Gmelin Handbook of Inorganic Chemistry

8th Edition

Pt
Platinum

Supplement Volume A 1

Technology of Platinum-Group Metals

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With 37 illustrations

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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

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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 NH_4^+ ions precipitated Pt as an insoluble salt from 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 $(NH_4)_2PtCl_6$ and precipitation of Pd as $PdCl_2(NH_3)_2$.

(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 H_2SO_4, then the oxidation of NH_3 to HNO_3, and thereafter in a whole range of new industrial processes.

The Modern Period

This period bas 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 form 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 ot 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 catalists, alumina-supported petroleum catalists, 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 μm. 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, pendlandite, 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 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 stock, 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.