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Background

Palladium is a very useful metal due to its many unique properties, making it a highly desired substance. Because of its low contact resistivity, palladium is used as a low-current electrical contact, primarily in telephone equipment and in integrated circuits. It is also used to strengthen gold-based dental alloys. The chief use of the metal is in the field of communications, where it is used to face electrical contacts in automatic switchgear. When annealed, it is soft and ductile, but cold working increases its strength and hardness. Therefore, it is used in some nonmagnetic watch and clock springs. It is also used in dentistry, for coating special mirrors, and in jewelry. When palladium is alloyed with gold, it is decolorized and called white gold.[1]

Palladium is often found in conjunction with other platinum-group metals, such as platinum, rhodium, iridium and others. The world's largest platinum-group mineral deposit is the Bushveld Complex of South Africa. The Sudbury deposit of Ontario, Canada and the Norilsk-Talnakh deposit of Siberia in Russia are other major deposits. In the United States, the Stillwater Complex in Montana is the largest deposit, but it is much smaller than the other world deposits.[2] This mine, located near Nye, MT, processed more than 400,000 metric tons of ore and recovered 10,200 kg of palladium in 1999. The United States imported 195,000 kg in 1999, mainly from Russia (48%) and South Africa (18%).[3]

The platinum group metals are found mainly in two types of primary deposits and in placers. The first type of primary deposit is composed of disseminations or local concentrations of the metals in olivene-rich rocks, dunite, and chromite. Iridosmine is the

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[1] http://www.webelements.com

[2] http://www.encyclopediabritannica.com

[3] http://minerals.usgs.gov

predominant component. The second type of primary deposit consists of magmatic nickel-copper sulfide deposits where platinum and palladium are major constituents. Placer deposits of the platinum metals are due to the erosion of primary deposits. The platinum group metals are the by-products when nickel and copper are extracted. In the South African primary deposits, all platinum group metals are present as well as iron, nickel, cobalt, copper, silver, and gold.[4]

Following are summaries of all the major techniques of processing and recovering palladium.

Treatment of Raw Materials Found with Nickel and Copper Sulfide Concentrate (Conventional Method)

A majority of all platinum-group metals are recovered from copper or nickel sulfide minerals. The flowcharts in Appendices I and II summarize the operations involved to recover the platinum metals. The ore deposits are mined underground and then concentrated by flotation.[5] Flotation is a mineral processing method used to separate and concentrate ores. Most minerals require coating with small amounts of chemicals or oils to make the finely ground particles hydrophobic so that they adhere to the air bubbles that carry them up to the froth. The gangue minerals are treated so that they are hydrophilic and sink to the bottom of the flotation cell.

The valuable minerals are then roasted to remove part of the sulfur. In a small blast furnace, the roasted ore is smelted with quartz, coke, and limestone to produce a furnace matte of iron, copper, and nickel sulfides. The matte product is blown in a

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[4] Hampel, Clifford A., *Rare Metals Handbook*, (NewYork: Reinhold Publishing Corporation, 1954), p.292.
[5] Hampel, p.295.

converter with basic lining to oxidize the sulfur and iron and remove most of it with the fluxes. This results in a matte that consists of approximately 80% copper and nickel, and the remainder is sulfur and almost all the platinum metals. The matte is treated to produce nickel by either the Mond carbonyl process or the electrolytic process.[6]

When nickel is refined by the Mond method, a residue from the carbon monoxide treatment is obtained. This product is roasted and then leached with sulfuric acid to remove any remaining copper and nickel. The resulting residue has a precious metals content of about 20%. The treatment with sulfuric acid dissolves almost all the silver and about one-third of the palladium. The sulfates of these metals are formed. By the Moebius process, the silver is recovered and purified electrolytically. The palladium is recovered from the anode slimes.[7]

If the matte is treated by electrolytic refining, copper and nickel are initially separated by the Orford process. The Orford process is known as the “tops and bottoms” method. By heating the matte with coke and sodium bisulfate, sodium sulfide dissolves copper sulfide rather than nickel sulfide. Two layers are formed when pouring the melt. The top layer consists of sodium copper sulfide and most of the silver and gold. It also contains a trace of platinum metals. The copper from the top layer is recovered and refined electrolytically. A small amount of platinum metals is also recovered from this refining. The bottom layer is made up of nickel sulfide and the bulk of the platinum metals. When the nickel is refined by electrolysis, more platinum metals are obtained. The anode slimes for both cases contain the precious metals. They are roasted and smelted to give secondary anodes that are also electrolyzed. The slimes from this

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[6] Hampel, p.295.
[7] Hampel, p.297.

treatment consist of about 2% platinum metals. However, they can be concentrated with suitable acid treatment until their platinum metals content is approximately 50%.[8]

Palladium, platinum, and gold are then extracted from the residual metal by applying an aqua regia treatment. Aqua regia is a mixture of concentrated nitric and hydrochloric acids. It is capable of dissolving palladium, platinum, and gold; a solution of chlorides results. First, the solution is treated with ferrous sulfate to precipitate gold by the following reaction:

$$3Fe^{2+} + AuCl_4^{-} \rightarrow 3\ Fe^{3+} + 4Cl^{-} + Au.$$

The Wohlwill electrolytic process is then applied to purify the impure gold. By adding ammonium chloride, platinum is precipitated next from the solution as ammonium chloroplatinate (IV). When isolated and dried, the precipitate is purified by igniting the metal and then redissolving it in aqua regia. This solution yields a pure ammonium chloroplatinate. The product is ignited, and a pure platinum sponge results. Thirdly, palladium is removed from the solution as diamine palladium (II) chloride. Excess amounts of ammonia are added first. Then hydrochloric acid is added and a yellow salt precipitates out. The reactions are shown below:

$$PdCl_4^{2-} + 4NH_3 \rightarrow Pd(NH_3)_4^{2+} + 4Cl^{-}$$

$$Pd(NH_3)_4^{2+} + 2HCl \rightarrow Pd(NH_3)_2Cl_2 + 2NH_4^{+}.$$

The salt is purified by dissolving it in excess ammonia and reprecipitating it with hydrochloric acid. A sponge of palladium metal results when the palladium compound is ignited.[9]

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[8] Hampel, p.297.
[9] Hampel, p.300.

The aqua regia extraction yields an insoluble residue. This residue is smelted with litharge and fluxes, resulting in a lead alloy. By using nitric acid, most of the palladium, platinum, and silver are removed from the alloy. This solution is separated from the insoluble residue and treated by the means previously described. The insoluble residue contains rhodium, iridium, ruthenium, and small amounts of osmium in concentrated form. Appendix II further maps out how these metals are isolated.[10]

Treatment of Raw Materials from the Merensky Reef in South Africa

Small particles of iron, copper and nickel sulfides are found in the platinum-bearing iron-chromite reef layers within the basic pyroxene deposit of the Bushveld Complex. The platinum exists in various forms such as a ferro-platinum alloy, sulfide, and arsenide of iron, copper or nickel. The platinum group metal content of the crude ore ranges from 4 to 6 grams per metric ton. It consists of 50-60% platinum and 20-25% palladium.[11]

The crude ores are first crushed and pulverized. By flotation processing, the sulfide concentrates containing these metals are separated and recovered. By gravity separation techniques, native platinum and their ferro-alloys are separated. A 25% copper-nickel matte is produced when the sulfide concentrates are smelted in an electric furnace. It is further desulfurized by oxidation in a converting process. This produces a high grade 75-80% copper-nickel matte that contains as much as 2 kg of platinum group metals per ton of matte. The high grade matte is water granulated and finely crushed. The base metals copper and nickel are leached from the matte by acid solution, which leaves a

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[10] Hampel, p.300.

[11] Benner, Linda S., et al, *Precious Metals: Science and Technology*, (Austin: International Precious Metals Institute, 1991), p.377.

residue containing most of the platinum group metals. The products become the raw materials for further recovery and refining of the platinum group metals.[12]

Solvent Extraction Technology

The degree to which separation is attained by means of traditional techniques used in refining platinum group metals is not considered efficient given the yields, complex operations, and expended labor. Much research and development has been geared toward replacing traditional processes with new solvent extraction technology since the early 1970s. The major advantages of employing solvent extraction processes include lower inventory due to the reduced overall processing time, higher separation efficiency, improved yields, higher product purity, flexibility, versatility and capability of continuous operation with process control.[13]

Solvent extraction technology is based on the physico-chemical characteristics of precious metal solution chemistry. These characteristics include the nature of the complex ionic species and their redox potentials. Methods vary with the kinds of extractants used, the rates of extraction, distribution ratios, and separation efficiencies. When solvent extraction technology is applied to commercial and industrial operations, various operational conditions must be considered before the processes are successful. Some points include efficiency and rate of back extraction, degradation and loss of extracts, and flexibility and versatility of the process. The differences in the forms of raw material, contents and grade of precious metals in them, and pretreatment methods also influence the solvent extraction technologies applied in commercial refineries. Newly

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[12] Benner, p.377.

[13] Benner, p.378.

developed solvent extraction methods have already been employed in several commercial refineries.[14]

INCO Acton Refinery Technique

INCO operates the solvent extraction process for precious metals recovery outlined in Appendix III. The raw material is copper electrorefining anode slimes, which are derived from nickel carbonyl gasification residues reprocessed in a copper converter. The raw material is attacked at 90-98°C with hydrochloric acid/chlorine gas. For silver and lead removal, the undissolved residues are attacked with nitric acid and fused with sodium hydroxide at 500-600°C. A hydrochloric acid/chlorine solution then dissolves the alkaline fusion salt. After removing excess chlorine from the solution, sodium hydroxide is used to neutralize the solution. Sodium bromate solution is added. The vapors of the ruthenium and osmium tetroxides are distilled away and absorbed in weak hydrochloric acid solution. Next, hydrolysis with sodium hydroxide is applied; base metals like copper are filtered out as solid hydroxides.[15]

After the solution is adjusted to contain a hydrochloric acid concentration of 3-4M, gold is extracted from the solution into dibutyl carbitol. Dilute, 1-2M hydrochloric acid is used to scrub the organic phase to remove base metals. By direct reduction with aqueous oxalic acid, gold is recovered from the scrubbed organic phase.[16]

Palladium is extracted into an organic phase with di-n-octyl sulfide. This results in a palladium-free aqueous raffinate phase. This scheme uses the lability of $PdCl_4^{2-}$ ion

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[14] Benner, p.379.
[15] Benner, p.380.
[16] Benner, p.380.

with respect to its ligand exchange rate. The reaction below explains the extraction exchange:

$$[PdCl_4^{2-}]_{aq} + 2[R_2S]_{org} \rightarrow [PdCl_2(R_2S)_2]_{org} + 2[Cl^-]_{aq}.$$

Dilute hydrochloric acid is used to scrub the organic phase. Palladium is stripped from the organic phase with an aqueous hydroxide solution to form $[Pd(NH_3)_4^{2+}]_{aq}$. This solution is neutralized using hydrochloric acid. The precipitate that forms is $Pd(NH_4)_2Cl_2$. The stripping reaction is described below:

$$[PdCl_2(R_2S)_2]_{org} + 4[NH_3]_{aq} \rightarrow 2[R_2S]_{org} + [Pd(NH_3)_4^{2+}]_{aq} + 2[Cl^-]_{aq}.$$

The palladium-free aqueous raffinate phase is then treated to recover platinum. The process is mapped out to also recover osmium, ruthenium, iridium, and rhodium.[17]

Matthey Rustenburg Refinery Technique

The solvent extraction process employed by the Matthey Rustenburg Refinery uses oxime/amine extractants. Appendix IV outlines the process flow chart. The precious metal raw materials are dissolved in hydrochloric acid/chlorine solution. Insoluble AgCl is formed. The precipitate is filtered and treated to recover silver metal. By implementing either of the solvation extraction schemes with tributyl phosphite (TBP) or with methyl isobutyl ketone (MIBK), gold is extracted into the organic phase in the form of $AuCl_4^-$. Other impurities such as iron and tellurium are also extracted when the organic phase is scrubbed with hydrochloric acid. Gold is reduced and recovered from the organic phase with the use of iron powder.[18]

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[17] Benner, p.382.
[18] Benner, p.382.

Palladium is extracted when a β-hydroxyoxime is applied. The following ligand exchange reaction occurs:

$$[PdCl_4^{2-}]_{aq} + 2[RH]_{org} \rightarrow [PdR_2]_{org} + 2[H^+]_{aq} + 4[Cl^-]_{aq}.$$

An organic amine reagent is added to accelerate the extraction since the ligand exchange rate is small. The organic phase is scrubbed with weak hydrochloric acid to remove base metal impurities. Palladium is stripped by using aqueous ammonium hydroxide solution. Palladium is then precipitated from the solution as $(NH_4)_2PdCl_6$ with hydrochloric acid. The extraction scheme continues with recovering the remaining precious metals as shown in the process flow chart.[19]

Lonrho Refinery Technique

Solvent extraction is applied as outlined in Appendix V to implement recovery of precious metals. The raw material considered here contains a relatively high content of secondary platinum group metals compared to the raw material feeds at other refineries. First, the raw material is treated for base metal removal by leaching with acid solution. Carbon reduction followed by aluminum reduction is applied to produce an aluminum precious metal alloy. The alloy is dissolved in hydrochloric acid. The remaining insolubles are dissolved in hydrochloric acid/chlorine solution. By diluting with water, silver is precipitated from the solution. Gold is reduced with a sulfur dioxide sparge. Then the solution is adjusted to a 0.5-1.0M acid concentration. This results in adjusting the secondary platinum group metal valence states to three.[20]

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[19] Benner, p.383.

[20] Benner, p.384-6.

By using an acetic acid derivative of a secondary amine (R_2NCH_2COOH), platinum and palladium are extracted from the solution. With hydrochloric acid, the two metals are stripped from the organic phase. To separate platinum from palladium, the principle used is the fact that $PdCl_4^{2-}$ is much more labile in its ligand exchange reactions than is $PtCl_6^{2-}$. A ligand exchange occurs to extract palladium from the raffinate into an organic sulfide phase forming $PdCl_2(RSR)_2$. With aqueous ammonia, $PdCl_2(RSR)_2$ is stripped from its organic phase as shown in the reaction below:

$$[PdCl_2(RSR)_2]_{org} + 4[NH_3]_{aq} \rightarrow 2[RSR]_{org} + [Pd(NH_3)_4^{2+}]_{aq} + 2[Cl^-]_{aq}.$$

By adding hydrochloric acid to the solution, palladium precipitates out in the form of $Pd(NH_3)_4Cl_2$. The process continues with recovering the remaining precious metals.[21]

Recovery and Refining from Scrap

The methods chosen to reprocess platinum-metals scrap depend on the various proportions of the platinum metals in the sample. A universal technique cannot be applied. Generally once the metals are dissolved, methods similar to those discussed in the recovery of the metals from ores are utilized.[22] In the case of palladium, the metal is soluble in aqua regia, hydrochloric acid, hot nitric acid, and chlorine. The pertinent reactions are as follows:

$$Pd + 3HCl + HNO_3 \rightarrow PdCl_2 + NOCl + 2H_2O$$

$$PdCl_2 + 2HCl \rightarrow H_2PdCl_4$$

$$3Pd + 18HCl + 4HNO_3 \rightarrow 3H_2PdCl_6 + 4NO\uparrow + 8H_2O$$

$$Pd + Cl_2 \rightarrow PdCl_2.$$

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[21] Benner, p.386.

[22] http://www.encyclopediabritannica.com

Palladium chloride in solution is reduced by reaction with copper or zinc powders:

$$H_2PdCl_6 + 3Zn \rightarrow 3ZnCl_2 + H_2\uparrow + Pd.$$

This reaction can also be used for palladium nitrate or sulfate in solution. Formic acid in a heated solution also reduces palladium chloride in solution by the reaction below:

$$H_2PdCl_6 + 2HCOOH \rightarrow 6HCl + 2CO_2\uparrow + Pd.$$

With alkaline formaldehyde, palladium chloride in solution reacts as follows:

$$H_2PdCl_6 + HCHO + 6NaOH \rightarrow CO_2\uparrow + 6NaCl + 5H_2O + Pd.$$

To obtain palladium of a higher purity, other processes include treating the palladium chloride in solution with ammonium chloride or ammonia. A red precipitate $PdCl_6(NH_4)_2$ or yellow precipitate $PdCl_2(NH_3)_2$ forms. The precipitates are calcined in a reducing atmosphere to produce palladium metal.[23]

The majority of palladium, platinum, and rhodium scrap comes from automotive catalytic converters. In the presence of iron or copper, the catalyst is melted at high temperatures to fuse the catalyst substrate and dissolve the metals in molten iron or copper. The resulting alloy is leached to dissolve the iron or copper. This leaves behind a concentrate of palladium, platinum, and rhodium, which is further refined by methods like those previously described. Appendix VI is an example of a process flow chart for recovering the metals.[24]

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[23] Benner, p.394.

[24] Benner, p.394.

Conclusion

Increasing demand for palladium, mainly from the automotive sector, has led to recent supply shortages.[25] These shortages are due to increased demand from the automotive industry compounded with export delays from Russia. The price of palladium has almost tripled in the past several years, from ~$130 in 1996 to ~$363 in 1999. In the United States alone, palladium demand has increased dramatically, from 2,300 kg in 1998 to 5,100 kg in 1999. This trend of increasing demand is expected to continue due to further demand from the automotive industry to comply with pending environmental regulations.

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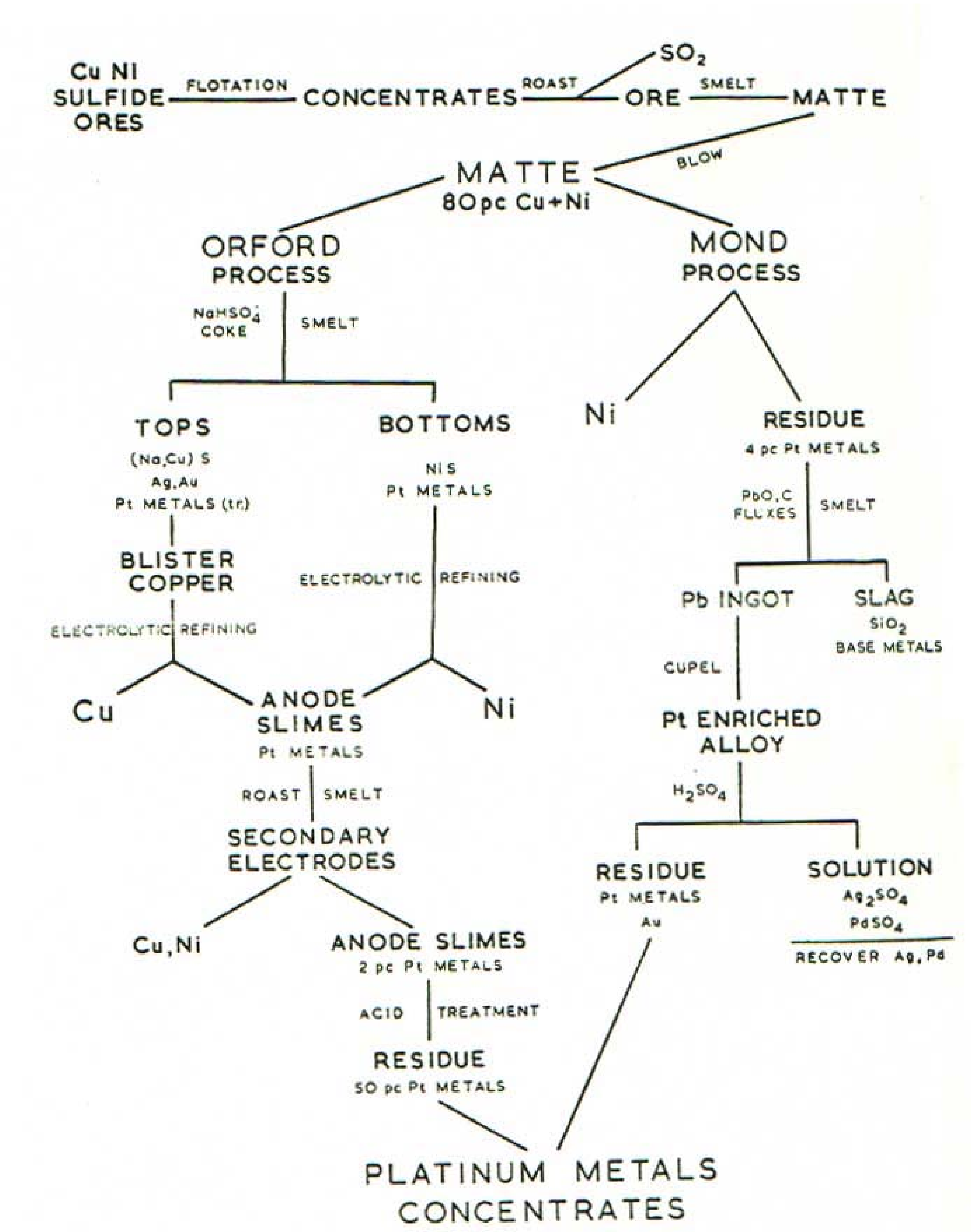
[25] http://www.usgs.gov

Appendix I: Flow Diagram of Ore to Platinum Concentrates[26]



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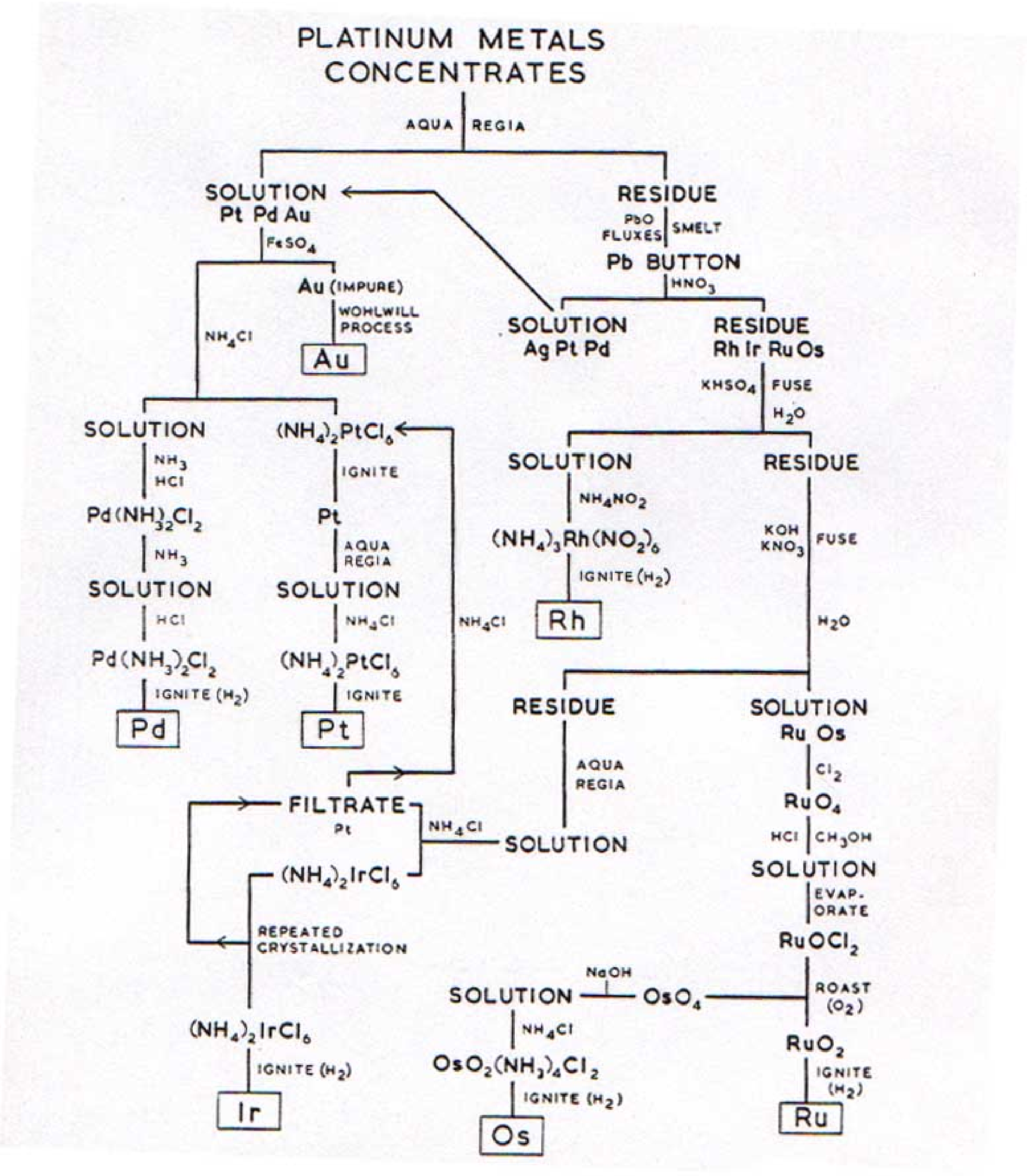
[26] Hampel, p.298.

Appendix II: Flow Diagram of Platinum Concentrates to Individual Metals[27]



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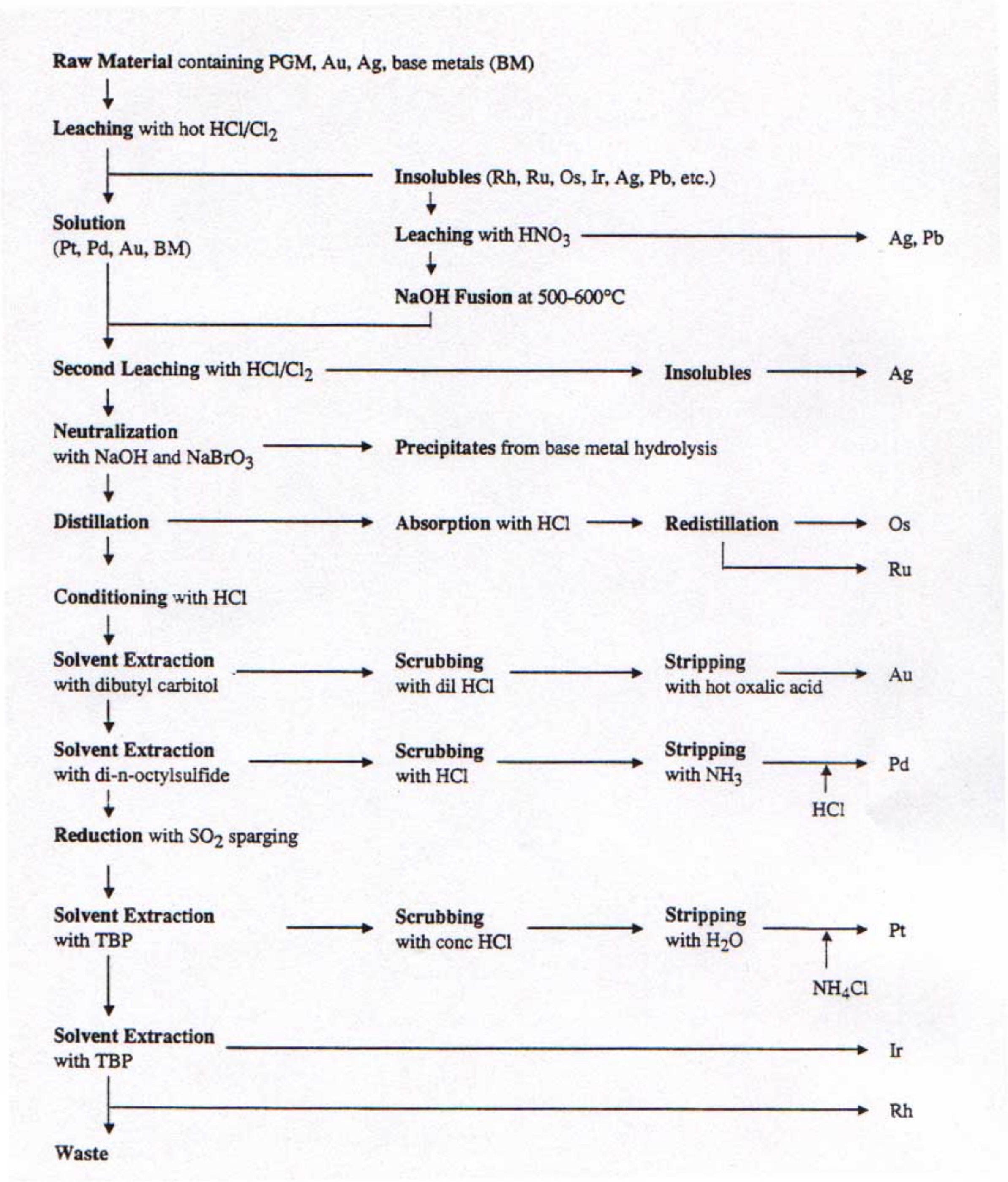
[27] Hampel, p.299.

Appendix III: Process Diagram of INCO Acton Refinery[28]



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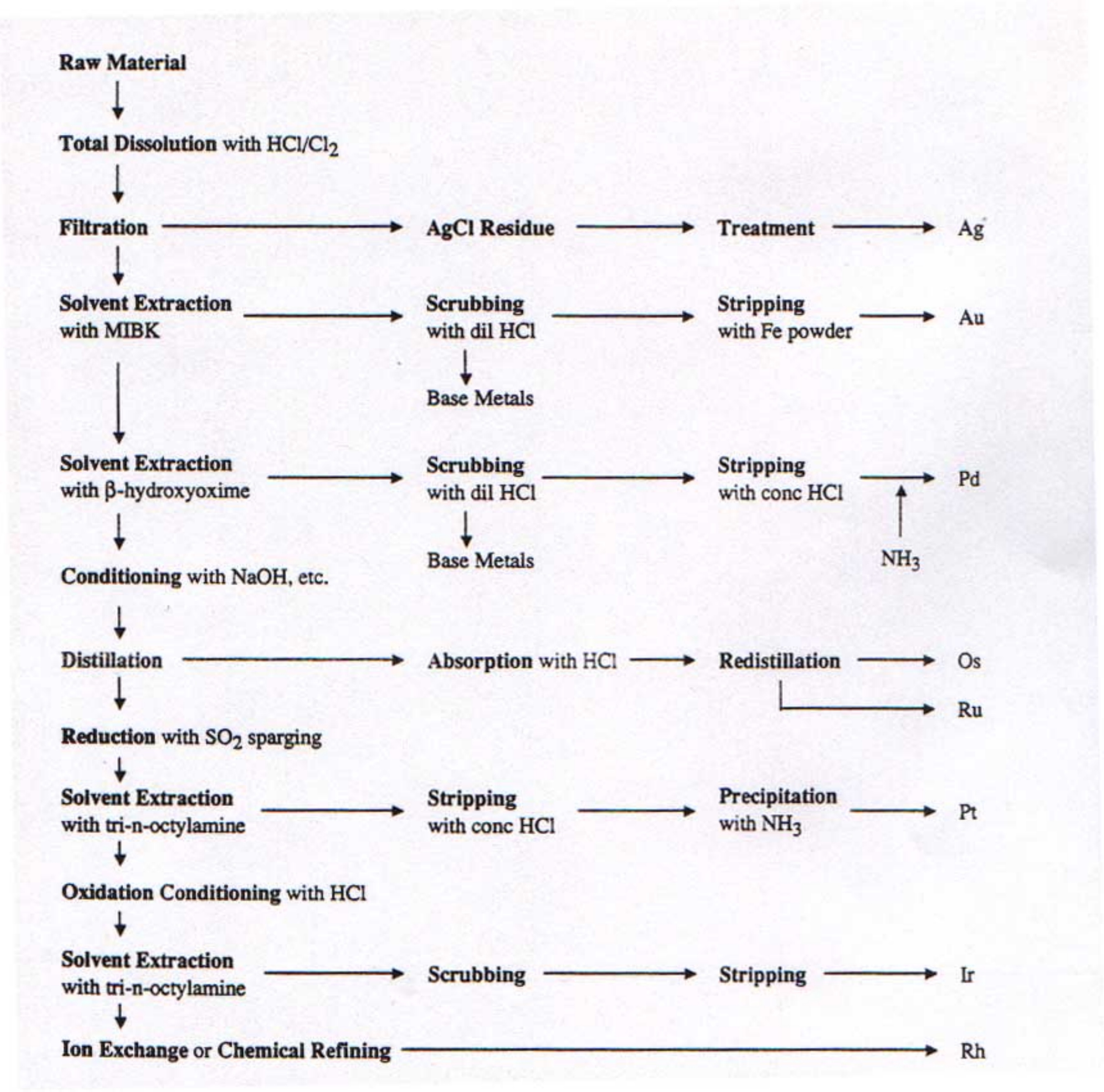
[28] Benner, p.381.

Appendix IV: Process Diagram of Matthey Rustenburg Refinery[29]



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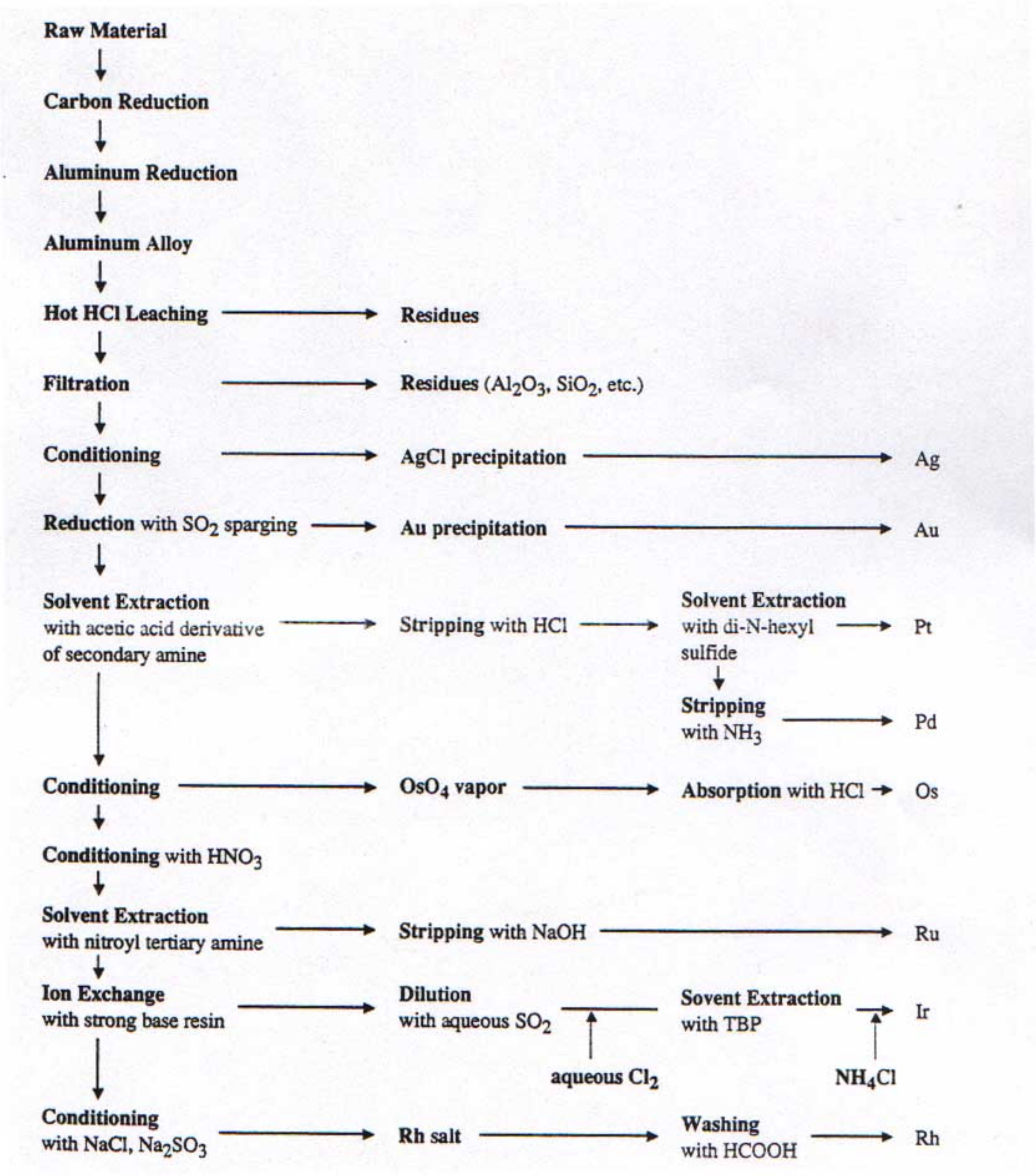
[29] Benner, p.383.

Appendix V: Process Diagram of Lonrho Refinery[30]



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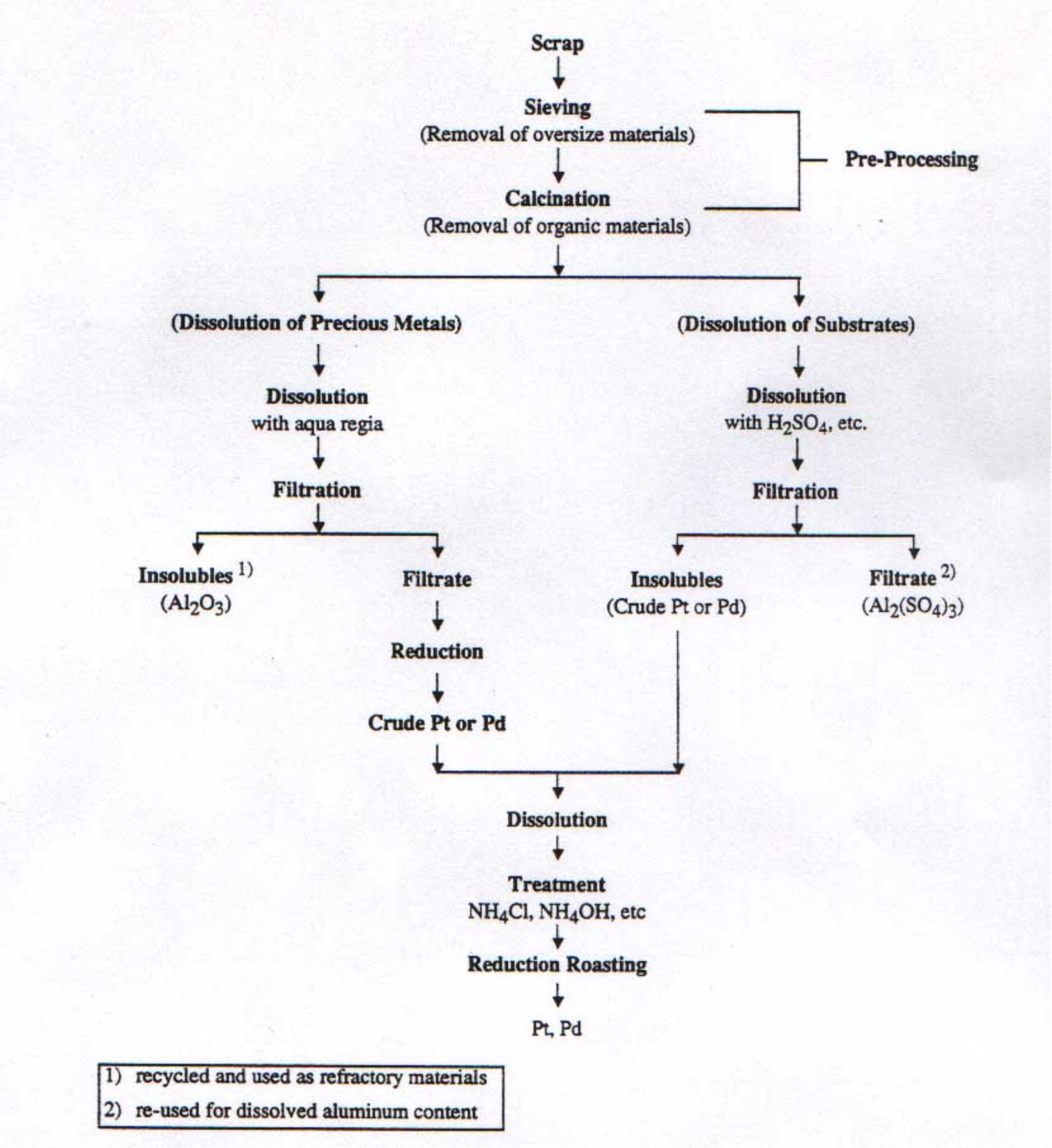
[30] Benner, p.385.

Appendix VI: Process Diagram of Spent Catalysts Recycling[31]



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[31] Benner, p.397.

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