

# Palladium Alloy Diffusion Process for Hydrogen Purification

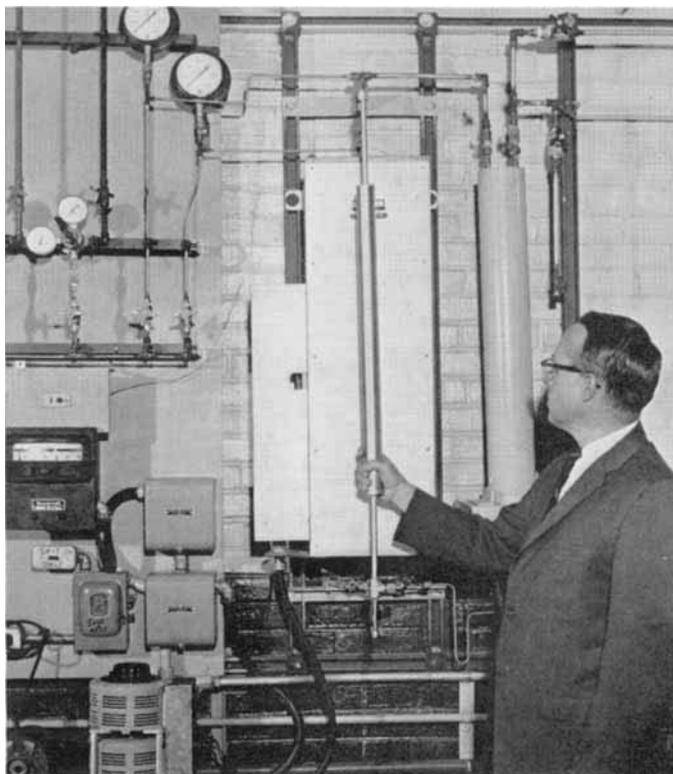
## FIRST COMMERCIAL-SCALE PLANT IN OPERATION

The development of a silver-palladium alloy having a hydrogen diffusion rate more than twice that of pure palladium, as well as a high degree of stability on heating and cooling in hydrogen, was described in *Platinum Metals Review*, 1960, 4, 130-131, by Dr J. B. Hunter, of J. Bishop & Co Platinum Works, Malvern, Pennsylvania. In the course of this article the author also outlined the design of a range of diffusion cells based upon this alloy suitable for laboratory, pilot plant and full-scale operation in the separation and purification of hydrogen. Since that time further design and engineering work have been carried out, and a number of relatively small-scale units have been put into service. Now

the first commercial-scale plant for volume production of high purity hydrogen has been put on stream. This is at the Los Angeles plant of the National Cylinder Gas Division of the Chemetron Corporation, where the installation is producing 115,000 cubic feet a day of hydrogen with an impurity level as low as 0.1 part per million.

The basic unit of the system consists of a bundle of thin-walled small diameter silver-palladium alloy tubes, manifolded together into a header, and assembled into an outer envelope. This construction provides a thin membrane for diffusion, coupled with high surface area in a small volume and adequate mechanical strength. Multiples of this unit

*Dr J. B. Hunter, of J. Bishop & Co Platinum Works, examining a single silver-palladium alloy diffusion cell in its test rig. Unit cells of this type are assembled in multiples to build commercial-scale plants such as the installation now on stream at the National Cylinder Gas Los Angeles plant*



can of course be assembled to provide the throughput required.

In the National Cylinder Gas plant the feed hydrogen, more than 99.7 per cent pure, is preheated to around 315°C, while the diffusion cells are maintained at the same temperature. The diffusion rate depends upon the partial pressure of hydrogen in the gas stream and the rate of circulation of the feed gas. The temperature of around 315°C is the minimum at which the rate of diffusion through the alloy becomes a practical proposition, but the hydrogen pressure differential across the alloy tube walls and the rate of bleed-off from the cells are factors which influence the economics of operating a diffusion unit.

The National Cylinder Gas installation employs electrolytic hydrogen, the 0.3 per cent of impurities consisting primarily of

oxygen, with some nitrogen, methane and water. Hydrogen produced from hydrocarbon reforming processes would of course contain also carbon monoxide and carbon dioxide, but these would not affect performance. The only impurities that do in fact interfere with diffusion are unsaturated hydrocarbons and sulphur, but the former can be removed by a hot air purge of the cells, while the latter can readily be removed by normal methods before being allowed to reach the diffusion unit.

The factors that led National Cylinder Gas to install their diffusion plant were mainly the safety, simplicity and ease of operation of the Bishop system. The unit has no moving parts, and the capital cost represents almost the total expense. Control of the process is simple, consisting only of analysis of the output stream.

## Surface Phenomena at Platinum Electrodes

### ADSORPTION OF CATIONS AT ANODIC POTENTIALS

When platinum electrodes are used for the anodic formation of persulphuric acid, the nature of the *cations* present has long been known to have a marked influence on the kinetics of the anodic oxidation; at any given potential, the rate of persulphate formation is diminished by the presence of alkali metal ions, the effect increasing in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ . Experiments on the anodic evolution of oxygen from perchloric acid, which is also influenced by the nature and concentration of the cations present, have shown that the platinum surface changes with time, chemisorbed oxygen being produced.

In a review paper recently published (*Electrochimica Acta*, 1961, 5, 265 – in French) Professor A. N. Frumkin, of the Institute of Physical Chemistry, Moscow, draws together a number of phenomena concerned with the surface of platinum anodes, and puts forward the view that the dipolar nature of the platinum-oxygen bond promotes the adsorption of cations. At high anodic polarisations, definite oxide films are formed, as indicated by earlier work. Cation adsorption has been directly demonstrated by the use of caesium ions labelled with  $\text{Cs}^{134}$ .

Both the adsorption of cations and the oxidation of the surface inhibit anodic oxidations such as persulphate formation and oxygen evolution. With the alkali metal ions, the cation effect increases in the order  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$ , undoubtedly the order of increasing specific adsorbability, when platinum is polarised anodically in 6N sulphuric acid and in electrolytes such as 5N  $\text{H}_2\text{SO}_4$ , 1N  $\text{Li}_2\text{SO}_4$ . Even 0.01N  $\text{Cs}^+$  has an appreciable influence. A similar although smaller effect of  $\text{Cs}^+$  can be found on the evolution of oxygen from the oxide-covered surface of passive iron.

In this important paper Professor Frumkin gives sixty-six references to earlier work in his own and other laboratories on the platinum anode. In view of the importance of platinum as a so-called “inert” electrode in electrolytic processes, in cathodic protection and in fundamental investigations, it is surprising that its actual “reactivity” has been relatively little studied; the paper is valuable in drawing attention to many points urgently needing further examination, as well as being an excellent summary of what is known to date.

T.P.H.