Diaphragm Cells for Chlorine Production

PLATINUM METAL OXIDE COATINGS ON TITANIUM ANODES

A symposium held in London in June, organised by the Electrochemical Technology Group of the Society of Chemical Industry, provided an opportunity for discussion of developments over the last ten years in the operation of diaphragm cells for chlorine production. Many of the papers presented outlined improvements in cell design and in diaphragm materials. Dimensionally stable anodes, made of titanium coated with a platinum-group metal oxide, are used in all the cells reviewed.

The electrolysis of brine is the main industrial process for the production of chlorine and its co-product, sodium hydroxide. Two types of electrolysis cell are used in the chlor-alkali industry; mercury cells in which the cathode is a circulating stream of mercury, and diaphragm cells in which anodic and cathodic liquors and products are separated by a diaphragm, usually of asbestos.

Cell Design

In an introductory lecture, Dr. M. G. T. Burrows of BP Chemicals described the stages in the development of the design of diaphragm cells from the late 1880s and compared the performance of four diaphragm cells now in commercial use. Operating data in this comparison included current range, anode area, current density, cell voltage, power consumption and current efficiency. The four types of cell reviewed were those licensed by Hooker, Diamond Shamrock, ICI/Solvay and de Nora/PPG. In all these cells the dimensionally stable anodes—titanium coated with an oxide of one of the platinum metals—make a significant contribution to their efficiency.

An analysis of the proportion of chlorine produced in diaphragm cells throughout the world showed a wide variation between countries, with the greatest proportion at present in the U.S.A. (73 per cent in 1975). However, because of environmental considerations, there are plans for the complete conversion of the Japanese chlorine industry to the use of diaphragm cells by 1978. In most western European countries, on the other hand, diaphragm cells were used for less than 20 per cent of chlorine production in 1975 and wholesale conversion from mercury cells is not foreseen.

The Dimensionally Stable Anode

The inventor of the dimensionally stable anode, Henri B. Beer (Scientific Research Society NV), described the sequence of his experimental work that culminated in the development of these anodes for the chlor-alkali industry. In 1956 he realised the potential value for the electrochemical industries of anodes made from titanium coated with platinum. The anode material was produced at first by electrodepositing platinum on to the titanium base, but in later work the coating was thermally deposited. Tests with both types of platinised titanium in brine electrolyses showed that thermal deposition gave a coated anode with some advantages over graphite, but with problems of platinum loss and passivation during electrolysis.

By 1965 investigation of the properties of titanium anodes coated with oxides of the platinum group metals had started. Oxides of the rutile type, such as are formed by

ruthenium and iridium, showed particular promise. Further improvement was achieved by thermal deposition on to titanium of mixtures of isomorphous oxides of platinum metals and non-platinum metals. Coated anodes of this type had very low overvoltages, were durable and could be used successfully at very high current densities. With some further refinements, these dimensionally stable anode materials have extensively replaced graphite in the chlor-alkali industry.

Mixed Oxide Coatings

A paper by Dr. Vittorio de Nora discussed the present applications and future development of dimensionally stable anodes. Titanium anodes coated with catalytically active isomorphous mixed oxides of a platinum group metal and a valve metal are used in the electrolytic production of chlorine, chlorates and hypochlorites. Special coatings have been developed for other processes such as the electrolysis of sea-water, nuclear effluents and sewage. The electrocatalytic activity of dimensionally stable anodes may be modified by the presence of doping agents, which replace part of the valve metal oxide, in the coating. Other types of dimensionally stable anodes, formed on sintered ceramic bases, are being developed for use in molten salt electrolysis, for example, in the production of sodium and aluminium.

Electrolysis of brine in diaphragm cells produces a caustic soda liquor that requires concentration before the separation of its main components—sodium hydroxide, sodium chloride and sodium sulphate. Dr. R. Winkler of Escher Wyss AG described in his paper various types of evaporation plant and discussed the economics of their operation.

Dr. G. van der Heiden of Akzo Zout Chemie reported results of a study of the fundamentals of diaphragm performance in terms of its permeability and electrical resistance. Permeability of an asbestos diaphragm is a function of its porosity, thickness, tortuosity and pore diameter and of the viscosity of the cell electrolyte. The electrical resistance of the diaphragm is a function of its porosity, thickness and tortuosity. Chemical degradation of the asbestos fibres during electrolysis limits diaphragm life.

Reduced Power Consumption

Technical advances in diaphragm chlorine cells developed by the Electrode Corporation were described by T. A. Liederbach of that company. Because of increasing energy costs, the emphasis of development programmes has been on the reduction of cell power consumption. The advent of the dimensionally stable anode made possible a power saving of about 20 per cent in diaphragm cells. A further power saving of 10 to 15 per cent resulted from the development in the early 1970s of expandable anodes and modified diaphragms, which together facilitated reduction of the cell electrolytic gap and, consequently, lowering of the cell voltage.

H. Shibata, Y. Kokubu and I. Okazaki of the Kureha Chemical Industry Co described the Kureha SK-Diacell, developed to replace mercury cells, and designed as a multi-cell unit that can use much of the electrical equipment previously required for the mercury cells. Layout of the diaphragm cell is similar to that of a mercury cell. The SK-Diacell has dimensionally stable anodes and asbestos diaphragms with a high degree of uniformity; it has been designed to operate at currents in the range 100 to 400 kA. Details were given of the performance over several months of an SK-Diacell operating at 330 kA.

The development of the Glanor Electrolyser by PPG Industries and Oronzio de Nora Impianti Elettrochimici was described by R. J. Scott of PPG. This bipolar diaphragm cell has dimensionally stable anodes. Four Glanor plants are now operating in Japan and one in the U.S.A.; others are under construction.

K. O'Leary of Diamond Shamrock reviewed his company's work on the development of semi-permeable membrane cells for chlorine production. Nafion membrane material, developed by du Pont, has been

modified and installed in a demonstration plant at Muscle Shoals, Alabama. In its first two months of operation the cell has shown a greater tolerance to load variations than the conventional permeable diaphragm cell.

At Dryden, Ontario, a Nafion membrane cell chlorine plant has been in operation since the beginning of this year. The plant was designed by Hooker Chemicals and Plastics Corporation for Dryden Chemicals Ltd. J. E. Currey and A. T. Emery reviewed the developments in Hooker membrane cell design and technology that led up to the commissioning of this plant.

Finally, Dr. S. F. Mellish of ICI Mond Division, using published information, gave an economic assessment of the performance of membrane cells by comparison with conventional diaphragm cells.

B. M. G.

Temperature Control in the Casting of Copper Alloys

Temperature control in the continuous or semi-continuous casting of copper alloys is vital to the production of sound material. For any given pouring temperature there are optimum rates of pouring and of cooling, and a new installation for the rapid and visible measurement of this temperature has recently been put in at Usine Metallurgiques Suisse Selve et Cie at Thun. The usual platinum: rhodium-platinum thermocouple not only records graphically but by means of an electronic circuit displays the temperature at any one of eight locations on a large luminous panel when a control button is activated. The operator can thus concentrate on the handling of the immersion pyrometer with an eye on the panel, which shows both the location and the temperature. The installation was supplied by Ets. Dr. Ness of Küssnacht, Switzerland, under the supervision of Dr. F. Roggen of Selve.