

Platinum Metals Activated Cathodes for the Chloralkali Industry

SIGNIFICANT ENERGY SAVINGS CAN BE ACHIEVED

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The chloralkali industry is one of the largest single electricity consumers in the world, and electricity costs can account for about sixty per cent of the running costs of a modern plant. This article, which is based in part upon a paper given at the Third London International Chlorine Symposium, organised by the Society of Chemical Industry, the Chlorine Institute and the Royal Society of Chemistry, which was held in London during June, considers the use in membrane cells of noble metal coated cathodes developed by Johnson Matthey and indicates some of the savings that can result. These coated cathodes, which are being evaluated by a number of chloralkali plant manufacturers, appear to act in a catalytic manner to reduce the cathodic hydrogen overpotential and thus the energy consumption.

The chloralkali industry is primarily concerned with the manufacture of chlorine and caustic soda (sodium hydroxide). Both of these products are well established chemicals, and their relatively large scale production in the nineteenth century formed one of the cornerstones of the European chemical industry.

In the past, several different methods have been used to prepare these products, but they are now made, almost exclusively, by the electrolysis of brine (aqueous sodium chloride). The overall reaction can be summarised by the equation:



All three chemicals produced have a cash value, although circumstances may dictate that in some cases the hydrogen be used as a fuel.

The chloralkali industry is truly large scale and there are brine electrolysis plants in well over 100 countries throughout the world. Japan, the U.S.A. and Western Europe have between them about 80 per cent of the chloralkali capacity of the free market economy countries of the world (1). Annual production

	1965/69	1980	1995*
Chlorine	16.3	31.3	56.3
Caustic Soda	18.8	33.1	59.0

*Estimate

figures for chlorine and caustic soda are shown in Table I (2).

There is scarcely any section of today's chemical industry which does not use one or other of these two chloralkali products at some stage in its processing routes. An approximate breakdown of usage in the U.S.A. is given in Table II(3).

Alternative Electrolytic Processes

There are three main electrolytic processes presently being operated in the world, namely diaphragm, mercury and membrane.

Up until about 15 years ago only diaphragm and mercury cells were in use, the diaphragm

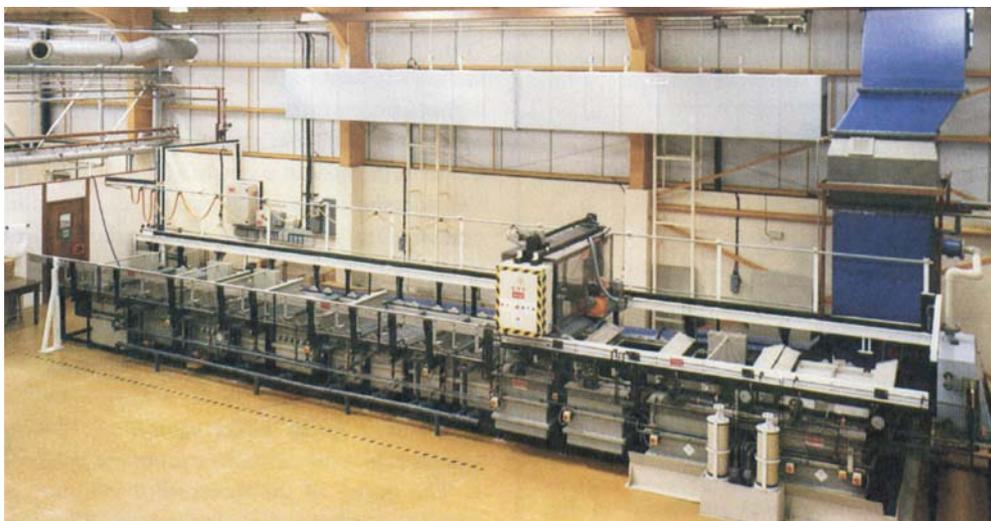


Fig. 1 Noble metal coated cathodes developed by Johnson Matthey for the chloralkali manufacturer appear to act in a catalytic manner, reducing the cathodic hydrogen overpotential and thus the energy consumption of this major electricity-using industry. At its Royston factory Johnson Matthey Chemicals Limited has the capacity to treat some 25,000 square metres of cathode area per year, and providing the nickel surface can be satisfactorily sand blasted prior to the coating operation there is no limit to the complexity of the cathode shapes that can be successfully coated

cell finding favour in the U.S.A. and the mercury cell predominating in Europe.

Recently, however, there has been considerable public concern regarding the use of asbestos (for diaphragms) and, also about

mercury pollution from the mercury cells. Indeed, in Japan, legislation has been passed which is aimed at phasing out mercury cell altogether by June 1986. There have therefore been external pressures brought upon the industry to develop alternative technology involving neither asbestos nor mercury. The idea of having an ion selective membrane is not new, but it has only become a practical possibility with the development of modern materials.

Diaphragm cells consume less energy per ton of product than do mercury cells, but the caustic soda produced from mercury cells is purer than that from diaphragm cells. The primary objectives in developing the membrane cell have been to produce caustic soda of a quality at least as good as that from the mercury cell with energy efficiency as good as, or better than that of the diaphragm cell. This has been achieved by positioning an ion selective membrane between anolyte and catholyte which does not permit the passage of chloride, from the brine anolyte input, into the catholyte nor does it allow the passage of the cathodically

Table II
U.S. Uses of Chloralkali Products
per cent

Industry	Chlorine	Caustic soda
Vinyl chloride	20	—
Pulp and paper	14	20
Chlorinated solvents	26	—
Propylene oxide	8	—
Petroleum production/ refining	—	5
Textiles	—	5
Aluminium production	—	4
Soaps and detergents	—	5
Waste/water treatment	4	—
Others a) inorganic	12	11
b) organic	7	38
Miscellaneous	9	12

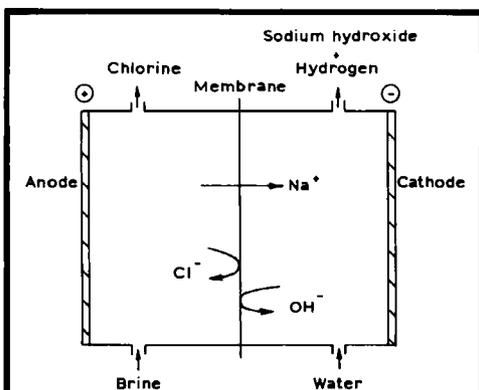


Fig. 2 The ion selective membrane allows the sodium, but not the chloride ion to pass from the brine feedstock into the catholyte. As a result the concentration of caustic soda produced in the membrane cell is higher than in a diaphragm cell, thus reducing the need for evaporation

produced hydroxide ion into the anolyte, see Figure 2.

A typical diaphragm cell catholyte contains about 15 per cent caustic soda and 20 per cent sodium chloride. In order to produce caustic soda which is acceptable to industry, the sodium chloride has to be removed. This is done by evaporation, crystallisation and removal of the solid sodium chloride. However the end product (about 50 per cent caustic soda) inevitably contains residual sodium chloride (typically about 1 per cent).

By its very nature, the ion selective membrane keeps chloride ions out of membrane cell catholytes, hence it is possible to achieve much higher concentrations of caustic soda in membrane cell catholytes (35 to 40 per cent) than was ever possible in a diaphragm cell catholyte. Considerably less evaporation is therefore necessary to achieve the 50 per cent caustic soda strength required by the market and the chloride level of this caustic soda is at the ppm level only. However, in addition to the extra cost of the membrane over and above that of a standard diaphragm, there are two factors which have to be offset against the energy savings achievable with the membrane cell:

1. The purity of the feedstock brine must be considerably better than that required for either mercury or diaphragm cells – in particular, alkaline earth impurities should be minimised in membrane cell catholytes otherwise they will precipitate out as hydroxides. If this precipitation occurs within the membrane, partial blockages, resistance to liquor flow and in extreme cases delamination and membrane rupture can occur.
2. The iron or mild steel cathodes traditionally used in diaphragm cells are not practical in the very much stronger caustic solutions found in membrane cell catholytes. Unacceptably high levels of corrosion are experienced with correspondingly reduced cathode lifetimes. The caustic soda produced is inevitably contaminated. In these circumstances many chloralkali

Table III
Relative Advantages/Disadvantages of the Diaphragm, Mercury and Membrane Cells

	Diaphragm	Mercury	Membrane
Energy consumption	low	high	lowest
Catholyte evaporation costs	high	nil	low
Caustic soda quality (with respect to sodium chloride)	poor	good	good
Brine purification cost	nil	minimal	considerable
Cost of membrane	no	no	yes
Use of mercury	no	yes	no
Use of asbestos	yes	no	no

plant manufacturers have substituted nickel coated steel, or better, solid nickel cathodes for the iron or mild steel cathodes used previously.

The relative advantages and disadvantages of the three types of electrolytic cells are summarised in Table III.

Energy Requirements in Membrane Cells

A summary of the factors contributing to the overall cell voltage of a membrane cell was given at the last London International Chlorine Conference in 1982 by Thomas (4). This is shown in Table IV. From this it can be seen that the cathode overpotential comprises about 10 per cent of the operating cell voltage and is one of the larger items contributing to the potential required over and above the thermodynamic minimum. There have been many attempts to reduce cathode overpotential by the application of surface coatings, but until recently those based on noble metals tend to have been dismissed on the grounds of cost.

Some aspects of the Johnson Matthey cathode coating are now described and performance data are given which demonstrate that this approach to reduce the cathode overpotential can be and is, a cost effective one.

Noble Metal Coated Cathodes

The work on noble metal coated cathodes began at the Johnson Matthey Research Centre several years ago and various noble metals and combinations of noble metals were examined. It was fairly quickly established that the high catalytic activity of these coatings was adversely affected by the presence of trace amounts of base metals such as iron or mercury. These coatings therefore operate most effectively in catholyte liquors containing low or sub ppm levels of iron. Such low iron levels are not found in diaphragm cell catholytes, hence the present generation of cathode coatings only finds application in membrane cells.

There is therefore an incentive to keep membrane cell catholytes substantially free of iron whether or not coated cathodes are used. Coating steel cathodes with an intermediate

	Volts	Voltage, per cent
Thermodynamic "minimum"	2.23	65
Membrane IR* drop	0.45	13
Cathode overpotential	0.35	10
Electrolyte IR* drop	0.22	6
Structural IR* loss	0.16	5
Anode overpotential	0.05	1
Cell voltage	3.46	

*IR is the voltage drop when the current (I) flows through resistance (R)

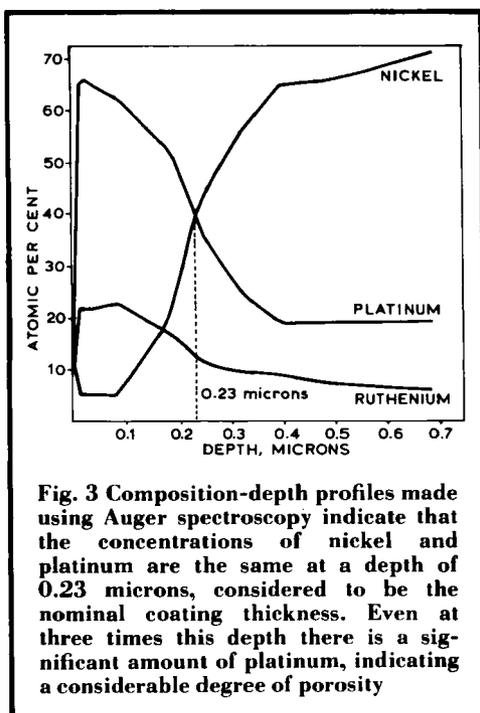
base metal, such as nickel, before application of the noble metal coating did not prove satisfactory. Even on a laboratory scale, it was found that the nickel coatings were more or less porous to the iron in the substrate material and the catholyte iron concentration inevitably increased to unacceptably high levels.

The problem has been avoided by not using any ferrous metal alloys in the internal cell construction. Thus the cathodes were made of solid nickel. This approach has been adopted by a number of chloralkali membrane plant manufacturers who appreciate that, although more expensive than steel, solid nickel cathodes offer distinct advantages in reducing membrane damage and avoids the cathode corrosion which inevitably occurs with steel in the high strength caustic liquors present in membrane cell catholytes. All the work described below therefore concerns the application of the noble metal coating to a solid nickel substrate.

Noble Metal Coatings

To be commercially successful any coating must be both effective, that is give the greatest reduction in hydrogen overvoltage, and adherent, under operational conditions.

Platinum was applied to a nickel substrate in a number of different ways including electrolysis (DC and pulsed plate), vacuum sputtering and as an organic dispersion. In all



these cases, however, the adherence was poor.

A number of binary mixtures were tested, and rather surprisingly it was found that certain combinations improved the adherence without reducing the effectiveness. The best coating to date taking cost and performance into account is that of a co-deposited platinum and ruthenium mixture containing:

3 to 3.5g platinum/m² of nickel surface, and
1 to 1.5g ruthenium/m² of nickel surface

and is much better than that obtained from either platinum or ruthenium alone.

These platinum/ruthenium coatings and the means by which they are applied are the subjects of patent applications world wide (5).

It is convenient to regard the noble metal cathode coating as a catalyst which reduces the hydrogen overpotential. This analogy will be developed later in the paper.

Coating the Cathode

The method of applying the noble metal coating to the nickel cathode substrate is described more fully elsewhere (5). A

wide variety of shapes have been coated and, providing the surface can be satisfactorily sand blasted during the pre-treatment stage, there is no limit to the complexity of forms to which the coating can be applied.

The noble metal coating is neither electrolytic, nor is it an electroless plate in the conventional sense. Most properly the operation can be described as an immersion plating process depending for its effect on the relative redox potentials of the metals involved. Johnson Matthey Chemicals Limited now has the capacity to treat some 25,000m² of cathode area per year at its Royston factory.

Nature of the Coating

Using standard figures for the specific gravities (SG) of platinum and ruthenium, it is possible to calculate the weighted specific gravity for any particular composition. Thus, taking the mean loading as 3.25g platinum/m² (with a SG of 21.45) and 1.25g ruthenium/m² (SG 12.45) the specific gravity of this particular composition can be calculated to be 18.95 (assuming ideal mixing). A simple calculation shows the coating thickness to be about 0.24μm.

An Auger depth profile of a nickel substrate coated with a standard platinum/ruthenium coating is shown in Figure 3. The nominal coating thickness is estimated as being that at which the platinum and nickel levels are the same, that is 0.23μm. In the calculation of the weighted specific gravity above, the individual metal specific gravities are those of the solid massive metals. However, from Figure 3 it will be noted that there are considerable quantities of platinum at nearly three times the nominal surface thickness. This indicates that the surface coating is porous to a considerable degree.

The porosity of the coating was confirmed by an ESCA study of the top 0.002μm of the surface which showed the presence of a small, but measurable (1.2 atomic per cent) amount of nickel. The existence of porosity is considered to be of prime importance since increased porosity indicates increased surface area and in

any catalytic process, factors which increase metal availability generally result in increased activity. In this instance, the increased activity shows as a reduction in hydrogen overpotential.

X-ray diffraction evidence indicates the presence of a cubic alloy phase which can best be described as a solid solution of ruthenium in platinum, with no evidence of any free ruthenium (hexagonal) being present.

Overpotential is dependent on electrode current density, the higher the current density, the higher the overpotential. If the surface of the electrode is roughened, the "true" surface area is increased and thus for a fixed current, the overpotential will decrease.

Examination of a standard coated cathode by scanning electron microscopy showed that the surface was covered with nodules about $1\ \mu\text{m}$ diameter and that these nodules were essentially platinum and ruthenium, see Figure 4.

It seems highly likely that this macro-surface roughening over and above that of the sand blasted substrate is an important factor in determining the final overpotential achievable by any given coating.

It was found that the morphology of the coatings changed with the deposition of increasing amounts of noble metals – in particular existing nodule growth as opposed to new nodule formation was observed.

Figure 5 shows the relationship between the

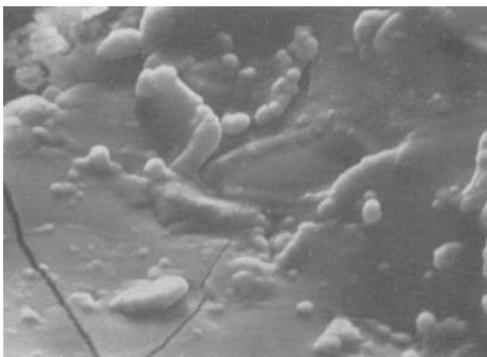


Fig. 4 Scanning electron microscopy of a standard coated cathode shows the surface to be covered with platinum/ruthenium nodules approximately 1 micron in diameter. This surface roughening is probably an important factor in determining coating performance

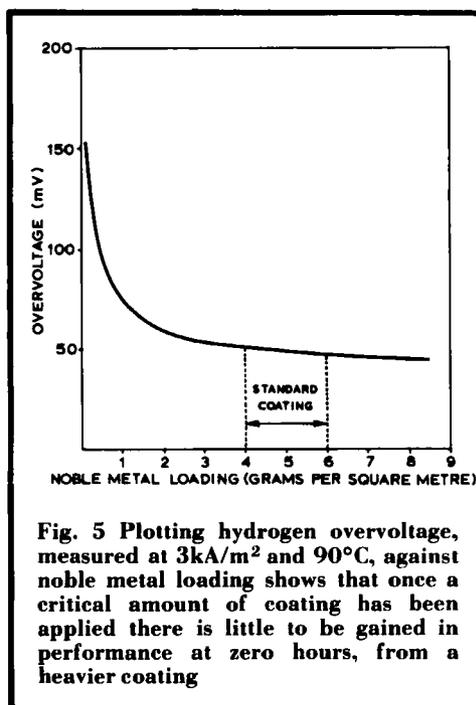


Fig. 5 Plotting hydrogen overvoltage, measured at 3kA/m^2 and 90°C , against noble metal loading shows that once a critical amount of coating has been applied there is little to be gained in performance at zero hours, from a heavier coating

observed overvoltage and the total noble metal loading. It also shows that a certain minimum amount of noble metal has to be exceeded for optimum performance, but above this level, the performance benefit (at zero hours) is minimal.

Measurement of Overpotential

Ideally measurements should be made under realistic plant operating conditions, that is at 90°C in 35 per cent caustic soda solution. However, the conventional mercury/mercuric oxide reference electrode used for making measurements at room temperature was found to be completely unsuitable for measurements at 90°C since the mercuric oxide dissolved at the higher temperatures thereby poisoning the working electrode. Accordingly a new reference electrode was developed for operating under these more extreme conditions (6), and is incorporated in the device illustrated in Figure 6. The measurements are made rapidly, and are reproducible and readily permit the calculation of the hydrogen overpotential on a cathode of any geometry.

The results that are obtained for the

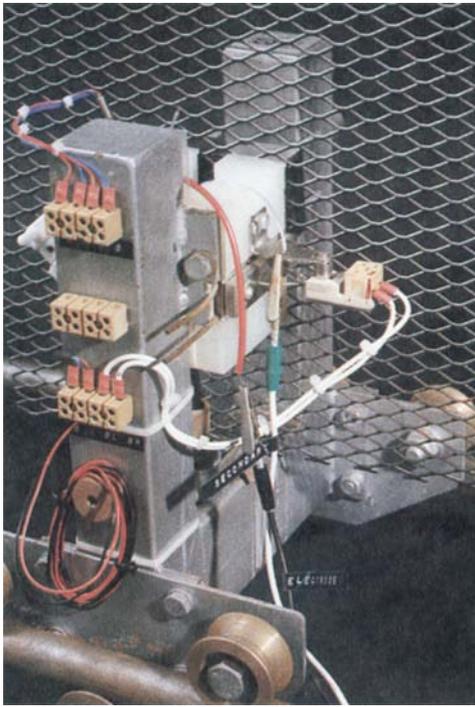


Fig. 6 Under realistic plant operating conditions the mercuric oxide from conventional mercury/mercuric oxide reference electrodes dissolves and poisons the working electrode. To enable measurements to be made at 90°C in 35 per cent caustic soda solution, a new reference electrode has been developed. Using a microcomputer and a frequency response analyser (Solatron FRA 1250) rapid and reproducible measurements can be made on cathodes of any geometry

standard coating are typically 50 to 70 mV at current densities of 3kA/m² in 35 per cent caustic soda solution at 90°C. This is shown in

Figure 5. While it is not unreasonable to expect that increasing the noble metal loading will prolong the cathode lifetime, the following durability data has been obtained with the standard coating. This is shown schematically in Figure 7. There is a slight, but perceptible upward trend which, if extrapolated, would indicate an overpotential of 160 to 180 mV after two years or so.

Similar encouraging results have been obtained with production scale membrane test cells using commercial brine feedstocks.

Economics

It is impossible in a paper such as this to give a definitive cost benefit analysis for every conceivable cell geometry. What is being considered below is the difference between a solid-nickel cathode system with and without a noble metal surface coating. Hence the cost of the nickel substrate is common to both situations and can therefore be ignored. The following assumptions have been made:

The noble metal cost is £35 per m².

The treatment charge is £50 per m², although this figure will obviously depend on the size, geometrical complexity and number of units to be treated.

A 200 mV saving is sustained for two years.

The quantity of electricity required per tonne of caustic produced is 700 kA h, assuming 95 to 96 per cent current efficiency.

Therefore a reduction of 140 DCkWh/tonne of caustic is to be expected. The cash value of

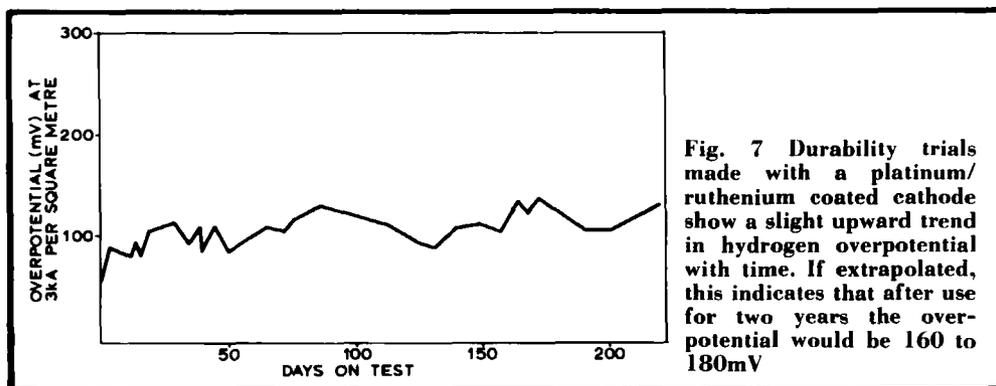


Fig. 7 Durability trials made with a platinum/ruthenium coated cathode show a slight upward trend in hydrogen overpotential with time. If extrapolated, this indicates that after use for two years the overpotential would be 160 to 180mV

such a saving is shown graphically for different cathode productivities in Figure 8.

The platinum/ruthenium coating can be thought of as a catalyst which lowers the overall energy consumption of the chloralkali electrolytic process. The performance of any catalyst inevitably deteriorates with time and there will come a time when the coated cathode performance approaches that of an uncoated cathode. However, Johnson Matthey has developed a technique whereby the noble metal coating can be removed and the stripped nickel cathode can be re-coated with fresh metal. Up to five coatings have been applied to test samples (1mm thick) without any deterioration in initial performance or adherence. The life of the nickel substrate is therefore at least five times that of the noble metal coating. Thus, because the platinum and ruthenium can be separated from the nickel substrate, recovered metal can be offset against future purchases. Hence the initial outlay for the noble metal is at least in part recoverable, making the overall net savings shown in Figure 8 even more attractive.

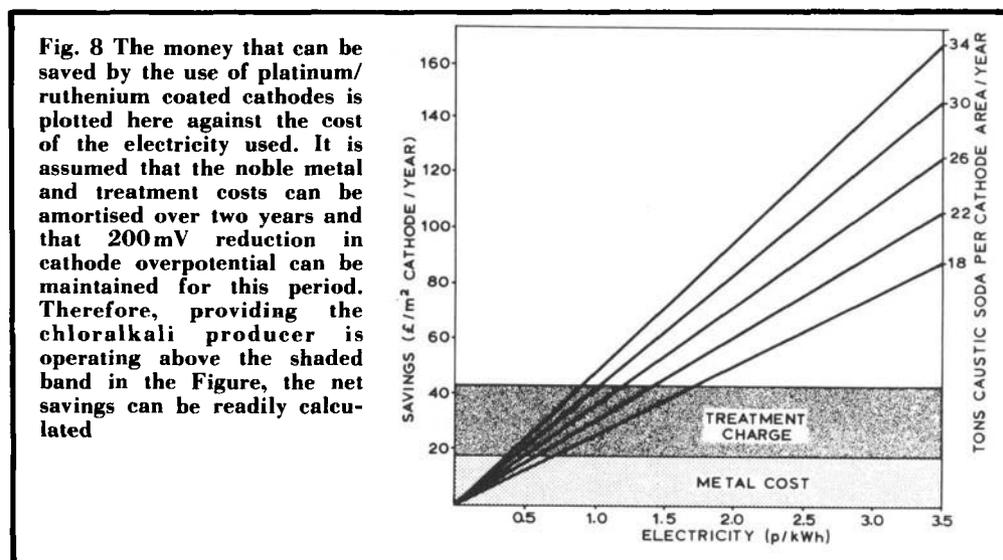
Future Developments

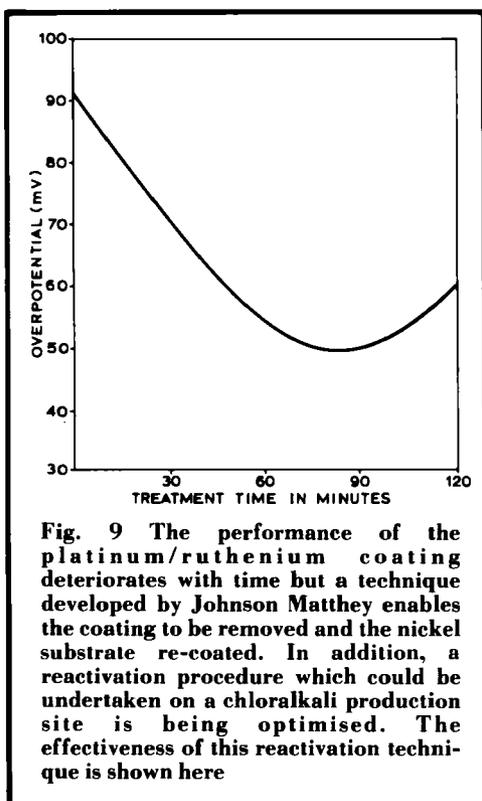
Because of the high price of the noble metals relative to other metals, there is always a desire by any prospective client, if he cannot avoid the

use of these materials altogether, to use as little as possible, and to make sure that what little he does use, lasts as long as possible. Figure 5 showed that a certain minimum amount of noble metal had to be exceeded before acceptably low overpotentials were obtained. Therefore, the platinum/ruthenium inventory is unlikely to decrease significantly from the present figures. Noble metal recovery has also been discussed, but it is readily accepted that the concept of an on-site reactivation procedure, thereby extending the coating lifetime, could well be of considerable interest to a client.

Recent developments have now shown that it is indeed possible to reactivate deactivated cathodes by a technique which could readily be accommodated on a chloralkali production site. Figure 9 shows the effectiveness of the reactivation procedure. There is still some way to go before reactivation can be offered as a fully optimised process but initial results look promising and durability tests are in progress.

The main cause of cathode deactivation is due to the build up of impurities in the catholyte — the role of iron in this respect has already been discussed. Another development under investigation therefore is to produce a cathode coating which is more poison resistant,





especially with respect to iron, than is the present one. This work too, is in its infancy, but a patent application has recently been filed (7).

Conclusions

Despite their relatively high cost, the noble metals have an important role to play in the chloralkali industry. Nowadays graphite is rarely used as an anode material, having been almost totally superseded by titanium coated with a noble metal, usually ruthenium.

From a consideration of its low hydrogen overpotential and its chemical stability there has always been a possibility that platinum could be incorporated into a chloralkali cathode with advantage. The primary objective of this paper has been to show that this can now be done with economic benefit. The cathode coating developed by Johnson Matthey is currently being evaluated by several chloralkali plant manufacturers and it is expected that with increased poison resistance and an on-site

reactivation package the noble metal activated cathode will become an even more attractive option.

Acknowledgements

I would like to place on record my gratitude to my colleagues at the Johnson Matthey Research Centre for providing much of the technical information on which this article is based.

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Platinum in the Glass Industry

Equipment made from platinum has been in use for glass making for over 150 years, and in spite of the relatively high cost of the metal the remarkable properties of platinum and some of its alloys are still encouraging their greater use for the production of household and industrial glasses. A recent article outlines the areas where platinum is being used cost effectively (D. Böttger, *Glass*, 1985, 62, (5), 177-178). The production of lightweight or thin walled bottles is regarded as important to the competitiveness of glass as a container material for the packaging industry. For this application optimum thermal homogenisation of the melt is a necessity and this can be achieved by the use of platinum components at key locations in the equipment.

For the manufacture of liquid crystal display glass there is no substitute for platinum feeders. Using platinum discharge nozzles heated directly by electricity it is possible to produce glass plates of equivalent quality to optical glass, at a thickness of less than 0.5mm. Considered to have advantages over both cathode ray tubes and conventional plasma displays, the flat display screen is also made of very thin (0.3 to 0.5mm) plates of a special glass that can only be manufactured by the use of a directly heated platinum feeder.