

overflow, which contains 40 per cent of the nickel leached out of the combined solutions, is pumped to the nickel sulphate crystallizer, while the thickener underflow is fed to the second-stage leach. The nickel may be recovered mainly as a sulphate, or as nickel powder or sintered briquettes, depending on the preference of the producer.

For the *second-stage leach*, the repulped first-stage residue is pumped into a large lead- and brick-lined autoclave with five stainless-steel compartments and six agitators. Copper-spent electrolyte is pumped separately into the first compartment of the autoclave. Oxygen is added to all five of the compartments, just below the agitation impellers. The reactions occur at temperatures of between 150 and 165 °C and at pressures of 10<sup>4</sup> kg/cm<sup>2</sup>, and involve principally the conversion of sulphides of nickel, copper, and cobalt to sulphates and the extraction of the iron and selenium. The autoclave discharge is depressurized in a flash tank before entering two pressure filters in series, leaving the upgraded precious-metal concentrate on the filters. The filter cake, which contains from 30 to 60 per cent PGM, depending on the nature of the leaching operation in the base-metal plant, is batch-dried and blended before being sent to the refinery.

About 80 per cent of the selenium content of the matte is recovered in the autoclave as cuprous selenite, which is filtered on a plate and frame filter coated with wood pulp, and then leached with a solution of sodium hydroxide. This is filtered once more, the filter cake being returned to the second-stage leach circuit. The filtrate solution is neutralized with sulphuric acid and then treated with aqueous sulphur dioxide to produce elemental selenites. The filtrate from the latter process is transferred to the copper electrowinning circuit.

The pregnant electrolyte solution, after the removal of the selenium, is pumped into a recirculating tank, where it is blended with the recycled electrolyte from the cell overflow. This blended electrolyte is pumped into the centre of a series of many electrolytic cells with overflows at each end. These cells have lead anodes and the copper is deposited at cathodes, which consist of stainless-steel blanks connected in parallel. The high-purity (99 per cent) copper is recovered weekly, and the spent electrolyte is pumped back to the first- and second-stage leaching circuits.

The filtered solution overflow from the thickener at the end of the first-stage leach circuit is pumped into a tube evaporative crystallizer with an external forced-circulation heater. The nickel sulphate crystal slurry from the crystallizer is centrifuged, and the crystals are dried in a rotary drier before bagging. The nickel sulphate hexahydrate crystals contain between 21 and 22 per cent nickel, with iron and chloride introduced extraneously as the main impurities.

#### 4.2.5. Primary Refining Methods

Classical methods of commercial PGM refining originated in Russia in the early 19th century, and many of the basic chemical steps in that original process remain

in use in modern refineries. A multitude of *batch-type* operations are involved in treating the solid materials with chemical liquids to extract one or more of the precious metals, which are then selectively precipitated. These initial wet-chemical methods were, however, exceedingly labour-intensive and slow, involving an extended hold-up in the plant before the pure metals were finally produced. In the modern equivalent of these processes, the order of precipitation may have been altered due to streamlining and environmental requirements, although the fundamental approach has not shown any drastic changes. The older wet-chemical methods have largely made way for more modern techniques, such as solvent extraction and ion exchange, which have revolutionized today's refining of the precious metals. These basic methods will now be reviewed.

#### (1) The Classical Chemical Methods of Primary Refining

The precious-metal concentrate from the leaching process and the base-metal refinery is treated with aqua regia (a mixture of hydrochloric and nitric acids), which dissolves the platinum, palladium, and gold, and leaves the other PGM as an insoluble residue.

(a) *Gold recovery.* The solution containing the soluble precious metals is heated to dryness and redigested repeatedly with hydrochloric acid to ensure the total removal of any remaining oxides of nitrogen. Gold is precipitated either by reduction with ferrous sulphate or sulphur dioxide gas, and then purified electrolytically; or is extracted by a water-immiscible solvent. The gold is then recovered by reduction with oxalic acid.

(b) *Platinum recovery.* The aqueous solution of platinum and palladium is heated with an ammonium chloride solution to precipitate an ammonium platinum chloride salt. Any impurities are removed by successive cycles of redissolution, solution, and precipitation, and the salt is finally decomposed by heating to produce the pure metal.

(c) *Palladium recovery.* Palladium is also recovered by precipitation of ammonium palladium chloride, and repeatedly dissolving and precipitating the salt to remove impurities. The salt is then treated with formic acid to obtain palladium metal.

After the removal of the soluble precious metals, the insoluble residue from the treatment with aqua regia is smelted with a mixture of lead carbonate, carbon, and borax plus a soda-ash flux. The flux forms a slag with any remaining silica, alumina, and base-metal impurities, and the remaining PGM are alloyed with the lead.

(d) *Rhodium recovery.* The insoluble residue remaining after the removal of the lead and silver is fused with molten sodium bisulphate at 500 °C, which renders the rhodium soluble as its sulphate, but leaves the other PGM unaffected. After cooling,



Shaft headgear at Karee  
(courtesy Lonrho Plc)