Extraction and Refining of the Platinum Metals

A COMPLEX CYCLE OF SMELTING, ELECTROLYTIC AND CHEMICAL OPERATIONS

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A major development in the world’s platinum industry took place in the early nineteen twenties when large deposits of platinum bearing ore were discovered in the Transvaal in South Africa. This led to the formation in 1931 of Rustenburg Platinum Mines Limited to work these deposits, and this company remains to this day the only platinum producer in South Africa and the only major producer in the world whose prime activity is the extraction of the platinum metals.

From the outset Johnson Matthey has been associated with Rustenburg, first in developing methods for the extraction of the platinum metals from these ores, and thereafter as smelters and refiners of the output from the mines.

This article describes the complex and lengthy cycle of operations required to effect complete recovery of the six platinum metals and to yield at the same time electrolytically refined copper and nickel.

Today the joint activities of Rustenburg and Johnson Matthey constitute the world’s largest source of the platinum metals in all forms. Together they ensure to industry throughout the world adequate and continuing supplies of these metals.

The earlier stages of the mining and recovery of the platinum metals from the Rustenburg Platinum Mines have been reviewed in some detail in this journal (1), while the geology of the Bushveld Igneous Complex and the platinum reefs—constituting an enormous reserve of platinum metals—which are mined by the Rustenburg company has also been described (2). This article deals with the succeeding stages of extraction and refining carried out in the smelting works and refineries of Johnson Matthey & Co Limited in order to bring the concentrates received from the mining company into marketable forms.

Operations conducted at the mine result in two products—a rich gravity concentrate which is passed directly to the wet process refinery of Johnson Matthey, and a converter matte that has been worked up from the flotation concentrate. This matte is cast and either prepared for shipment to the Johnson Matthey smelter at Brimsdown in the United Kingdom or sent to Matte Smelters (Pty.) Limited, a company formed in South Africa in 1952 as a joint subsidiary of Rustenburg Platinum Mines and Johnson Matthey in order to cope with the increasing output from the mines. The process operated at this plant, which is adjacent to the Rustenburg mine, is essentially the same as the primary stages of the Brimsdown process.

During the past thirty years the quantities of matte received at the Brimsdown refinery have increased, and in 1950 a new plant was
added, bringing the site for treating Rustenburg matte at Brimsdown up to a total area of ten acres.

Improved techniques and more modern equipment are always under review, but the basic process for extraction of the platinum metals has remained essentially the same.

Rustenburg converter matte contains about 46 per cent of nickel and 28 per cent copper, together with some other base metals and sulphur. The platinum group metals, together with some gold, total about fifty ounces to the ton. The complete process of extraction consists essentially of enriching this matte to approximately 65 per cent content of platinum metals and then treating this concentrate with acids to separate the individual platinum group metals from each other, followed by final refining.

Operations to achieve this can roughly be divided under three headings:

1. Smelting operations, where the original matte is broken down to yield metallic nickel and copper anodes.
2. Electro-refining operations, where these anodes are dissolved electrolytically to produce pure nickel and copper and an anode slime containing the precious metals.
3. Chemical operations, for the separation and refining of the individual metals.

Smelting Operations

Converter matte from Rustenburg arrives at the Brimsdown smelter in bags of about 150 pounds each. It has been crushed to three-inch size. After weighing and sampling the first operation is to separate the nickel and copper sulphides. This is done by making use of the fact that molten sodium sulphide is completely miscible with copper sulphide and completely immiscible with nickel sulphide, so that if the converter matte is melted with sodium sulphide two fractions separate out—a sodium sulphide/copper sulphide layer floating on a nickel sulphide layer. Furthermore, a nickel matte with a deficiency of sulphur is an excellent collector of the platinum group metals; therefore under suitable conditions a nickel matte can be produced that is low in copper and will contain the platinum group metals. At Brimsdown this operation is mainly carried out in a blast furnace, although six-ton
reverberatory furnaces are also used. The blast furnace is water-jacketed for its full height and has a rectangular hearth measuring \(72 \times 36\) inches. Converter matte, salt cake (sodium sulphate) and coke are fed in and the molten materials run into a settler where the sodium sulphide/copper sulphide top layer flows continuously into a ladle, while the bottom layer of nickel matte is tapped intermittently. By careful control of temperature and sulphur content a nickel matte can be obtained containing little copper and all the platinum metals, whereas any gold will have followed the copper sulphide into the “tops” layer.

The first stage of the smelting operations is a blast furnace treatment to separate nickel matte containing very small amounts of copper and practically all of the platinum metals.

The copper tops are then either poured into a five-ton reverberatory holding furnace or directly into a horizontal-type copper converter. The converter is lined with magnesite brick and capable of taking charges up to five tons. By blowing air through the molten top considerable heat is generated and sodium sulphate is first formed. This is tapped off as a watery liquid and used again in the blast furnace. Silica is then added to the converter to flux iron oxide and any excess soda; this slag is also poured off and the residual copper sulphide blown down to blister copper in the normal way. The blister copper is tapped into a ladle and poured directly into one of three small reverberatory furnaces. The copper is then further refined and cast into moulds.

Casting the enriched nickel matte into pigs. These are then crushed, ground and roasted.
The ground nickel matte is roasted in this battery of oil-fired furnaces. The nickel oxide produced is then reduced to metal and cast into anodes.

to make anodes for the electro-refinery.

In the meantime, nickel matte from the blast furnace operation is broken, crushed and ground in ball mills to 20 mesh. This material is then roasted to nickel oxide in oil-fired 17-feet diameter Herreschoff type furnaces with two hearths separated by an air gap. Ground nickel matte is fed through a hopper on to the top hearth which is kept at a low temperature; it then falls through to the lower hearth which is kept at 900° to 950°C. After cooling, the resultant nickel oxide is briquetted with anthracite coal and sand. These briquettes are next charged into an oil-fired reverberatory type furnace, where the oxide is reduced to metal and tapped into anode moulds. These anodes, which contain practically all the platinum metals, are then passed into the electrolytic nickel refinery.

**Electro-Refining Operations**

Copper anodes from the converter process are dissolved electrolytically using an acid copper sulphate solution as an electrolyte. The products of this operation are pure copper cathodes and an anode slime which may contain gold and small quantities of the platinum group metals.

The cells are constructed of rubber-lined concrete. Internal measurements are approximately $8\frac{1}{2} \times 2 \times 3$ feet. The warmed electrolyte is fed in at one end and overflows from the other into a launder running between the lines of cells. From the launder the liquid is pumped to overhead tanks where its heat is maintained, and by gravity flows to a manifold which feeds it back to the cells. During electrolysis the electrolyte tends to accumulate nickel and quantities have to be bled off occasionally and replaced by pure copper sulphate. The impure electrolyte is treated for recovery of the copper sulphate and the nickel sulphate is passed to the nickel refinery. There are 21 anodes and 20 cathodes in each cell and a current of $15\frac{1}{2}$ amp per square foot is maintained. The quantity of anode slime formed by the dissolving of these anodes is small and falls to the bottom of the cells, where it is periodically recovered.

The dissolving of the nickel anodes follows the same general pattern, the products
The electrolytic nickel refinery at Brimsdown. Here pure nickel cathodes are produced, while the platinum metals accumulate in the anode residues and are removed for the separation and refining of the individual metals being pure nickel cathodes and an anode slime containing the bulk of the platinum group metals. In this case the electrolyte is a neutral solution of nickel sulphate containing boric acid as a buffer and has to be continually purified to produce a pure cathode. Copper and iron are present in the anodes and being more electro-negative than nickel must be removed from the electrolyte or they will deposit on the cathode as impurities. To achieve this each cathode is placed in a calico bag with purified electrolyte flowing into it, so that the cathode will grow in clean liquor. The stripped liquor flows out of the bag laterally and picks up the impurities from the solution of the anode. This liquor flows out of each cell into a launder and is pumped across to large circular treatment tanks where it is heated to approximately 70°C. An emulsion of nickel carbonate is added to adjust the pH and air is blown through to hydrolyse out the iron. After this any copper present is precipitated and the contents pumped through a filter press to separate out the solid impurities.

The filtered liquor is stored in overhead tanks ready for feeding back to the cells. As in the copper refinery, the cells are constructed of rubber-lined concrete and 24 cells make up one unit. Internal dimensions of the cells are about $11\frac{1}{2} \times 2 \times 2\frac{1}{2}$ feet. There are 21 anodes and 20 cathodes in each cell and the current density is $12\frac{1}{2}$ amp per square foot. Anodes and cathodes in each cell are in parallel.

The quantity of slime produced by the nickel anodes is far greater than from the copper anodes and although a little falls to the bottom of the cells the majority adheres to the anode and has to be scraped off. This is normally done every 100 running hours, both to bring the platinum metals forward and to stop the anodes becoming passive.

During all the processes that have been described so far slag, residues and flue dust have been produced. Normally these are worked into a previous stage of the process, but in primary work several products result which although poor in values compared with the initial matte are far too valuable to be
thrown away. These are collected, blended with suitable fluxes and smelted in a blast furnace to a matte which is blended in with the original matte at the beginning of the process.

**Chemical Operations**

From this stage onwards the concentration of the platinum group metals is more rapid and the processes entirely chemical. First the slime is subjected to roasting and leaching attacks to remove the last of the copper, nickel, iron and sulphur. This produces an enriched slime running approximately 65 per cent of the platinum group metals and gold.

At this point the platinum-bearing gravity concentrates shipped from South Africa join those produced in the Johnson Matthey smelting plant, and together enter the wet process refinery. Here they are treated for complete elimination of base metals, and the platinum metals are brought into solution for their separation and individual refining. The solutions handled are usually highly concentrated, extremely valuable and very corrosive. Handling is therefore carried out by employing the simplest possible methods, including siphoning and gravity draining, and use is made of glass-lined vessels, glass pipelines and glandless pumps of chemically resistant materials.

The complete cycle of treatment is very complex and can only be briefly outlined here. Basically the separation and refining of these six closely allied metals involves their precipitation as complex salts followed by successive stages of recrystallisation and then by calcination, under carefully controlled conditions in electrically heated muffle furnaces, to produce the metals in the form of sponges or powders suitable for melting and working.

Initial treatment comprises digesting with aqua regia to produce a solution containing the major portion of the gold, platinum and palladium as chlorides, the residue comprising the more insoluble metals, iridium, rhodium, ruthenium and osmium. The solution is reduced by adding ferrous chloride to remove the gold. The addition of ammonium chloride to the filtrate precipitates impure ammonium chloroplatinate, which is calcined to a crude platinum sponge, redissolved, reprecipitated...
This section of the wet process refinery – the largest of its kind in the world – handles the precipitation, redissolving and reprecipitation of platinum and palladium. It is arranged on the cascade system to facilitate the movement of solutions.

As pure ammonium chloroplatinate and calcined again to give pure platinum sponge.

The filtrate from the ammonium chloroplatinate is oxidized, and excess of ammonium chloride added to precipitate the palladium as a crude ammonium salt. This is redissolved in ammonia to form a tetrammino palladium chloride, which on acidification precipitates palladium diammino dichloride. This salt is then calcined to pure palladium sponge.

The other four metals are extracted from the original insoluble residue, first by fusion with alkaline and oxidising fluxes, followed by dissolution in water and then by distillation.

In this part of the refinery the four "insoluble" metals – ruthenium, rhodium, iridium and osmium – are extracted and separated as their complex ammonium salts.
The final stage in the refining operations — platinum sponge is being melted in a high frequency induction furnace for casting into ingot form

of ruthenium and osmium as volatile oxides. These distillates are then treated in a similar way to the solutions of the soluble metals, by precipitation of their complex salts and calcination to metal.

The solution remaining after distillation contains the iridium and rhodium, which are recovered as sodium salts, followed again by precipitation of their complex ammonium compounds and calcination.

The whole of the plant, the largest of its kind in the world, is arranged on the cascade system, so that all movement of liquids is by gravity. The methods employed achieve an extremely high degree of purity in each of the metals. For example, routine production of platinum yields a metal of 99.99 per cent purity, while additional steps in refining metal required for special purposes give a product totalling only a few parts per million of impurities.

In every case the metals produced are subjected to chemical and spectrographic analysis. After meeting the specified requirements, the sponges are converted to solid metal—or to alloys—either by melting in high frequency induction furnaces or by the method of powder metallurgy, followed by forging and rolling.

From this refinery the six platinum metals are supplied in pure form to independent fabricators and users throughout the world, to Johnson Matthey associated companies in the United States, Canada, South Africa, Australia, Belgium and Italy, and to the company's London manufacturing centre.

References

1 C. B. Beath, R. J. Westwood and C. A. Cousins
2 C. A. Cousins