Availability of the Platinum Metals

A SURVEY OF PRODUCTIVE RESOURCES IN RELATION TO INDUSTRIAL USES

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Increasing industrial uses of platinum and its associated metals — palladium, rhodium, ruthenium, iridium and osmium — have occasionally given rise to doubts as to the future availability of adequate supplies. This has sometimes discouraged research workers from considering the advantages of these metals in their search for new routes or for new products in the chemical and allied industries. This paper, presented at the Symposium on the Platinum Group Metals organised by the American Chemical Society during its meeting in New York in September, outlines the very substantial productive resources now associated with these metals and relates them to the trends in their applications in industry.

Every chemist is familiar with the six metals of the platinum group, and most will be well aware of the chemistry of their complex salts upon which their separation and refining — as well as their methods of analysis — are based. Not so much is known about the extraction of these metals from their ores or about the scale upon which these operations are conducted to provide the chemical and other industries with their needs, and in consequence misconceptions have sometimes arisen as to their availability for new products or processes.

It is the intention in this paper to outline the chemistry of the extractive methods employed, to submit data on the present and future supply position, and to put into perspective some of the trends in the applications of the platinum metals in their major areas of growth.

Before we turn to this discussion, however, there are a few essential factors that must be made clear:

(1) Unlike gold, platinum is not used for monetary or speculative purposes, and only to a limited extent for decorative uses. We are dealing with an industrial metal, vital to a number of chemical or metallurgical processes which, taken together, account for between 80 and 90 per cent of the total demand.

(2) Platinum and its allied metals are used in industry only where their inherent properties are essential to a successful operation or process. Many established uses of fifty or a hundred years ago have disappeared with the advent of new and cheaper materials, while many newer applications have become established.

(3) By comparison with the base metals, a very high proportion of the platinum metals used in industry is refined and re-used repeatedly, often without change of ownership. Figures for production therefore relate only to newly-mined metals to meet increasing demands from technologically advanced industries. A considered estimate of the total amount of platinum in circulation in the world to-day would be between 25 and 30 million troy ounces.

(4) There has been a great deal of discussion about a shortage of platinum
The shallower portions of the Rustenburg platinum mines are worked from inclined haulages such as this, sited about 2,500 feet apart, while the deeper areas have been opened up by means of five vertical shafts ranging in depth from 500 to 2,500 feet. A further shaft is now being sunk to exploit the ore body to a depth of 3,000 feet. All together some eighteen miles of outcrop are being mined. Rustenburg is the largest underground mining operation in South Africa, employing over 20,000 workers, and is the largest producer of platinum metals in the world. Total reserves in this part of South Africa have been estimated to be in excess of 200,000,000 ounces of platinum for industrial uses during the last few years. In fact there has been no absolute shortage, and although demand has increased very substantially, almost all industrial needs have been met by the main primary sources, South Africa, Canada and Russia. The impression of shortage has stemmed from the wide disparity in the selling prices for South African and Canadian platinum, on the one hand, and that for the metal coming from Russia and certain other minor producers. The shortage is thus one of relatively low-cost platinum only. The widely held belief that Russia has withdrawn as a major supplier to the West is untrue. In fact the amounts exported year by year have remained fairly constant, although constituting a diminishing proportion of a larger usage.

(5) Increased supplies of new metal can be made available, the only condition being that responsible forecasts of usage are provided upon which to base further programmes of expansion in mining and smelting facilities. At any conceivable rate of production the ore reserves available will ensure continuity of operations at the South African mines well into the next century.

Sources of the Platinum Metals
Prior to World War I the greater part of the then modest needs for the platinum metals was met from alluvial or placer deposits in Russia and the Republic of Colombia, but this type of primary material now represents only a very minor part of world production, the two remaining sources today being Goodnews Bay in Alaska and the Compania Minera Choco Pacifico in Colombia.

The discovery of extensive deposits of platinum-bearing copper-nickel ores in
The ore is first crushed in a series of jaw crushers and is then fed to the primary and secondary ball mills.

Canada and South Africa some forty or fifty years ago has given rise to a major industry which now provides by far the greater part of the Western world's needs, while broadly similar deposits in the Urals and elsewhere in Russia have been worked more recently. In all these three major producing countries the platinum content of the mineral runs only to a fraction of an ounce per ton, and many millions of tons of ore have therefore to be mined, milled and smelted each year. The processes of extraction involve basically the smelting and then the electro-refining of copper and nickel, followed by the recovery, separation and refining of the platinum metals themselves.

South Africa differs, however, from Canada and the USSR in one important respect. The Rustenburg mines in South Africa are worked primarily for the platinum metals, yielding copper and nickel as by-products, whereas the International Nickel and Falconbridge mines in Canada, and also the Russian deposits, are essentially sources of copper and nickel with the platinum metals as by-products. This difference is of major importance in enabling the South African mines to respond more quickly and effectively to increasing demand, and output from this source has been increased more than fourfold over the past five years, with further expansion already in hand. Rustenburg is in fact the world's largest source of platinum, and the only major mine whose main activity is the production of the platinum metals.

For this reason, although methods of extraction in other countries are broadly similar, it is the techniques adopted by Rustenburg and by their refiners Johnson Matthey that will be mainly described here.

**Extraction and Refining**

The deposit worked by Rustenburg Platinum Mines forms part of the Merensky Reef of the Bushveld Igneous Complex. This reef, named after the geologist Hans Merensky who was responsible for the prospecting programme that led to its discovery in the 1920s, has been traced on outcrop a distance of some 75 to 80 miles along both the eastern and western limbs of the Complex. The eighteen miles of outcrop which are mined at the two operations, the Rustenburg section a few miles to the East of the town,
and the Union section about sixty miles to the North, are considered to contain the highest grades of the entire Complex.

Platinum values at these two sections show a very even tenor, the platinum being partly in the form of native metal, invariably alloyed with iron as ferro-platinum, and partly as the sulphide, arsenide and sulph-arsenides, these always occurring in intimate association with the sulphides of iron, copper and nickel. Associated with platinum, the predominant metal, are smaller proportions of palladium, ruthenium, rhodium, iridium and osmium, in this descending order of concentration.

The platinum-bearing reef averages only some twenty inches in thickness, but its regularity makes for relatively straightforward mining. It persists to depths beyond the limits of practical mining, and the reserves down to a depth of 3,000 feet are immense.

The length of strike and the comparative shallowness of the deposit have made possible the rapid development of large areas of ground whenever a greater demand for platinum has arisen—one reason why Rustenburg has been able to follow world demand so closely. In the shallower portions of the deposit inclined haulages are sited about 2,500 feet apart, while the deeper areas have been opened up by means of five vertical shafts ranging in depth from 500 to 2,500 feet. A further shaft is currently being sunk to exploit the ore body to a depth of 3,000 feet.

The ore is first crushed in a series of jaw crushers and fed to the ball mills which are in closed circuit with hydrocyclone classifiers. This stage is followed by gravity concentration on corduroy tables to separate the coarse particles of platinum-bearing minerals and the free metallic particles. The corduroy concentrate is dressed on an elaborate system of shaking tables up to a final high grade concentrate which is sent directly to the Johnson Matthey refineries in England.

The tailings from the tables are returned to the mill circuit, the final pulp from here

*Flotation concentrates are smelted to a copper-nickel-iron matte. This is cast into moulds, broken up and sent to the refineries for extraction of copper, nickel and the six platinum metals*
In the electrolytic nickel refineries pure nickel cathodes are produced while the platinum metals accumulate in the anode residues and are removed for separation and refining being treated in a series of thickeners before going to the flotation plant, which recovers most of the remaining platinum-bearing minerals. The flotation concentrates, consisting mainly of nickel, copper and iron sulphides with the balance of the platinum metals, are thickened, filtered, dried and pelletised, ready for the smelter.

The initial stage in the recovery of the platinum metals is to smelt to a copper-nickel-iron matte in a series of blast furnaces. This matte is then tapped periodically into ladles, transferred to a group of converters, and blown to a high-grade matte which is cast into moulds and then broken up in a jaw crushe. Part of this converter matte is shipped to the Johnson Matthey smelter in England, the balance being treated by Matte Smelters, a joint subsidiary of Johnson Matthey and Rustenburg, in a plant adjacent to the mine.

Rustenburg converter matte contains about 46 per cent of nickel, 28 per cent of copper, together with small amounts of other base metals and sulphur. The content of platinum group metals is about 50 ounces troy per ton (0.15 per cent). The treatment of this material may be divided into two steps, first the removal of nickel and copper to produce a rich platinum group metal concentrate, followed by chemical treatment of this concentrate to separate and purify the individual metals.

Two processes are in operation to achieve the first aim. The older process, the Orford or top-and-bottom process, involves the smelting of the copper-nickel matte with sodium sulphide. This results in the formation at high temperature of two immiscible liquids, a heavier nickel sulphide phase containing the platinum group metals and a lighter sodium copper sulphide phase containing gold, silver and only minor amounts of platinum group metals. These two liquid phases are separated and allowed to solidify. The sodium copper sulphide is blown with air in a Bessemer converter to produce blister copper which is further refined and
then cast into anodes. These are electrolytically refined to produce marketable copper, leaving an adherent anodic residue containing the noble metals present in the copper "tops". The nickel sulphide "bottoms" are ground, roasted, and the resultant nickel oxide reduced to metal which is cast into anodes. These are also refined electrolytically to produce pure nickel and an anodic residue containing the platinum metals. The residues from the copper circuit and the nickel circuit are together roasted and leached with sulphuric acid to produce a concentrate, containing about 65 per cent of platinum group metals.

The second process being operated to produce a platinum group metal concentrate from the matte involves the leaching with sulphuric acid under pressure of the finely ground matte. This results in the removal of copper and nickel as sulphates followed by their recovery by normal electro-refining techniques. The residue, containing the platinum metals, is treated to remove iron oxide and to produce a concentrate suitable for chemical refining.

Final concentration and separation of the platinum metals is carried out in the Johnson Matthey refinery in England, but an additional refinery is now under construction in South Africa to supplement supplies by treating some part of the output of Matte Smelters.

It is only possible to outline briefly the chemical treatment of these concentrates, and this account gives only a simplified picture. The concentrate is first attacked with aqua regia to dissolve gold, platinum and palladium, the residue comprising the more insoluble metals iridium, rhodium, osmium and ruthenium. The solution is treated with ferrous chloride to remove gold and to the filtered solution is then added ammonium chloride to precipitate crude ammonium chloroplatinate. This is calcined and the impure sponge re-dissolved. Ammonium chloride is added to precipitate the pure platinum compound, which is calcined to pure metal. The filtrate from the crude ammonium chloroplatinate is oxidised to precipitate ammonium chloropalladate. This is dissolved and decomposed by boiling with water to produce a solution of ammonium chloropalladid. Ammonia is added to convert the palladium to tetraminepalladous chloride. On acidifying the solution with hydrochloric acid there is precipitated diaminedichloropalladium which is calcined to yield pure palladium sponge.

The original insoluble residue is fused with oxidising alkaline fluxes and the cooled melt leached with water. Osmium and ruthenium are removed and separated by distillation of their volatile tetroxides, being subsequently converted to metal by thermal decomposition of a suitable compound. The iridium and rhodium remaining in the solution after distillation are recovered as sodium chlorocomplexes which are converted to ammonium compounds for calcination to metal.

All these calcinations are carried out under carefully controlled conditions in electrically heated muffle furnaces, to produce the metals as sponges or powders suitable for melting.

**World Production**

Dealing first with South Africa, Rustenburg, whose output has been increased from some 200,000 ounces of platinum in 1963 to 850,000 ounces a year at present, has a further expansion programme in hand to yield 1,000,000 ounces a year by 1971, and has just announced plans to increase production to 1,200,000 ounces by 1973.

Corresponding increases have, of course, taken place in the output of the other members of the platinum group of metals — palladium, rhodium, ruthenium, iridium and osmium.

This has been achieved by very substantial capital expenditures on the sinking of new shafts, the installation of additional grinding, milling and flotation equipment, and the building of an additional modern smelting plant, together, of course, with a consequent expansion in all the facilities and services. The expenditure involved in the expansion...
The initial stage in the Johnson Matthey wet process refinery involves digestion of the enriched concentrates with aqua regia to dissolve the platinum and palladium, leaving the iridium, rhodium, ruthenium and osmium as insoluble residues to be treated separately.

programme over the seven years 1967 to 1973 will probably exceed $130 million. Today Rustenburg constitutes the largest underground mining operation in the Republic of South Africa, its two mines together extending more than eighteen miles from one end to the other, and providing about 60 per cent of the Western world's needs of platinum.

By the end of the present year there will be a new South African producer, Impala Platinum, from which can be expected an output of about 50,000 ounces in 1970, rising perhaps to 150,000 ounces in two years' time.

The output from Canada is likely to be upwards of 200,000 ounces a year, and no significant change is expected from the existing smaller producers.

There is unfortunately no real basis for estimating production from the USSR, but this is undoubtedly geared to her growing outputs of nickel and copper. All that can be said is that after taking care of her internal and expanding needs of platinum, something like 300,000 ounces of metal a year have been exported.

Thus a total annual output from the Western world of over 1,500,000 ounces will be available in the early seventies, and it is reasonable to assume that this will be supplemented by whatever the USSR may contribute to Western supplies.

Palladium naturally follows the same trend in expanding output as platinum itself, but here the relationship between individual producers is somewhat different. The Canadian ores contain more palladium than platinum, while in South Africa the reverse is the case. Western World production from these two sources together with the minor producers is now running at around 550,000 ounces a year, with the USSR overtopping this figure considerably. Looking ahead some five years or so, Rustenburg, within the framework of its present expansion plans, could produce around 500,000 ounces a year. To that could be added rather less than 100,000 ounces from Impala, depending upon this producer's aspirations in platinum.

Canadian output should continue to provide between 250,000 and 300,000 ounces a year, and other sources will make a modest contri-
This section of the Johnson Matthey refinery – the largest of its kind in the world – handles the precipitation, re-dissolving and re-precipitation of platinum and palladium.
weight of gauzes that most plants carry as spares. Nitric acid manufacture represents the largest direct platinum metal consuming process, in that a small but significant proportion of the gauzes installed is irrecoverably lost in the high temperature oxidising conditions encountered in the plant. This metal loss represents only 3 to 4 per cent of the total costs of manufacturing nitric acid, and the recently developed platinum recovery process using gold-palladium gauze immediately below the platinum gauzes should serve to reduce appreciably even this small proportion of the costs contributed by the use of platinum.

The major outlet for nitric acid is in the manufacture of nitrate fertilisers for which the demand is growing steadily throughout the world—particularly in the underdeveloped countries. The ammonia oxidation route to nitric acid is now very well established and is unlikely to be superseded by alternative processes in the foreseeable near future. Alternative catalysts, using transition metal oxides such as cobalt oxide, have been studied for a number of years as possible alternatives to platinum, but their relatively short operating lives makes it unlikely that they will find acceptance in the industry for the time being.

In the very long term, it is possible that the nitric acid route to nitrogen fixation may be replaced by direct fixation processes using homogeneous catalysts. The platinum metals, particularly ruthenium, have been intensively studied to provide suitable catalysts for such a process, but at the present time no viable route is in sight.

Atmospheric Pollution

The excellent catalytic properties of platinum—particularly as an oxidation catalyst—make it likely that it will be used in a number of systems designed to oxidise undesirable or harmful organic odours or other atmospheric pollutants. The pollution control industry is a comparatively new one, and is growing very rapidly as increasing public attention is focused on the problem in almost every country, while legislative pressures mount to force offenders to adopt suitable control systems. Already platinum catalysts are used to oxidise a number of unpleasant pollutants in several industries, for example in wire enamelling, in abattoirs and in meat or fish processing. Platinum catalysts are also increasingly adopted by the nitric acid industry to reduce the harmful and corrosive nitrogen oxides that are emitted with the tail gases from most plants.

The problems resulting from the emission of unburnt hydrocarbons, carbon monoxide and nitrogen oxides in the exhaust gases from internal combustion engines have received a...
World production of chlorine by the electrolysis of brine is about 25 million tons a year. Some large estimates of platinum consumption as platinised-titanium anodes in this industry are now unlikely to be realised since the development of a ruthenium oxide coating on titanium.

great deal of attention. Several platinum-containing catalyst systems have already been developed and await commercial exploitation. Legislation under consideration in several countries—notably in the USA—could dramatically affect the future of platinum consumption in this field in one of two ways: either the conventional petrol engines will have to be universally fitted with catalytic or other exhaust gas purification systems, or the use of lead additives may be increasingly controlled, resulting in a corresponding increase in the need for platinum in petroleum reforming operations. Either way, it seems likely that public pressures for the need to control atmospheric pollution in the urban centres of the world's industrial countries will result in a demand for platinum using systems, although, of course, modifications to engine design may also help to overcome part of the problem.

Petroleum Reforming

The recent introduction of rhenium into reforming catalysts has a synergistic effect on the performance of the platinum, and some catalyst manufacturers have been able to make use of this to give improved performance while maintaining the same platinum percentages in their products. In other cases a lowering of platinum levels has been made possible, at least for the time being. It is still clear that the more platinum contained in a reforming catalyst, the better is its performance. The continual increase in operating severities coupled with the rising demand for high octanes and for aromatics will almost certainly require an increasing level of supply of platinum to the petroleum industry, but this increase will probably be spread over a number of years.

Fuel Cells

Fuel cells have for a long time been under intensive development for a number of applications. Among the favourite potential applications has been the electrically powered motor-car, using the fuel cell as an alternative to the internal combustion engine. Early work in the development of fuel cell systems indicated that the platinum metals were supreme in their combination of catalytic and
corrosion resistant properties. More recent work, however, based on the erroneous assumption that insufficient platinum would be available for their future needs, has led researchers to develop some potential alternatives to platinum in certain applications. Although it now seems unlikely that platinum electrocatalysts will find applications in fuel cells for major mass market applications, it is very probable that specialised fuel cells for selected applications will use them. Considerable effort is being devoted towards providing platinum electrocatalysts that make much more effective use of the platinum component than has been possible hitherto, and indications are that this work will be successful.

**Chlorine Production**

The use of platinised-titanium anodes in the production of chlorine and chlorates by the electrolysis of brine has received considerable attention in recent years, and some very large estimates of platinum and iridium-platinum consumption have been made. At present, however, it appears likely that while iridium-platinum deposited on titanium anodes will be used for chlorate production, ruthenium oxide on titanium will be preferred in the very much larger chlorine manufacturing industry.

**Organic Electrosynthesis**

The field of organic electrosynthesis is receiving very considerable attention from research workers in the universities and in industry. Here also selective electrocatalysts are required, and it is possible that some systems may be developed using platinum metals on suitable supports.

**Heterogeneous Catalysis**

Other than in petroleum reforming operations, platinum is not at present widely used in industrial heterogeneous catalytic systems. Palladium is much more widely employed, particularly in liquid phase hydrogenation reactions. Hydrogenation of a wide range of compounds has grown very markedly in recent years in the general chemical, dyestuffs and pharmaceutical industries, and the future application of platinum group metal catalysts, particularly palladium, supported...
The manufacture of glass fibre involves the rapid flow of glass at around 1,400°C through a series of orifices which must retain their size and alignment. The electrically heated bushings are universally made in rhodium-platinum alloys

on a range of suitable carriers is likely to increase significantly.

**Homogeneous Catalysis**

Organo-metallic chemistry is the most rapidly expanding of all branches of chemistry and although the use of compounds and organic complexes of the platinum metals as homogeneous catalysts is only in its industrial infancy at present, this is a field of application likely to grow dramatically in the next decade. Rhodium in particular has been found, in its numerous complexed forms, to be a most effective homogeneous catalyst in hydrogenation, hydroformylation, carbonylation and other reactions, while ruthenium complexes are also showing indications of great potential usefulness.

**Viscose Rayon**

Substantial amounts of platinum are in use in the viscose rayon industry in the form of spinnerets made from platinum-gold or rhodium-platinum alloys, but recovery and re-use are virtually complete and this industry does not therefore create a significant demand for new metal.

**Electrical Uses**

For the electrical industry no major change in the usage of platinum (or rhodium with which it is so often alloyed) is foreseen. Light duty contacts, electric furnace windings, thermocouples, cobalt-platinum alloy permanent magnets, resistance thermometers and precision potentiometers represent the major applications in this field, while metalising preparations based upon platinum, palladium and ruthenium are growing in demand for capacitors, resistors and other thick film electronic components.

Some 60 per cent of the total usage of palladium is in the electrical industry mainly for telephone contacts in the cross-bar switching system adopted in the USA and Japan. This system will eventually be superseded by the electronic exchange, but it is not expected that the demand for palladium will fall for a further year or two.

In light duty contact applications, particularly for sliding surfaces such as slip-rings, electrodeposited rhodium has for many years been established and is growing in usefulness.
Improved methods of electrodepositing both palladium and ruthenium have more recently shown the advantages of these two metals, the former in replacing gold in electronic applications and the latter as a less expensive alternative to rhodium.

**Glass Manufacture**

The protection of refractories from attack by molten glass—and thus the avoidance of contamination—is a major problem in the glass manufacturing industry, and a large and growing demand for platinum arises here. Stirrers, tank blocks and other equipment controlling the flow of molten glass are thus clad with platinum sheet of about 0.25 mm in thickness, and it has been well established that this practice has always resulted in the production of a particular type of glass at a more economic price either by the production of a purer glass or of one with greater freedom from defects.

The manufacture of glass fibre—an industry that has grown rapidly and that is now expanding considerably in less well-developed countries—involves the rapid flow of glass at around 1400°C through a series of orifices which must retain their size and alignment. Platinum, or more generally 10 per cent rhodium-platinum, is universally employed for the construction of the trough-shaped bushings used in this process. The cost of the platinum employed, including the interest on the investment and the refining and remanufacturing of the bushings, represents only about 3 per cent of the selling price of the glass fibre.

**The Future**

To sum up these trends in the demand for platinum and its allied metals is not a simple matter, but irrespective of the several uncertainties in the situation or of short-term fluctuations in consumption, the overall picture remains one of growth based upon increasing industrialisation and upon the normal growth of the established applications. Rustenburg has demonstrated clearly over the years its determination to meet this growing demand. Its most recent announcement of yet another programme of increasing productive capacity to yield 1,200,000 ounces of platinum a year by 1973—with, of course, corresponding increases in the output of the other platinum group metals—gives any reassurance that might still be needed on their long-term policy. Simply and briefly expressed, this is to take all steps that might be necessary, jointly with Johnson Matthey as smelters and refiners, to ensure to industry throughout the world adequate and continuing supplies of the platinum metals.

In making this latest decision to expand still further, the possibility has been faced that it could conceivably give rise to some excess of capacity and a situation of over-supply. On the other hand, should it be found that the projected output is not likely to be adequate for the indicated demand, there will be no hesitation on the part of Rustenburg in increasing still further the mines' productive capacity, or on Johnson Matthey's part in extending once again their smelting and refining facilities.

The question then arises of how long production at this or any higher rate can be continued. It is difficult to assess with any high degree of accuracy the amount of platinum contained in the South African deposits and so to give an indication of the potential reserves of metal, but prospecting operations which have been carried out by Rustenburg for many years on the Merensky Reef have enabled it to build up a comprehensive knowledge of the potentialities of both the very substantial areas over which it has mining rights and of the remaining areas. To arrive at a realistic estimate of the total reserves, account must be taken of the grade of ore available and the feasibility of mining operations at increasing depths. Within this framework, and assuming reasonable price levels for an arbitrarily selected period of the next 30 years, it is estimated that the overall reserves of platinum that could be economically exploited during this period amount to not less than 200 million ounces.