

prepared for solvent extraction by methyl isobutyl ketone (MIBK) by adjusting the concentration of hydrochloric acid.

(a) *Gold recovery.* MIBK extraction is used to remove the gold, as well as any iron and tellurium, from the pregnant solution. The organic phase is heated with hydrochloric and oxalic acids to precipitate a pure gold sponge, which is removed by filtration. The iron-tellurium residue solution is disposed of, and the aqueous phase is passed on to the next solvent-extraction step to recover the palladium.

(b) *Silver recovery.* Prior to the recovery of palladium, the acidity of the solution is reduced by evaporation to a low volume, and the solution is then rediluted with water. During this process, a substantial amount of the silver is precipitated as insoluble silver chloride, which can be removed by filtration.

(c) *Palladium recovery.* This is undertaken by solvent extraction using an oxime reagent, which also extracts small amounts of platinum and copper from the solution. The organic phase is stripped with hydrochloric acid, and can be re-used. The acid palladium solution is then treated with a controlled quantity of ammonium hydroxide to produce a palladium ammonium chloride salt. After filtration, this salt is dissolved in further ammonium hydroxide. Any insoluble impurities are filtered off, and a pure diamine is precipitated with hydrochloric acid. Calcination of this salt produces a 99.98 per cent pure palladium sponge.

(d) *Platinum recovery.* The aqueous raffinate from the palladium extraction is used directly for the platinum solvent extraction, which is carried out with an organic amine. The organic phase, which contains all the platinum and small amounts of iridium, lead, and copper, is stripped with hydrochloric acid. Hydrolysis removes these trace impurities, allowing for the precipitation of a pure ammonium chloroplatinate by addition of a saturated solution of ammonium chloride.

The stripped solution is available for re-use, and calcination of the platinum salt at temperatures between 400 and 500 °C in air yields a 99.98 per cent pure platinum sponge.

(e) *Ruthenium recovery.* The aqueous raffinate from the platinum is passed directly to the ruthenium recovery circuit. The process relies on the volatility of ruthenium tetroxide. The ruthenium is oxidized by the addition of sodium chlorate at boiling temperature. After the majority of the ruthenium has been removed, the last traces are distilled using sodium bromate. The ruthenium tetroxide is collected by hydrochloric acid circulating in a scrubber. Ammonium chlororuthenate salt is precipitated with ammonium chloride, filtered and washed, then calcined to produce a

pure ruthenium sponge.

After distillation of the ruthenium, the solution is treated with sodium bicarbonate to bring it to a pH of 5. The hydrolysis cake contains all the rhodium and iridium; the sodium, nickel, and much of the copper are removed by filtration. The cake is then dissolved in hydrochloric acid, and the resulting solution is concentrated by evaporation.

(f) *Iridium recovery.* The solution containing the iridium and rhodium is now submitted for the solvent extraction of iridium. The solution obtained by dissolving the hydrolysis cake is boiled with hydrochloric acid while hydrogen peroxide is added. This produces tetravalent iridium, which can be extracted using an organic amine. The organic phase containing the iridium, with traces of rhodium and lead, is stripped with hydrochloric acid containing a reducing agent. An impure ammonium chloriridate is precipitated by adding saturated ammonium chloride solution, and the salt is purified by redissolution and reprecipitation. The eventual product is calcined to produce a pure iridium sponge.

(g) *Rhodium recovery.* The aqueous raffinate from the iridium solvent-extraction process contains rhodium, as well as deleterious quantities of nickel, copper, and lead. The lead is removed by precipitation as lead sulphate, but this is effective only at low concentrations of chloride ions. Any excess of hydrochloric acid is therefore removed by evaporation and redilution, before the sodium sulphate solution is added in order to precipitate the lead. The purified solution is contacted with an ion-exchange resin, which absorbs the rhodium. The effluent containing the residual base metals is treated by cementation to recover any traces of remaining PGM before it is finally discarded. The ion-exchange resin is eluted with hydrochloric acid and, after clarification, ammonium chloride is added to produce so-called 'Claus' salt (chloropentamminerhodium chloride). This salt is purified by dissolution in sodium hydroxide solution and reprecipitation. It is then calcined to produce a ruthenium sponge, which is typically 99.98 per cent pure.

4.2.6. Secondary Refining Methods

The secondary refining of scrap or discard materials is reported to account for approximately one third of the annual PGM production that enters the supply market, and constitutes a significant source of the PGM activity, owing to the rarity of the metals and their elevated prices. Because of their noble character, the PGM are virtually indestructible in most industrial uses, and they can therefore be recycled by secondary refining.

The lower the quality of the PGM contained in the scrap, the further back it must enter the refining process, and the higher the cost of recovery of the PGM. It is, however, extremely difficult to provide details of PGM recycling because of the extreme diversity of the source materials. Each class of scrap must be considered separately, and the potential of each refining route for a particular class of scrap material must be assessed and tested before a suitable process can be selected.

High-grade scrap is usually classified as containing in excess of 10 per cent PGM. It is usually melted before either being subjected to a chlorine treatment to volatilize the base metals, or it may follow the conventional refinery process outlined above. Low-grade scrap containing less than 10 per cent PGM is melted in an electric-arc furnace or coke-fired blast furnace with suitable fluxes to produce fluid slags of low value. The PGM are gathered in suitable collectors like lead, iron, nickel-copper sulphides, or copper metal to reduce

health and environmental hazards. After casting, the collector material is separated from the slag and leached with a suitable acid to remove the base metals. The rich concentrate is dissolved by chlorine gas and hydrochloric acid, and then follows the conventional refining route. Combustible scrap materials, such as carbon-supported platinum catalysts, must be incinerated before further treatment. Solutions or liquids containing the PGM are commonly absorbed by combustible materials such as sawdust, and the resulting mass incinerated. The treatment of the ash depends on the concentration of the contained PGM and the base-metal impurities. Platinum and palladium contained in alumina-supported catalysts are subjected to high-temperature attack with concentrated sodium hydroxide, leaving a solid residue which is fairly rich in PGM. This residue is dissolved by chlorine gas and hydrochloric acid, and then refined by the techniques outlined above.