# A Pseudo-Problem of Pollution

**Trace Metals in the Environment, Volume 4 – Palladium & Osmium**

By IVAN C. SMITH, BONNIE L. CARSON AND THOMAS L. FERGUSON

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Although there are numerous publications describing the toxicology and environmental impact of the better known metals such as lead, cadmium and mercury, information on the less common metals is not as readily available. The Mid-West Research Institute has therefore undertaken a programme initiated by the National Institute of Environmental Health Sciences to assemble information on the natural occurrence, processing, use, human and animal health effects, and environmental impacts of a series of selected trace elements. The fourth book of this series is concerned with palladium and osmium.

A problem with books of this nature is that probably because of the paucity of information on environmental and health effects the supporting chapters tend to form a disproportionately large part of the book. The section on palladium contains only nine pages on losses to the environment and five on the physiological effects of palladium and its compounds, while there are thirty seven on occurrence, economics, processing and uses. These are supported by no fewer than sixty pages of appendices containing tables on sources, production figures, imports, exports, stocks, sales, principal uses and the firms involved, and sub-sections on the chemistry and analysis of palladium.

One serious criticism is that with one exception the references only go up to 1973; thus by the time of publication the book was already five years out of date. Repeated mention is made in the text of increased losses of palladium to the environment resulting from greater use of the metal in automobile emission control devices, and recommendations are made regarding epidemiological, toxicological and other studies that should be undertaken to evaluate its effect on the environment. In fact many such studies have already been reported and "scare" reports dismissed. A sub-committee of the American National Research Council has made a study for the Environmental Protection Agency to establish a broad background of information on the medical, biological and environmental affects of selected pollutants, to evaluate that information and to recommend studies aimed at remedying information inadequacies or gaps. The conclusion they reached on this use of the platinum group metals is therefore worth quoting:

> "The newest and most extensive use of the platinum group metals is in catalysts for purifying exhaust from automobiles. Minute quantities of platinum or palladium (about 1–3μg/mile or 0.6–1.9μg/km) are emitted from the exhaust systems of automobiles equipped with catalytic converters; much of this material may accumulate alongside roadways. However, this material is in a chemical form that is physiologically innocuous (no detectable soluble salts) and it is concluded that such emission poses no threat to the environment. Because there is no evidence that platinum metal can be methylated by microorganisms and solubilised in the same way that mercury is methylated, this deposited material should not have an adverse effect on the environment"(1).

Although the authors are concerned that the loss of palladium(II) compounds to waste water streams may be in sufficient concentrations to be toxic to aquatic organisms they offer little information on this.

The chapters on sources, processing and uses are interesting but the lack of recent information does show through and there are some unfortunate omissions, particularly in discussing the primary sources of the platinum metals in South Africa.

The section on osmium is significantly shorter than that on palladium, reflecting the relative occurrence and uses of the two metals. The major sources of osmium loss to the environment are thought to occur as the volatile tetroxide during pyrometallurgical refining, and in the waste water resulting from its use as the catalyst in the preparation of steroids and as a stain for tissue samples being prepared for electron microscopy. However, no localised loss of osmium sufficiently large to create an obvious environmental hazard was identified. The toxicity of osmium tetroxide is well recognised and could pose a serious health hazard to operators unless handled with adequate caution.

The end result is that the authors have produced a book that will probably disappoint environmentalists but which could be a useful source book for others.

C.W.B.

### Reference

1 "Platinum-Group Metals", by Subcommittee on Platinum-Group Metals, Committee on Medical and Biologic Effects of Environmental Pollutants, National Academy of Sciences, Washington, D.C., 1977, p. 175

# Hydrogen Diffusion through Palladium Alloys

## SOLUBILITY GRADIENTS EXPLAIN PERMEABILITY BEHAVIOUR

Diffusion through palladium–silver membranes is now a well established commercial route for the production of ultra high purity hydrogen. Continuing attempts to find better membrane materials have shown that palladium alloyed with the rare earth elements cerium or yttrium has certain appreciable advantages, although poisoning of the membrane surface can make evaluation of the materials difficult, particularly at low differential pressures, and may also limit permeability.

Recent work carried out at the University of Birmingham using equipment constructed to avoid contamination of the surface has now been reported by D. T. Hughes and I. R. Harris (*J. Less-Common Metals*, 1978, **61**, (2), 2–21). Permeability and solubility measurements were made on palladium-25 atomic per cent silver, palladium-5.75 atomic per cent cerium and palladium-8 atomic per cent yttrium, over a temperature range 20 to 500°C and at differential pressures of 3.4 and 6.8 atmospheres of hydrogen. It is believed that the stringent precautions taken to clean the measuring system have enabled the intrinsic permeability of the materials to be measured.

When the surface processes are unimpeded by poisoning, the rate controlling factor for the permeation of hydrogen through the membrane is the diffusion of hydrogen through the bulk material. The results confirm the greater permeability of the yttrium containing alloy, especially at the higher temperatures, although below 250°C the difference is small. The figures for the cerium alloy show that at the lower differential pressure the permeability is practically the same as for the silver alloy at all temperatures, while at the higher pressure difference the rate is slightly lower in the range 200 to 350°C but slightly greater above 350°C.

Hydrogen solubility measurements were also made under the same experimental conditions, thus enabling the concentration difference between the high and low pressure surfaces of the membrane to be obtained. Diffusion coefficients calculated from these solubility and permeability data showed very similar values for all three alloys. However, it was found that the hydrogen solubility in the yttrium containing alloy is greater than for the other two materials at most conditions of temperature and pressure. The solubility–temperature relationships for this alloy are similar to that of the palladium–silver alloy, but the cerium alloy exhibits some unusual features. In particular, above 250°C, the hydrogen solubilities for the palladium–cerium alloy show a lower temperature dependence than the other two alloys, especially in the measurements made at a hydrogen pressure of 1 atmosphere.

Solubility measurements have shown therefore that the permeability behaviour of the alloys examined is a result of the intrinsic differences in the hydrogen solubility rather than differences in diffusion coefficients. This is supported by the fact that independently determined solubility data can be used with success to analyse the differences in the permeability versus temperature curves. As well as confirming the superior performance of the palladium–yttrium alloy the work has also demonstrated the meticulous care which is required to avoid poisoning of the membrane surfaces during work with these rare earth containing alloys. I. E. C.