and other processors of gold, including Rand Refinery itself, produce various gold- and silver-bearing by-products from which the gold and silver are most efficiently recovered by pyrometallurgical processes. These materials are thus delivered to the smelter department of Rand Refinery where the treatment process is generally as shown in Figure 10.20, the end product being Doré bullion which is delivered to the refinery for electrolysis.

There are six basic operations involved: sampling, blending and sintering, blast furnace smelting, cupellation, pan furnace smelting and fume collection.

10.4.5.2 Sampling
Over 300 tons of material are received for treatment every month, containing some 450 kg gold and 1 200 kg silver. By far the largest component is borax slag from mine smelting operations, followed by miscellaneous concentrates, ashes, bricks, pots and liners, activated carbon, jewellers' "sweeps", base bullion bars, computer scrap and various sweeps from the refinery's gold and silver refining branches.

Considerable effort has been put into developing reliable and accurate sampling methods for these materials. The first prerequisite is that the material
be fine enough to pass through a 2 mm screen; therefore all oversize materials are crushed in a Symons crushe prior to sampling. To sample accurately material with a bulk density of 2 - 3 t/m³ containing gold bullion particles of density up to 18 t/m³ is not easy, and a further prerequisite is that the gold particles be distributed uniformly throughout the bulk. To achieve this condition each lot of material is charged via a pneumatic conveying system to either a 2 m³ or a 6 m³ conical mixer and allowed to mix for approximately fifteen minutes. The mixer is then discharged into 0,2 m³ drums and two "rod samples" are taken from each drum. The rod samples are accumulated to give a 20 - 30 kg sample representative of the whole. In theory, much larger samples are necessary to achieve the desired accuracy of ± 2,5% but experience has justified the technique described. Experience has also proven the necessity of achieving thorough mixing; providing this is done, the rod sampling technique is adequate and there is no need for elaborate sample-splitting operations. After mixing and sampling, the complete lot is weighed to obtain its wet mass. Two small moisture samples are withdrawn from the main sample, weighed, dried in an electric oven and reweighed to enable the true dry mass of the material to be calculated. The remaining sample material is coned and quartered and split into 'A' and 'B' fractions which are then reduced to suitable form for assay, as shown in Figure 10.21. Screening of the metallics is essential to leave the bulk of the sample more uniform in
value. The metallics and fines are assayed separately and the assays combined according to the masses of the different fractions.

The above sampling method applies to the majority of materials received, but metallics and bars require special techniques normally involving melting and fluxing with galena, followed by sampling of the lead metal and matte produced.

After sampling, weighing and assaying, all materials are purchased from the depositor and stored pending treatment.

10.4.5.3 Blending and sintering

Having reduced all materials to fines to ensure accurate sampling, the next step is to agglomerate these fines into a form suitable as feed for the blast furnace. The sinter process was chosen in preference to pelletising or briquetting because of the superior physical characteristics of sinter with regard to size, strength and porosity.

All purchased materials are analysed not only for gold and silver but also for the chemical components which affect blast furnace and sinter plant performance. These are silica, iron, lime, alumina, zinc, lead, copper, sulphur and arsenic. From the stock of materials available, a sinter charge of roughly 250 tons is calculated, chemical composition of the total charge being ad-
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justed by the addition of iron mill scale, pyrite and coke breeze. The charge calculation is governed by the requirements of good quality sinter, minimum barren flux usage and good blast furnace slag. Generally speaking, the rules are:

i) Borax slags must comprise less than 35%. Above this figure the sinter bed slags over, restricting the sintering action.

ii) The approximate composition must be:

\[ \text{SiO}_2, 12-20\%; \text{Fe}, 18-24\%; \text{S}, 6-8\%; \text{Pb}, 8-10\%. \]

iii) Alumina must be less than 8% to avoid forming a viscous blast furnace slag.

iv) Excessive zinc must be avoided, also to prevent the formation of viscous slag.

The total calculated charge is divided into identical 15 ton batches. Each batch must be thoroughly mixed to give a uniform feed to the sinter plant and this is done by heaping all materials on the floor and turning over the heap several times with a front-end loader, dust being suppressed by means of water sprays. This method of blending the charge has proved to be the simplest and most economic way of achieving the required throughput of some 40 tons per day of blended feed.

The blended mix is loaded into drums which are in turn discharged by a fork-lift truck into a hopper from which feed material is elevated to the sinter plant.

The object of the sintering process, as previously stated, is to agglomerate the feed prior to smelting in the blast furnace. In practice, this agglomeration is achieved by igniting the fuel constituents in the blended mix laid on the sinter strand. The heat generated by the combustion reaction is sufficient to soften many ingredients and to produce localised melting and slagging of the lower melting point materials such as litharge, borax slag and matte. The resulting product, after the hot zone has passed through the bed, is a hard porous frit, ideal for the blast furnace. The two fuels used are pyrite (FeS₂) and carbon in the form of coke breeze, although recently breeze has been largely replaced by activated carbon, which is now being received from the mines in increasing amounts.

The sinter plant itself is a small conventional down-draught machine as depicted in Figures 10.22 and 10.23. One of the main features is the use of \(-25 + 6\) mm recycle material as a hearth layer to protect the grate bars.

The important parameters are as follows:

- Feed moisture = 9\% - determined by carbide bomb apparatus.
- Bed depth = 175 mm + 50 mm hearth layer
- Strand width = 1.0 m
- Strand speed = 0.18 m/min (but variable)
- Down draught = 1.9 m³/sec each windbox, at 250-450 mm w.g.
- Rated output = 35 t/day product + 10 t/day recycle.

10.4.5.4 Blast furnace smelting

The general theory of blast furnaces can be found in most metallurgical text-
books, so it is more important to describe here the metallurgical principles governing Rand Refinery's specific operation.

The basic process is the reduction of the lead oxides in the charge to metallic lead, which percolates through the charge column and collects the precious metals. At blast furnace temperatures the basic oxides combine with silica and other gangue materials to form slag which, having been freed of its precious metal content by the lead, is low enough in value to be discarded. Sulphides present in the charge cause the formation of a matte phase which serves to recover the copper content of the charge and also collects silver.

The important reactions are:

\[ 2C + O_2 \rightarrow 2CO \]  \hspace{1cm} (10.16)
\[ \text{PbO} + \text{CO} \rightarrow \text{Pb} + \text{CO}_2 \]  \hspace{1cm} (10.17)

Reaction (10.16) generates most of the heat within the furnace, so there must always be sufficient coke included in the charge, not only to ensure a stable operation, but also to prevent the formation of carbon dioxide which
occurs in preference to carbon monoxide at lower temperatures, i.e.

\[ C + O_2 \rightarrow CO \] \hspace{1cm} (10.18)

The proportion of carbon converted to CO rather than CO$_2$ is most important since it affects the degree of reducing conditions and hence the extent of reaction (10.17). This explains the success of the oxygen enrichment technique in which increased oxygen and reduced nitrogen contents of the air blast cause more efficient combustion, hence hotter conditions and a higher CO:CO$_2$ ratio, thereby increasing the lead formation by reaction (10.17). A further benefit of oxygen enrichment, indeed the main reason for its use, is that the more efficient combustion permits the use of less coke per unit charge and allows a higher feed rate.

The composition of the slag leaving the furnace must be carefully controlled. The slag formation reaction can be written:

\[ x \text{SiO}_2 + y \text{FeO} + z \text{CaO} \rightarrow x \text{SiO}_2.y \text{FeO}.z \text{CaO} \] \hspace{1cm} (10.19)

In practice the ratio of \((y + z):x\), i.e. the amount of iron and calcium oxides combining with the silica, must be sufficient to displace lead oxide from the slag. Unless this is so, the silver and gold in the slag will be unacceptably high. The ratio of \(x:y:z\) is also very important to ensure a fluid, low melting point slag. Figure 10.24 illustrates this point.
Figure 10.24. CaO-FeO-SiO$_2$ phase diagram (after Levin et al., 1969).

It can be seen that the lowest melting point slags are found where SiO$_2$ : FeO : CaO is 35 : 46 : 18, corresponding to an olivine-type slag. Because of the other constituents present such as zinc oxide, alumina and magnesia, which raise the melting point, and borax, which lowers the melting point, slag analyses obtained in practice are as follows:

- SiO$_2$ = 20 – 24%
- FeO = 35 – 39%
- CaO = 11 – 14%
- Al$_2$O$_3$ = 6%
- B$_2$O$_3$ = 5%
- Pb = 1%
- MgO = 2%
- MnO = 1%
- Cu = 0.3%
- S = 1%
- Na$_2$O = 2.5%

Figure 10.24 clearly shows that deviating too far from these values moves the slag into areas of rapidly increasing melting point and hence difficult furnace operations.

The physical condition of the charge is also very important. All components should be of approximately the same size to avoid segregation of...
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the materials as they are fed into the shaft and to ensure an even distribution
of the gases as they rise through the column. If "channelling" of the blast
is allowed to occur, the hot zone of the furnace rises from its normal level
(just above the tuyères) and furnace operation becomes difficult. This is why
the sinter quality is so important; the sinter must be strong enough to with­
stand the weight of the burden above without becoming finely crushed.

Rand Refinery's furnace is a modified lead blast furnace with a rect­
angular hearth of area 1,22 m$^2$ and four tuyères on either side. The hearth
slopes towards the lead taphole, which is in the centre of one side, whilst
the slag overflows a slag notch at the front end of the furnace. If necessary
the slag can be run out of a notch at the opposite end. The furnace is water­
jacketed to a height of 1,5 m then lined for the remaining 4,5 m with high­
alumina firebrick. A fan delivers up to 90 m$^3$/min of air to the tuyères via
a bustle pipe into which oxygen is injected to an enrichment level of 2,5%
(i.e. the air blast is 23,5% oxygen). At the top of the shaft, a cast iron collar
is fitted through which the charge descends. The off-gases are drawn from
around the collar into a side offtake and thence to the flue system.

The furnace charge, generally comprising coke, sinter, litharge, return
matte and the requisite fluxes, is carefully calculated and adjusted daily to
maintain the slag, lead and matte compositions within the correct limits.
Metallic iron (turnings and chopped discarded drums) is added to reduce lead
from the matte while limestone and iron mill scale are added to adjust the
slag composition. The various ingredients are each weighed into a scale car
and transferred into a feed skip which tips directly into the top of the fur­
nace. Slag and matte overflow the hearth continuously via the slag notch
into three settling pots in series. Slag overflowing the third pot is granulated
in a water launder, conveyed to a storage bin and sold for use as a grit blasting
medium or as a colour additive to glass. The assay of the slag is normally
around 1 g/t Au and 50 g/t Ag.

Matte, being denser than slag, collects in the bottom of the settling pots
and is tapped periodically into pig moulds and recycled to the furnace, both
directly and via the sinter, until its copper content exceeds 30%. At this point
the lead tapping becomes difficult due to copper dross freezing in the taphole.
The matte is therefore withdrawn from the circuit and accumulated for sale
to a suitably equipped refinery which can extract the copper, lead, gold and
silver. Matte for sale typically analyses 30% Cu, 15% Pb, 20% Fe, 20% S,
0,5% As, 400 g/t Au and 8 000 g/t Ag. The lead bullion is tapped every
four hours into pig moulds and the solidified ingots, each weighing 25 kg
and assaying typically 1% Au and 3,5% Ag, are delivered to the cupel
furnace.

Blast furnace throughput is around 40 tons of total charge per day, in­
cluding 10 tons of new material. The furnace is operated for campaigns of
three months after which the flues must be cleaned and the accretion in the
shaft removed.

10.4.5.5 Cupellation
The cupel is an oil-fired, brick-lined furnace as shown in Figure 10.26, with
The refining of gold

Figure 10.25. Blast furnace slag and matte stream.

A tiltable, removable hearth (referred to as a "test") made of rammed magnesite. The lead bullion is loaded into the feed chute where it melts and trickles down into the hearth. A low pressure jet of air across the hearth causes the lead to oxidise to litharge and directs this litharge into a shallow channel and thence into a collecting pot. Any other base metals are also oxidised and removed either as fume or with the litharge. The silver and gold are not oxidised and, being denser than lead and litharge, settle in the bottom of the hearth and accumulate until the hearth is full. At this point, lead addition is stopped, the temperature raised and fluxes sprinkled over the melt to remove the last traces of lead as a slag. The cleaned Doré bullion is ladled out into flat anode moulds. More than one ton of these anodes, assaying roughly 70% Ag, 30% Au and up to 0.2% Pb and 0.6% Cu, are delivered each month to the electrolytic silver section.

10.4.5.6 Pan furnace smelting

The pan furnace is a small, oil-fired reverberatory with a hearth area of 6 m². In the past this was used for smelting purchased materials using a lead collection technique similar to that of the blast furnace. However, the residue slag was never low enough in value to be discarded and so had to be retreated in the blast furnace. Because of the adverse economics, this process has been discontinued and the furnace is now used only to reduce surplus litharge from the cupel furnace back to lead metal. The process is quite straightforward, involving the charging of batches of 5 t litharge plus 0.6 t coal, firing for four hours and tapping into pig moulds.

The lead is sold to a lead works, where the residual gold and silver are
Figure 10.26. Diagram of cupel furnace.
extracted by drossing with sawdust and zinc in a Parkes kettle, the drosses being returned to the Refinery's blast furnace circuit.

10.4.5.7 Fume collection
Because of the lead hazard, all operations in the smelter must be vented to efficient gas-cleaning equipment before the gases are released to atmosphere. Their precious metal content makes it economically imperative to recover the dust and fume. A further contaminant in the gas stream is sulphur dioxide; its concentration is too low to permit economic extraction and it is therefore dispersed via a 61 m stack. Fumes from all the furnaces and the sinter plant are extracted via an underground flue system leading to four identical electrostatic precipitators of the tube and wire type. The electrodes are 1.6 mm-diameter titanium wires suspended in 280 mm-diameter tubes. Electrode current is 1 mA at a maximum potential of 65 000 V. The linear gas velocity is 0.76 m/sec.

Since the dust consists mainly of heavy metal oxides which are difficult to ionise, the precipitators are only about 60% efficient, so the gas stream from the precipitators is passed to a bag filter plant. Precipitated dust assays typically 25% Pb, 11% Zn, 400 g/t Au, 800 g/t Ag, and is recycled to the sinter charge. The bag filter has a designed capacity of 34 m$^3$/sec and consists of 48 compartments, total cloth area 2880 m$^2$, two compartments at a
time being cleaned "off line" by the action of a pulsating reverse air flow. The low air : cloth ratio of 0.7 m/min results in a very high filtration efficiency of around 99.9% and minimum failures of the "Dralon T" filter sleeves. The bag dust recovered, assaying typically 40% Pb, 15% Zn, 60 g/t Au, and 800 g/t Ag, is pelletised and recycled to the sinter charge.

10.4.6 Assaying and chemical analysis
It is essential that the assay and analysis of all samples are of the highest integrity because of the value of the materials being handled. Errors in the assay of purchased or sold materials could cause either the Refinery or the depositor to suffer financially, while errors in the process control sample analyses could lead to expensive metallurgical losses and process failures. The assay and analytical techniques used at the Rand Refinery are fully described in the book *Assay and Analytical Practice in the South African Mining Industry* (Lenahan and Murray-Smith, 1986).

One of the main features of the assay procedure, designed to ensure the required accuracy, is that routine gold assays are done on a twin-stream duplicate system to reveal any errors or bias which would otherwise go undetected. The assay department is therefore divided into two separate assay offices, each with its own staff, equipment and rooms. Despite the duplication of labour and equipment, the cost is no greater than running a single stream with the comparable degree of control.

10.5 Future Developments
In any business it is essential to seek ways and means of improving process efficiency and the working environment by developing and incorporating new technology. Precious metal refining is no exception to this rule.

At the time of writing this chapter (1985), Rand Refinery is embarking on a project to refurbish the smelter plant. The plans include the adoption of electric furnace smelting to replace the sinter plant/blast furnace route. This will lead to increased capacity, improvements in air quality index, reduction in operating costs and a reduction in the labour requirement. For similar reasons the cupel furnaces will be replaced by a top-blown rotary converter — a high intensity, energy efficient reactor. The same converter furnace will also be used for the litharge reduction, simply by changing to reducing conditions. The latest mechanical handling techniques will also be introduced to save labour and eliminate dust emission. Further, there are medium term plans to rebuild the refinery, incorporating sophisticated electronic/electrical equipment applied to new induction furnaces, improved mechanical handling and ventilation, and process changes designed to eliminate the aqueous effluent from the silver refinery. Computers have already found applications in the analytical field, are currently being applied to the metallurgical accounting system, and in the future will undoubtedly be used for on-line process control of the smelting and refining operations.
10.6 References

