TRACE METALS IN THE ENVIRONMENT

VOLUME 4—Palladium/Osmium

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ANN ARBOR SCIENCE
PUBLISHERS INC
P.O. BOX 1425 • ANN ARBOR, MICH. 48106

Published 1978 by Ann Arbor Science Publishers, Inc.
P.O. Box 1425, Ann Arbor, Michigan

Library of Congress Catalog Card Number 77-088486
ISBN 0-250-40217-3
Manufactured in the United States of America

The work upon which this publication is based was performed pursuant to Contract No. N01-ES-2-2090 with the National Institute of Environmental Health Sciences, Department of Health, Education, and Welfare.

PREFACE

In 1972, the National Institute of Environmental Health Sciences initiated a program with Midwest Research Institute to assemble information on production, usage, natural environmental levels, anthropogenic sources, human and animal health effects, and environmental impacts of selected trace elements. This book on palladium and osmium is one of a series of comprehensive documents which has resulted from that program. Scientists in many disciplines should find this work to be of value.

The authors wish to express their appreciation to Dr. Ernest Angino of the University of Kansas; Dr. Thomas O'Keefe and Dr. Arthur Morriss of the University of Missouri, Rolla; Dr. Roscoe Ellis of Kansas State University; and to our colleague at Midwest Research Institute, Mrs. Connie Weis, for assistance with this book.

The authors wish to express their thanks to Dr. Harold Orel for editorial comments and to Miss Audene Cook and her staff for typing the manuscript. We also wish to acknowledge the information provided us by Mr. Howard Martin of Martin Metals, Inc.; Mr. David Luning of Matthey Bishop, Inc.; Mr. Larry Greenspan and Mr. N. F. Carsillo of Engelhard Industries Division; Mr. A. Dipiazzo, Goldsmith Brothers, Division of National Lead; Dr. William D. Balgord of the New York State Environmental Conservation Department; Dr. Bruce Gonser, retired, of Columbus, Ohio; Dr. Willard Hoehn of G. D. Searle Company; and numerous other spokesmen for industry and government regulatory agencies.

Finally, we especially acknowledge the support, encouragement, and patience of Dr. Warren T. Piver (project officer) and Dr. Hans Falk of the National Institute of Environmental Health Sciences.

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SUMMARY

This report summarizes available information on the natural occurrence, processing, uses, and disposal of palladium and its compounds. We have estimated losses of palladium to the environment during these activities, attempted to identify the forms that the lost palladium assumes, and assessed human-health hazards associated with environmental contamination by palladium.

The principal findings of the report may be summarized as follows:

A large fraction of the world's primary production of platinum-group metals--ruthenium, rhodium, palladium, osmium, iridium, and platinum--is recovered as a by-product of copper and nickel sulfide-ore refining. The rest is recovered from placer deposits of platinum-group metals and gold and from lead and gold ores.

The principal sources of platinum-group metals in the world are the Bushveld Complex of South Africa; the Sudbury District of Ontario, Canada; and the regions of Norilsk and the Kola Peninsula of the USSR. Minor sources are placer deposits in Alaska, Columbia, Ethiopia, Japan, Australia, and Sierra Leone.

The major domestic source of platinum-group metals is secondary recovery from metal scrap, chiefly electronics scrap. The amount of palladium refined from used sources was 161,099 troy ounces in 1971. The amount refined without transfer of ownership (toll refined) in 1971 was 593,842 troy ounces.

Most of the <u>new</u> platinum-group metals recovered in the U.S. are by-products of copper sulfide-, lead-, and gold-ore refining. Industrial contacts estimated that 75-95% of the new palladium recovered each year in the U.S. is from copper refining. Possibly as much as 15% is recovered as a by-product from lead refining. The amount of new domestic palladium refined in 1971 was 32,102 troy ounces.

Chief free-world producers of palladium include International Nickel Company of Canada, Ltd. (INCO); Falconbridge Nickel Mines, Ltd., Sudbury, Ontario; and Rustenburg Platinum Mines, Ltd., of South Africa. Most of the Canadian and South African production is refined in England. Soviet platinum metals are refined in the USSR and distributed to the U.S. directly or via European countries. Chief refiners and distributors of new palladium produced in the U.S. are the major copper refiners; Engelhard Industries, Inc.,; and Matthey Bishop, Inc.

Reported sales of palladium to industry have been assumed to closely approximate domestic consumption. The average amount of palladium sold annually to industry from 1962 to 1971 was 677,608 troy ounces. The average annual fraction used by the various industries in that period was electrical, 57.38%: chemical, 25.73%; dental and medical, 7.55%; jewelry and decorative, 2.83%; petroleum, 2.52%; glass, 0.42%; and miscellaneous and undistributed, 3.42%.

Noncatalytic uses of palladium comprise about 70% of all palladium consumed by industry. About 50% is used as electrical contacts in telephone equipment. Other applications include hydrogen-diffusion apparatus and cladding of process equipment.

Palladium is used in the chemical industry primarily for catalysts in the hydrogenation of intermediates in the production of pharmaceuticals, fragrances, pesticides, dyes, etc., and in the anthraquinone process for hydrogen peroxide production. Palladium(II) compounds are used widely for catalyzing oxidation and carbonylation reactions, especially in commercial processes for producing vinyl acetate, acrylic acid, and acetaldehyde. Supported palladium or palladium zeolite catalysts are used for hydrocracking in petroleum refining.

A major new use for palladium (> 100,000 troy ounces per year) is in the catalytic muffler for oxidation of hydrocarbons and carbon monoxide and reduction of nitrogen oxides in automobile-exhaust emissions.

We estimate that the average annual loss of palladium to the domestic environment in recent years has been about 244,000 troy ounces, distributed among losses to the atmosphere, during copper smelting 1,200, losses during primary and secondary refining 44,000, petroleum refining 50-340, electrical uses 39,000, and chemical-industry catalysts 160,000 troy ounces.

Annual losses of palladium to the environment will increase with the introduction of catalytic automobile-emission-control devices. It is presently estimated that 10 million vehicles will be equipped annually with catalytic mufflers and that a muffler's average life will be approximately 5 years (50,000 miles). Using estimates of 0.01 troy ounce per converter per automobile, 40% catalyst attrition during the useful life of the catalyst, and up to half of this attrition occurring during the first year of operation, one calculates that 8,000-20,000 troy ounces of palladium would be lost from this source in 1975 and that the annual loss will approach 40,000 troy ounces by 1979. This loss is expected to occur as fine particulate palladium metal or as some unknown palladium compound. No information was found on the hazards of breathing fine palladium particulates.

The remainder of the palladium in spent mufflers will likely be discarded to the environment until such time as platinum-palladium prices or the number of spent mufflers justify recovery. Estimated value of residual platinum and palladium in spent mufflers will approach $33 million annually by 1979, based on current metal prices.

A significant fraction of the average annual loss of palladium to the domestic environment during processing, traditional uses, and disposal is in the form of innocuous palladium metal or palladium alloys. The concentration of palladium emissions as metal or oxide particulates or vapors to the atmosphere during domestic copper smelting is thought to be too low to pose any hazards. The 39,000 troy ounces of palladium expected to be lost annually in unrecycled electrical equipment is too widely disseminated to pose a health hazard. Losses of palladium metal or alloys used as petroleum-refining catalysts are estimated to be 50-340 troy ounces per year. Palladium metal or alloys lost to the environment from brazing alloys, dental alloys, jewelry, and glass coatings and from fabrication of palladium and its alloys (except in the case of electroplating wastes) are believed to be innocuous and of little environmental hazard.

However, a significant amount of the average annual loss of the estimated 160,000 troy ounces of palladium per year lost by the chemical industry must be in the form of palladium(II) compounds in wastewater streams. Moreover, loss of palladium(II) compounds by refiners and small electroplaters to wastewater streams may be sufficiently concentrated to be toxic to aquatic organisms.

Palladium and its compounds have not caused any recognized acute or chronic toxic effects in humans. However, the carcinogenicity of palladium(II) compounds in rats and mice, as well as the toxicity of these compounds to mammals, microflora, fish, and a higher plant (Kentucky bluegrass) are causes for environmental concern. Although palladium poses no urgent problem to humans, its toxicity to lower life forms suggests that palladium losses to the environment should be appraised regularly, that recycling of palladium-containing wastes should be increased, and that epidemiological studies in areas where palladium losses are expected to be high would be useful to determine whether palladium poses any human-health problems.

The appendices include the tables and figures and brief summaries of the physical and chemical properties and the analytical chemistry of palladium and its more common compounds.

I. INTRODUCTION

This document summarizes information available from published and company literature and industrial contacts on the natural occurrence, processing, uses, and disposal of palladium and its compounds. Suppliers and dealers were reluctant to disclose information on amounts sold to specific consumers. Amounts of palladium catalysts used in specific industrial processes could not be determined so that losses could only be estimated within a reasonable order of magnitude. The probable losses, distribution pathways, and ecological consequences of palladium presented in this report have been based primarily on subjective evaluations.

The findings of this study are presented in the following eight major sections: Sources, Economics, Processing, Uses, Losses to the Environment, Physiological Effects, Human Health Hazards, and Conclusions and Recommendations.

Appended to this report are tables supporting the textual discussions (Appendix A); tabulations of the physical properties of palladium, its common compounds, and alloys (Appendix B); a summary of the inorganic and organic chemistry of palladium compounds, including tabulations of the corrosion resistance of palladium to various inorganic compounds (Appendix C); and a discussion of analytic methods for determining palladium (Appendix D).

II. SOURCES OF PALLADIUM

The palladium content of the earth's crust is estimated to be 0.01-0.02 ppm.[1/] Concentrations of palladium found in various natural minerals, soils and sediments, and other materials collected from a variety of geographical locations throughout the world are shown in Table A-I (page 61).

Palladium recovered for commercial use was obtained almost entirely from placer deposits until the 1920's. Since then the situation has been drastically altered by the discovery of plantiniferous lodes in Canada and South Africa. Today, a large fraction of the free-world production of platinum metals is recovered as a by-product of copper and nickel sulfide-ore refining.

Following are brief descriptions of the commercial sources and chemical forms of palladium found in nature and of the scrap materials that supply a large fraction of palladium consumed each year in the United States.

A. Natural Sources

The six platinum-group metals (platinum, palladium, ruthenium, rhodium, iridium and osmium) commonly occur in nature as two intergrown alloys.2/ However, these metals also occur as minerals in sulfide-ore bodies.

Alloys of the platinum metals are recovered primarily from placer deposits. The alluvial deposits in Canada were formed by weathering and erosion of dunite and serpentinite. Deposits of similar peridotites and perknites are the source of platinum metals in most placer deposits known in the world. In placer deposits, the two alloys are invariably mixed. One alloy has a high platinum content; a lower iridium content; and small contents of ruthenium, palladium, rhodium, and osmium. The second alloy consists mainly of iridium and osmium with considerable ruthenium; less rhodium and platinum; and very small amounts, if any, of palladium. Natural alloys and intermetallic compounds of palladium as well as the palladium content of these materials are shown in Table A-II (page 62).

The other workable deposits of platinum metals occur mainly as platinum minerals in nickel-copper, copper, and copper-cobalt sulfides that are genetically related to basic or ultrabasic rocks. The platinum metals occur mainly in sperrylite, cooperite, and other platinum and palladium minerals. Table A-III, page 63, contains a list of natural palladium compounds that have been identified. Small amounts of native platinum metals and alloys are often present in these mineral deposits.

Other natural sources include platinum minerals or native platinum alloys in copper and related ores indigenous to contact metamorphic and other types of ore bodies, including vein systems; native platinum metals in gold ores of quartz veins and other free gold ores; and meteorites. Noble metal abundances in meteoritic material are several orders of magnitude greater than in terrestrial material. The average crustal abundance of palladium is 0.01-0.02 ppm. Accretion of interplanetary dust by the earth may be the major source of palladium in deep-sea manganese nodules, rather than terrestrial-rock weathering.3/ Palladium was not detected in the principal U.S. rivers in a 1958-1959 study.4/

Palladium has been detected in other minerals used commercially. Less than 1-ppm palladium was found in coal taken from single mines in the Pittsburgh and Upper Freeport seams in Allegheny County, Pennsylvania.5/ Palladium has also been detected in 16 samples of calcium phosphate fertilizer, including three from North America.6/

The principal sources of platinum metals in the world are the Bushveld Complex of South Africa, the Sudbury District of Canada, and the regions of Norilsk and the Kola Peninsula of the USSR.7/ Minor sources are placer deposits in Alaska, Colombia, Ethiopia, Japan, Australia, and Sierra Leone.

The Sudbury District of Ontario, Canada, contributes about one-third of the free-world production of platinum metals. The platinum-bearing ores are nickel-copper, copper, and copper-cobalt sulfides; native platinum metals or their alloys are usually absent in these ores.

South Africa produces most of the remaining two-thirds of the free-world's platinum metals, primarily from the nickel-copper lodes of Transvaal.

The estimated amounts of palladium in the platinum-group metals recovered from Canadian, Soviet, and South African sources are 42.9%, 60.0%, and 25.1%, respectively.8/ This compares with platinum contents of 43.4%, 30.0%, and 71.2% for the same sources. Platinum metals produced in the USSR are high in palladium and may account for as much as 80% of the world production of that metal.9/

Platinum metals have been found in 22 of the United States, but only Alaska is a major producer. The principal sources in Alaska are the Goodnews Bay District, Western Alaska, and a copper lode on Kasaan Peninsula in Southeastern Alaska. The latter was worked for several years, but is now closed. The Goodnews Bay District produced 3% of the world output of platinum-group metals in 1963.9/ Alaskan placer platinum metals, however, contain < 1% palladium.2/ In California and Oregon, small amounts of platinum metals are recovered as a by-product of gold placer mining.

Most of the platinum metals recovered from primary domestic sources are by-products of copper sulfide, lead, and gold ore refining.10/ Industrial contacts estimated the amount of palladium recovered from copper refining to be 75-95%11/ and 90%.12/ A small amount is recovered as a by-product of lead refining,13/ possibly as much as 15%.11/

B. Metal Scrap

Secondary recovery from metal scrap is the major domestic source of platinum-group metals, and accounts for about 10% of the new metal requirement. Most spent catalysts, however, are refined on a toll basis without transfer of ownership to the refiner.7/ "Toll refining," therefore, is categorized separately from secondary refining of metal scrap in that it does not represent a source of additional metal.

The three categories of scrap are: (1) mechanical fabrications of platinum-group alloys and spent solutions having a high precious-metal content; (2) filter media containing trapped precious metal and spent supported catalysts that can be refined but require prior preparation; and (3) materials with such small amounts of precious metal that smelting is the only economical method of removal, e.g., process residuals, mint and jewelers' sweeps, and composite materials containing both precious metals and commercially interesting base metals. Scrap sources include brazing alloys;