



# Gmelin Handbook of Inorganic Chemistry

8th Edition

## Pt Platinum

Supplement Volume A 1

Technology of Platinum-Group Metals

With 37 illustrations

### AUTHORS

G. J. Bernfeld, Council for Mineral Technology, Randburg,  
Republic of South Africa

A. J. Bird, Johnson Matthey Research Centre, Reading,  
Great Britain

R. I. Edwards, Council for Mineral Technology, Randburg,  
Republic of South Africa

Hartmut Köpf, Technische Universität Berlin

Petra Köpf-Maier, Universität Ulm, Bundesrepublik  
Deutschland

Christoph J. Raub, Forschungsinstitut für Edelmetalle  
und Metallchemie, Schwäbisch Gmünd, Bundesrepublik-  
Deutschland

W. A. M. te Riele, Council for Mineral Technology, Randburg,  
Republic of South Africa

Franz Simon, Degussa AG, Schwäbisch Gmünd,  
Bundesrepublik Deutschland

Walter Westwood, Johnson Matthey Research Centre,  
Reading, Great Britain

### EDITORS

Gary J. K. Acres, Johnson Matthey Corporate  
Development (Technology), London, Great Britain

Kurt Swars, Gelnhausen, Bundesrepublik Deutschland



System Number 65

Springer-Verlag Berlin · Heidelberg · New York · Tokyo 1986

# Gmelin Handbook of Inorganic Chemistry

8th Edition

Ir	<ul style="list-style-type: none"> <li>* Iridium Main Volume - 1939</li> <li>* Iridium Suppl. Vol. 1 (Metal Alloys) - 1938</li> <li>* Iridium Suppl. Vol. 2 (Compounds) - 1938</li> </ul>
Os	<ul style="list-style-type: none"> <li>* Osmium Main Volume - 1939</li> </ul>
Pd	<ul style="list-style-type: none"> <li>* Palladium 1 (Element) - 1941</li> <li>* Palladium 2 (Compounds) - 1942</li> </ul>
Pt	<ul style="list-style-type: none"> <li>* Platinum A 1 (History, Occurrence) - 1938</li> <li>* Platinum A 2 (Occurrence) - 1939</li> <li>* Platinum A 3 (Preparation of Platinum Metals) - 1939</li> <li>* Platinum A 4 (Detection and Determination of the Platinum Metals) - 1940</li> <li>* Platinum A 5 (Alloys of Platinum Metals: Ru, Rh, Pd) - 1948</li> <li>* Platinum A 6 (Alloys of Platinum Metals: Os, Ir, Pt) - 1951</li> <li>* Platinum B 1 (Physical Properties of the Metal) - 1939</li> <li>* Platinum B 2 (Physical Properties of the Metal) - 1939</li> <li>* Platinum B 3 (Electrochemical Behavior of the Metal) - 1939</li> <li>* Platinum B 4 (Electrochemical Behavior and Chemical Reactions of the Metal) - 1942</li> <li>* Platinum C 1 (Compounds up to Platinum and Bismuth) - 1939</li> <li>* Platinum C 2 (Compounds up to Platinum and Cesium) - 1940</li> <li>* Platinum C 3 (Compounds up to Platinum and Iridium) - 1940</li> <li>* Platinum D (Complex Compounds of Platinum with Neutral Ligands) - 1957</li> <li>* Platinum Suppl. Vol. A 1 (Technology of Platinum-Group Metals) - 1986 (present volume)</li> </ul>
Rh	<ul style="list-style-type: none"> <li>* Rhodium Main Volume - 1938</li> <li>* Rhodium Suppl. Vol. B 1 (Compounds) - 1982</li> <li>* Rhodium Suppl. Vol. B 2 (Coordination Compounds) - 1984</li> <li>* Rhodium Suppl. Vol. B 3 (Coordination Compounds) - 1984</li> </ul>
Ru	<ul style="list-style-type: none"> <li>* Ruthenium Main Volume - 1938</li> <li>* Ruthenium Suppl. Vol. - 1939</li> </ul>

## Volumes published on Platinum-Group Metals

- Ir**     \* Iridium Main Volume – 1939  
          \* Iridium Suppl. Vol. 1 (Metal, Alloys) – 1978  
          ° Iridium Suppl. Vol. 2 (Compounds) – 1978
- Os**     \* Osmium Main Volume – 1939  
          \* Osmium Suppl. Vol. 1 – 1980
- Pd**     \* Palladium 1 (Element) – 1941  
          \* Palladium 2 (Compounds) – 1942
- Pt**     \* Platinum A 1 (History, Occurrence) – 1938  
          \* Platinum A 2 (Occurrence) – 1939  
          \* Platinum A 3 (Preparation of Platinumum Metals) – 1939  
          \* Platinum A 4 (Detection and Determination of the Platinumum Metals) – 1940  
          \* Platinum A 5 (Alloys of Platinumum Metals: Ru, Rh, Pd) – 1949  
          \* Platinum A 6 (Alloys of Platinumum Metals: Os, Ir, Pt) – 1951  
          \* Platinum B 1 (Physical Properties of the Metal) – 1939  
          \* Platinum B 2 (Physical Properties of the Metal) – 1939  
          \* Platinum B 3 (Electrochemical Behavior of the Metal) – 1939  
          \* Platinum B 4 (Electrochemical Behavior and Chemical Reactions of the Metal) – 1942  
          \* Platinum C 1 (Compounds up to Platinumum and Bismuth) – 1939  
          \* Platinum C 2 (Compounds up to Platinumum and Caesium) – 1940  
          \* Platinum C 3 (Compounds up to Platinumum and Iridium) – 1940  
          \* Platinum D (Complex Compounds of Platinumum with Neutral Ligands) – 1957  
          \* Platinum Suppl. Vol. A 1 (Technology of Platinum-Group Metals) – 1986  
          (present volume)
- Rh**     \* Rhodium Main Volume – 1938  
          Rhodium Suppl. Vol. B 1 (Compounds) – 1982  
          Rhodium Suppl. Vol. B 2 (Coordination Compounds) – 1984  
          Rhodium Suppl. Vol. B 3 (Coordination Compounds) – 1984
- Ru**     \* Ruthenium Main Volume – 1938  
          \* Ruthenium Suppl. Vol. – 1970

\* Completely or ° partially in German



# Gmelin Handbook of Inorganic Chemistry

8th Edition

**Gmelin Handbuch der Anorganischen Chemie**

**Achte, völlig neu bearbeitete Auflage**

Prepared  
and issued by

**Gmelin-Institut für Anorganische Chemie  
der Max-Planck-Gesellschaft  
zur Förderung der Wissenschaften**

**Director: Ekkehard Fluck**

Founded by  
8th Edition

**Leopold Gmelin  
8th Edition begun under the auspices of the  
Deutsche Chemische Gesellschaft by R. J. Meyer**

Continued by

**E. H. E. Pietsch and A. Kotowski, and by  
Margot Becke-Goehring**



**Springer-Verlag Berlin · Heidelberg · New York · Tokyo 1986**

Gmelin-Institut für Anorganische Chemie  
der Max-Planck-Gesellschaft zur Förderung der Wissenschaften

ADVISORY BOARD

Dr. J. Schaafhausen, Chairman (Hoechst AG, Frankfurt/Main-Höchst), Dr. G. Breil (Ruhr-chemie AG, Oberhausen-Holten), Dr. G. Broja (Bayer AG, Leverkusen), Prof. Dr. G. Fritz (Universität Karlsruhe), Prof. Dr. N. N. Greenwood (University of Leeds), Prof. Dr. R. Hoppe (Universität Gießen), Dr. H. Moell (BASF-Aktiengesellschaft, Ludwigshafen), Prof. Dr. H. Nöth (Universität München), Prof. Dr. G. zu Putlitz (Universität Heidelberg), Prof. Dr. A. Rabenau (Max-Planck-Institut für Festkörperforschung, Stuttgart), Prof. Dr. Dr. H. A. Staab (Präsident der Max-Planck-Gesellschaft, München), Prof. Dr. Dr. h.c. mult. G. Wilke (Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr)

DIRECTOR

Prof. Dr. Dr. h.c. Ekkehard Fluck

DEPUTY DIRECTOR

Dr. W. Lippert

CHIEF EDITORS

Dr. K.-C. Buschbeck – Dr. H. Bergmann, F. Füssel, B. Heibel, Dr. H. Katscher, Dr. R. Keim, Dipl.-Phys. D. Koschel, Dr. U. Krüerke, Dr. H. K. Kugler, Dr. P. Merlet, Dr. E. Schleitzer-Rust, Dr. A. Slawisch, Dr. F. Schröder, Dr. B. v. Tschirschnitz-Geibler, Dr. R. Warncke

STAFF

D. Barthel, Dr. N. Baumann, Dr. W. Behrendt, Dr. L. Berg, Dipl.-Chem. E. Best, Dipl.-Ing. V. A. Chavizon, E. Cloos, Dipl.-Phys. G. Czack, I. Deim, Dipl.-Chem. H. Demmer, R. Dowideit, Dipl.-Chem. M. Drößmar, M. Engels, Dr. H.-J. Fachmann, Dr. J. Faust, Dr. W.-D. Fleischmann, V. Frick, Dr. R. Froböse, G. Funk, Dipl.-Ing. N. Gagel, E. Gerhardt, Dr. U. W. Gerwarth, M.-L. Gerwien, Dipl.-Phys. D. Gras, C. Gorr, H. Hartwig, Dipl.-Min. H. Hein, G. Heinrich-Sterzel, H.-P. Hente, H. W. Herold, U. Hettwer, Dr. I. Hinz, Dr. W. Hoffmann, Dipl.-Chem. K. Holzapfel, Dr. S. Jäger, Dr. J. von Jouanne, H.-G. Karrenberg, Dipl.-Phys. H. Keller-Rudek, Dr. L. Kießling, Dipl.-Phys. E. Koch, Dr. E. Koch, Dipl.-Chem. K. Koeber, Dipl.-Chem. H. Köttelwesch, R. Kolb, E. Kranz, Dipl.-Chem. I. Kreuzbichler, Dr. A. Kubny, Dr. P. Kuhn, Dr. W. Kurtz, M. Langer, Dr. A. Leonard, Dipl.-Chem. H. List, H. Mathis, E. Meinhard, K. Meyer, Dr. M. Mirbach, Dr. U. Neu-Becker, K. Nöring, Dipl.-Chem. R. Nohl, Dipl.-Min. U. Nohl, Dr. W. Petz, I. Rangnow, Dipl.-Phys. H.-J. Richter-Ditten, Dipl.-Chem. H. Rieger, B. Riegert, E. Rieth, A. Rosenberger, Dr. B. Roth, E. Rudolph, G. Rudolph, Dipl.-Chem. S. Ruprecht, Dr. R. C. Sangster, V. Schlicht, Dipl.-Chem. D. Schneider, Dipl.-Min. P. Schubert, A. Schwärzel, Dipl.-Ing. H. M. Somer, E. Sommer, M. Teichmann, Dr. W. Töpfer, Dipl.-Ing. H. Vanecek, Dipl.-Chem. P. Velić, Dipl.-Ing. U. Vetter, H.-M. Wagner, Dipl.-Phys. J. Wagner, R. Wagner, Dr. E. Warkentin, Dr. B. Wöbke, K. Wolff, U. Ziegler

CORRESPONDENT MEMBERS OF THE SCIENTIFIC STAFF

Dr. J. R. Clark, Dr. D. B. Gerth, Dr. J. L. Grant, Dr. K. Rumpf, Dr. K. Swars, Dr. U. Trobisch, Dr. B. Vance

EMERITUS MEMBER OF THE INSTITUTE

Prof. Dr. Dr. E. h. Margot Becke

CORRESPONDENT MEMBERS OF THE INSTITUTE

Prof. Dr. Hans Bock

Prof. Dr. Dr. Alois Haas, Sc. D. (Cantab.)

## Preface

Like most supplement volumes of the platinum-group metal series, Platinum Suppl. Vol. A 1 has been written by an international team of specialists. It comprises technological data of all six platinum-group metals and their technically relevant alloys and compounds.

The volume starts with a review on the recovery of the platinum-group metals (23 pages); the next 42 pages are devoted to processes for separating and refining the PGM in order to obtain metals of high purity. The electrodeposition of the PGM and their alloys is treated on 26 pages. The by far most extensive section deals with PGM and their alloys and compounds in catalysis. After a historical survey and a list of important reviews on PGM catalysis, the catalytic properties of the metals are treated in a general way, followed by unsupported metals and alloys including preparation of catalysts and their reactions in various industrial processes. The role of supported metals and alloys is described in a similar manner. This is followed by an extensive description of the preparation and the reactions of PGM compounds with various nonmetals and their catalytically active role in a number of industrial processes (226 pages).

The last chapter (21 pages) is a compilation of data on the medical use of cytostatic platinum compounds.

Gelnhausen, December 1985

Kurt Swars

## Table of Contents

	Page
<b>Technology of the Platinum-Group Metals</b>	1
<b>1 Review on the Recovery of the Platinum-Group Metals</b>	1
<b>1.1 Historical Perspective</b>	1
Period of Discovery, 1750 to 1820	1
First Industrial Period 1820 to 1900	1
Second Industrial Period 1900 to 1960	2
The Modern Period	2
<b>1.2 Sources of Platinum Metals</b>	2
Primary Metal	2
Secondary Metals	3
<b>1.3 The Production of PGM Concentrates from Sulphide Ore-bodies</b>	4
<b>1.4 Production of PGM Concentrates from Low-Grade Scrap and Other Minor Sources</b>	6
The Copper Smelting – Refining Route	6
The Lead Smelting and Refining Route	7
Auto-Exhaust Catalysts	8
<b>1.5 The Refining of Platinum Metal Concentrates</b>	8
General Principles	8
The Chemistry of Aqueous Chloride Solutions of the Metals	9
The Standard Process	10
Alternative Classical Procedures	13
<b>1.6 Solvent Extraction Techniques</b>	15
General Principles	15
Anion Exchange	15
Ligand Exchange Systems for Pd Extraction	17
Commercial Solvent Extraction Processes	18
<b>1.7 Other Modern Techniques</b>	19
Pre-Leach Treatments	19
Chlorine/Hydrochloric Acid Leaching	20
Ion Exchange	20
<b>1.8 Analytical Techniques</b>	21



	Page
<b>2 High Purity Platinum-Group Metals</b>	24
2.1 Introduction	24
2.2 Production of Pure Platinum-Group Metals	30
2.2.1 Commercial Refining Using Sequential Precipitation	30
2.2.2 Solvent Extraction Methods	30
2.3 Preparation of High Purity Platinum-Group Metal Powders by Chemical Precipitation Methods	38
Platinum	38
Palladium	39
Ruthenium	40
Rhodium	41
Osmium	41
Iridium	42
2.4 Melting, Casting and Mechanical Working	42
2.5 Thin Films of High Purity Platinum-Group Metals	43
2.5.1 Volatilization Methods	43
Pyrolysis of Halides	44
Pyrolysis of Carbonyls and Carbonyl Halides	47
Pyrolysis of Acetylacetonato and Fluoroacetylacetonato Complexes	47
Pyrolysis of Cyclopentadienyls	47
Pyrolysis of Alkyl and Aryl Derivatives	47
2.5.2 Electrodeposition	50
2.5.3 Vacuum Evaporation and Sputtering	51
2.6 Zone Refining of Platinum-Group Metals	51
2.6.1 General Remarks	51
2.6.2 Platinum	52
2.6.3 Palladium	54
2.6.4 Rhodium	54
2.6.5 Iridium	57
2.6.6 Ruthenium	57
2.6.7 Osmium	59
2.7 Testing High Purity Platinum-Group Metals	60
Review	60
Spectrographic Methods	61
Activation Methods	62

	Page
Mass Spectrograph Methods .....	63
The Atom Probe .....	64
Gas Analysis .....	64
Determination of Carbon and Sulphur .....	64
Electrical Resistivity and Electromotive Force Tests for Purity .....	65
<b>3 Electrodeposition of the Platinum-Group Metals</b> .....	66
<b>3.1 Electrodeposition of Ruthenium</b> .....	66
<b>3.2 Electrodeposition of Rhodium</b> .....	68
Introduction .....	68
Applications of Rhodium Electrodeposits .....	69
Historical Survey on Rhodium Plating .....	70
Aqueous Electrolytes for Electrodeposition of Rhodium .....	70
Electrolytes for Deposition of Rhodium Alloys .....	75
Electrolytes for Electroless Deposition of Rhodium .....	76
Electrodeposition of Rhodium from Molten Salts .....	77
<b>3.3 Electrodeposition of Palladium</b> .....	77
General Properties of Palladium Electrodeposits .....	78
Hydrogen in Electrodeposited Palladium .....	79
Palladium Electrodeposition Processes .....	80
Acid $\text{PdCl}_2/\text{HCl}$ and $\text{Pd}(\text{NO}_3)_2/\text{H}_2\text{SO}_4$ Electrolytes .....	80
The Alkaline $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ Electrolyte .....	80
The Alkaline $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ Electrolyte (P-Salt Type) .....	81
Other Alkaline Pd Electrolytes .....	81
Electrodeposition of Pd Alloys .....	82
<b>3.4 Electrodeposition of Osmium</b> .....	85
<b>3.5 Electrodeposition of Iridium</b> .....	86
<b>3.6 Electrodeposition of Platinum</b> .....	87
Electrolytes Based on Platinic Chloride .....	87
Electrolytes Based on Diammino-dinitritoplatinum ("P" Salt) .....	89
Electrolytes Based on Alkali-Hydroxyplatينات .....	89
Electrodeposition of Pt from Salt Melts .....	90
<b>4 Platinum-Group Metals, Alloys and Compounds in Catalysis</b> .....	92
<b>4.1 Introduction</b> .....	92

	Page
<b>4.1.1 The Historical Background to Platinum-Group Metal Catalysis</b>	92
The First Period to 1836	93
The Second Period, 1836 Onwards	94
The Third Industrial Period, 1838 Onwards	95
<b>4.1.2 Catalyst Literature</b>	97
Congress, Symposia etc., Reports	98
Patent Literature Reviews	98
Periodical Literature	99
Reviews of Platinum Metal Catalysis	100
<b>4.1.3 Platinum-Group Metal Catalysis</b>	104
Industrial Platinum Metal Catalysis	107
<b>4.2 The Unsupported Metals and Metal Alloys</b>	120
<b>4.2.1 Preparation and Physical Properties of Industrial Unsupported Metal and Metal Alloy Catalysts</b>	123
Preparation of Metal Blocks	124
Thermal Decomposition of Salts	124
Hydrogen Reduction of Oxides and Hydroxides	125
Reduction of Aqueous Solutions of Metal Salts	126
Raney and Urushibara Skeletal Catalysts	127
Promoted Metal Blacks	129
Pseudo-organometallic or Solvated Metal Atom Dispersed (SMAD) Catalysts	131
Nascent Platinum Metal Blacks	131
Physical Properties of Platinum-Group Metal Blacks	132
Gauze Manufacture and Properties	142
Electrode Fabrication	143
<b>4.2.2 Reactions</b>	143
Hydrogenation	147
Dehydrogenation	164
Oxidation	167
Energy Generation	173
<b>4.3 Supported Metal and Metal Alloy Catalysts</b>	174
<b>4.3.1 Preparation and Reactions</b>	174
Catalysis in the Petroleum Industry	175
Automobile Emission Catalysts	188
Control of Toxic Emissions, Odour and Solvent Streams	191
Catalytic Combustion	192
Fischer-Tropsch Catalysis for Liquid Fuels	193
<b>4.4 Platinum-Group Metal Compounds in Catalysis</b>	196
<b>4.4.1 Platinum-Group Metal Hydrides</b>	203
Platinum-Group Metal Hydride Preparation	206
Reactions	207

	Page
4.4.2 Platinum-Group Metal Borides	213
Preparation of Boride Catalysts	215
Chemical and Physical Properties	217
Reactions	219
4.4.3 Platinum-Group Metal Compounds with Group IV Elements	224
Carbides	225
Graphite Intercalate Compounds	227
Reactions of Carboxylate, Cyanide and Phthalocyanin Heterogeneous Catalysts	232
Silicides	233
Silicates	235
4.4.4 Platinum-Group Metal Compounds with Group V Elements	240
4.4.5 Platinum-Group Metal Compounds with Group VIA Elements	243
Oxides	247
Oxides as Catalytic Metal Precursors	248
Oxides as Catalysts	255
Ruthenates, Perruthenates, Ruthenium Tetroxide and Osmium Tetroxide as Oxidation Catalysts	261
Oxides as Electrocatalysts	276
Chalcogenides	280
Preparation	283
Reactions	287
4.4.6 Platinum-Group Metal Compounds with Halogens	299
Preparation	300
Reactions	300
Industrial Processes	308
4.4.7 Homogeneous Catalysis	310
Hydroformylation	310
Carbonylation	312
Homogeneous Hydrogenation	313
Hydrosilation	314
Olefin Oligomerisation and Telomerisation	315
Developments in Homogeneous Catalysis	316
<b>5 Medical Use of Cytostatic Platinum Compounds</b>	<b>318</b>
<b>5.1 Detection of the Biological Activity of Platinum Compounds</b>	<b>318</b>
<b>5.2 Antitumor Effect of cis-Diamminedichloroplatinum(II) in Animals</b>	<b>318</b>
<b>5.3 Clinical Trials with cis-Diamminedichloroplatinum(II)</b>	<b>320</b>
5.3.1 Genito-Urinary Tumors	320
5.3.2 Carcinomas of the Head and Neck	322
5.3.3 Bronchogenic Tumors	322
5.3.4 Miscellaneous Tumors	322
<b>5.4 Organ Distribution and Pharmacokinetics of cis-Diamminedichloroplatinum(II)</b>	<b>327</b>

	Page
<b>5.5 Side Effects and Toxicity of cis-Diamminedichloroplatinum(II)</b> .....	328
<b>5.6 Structure-Activity Relation and Cytostatic Platinum Complexes of the "Second Generation"</b> .....	330
Structure-Activity Relation .....	330
Platinum Complexes of the "Second Generation" .....	332
Other New-Developed Cytostatic Platinum Compounds .....	334
<b>5.7 Cytostatic Complexes of Platinum Metals Other than Platinum</b> .....	336
<b>5.8 Outlook</b> .....	338
<b>Table of Conversion Factors</b> .....	339



# Technology of the Platinum-Group Metals

## 1 Review on the Recovery of the Platinum-Group Metals

### 1.1 Historical Perspective

No definite date can be ascribed to the discovery of platinum; rather it became gradually known to the Western World as a distinct metal of unique properties over a period of two centuries, between 1500 and 1700. The first source to be exploited was the placer deposits in New Granada (now Colombia) where it was initially regarded as a nuisance in the gold extraction operations. By about 1750 however it was beginning to be exploited for its own sake and had found uses for decorative purposes.

The development of the technology of these metals can be divided into four stages:

#### Period of Discovery, 1750 to 1820

During this period major progress was made in separating the various platinum metals and in establishing many of the basic characteristics of their chemistry. Thus, for example Scheffer established in 1751 the fact that  $\text{NH}_4^+$  ions precipitated Pt as an insoluble salt from  $\text{Cl}^-$  solutions – a technique used in its recovery and refining up to the present day. By 1804 various techniques had been used to isolate five of the six metals (Pt, Pd, Rh, Os, Ir) from Colombian ores.

At the same time much attention was also paid to the physical metallurgy of the new metals, especially of Pt and to methods of fabricating them.

The techniques of extraction, refining, and fabrication developed during this period thus laid the foundation for the industrial exploitation of the metals.

#### First Industrial Period 1820 to 1900

This period is distinguished by four major developments in the industrial applications of the platinum metals. These were:

- (a) The development of industrial-scale integrated refining processes for the metals. Starting with Breant in 1822, these processes included steps such as aqua regia leaching, distillation of Os, precipitation of Pt as  $(\text{NH}_4)_2\text{PtCl}_6$  and precipitation of Pd as  $\text{PdCl}_2(\text{NH}_3)_2$ .
- (b) The establishment of industrial companies whose major business was the extraction, refining, and fabrication of the platinum metals. These include Johnson Matthey, Hereaus, and Desmontis Quennessen early in the period, and Bishop and Baker-Engelhard later on.
- (c) The establishment of international trade in the metals and their ores, firstly from Colombia alone, but later and almost exclusively from new deposits in Russia.
- (d) The development of satisfactory methods of fabricating the metals and their usage as corrosion-resisting linings, especially in sulphuric acid boilers – the major use for Pt till after the turn of the century.

## Second Industrial Period 1900 to 1960

Platinum metals were obtained from a wide variety of sources during this period. Placer deposits in Colombia and Russia were still exploited, but the recovery of byproduct platinum metals from Cu-Ni ores from Sudbury, Canada became an important source from about 1920 and by the late 1930s this source was dominant in the market. This situation continued until the late 1940s, when deposits in South Africa and, somewhat later, in Russia, also of the Cu-Ni sulphide type, became of increasing importance.

During this period the refining processes developed during the nineteenth century became standardised to a large extent. This is best illustrated by the Inco process which with minor variations was almost universally used until the 1970s.

Because of the change in the nature of the ores from which PGM were derived, new methods also had to be developed for the early stages of concentration. These techniques only reached their full maturity with the development of the South African and Russian deposits, however.

Uses of the PGM continued to grow during this period and their catalytic properties began to be exploited, firstly in the production of  $\text{H}_2\text{SO}_4$ , then the oxidation of  $\text{NH}_3$  to  $\text{HNO}_3$ , and thereafter in a whole range of new industrial processes.

## The Modern Period

This period has been marked by the vast increase in the range and amount of usage of the PGM. Accompanying this has been the virtual elimination of primary sources of PGM other than Cu-Ni sulphide deposits, and the dominance of the Russian and South African deposits.

At the same time the recovery of the metals from secondary materials, i.e. their recycling, has become a major factor in the industry. The secondary refining industry is probably almost as large as the primary, and will probably continue to expand in the future.

Technologies have been developed to a high level of sophistication to extract and concentrate the metals from ores containing only a few parts per million into concentrates.

Beginning in about 1970, the principles and techniques of modern inorganic chemistry have been used very effectively to analyse the conventional process for the refining of the concentrates and to improve these methods. A feature of newer refining processes has been the introduction of solvent extraction and ion-exchange methods to the industry, and it appears probable that these techniques will become standard within the industry in the near future.

## 1.2 Sources of Platinum Metals

### Primary Metal

As outlined previously, various sources have at various times dominated the supply of PGM. From about 1960 onwards, PGM associated with Cu-Ni deposits became by far the dominant source, and today about 98% of the total world production of primary PGM is derived from only three sources, i.e. sulphide deposits in Canada, USSR, and South Africa.

These three sources have in common a low PGM grade (2 to 10 ppm), and in general a very close association between the PGM minerals and the base metal sulphide minerals. This means that, in general, recovery of the PGM separately from the base metal sulphides is not

possible by physical methods such as gravity separation. Thus, the major amount of PGM is recovered as a byproduct of the processes used for recovery of the much larger amounts of base metals that accompany them.

In other respects these three deposits are somewhat different. In the case of the Russian and Canadian deposits, the ratio of (Cu + Ni)/PGM is so high that these deposits are in essence mined for their base metal content, the PGM being merely byproducts. In the Bushveld Igneous Complex (BIC) deposits in South Africa, the reverse is true, ~60% of the revenue being obtained from the PGM, and <40% from the base metals.

In addition, Pt is the major PGM found in South African ores, whereas Pd is the major in Russia and Canada. South Africa therefore dominates the world Pt market whereas the USSR dominates the Pd market.

A further source of supply is beginning to be exploited in South Africa. This is the "UG-2" chromitite seam, underlying the main Merensky Reef. This contains a low sulphide mineralisation in a chromitite seam, and, associated with these sulphides are PGM. The ratio of individual PGM in this ore is quite distinct to that of the Merensky Reef, and it is in particular much richer in Ru and Rh than the Merensky.

The reserves of PGM available in South Africa are reputed to be in excess of 42000 t. This includes those in the Merensky Reef and the UG-2 reef, where exploitation has only just begun.

## Secondary Metals

The consumption of PGM by industry increased by a factor of ~50 between 1930 and 1980. This vast increase in consumption has been matched by the growth of the secondary metal industry since most of the metals are used in products from which they may eventually be recovered for recycling. The major uses of the metals today are as follows:

electrical and electronic usage 40%; chemical industry (catalysts) 30%; auto-exhaust catalysts 10%; petrochemical catalysts 10%; fabricated ware 10%.

Recycled material from these uses falls into one of two categories:

- (I) high and medium grade scrap includes supported and gauze catalysts, fabricated ware, etc., and usually has a PGM content of >10%, or is associated with an easily separated substrate (e.g. carbon supported catalysts). These materials can be recycled directly to a secondary refinery for treatment and recovery of the individual PGM.
- (II) low-grade scrap. This includes much material from the electronics industry in the way of obsolete equipment and production scrap, and the PGM are usually present in low amounts on mixed metallic/non-metallic materials. Certain low-grade catalysts, e.g. auto-exhaust catalysts, alumina-supported petroleum catalysts, etc. also fall into this category, as well as low-grade byproducts from the secondary refiners themselves. These materials are usually treated by Pd or Cu smelters, and are removed from the base metal circuits in the form of byproducts where they may be sufficiently concentrated to allow final refining to take place.

By 1981 it is estimated that ~100 t p.a. of PGM scrap in one form or another was being recycled via secondary metal refiners. This may be compared with total world production of new metal of ~200 t p.a. in that year.

### 1.3 The Production of PGM Concentrates from Sulphide Ore-bodies

Almost all ores that are treated today for their PGM content contain less than 10 ppm PGM in association with a relatively large amount of Cu, Ni, and Fe sulphides. The initial steps in the recovery of the PGM are thus very closely related to the recovery of the associated base metals, and the processing only becomes distinct once a concentrate containing the PGM can be separated from the base metals.

The following description of the early stages in the processing of the ore applies to the South African producers. The technology used by Russian and Canadian producers is similar in principle but does vary somewhat in detail, as a result of the slightly differing mineralogy of these deposits.

The ore is first crushed and then milled to the desired "liberation" size. On South African ores of a relatively fine-grained character, this is usually  $75\% < 70\ \mu\text{m}$ . The finely ground ore may then be treated by a gravity separation technique to remove some of the PGM ( $\pm 20\%$ ) as a rich As/Te heavy mineral concentrate, although this is by no means essential. This concentrate is rich enough to be treated directly by the PGM refinery.

The sulphide minerals are then recovered from the ore by froth flotation. Usually  $\sim 5$  to 10% of the ore appears in the concentrate, and this contains  $\pm 80\%$  of the PGM and Cu and Ni sulphides. The grade of PGM in the concentrate is thus  $\sim 100$  ppm and the nickel content 5 to 10%.

The flotation process may be varied to include differential flotation of Ni and Cu minerals. Thus, at Inco, it has been found possible to selectively float chalcopyrite, pentlandite, and pyrrhotite to produce separate concentrates for processing. This may be a distinct advantage for further processing, especially if the PGM are only of minor economic significance, but this does not apply to South African ores.

Further upgrading of the concentrate usually takes place by smelting. This was formerly done in blast furnaces, but all new plants have been built on the basis of electric smelting.

The concentrate, dried and sometimes agglomerated, is fed via chutes between the electrodes to form a cold top.

The electrodes usually in an in-line pattern, are spaced  $\sim 1.5$  to 2 m apart, and heating takes place by means of the ohmic resistance of the molten slag layer between the electrodes. The sulphide minerals melt and collect at the bottom of the furnace as a matte layer, which is tapped off intermittently while slag runs over an end weir continuously.

Typical operation is at a temperature of 1250 to 1350°C. The composition of the matte produced – "green matte" is dependent on the Ni and Cu content of the concentrate. In South Africa a typical composition would be Fe 40%, Ni 20%, Cu 10%, S 30%, PGM 500 to 1000 ppm. Recovery of valuable metals in the matte is very high – usually  $> 98\%$ , so that the slag is normally discarded, although at Rustenburg Platinum Mines (RPM) a slag grinding/flotation circuit was formerly used.

Although the operation is in essence a melting, some incidental oxidation of sulphur takes place, and the furnace off-gases contain a low concentration, 1 to 2%, of  $\text{SO}_2$ . This is of considerable concern from the atmospheric pollution that results. Furnace gas is also very dusty and is cleaned before discharge to atmosphere via a tall stack, the dust being returned to the furnace.

The matte phase formed in this operation is an excellent collector of the precious metals, and losses in the slag are almost entirely due to mechanical causes (entrainment of matte prills). It is also an excellent collector of various other minor constituents of the ore, such as Se, Te, As, Sb, Pb, Co, Bi, etc., and these are thus concentrated along with the PGM.