

Platinum Metals from Nuclear Fission

AN EVALUATION OF THEIR POSSIBLE USE BY INDUSTRY

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Metals of the platinum group are being produced in appreciable and growing quantities as by-products of nuclear fission in atomic reactors. It has been suggested that rhodium, palladium and ruthenium might possibly be separated in the reprocessing of spent fuel and be used in industry but from calculations recently made it is now shown that their levels of radioactivity would be unacceptably high and their use would entail a risk of contamination of world stocks of all the platinum metals. The growth of mining operations is expected to provide ample supplies of all the platinum group metals and there is no prospect of exhausting mineral resources in the foreseeable future.

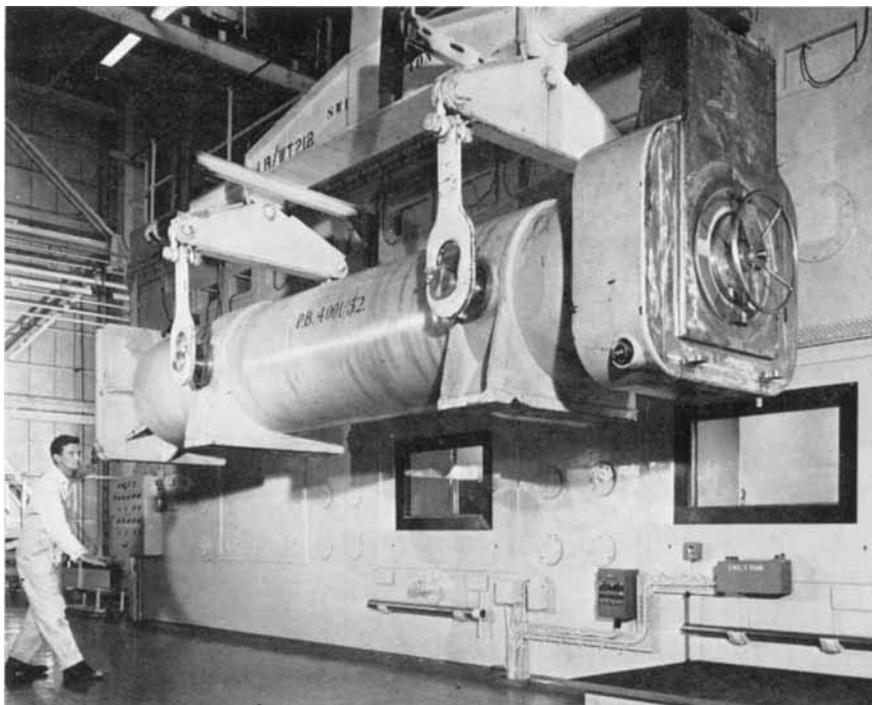
The growth in the generation of electrical power from nuclear fission is giving rise to transmutation elements in significant quantities. Of the many created, those in the platinum group might appear worthy of consideration for commercial use (1). Indeed this has been suggested by staff at Battelle-Northwest working on behalf of the United States Atomic Energy Commission (2, 3) and assessments of them are being undertaken (4), but after careful study of available information on the platinum group metals potentially recoverable from atomic wastes

we have reached the following general conclusions:

- (1) There are adequate mineral reserves under development and the recovery of fission products is not therefore imperative.
- (2) The platinum group metals are not destroyed in industrial use but are recycled many times through the refineries. Radioactive contamination of this recycled pool would introduce irreversible hazards.
- (3) The cost of recovering fission products and of decontaminating them (so far as may be possible) is likely to be high since the processing must eliminate any risks of the escape of very dangerous wastes in any form whatsoever.
- (4) For some years industrial demand has been for more platinum; in matching this demand by mining natural ores there has been a more than adequate generation of the associated metals of the group.

Much of the quantitative information supporting these conclusions has been published previously (3, 5) but we will repeat salient points and give some new data based on studies made by the United Kingdom Atomic Energy Authority (6), to whom we are grateful for discussions.

Of the platinum group metals only ruthenium, palladium and rhodium are produced in significant amounts during the nuclear fission of uranium and plutonium.



Stringent precautions are needed to prevent the escape of radioactivity during the reprocessing of nuclear fuel. Movement of material within a reprocessing plant requires special flasks

However, we do not propose to discuss ruthenium in detail since its radioactivity is high and long-lived and also its industrial importance is very much less than that of palladium or rhodium.

Fission Palladium

Palladium has its principal use in electrical contacts but it is also important for catalysts and for alloys used in the diffusion purification of hydrogen. World usage has climbed from half a million ounces troy in 1962 to more than one million ounces troy per annum at present and the demand shows no sign of abating. However, the demand for platinum, which is only available from natural sources, is rising at a similar rate and mining operations for platinum yield enough associated palladium to meet the increased demand. Russian deposits appear to yield more palladium than platinum; South African deposits yield about one ounce of palladium for three of platinum. Hence, with world

production of platinum group metals probably exceeding 4,000,000 ounces this year, something of the order of 1,800,000 ounces of palladium will be mined.

It has been forecast that fission palladium will be produced by 1990 at a rate equal to that of natural palladium (70,000 ounces troy in the U.S.A. alone by 1980 (7)). However, it contains about 15 per cent of the isotope ^{107}Pd . This is not found in nature and is a stable beta emitter with 7×10^6 years half-life. The activity is expected to be 100 millicuries per kilogram of the recovered product. Although the energy of the beta radiation is low (0.035 MeV) such material could not be handled with bare hands. It could conceivably cause skin damage if used in jewelry, and silver recovered from scrap palladium-silver alloys might well ruin film if re-used in photography without perfect removal of the palladium. Of the 22 isomers and isotopes of palladium only ^{107}Pd has a significantly long half-life.

Fission Rhodium

Rhodium has very important uses, chiefly as 10 to 20 per cent rhodium-platinum alloys in gauzes for the production of nitric acid by catalytic ammonia oxidation, for glass melting apparatus and in wire for thermocouples. Again it may be noted that the amounts of rhodium and platinum from natural sources are in the right ratio of production to meet demands for them. From South African sources alone around 100,000 ounces of rhodium will be mined this year together with about 1,200,000 ounces of platinum. This amount of rhodium is in itself almost enough to cope with world demand (outside Russia).

Fission rhodium is expected to arise in quantities equal to present usage by 1980 (3) and if suitable it could supplement natural resources. This would be particularly important if the rate of usage of rhodium should grow more rapidly than that of platinum or if Russian supplies should fail. It is therefore more important than in the case of palladium to examine prospects for the fission product. Of the isotopes of rhodium only ^{102}Rh occurs as a fission product with significant half-life. It has two isomers, both gamma emitters, with half-lives of 206 days and 2.9 years. Present estimates, in the absence of experimental results, suggest that, for power reactors, there might be initial activities of 200 and about 10 millicuries per kilogram of total rhodium. After storage for three years the activity of the 206-day isomer would be nearly equal to that of the 2.9 year isomer (i.e. each about 10 millicuries per kilogram). This latter figure will be used in discussing the dose rates of radiation in certain practical cases.

Let us assume that three-year "cooled" fission rhodium is alloyed with natural platinum to produce 10 per cent rhodium-platinum alloy. A typical gauze catalyst bed for nitric acid production 8 feet (2.4 metres) in diameter would contain 2 kilograms of rhodium and would give a dose rate of 10 millirad per hour at an axial distance of

6 feet (2 metres). The maximum ambient level permitted under the Unsealed Sources Act (uncontrolled conditions) is 0.75 millirad per hour or 2.5 millirad per hour with prescribed precautions. Such gauze could not be touched with bare hands and its fabrication, particularly during weaving, would be attended by difficult problems of remote control, while its installation in the nitric acid plant could not be undertaken by the normal personnel.

Consider a piece of rhodium-platinum alloy sheet one millimetre thick such as a disc of two square feet (900 cm^2) used in glass melting apparatus. It would give a contact dose rate of 750 millirad per hour and a dose rate of more than 50 millirad per hour at an axial distance of 30 centimetres. Thus the complex cutting, forming and welding operations involved in making glass melting apparatus would have to be performed under extreme difficulty and expensive precautions would be required of the user.

Similarly a rhodium-platinum twin thermocouple with wire 0.5 mm diameter would give a contact dose rate of about 50 millirad per hour when the wires were stretched out in a straight line and, of course, much more when coiled up for storage.

Problems of Decontamination

When reprocessing spent fuel elements the fission products are removed and apart from uranium and plutonium they are finally stored in the form of nitric acid solutions. Most of the numerous elements contained in these solutions are highly radioactive and possess no commercial value at present. The solutions, which are stored in cooled tanks, represent a growing problem of disposal, the ultimate answer to which may involve evaporation and encapsulation as a glass (8, 9).

The ratio of the activities of unwanted elements to those wanted (rhodium and palladium) is in the region of 1,000 million to 1. The U.S.A.E.C. estimate of the activity



Platinum-bearing ore is transported from the mines by the train load. Here loading is taking place at the Bleskop shaft, one of the many shafts at Rustenburg Platinum Mines in South Africa. The mineral reserves are immense and the recovery of fission product platinum group metals is not therefore imperative

of fission rhodium of 5 to 10 millicuries per kilogram is the figure after achieving a decontamination factor of 1,000 million from the original waste solution. Our comments on the difficulties inherent in using fission rhodium in industry assume that this decontamination factor has been achieved! At best, to do so will involve expensive and difficult processing to avoid the hazards of the material.

Some 3,000 ounces troy of fission rhodium are expected to arise in the United Kingdom in each of the next five years. The world total is considerably bigger but it is still small compared to the South African mined output of around 100,000 ounces in 1970.

The present rise in the mining of natural platinum group metals is likely to keep pace with the increasing use of atomic power worldwide. It must be remembered that the platinum group metals are not destroyed in use but are mostly returned to the refineries

for repurification and re-use. The metals in fact are recycled many times. Addition of 1 per cent of fission rhodium to the world supply on a continuous basis would therefore produce a mixture with an activity in the region of 50 to 100 microcuries per kilogram. An ingot of this weight could be handled fairly safely, but the material could not with impunity be used in critical applications such as implant surgery nor could it be brought near photographic apparatus. This is the hypothetical case of complete dispersal of the fission product in the natural one, but any practical situation is likely to lead to some alloys of much higher activity.

Of course the recovery and sale of the fission platinum group metals might be expected to pay in part or in whole for the costs of disposal of radioactive wastes, while the chemical investigations required would contribute to the fund of new technology, but the dangers of rendering world circuits

of platinum and the other precious metals radioactive suggest to us that such a grave step should be avoided – at least for so long as natural supplies of the platinum group metals can keep pace with industrial needs. The platinum mines do in fact possess the capability of expansion to meet such increased demands. This makes it unnecessary to consider using fission metal at present (5).

Finally we cannot advocate the use of materials which might raise rather than reduce the amount of environmental pollution.

References

- 1 *INCO Reporter*, 1968, (October)
- 2 C. A. Rohrmann, *Engelhard Ind. Tech. Bull.*, 1968, 9, (2), 56-61
- 3 *Ibid.*, *U.S.A.E.C. Rept BNWL-SA-2786*, 1969, (Sept.), 24 pp
- 4 *U.S.A.E.C. Rept BNWL 1010*, 1969, (Feb.), 39
- 5 L. B. Hunt and F. M. Lever, *Platinum Metals Rev.*, 1969, 13, (4), 126-138
- 6 U.K.A.E.A., private communication, 1969
- 7 *Chem. engng News*, 1970, 48, (4, Jan. 26), 49
- 8 *Platinum Metals Rev.*, 1965, 9, (3), 89
- 9 *Ind. engng Chem., Process Des. Dev.*, 1969, 8, (1), 36

Dimensionally Stable Electrodes

PAPERS AT THE ELECTROCHEMICAL SOCIETY MAY MEETING

Platinum metals have many and diverse applications in electrochemistry; hence it was no surprise that they formed the subjects of several papers at the May meeting of the Electrochemical Society in Los Angeles. Of particular interest is the fact that three of these papers dealt with the dimensionally stable electrodes under development by Oronzio de Nora-Impianti Elettrochimici di Milan.

Dimensionally stable electrodes preserve their shape and voltage characteristics even under the most severe conditions of anodic attack prevailing in brine electrolysis, whereas the graphite electrodes generally in use at present are eroded and require frequent maintenance to keep voltage losses to a minimum. The dimensionally stable electrodes consist of a thin film of ruthenium oxide deposited on titanium and were developed from the work of H. Beer, of Magnetochemie N.V. in the Netherlands.

Vittorio de Nora described at Los Angeles the characteristics and advantages of dimensionally stable electrodes. After fabrication of the titanium it is coated with ruthenium oxide, which has low overvoltage and good corrosion resistance. The main applications of these electrodes have been in chlorine and chlorate production where a saving in electrical power consumption of over 20 per cent is claimed. Chlorine produced by this means is purer, no further plant to eliminate oxygen and carbon dioxide being required. Hydrogen content is less too. Furthermore, the anodes tolerate much less pure brine feed so that new plant can be constructed more

cheaply. Such electrodes have been operating for more than two years, apparently with no reduction in performance.

De Nora suggested that the electrodes could be adapted to electro-organic oxidation processes and to the electrowinning of such metals as copper and cobalt.

H. S. Holden and R. E. Loftfield, of Electrode Corporation, reporting on practical problems of introducing dimensionally stable electrodes to the chlor-alkali electrolysis process, said that it was possible to make them compatible with the widely differing operating conditions found in commercial mercury and diaphragm cell rooms.

M. M. Jaksic, from the Yugoslav Institute of Chemistry, Technology and Metallurgy described how, on the basis of kinetic, hydrodynamic and polarisation measurements, a chlorate cell was scaled up from 2.0 A rating load to an optimum industrial rate of 40,000 A with efficient operation still possible at 60,000 A. The optimum rate was obtained with an anode current density of about 30 A/dm², which gave a current efficiency of 96 to 98 per cent at 80°C and low overvoltage.

Two other related papers were also of interest. C. C. Lu, K. Fueki, T. Mukaibo and S. Asakura reported that periodic pulse activation of the platinum anode during brine electrolysis maintained its lower over-voltage indefinitely, while E. H. Cook and M. P. Grotheer showed that platinum anode weight loss during sodium perchlorate production depends on the fraction of sodium chlorate converted.