International Conference
on

LOCAL GENERATION AND USE OF CHLORINE AND HYPOCHLORITE

held at

The Zoological Society
Regent's Park, London NW1

on

14th – 16th October 1980

Society of Chemical Industry
Electrochemical Technology Group

LOCAL GENERATION AND USE OF CHLORINE AND HYPOCHLORITE

CONTENTS

Note

The opinions expressed in these papers are those of the authors and do not necessarily represent those of the Conference organisers.

THE CHLORINE INDUSTRY'S VIEW OF THE MARKET

PRODUCTION AND USES

Chlorine has been used commercially in the UK since Lancashire bleachers first absorbed it into milk of lime in the 1780's. Its use as a bleach increased considerably following Charles Tennant's discovery in 1799, that chlorine was absorbed by dry slaked lime and could be transported to the bleacher's works as a powder. However the chlorine industry we know today had to await firstly the invention of electric power generators and then the introduction of the electrolytic cell. In the UK it could be said to date from the first industrial use by Castner of his mercury cell process in 1897. Since then the production of chlorine in the UK has grown steadily - as shown in Table I - from the 30 tons produced in that first year to the 1.05 million tons made last year by the four producing companies on their nine different sites.

At the time that processes were being developed to manufacture chlorine by electrolysis the problems of liquifying chlorine on a commercial scale were also being overcome. Thus it became possible to transport chlorine from producing to consuming works and make it available in liquid form to support the demand of the growing synthetic dyestuffs industry for chlorinated organic substances which were not easily prepared from bleaching powder.

As a consequence of liquid chlorine becoming more freely available many new uses and processes were discovered and developed so that the old pattern of usage, heavily weighted to the bleaching of textiles, has changed completely. So much so that bleaching powder itself is no longer made in this country and textile and paper bleaching operations account for less than 1% of UK annual chlorine production. The biggest single use for chlorine nowadays is in the manufacture of ethylene dichloride which is the first step in the manufacture of PVC and a number of chlorinated solvents. However PVC manufacture, though the largest outlet, only accounts for about one third of the chlorine produced annually, whilst the manufacture of chlorinated solvents accounts for a further eighth.

Most of the chlorine produced finds its way into one of the large number of other chlorine consuming processes which use from tens of thousands of tons a year down to only a few tons and cover a very wide range of the country's industrial and domestic activity. For example about 30 000 tpa of chlorine is used to manufacture metal chlorides; some like titanium tetrachloride in large quantities and others like the chlorides of tin and copper in relatively small amounts. About 1,000 tpa is used in the refining of scrap aluminium and precious metals. Phosphorous chlorides and oxychlorides are needed in substantial quantities for use in the manufacture of plasticisers and in organic syntheses. About 130,000 te of electrolytic chlorine are needed each year to satisfy the market demand for hydrochloric acid.

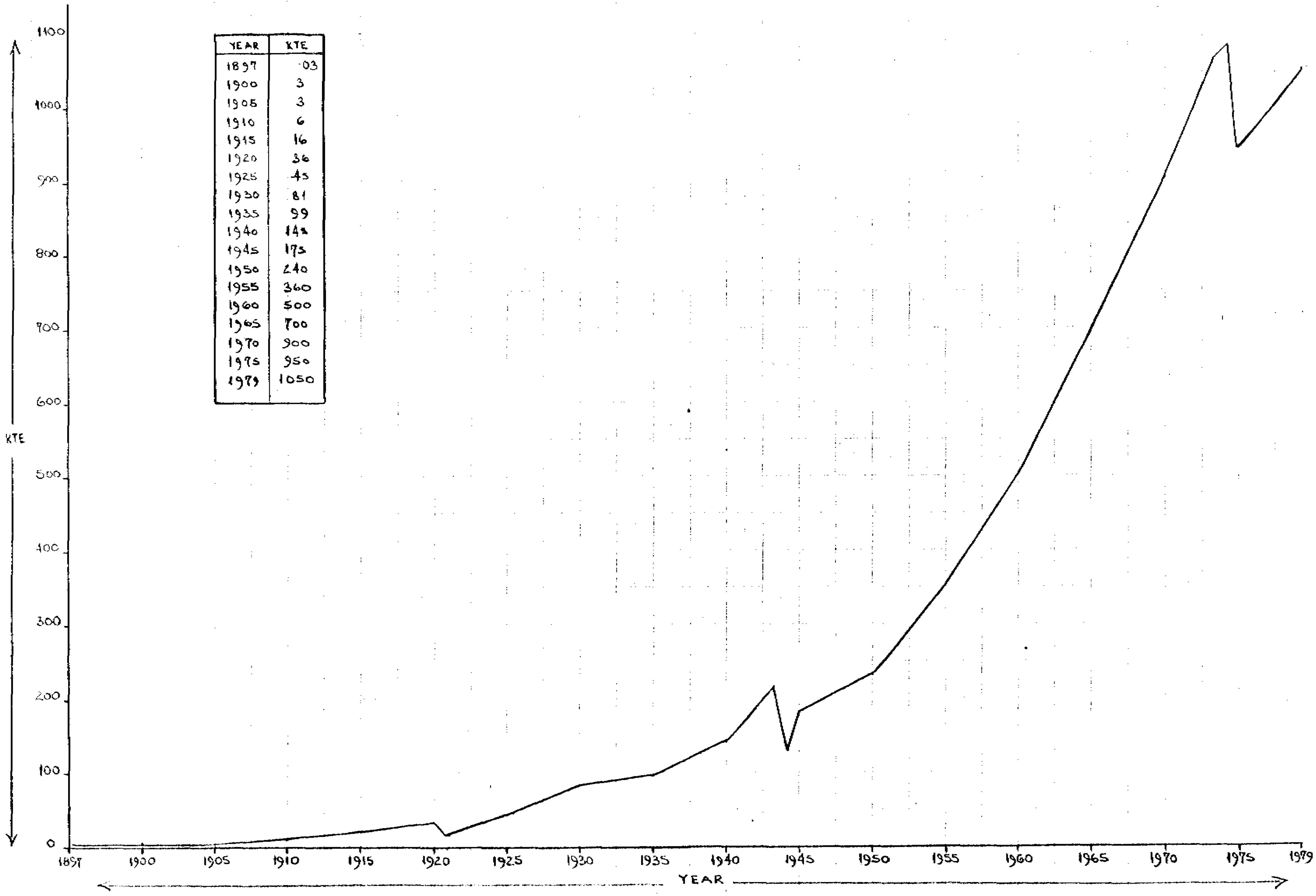
On the border line between inorganic and organic chemistry there is another large use for chlorine in the manufacture of phosgene needed to produce isocyanates for conversion into polyurethanes.

In organic chemistry itself the reactive nature of chlorine and its affinity for hydrogen lead to the most diverse and numerous of its uses. The direct chlorination of benzene and its near relatives for example provides many chlorinated aromatic compounds for use in their own right as disinfectants,

TABLE I

U.K. CHLORINE PRODUCTION - '000 TE

YEAR	KTE
1897	·03
1900	3
1905	3
1910	6
1915	16
1920	36
1925	45
1930	81
1935	99
1940	145
1945	175
1950	240
1955	360
1960	500
1965	700
1970	900
1975	950
1979	1050



insecticides and herbicides, or as precursors in organic syntheses leading to pigment, dye and pharmaceutical products.

Similarly the chlorination of aliphatic compounds, other than ethylene which has already been mentioned, leads directly to large tonnages of agricultural chemicals and to compounds which are valuable tools in the synthesis of other chemicals needed, for example, in petrol and lubricating oils, in dyestuffs and pharmaceuticals, and in paints.

Besides these uses about 13 000 tons a year of chlorine are still needed for their sterilising action in the treatment of potable water, and about the same amount for dealing with algae and mussels in industrial cooling water; beside which there are a host of smaller miscellaneous uses including the original bleaching application. Many of these applications can be carried out using sodium hypochlorite, the manufacture of which represents another major outlet for chlorine.

In fact the range of end uses is so diverse that chlorine consumption has now become as good an indicator of a nations industrial activity as sulphuric acid used to be 50 years ago.

However, despite the diversity of products manufactured and the number of customers using chlorine, it is interesting to note that more than 85% of it is used by the four UK producing companies on their own sites. The remainder is distributed to a large number of customers whose needs are met by delivery in bulk by road, rail, ship or pipe-line, which accounts for 84% of the external sales; in drums, accounting for a further 12%; and in cylinders, accounting for the remaining 4%. Whilst delivery in cylinders is the oldest of these methods it is worthy of note that delivery in bulk by rail has been carried out for rather more than 50 years and by road for a little under 50 years. The UK safety record associated with these two bulk delivery operations has been entirely satisfactory,as will be shown in the following paper.

As might be expected the majority of external supplies go to users of small quantities of chlorine, as illustrated in Table II.

TABLE II

Annual Chlorine Consumption - tes	0-10	10-25	25-100	100-250	250-1000	1000+
% of Total						
Number of Sites	86.5	6	4.5	1.5	1	0.5

There are a number of outlets where the customer finds it advantageous to get the sterilising or oxidising effect of chlorine by taking it in solution as sodium hypochlorite. The market for sodium hypochlorite solution,expressed in terms of chlorine, is equivalent to almost 25% of the external chlorine market. The dominant use is that of rebottling for the domestic bleach market, but in addition there is significant industrial use, some effluent treatment use and some bleaching use.

MEETING THE CUSTOMER'S REQUIREMENTS

Those consumers who purchase their chlorine from the major producers have a number of basic requirements which they share with most consumers.

Clearly they want a pure product, and this aspect is covered by British Standard 3947:1976 with which chlorine produced in this country complies. About half a dozen consuming processes require chlorine with a specially low bromine content and their requirements can be met by supply from those producing works using salt with a low sodium bromide content. The other important requirement is that the chlorine should be dry. This is chiefly because of the corrosive nature of wet chlorine, but is also a process requirement for some operations such as titanium tetra-chloride manufacture or aluminium refining. In this respect the BS limit of 100 ppm is easily achieved.

Like most consumers they do not want to pay more for their raw materials than they have to. Chief among the cell room costs of chlorine is the price the producer has to pay for his electricity. The chlorine industry uses about 1.5% of the electricity generated in the UK and electricity accounts for three quarters of the cell room variable costs. The efficient use of electricity is therefore of paramount importance.

Large scale manufacture offers well established advantages in terms of capital and operating costs per ton of product. It allows brine purification, for example, to be carried out on a large and economic scale, indeed in some works the cost is shared with other products.It allows the best technology and the best technical people to be concentrated at the point of production, so that the most efficient operating conditions can be achieved in existing units and so that the process can develop continuously as technology advances.

It is important when comparing the cost of using one chemical with another, or of one method of manufacture with another, to take into account all the costs involved. Capital cost must be taken into account, including those for storing and metering the product, the cost of maintenance and the appropriate rate at which capital must be depreciated. Cost figures for local generation available so far indicate that a high capital depreciation rate can be required for these units together with high maintenance costs and high total power costs. Manpower costs must also be correctly alocated both for operation and maintenance.

In many parts of the world the well established advantages of scale in manufacture are dissipated in transport costs, but in this small island we are fortunate that most consumers, certainly the large ones, are not very far from a producing works. Nearly 90% of the external sales of chlorine are to sites within 100 miles of a producing works. The corresponding figure for sodium hypochlorite is over 80%; however, of the remaining 20% more than 100 miles from a producing works, almost half is to small lot business handled by distributors.

Also, like most consumers, they prefer a 'ready to use' product. They have their own expertise directed to the efficient running of their own processes and to dealing with the associated problems. There is not much incentive to get involved in electro-chemical engineering processes if the pure product can be delivered to their premises at costs which are comparable with or lower than those they would incur producing it themselves.

Security of supply is important to most customers. In the hands of the major producers chlorine production is a reliable continuous process. In addition the producing works have storage capacity which is large by their customers standards, and customers themselves can, without difficulty, store several weeks requirements on their own premises.

Apart from the more obvious needs of the consumer mentioned above it is traditional for chlorine producers to provide their customers with technical assistance based on their own detailed and extensive knowledge of the product and how its use is developing not only in this country but throughout the world.

The safe use of this product is of equal importance to the supplier as to the consumer. In this field also the producer takes an active interest, offering advice about the arrangements customers make for handling the product, responding to technical queries; and, if the need arises, offering immediate assistance at any time of the day or night by means of the Chemical Emergency Service "Chlor Aid" scheme operated jointly by all the producers.

Despite the very high standards of safety achieved in the use of large quantities of this basic chemical, industry is continually looking to ways of maintaining the excellent record. Recently these have included refinements to the way drums and cylinders are transported, and modifications to the road and rail tanker wagons carrying chlorine in bulk. Also earlier in the year the Chemical Industries Association, having reviewed the standards of design currently adopted in the UK, those advised by the Bureau International Technique du Chlore in Europe and the Chlorine Institute of America, produced "Guidelines for Bulk Handling of Chlorine at Customers Installations" which seek to harmonise the advice given to users of chlorine in bulk and to maintain the traditional high design standards.

Customers using sodium hypochlorite have similar requirements which large-scale producing sites are well able to meet. The quality of the product is important in respect of stability and appearance. The introduction of plastic materials of construction in the manufacturing plant and handling equipment in recent years has significantly improved sodium hypochlorite quality.

LEGISLATION

The Health and Safety at Work etc. Act has had practically no effect on the supply of chlorine to external customers because the standards already adopted exceeded those required by the Act.

The impending Hazardous Installations (Notification & Survey) Regulations will affect perhaps two dozen customers whose installations are large enough to be surveyable; but what will be required of them is not significantly different from the present practice for the majority of these installations. They will, however be required to demonstrate this and produce a formal reponse to the HSE.

There may eventually be corresponding "Dangerous Substances" (Conveyance by Road) Regulations, though the consultative document fell so far short of offering a satisfactory framework for legislation that these are not expected to appear in the near future.

In the meantime the regulations which have an indirect influence are the ADR[*] and RID[+] covering respectively road and rail movement in bulk. There was, towards the end of 1977, a Continental Western European suggestion that the movement of chlorine in bulk by road should cease. However the proposal was not based on any careful comparison of the relative merits of transport by rail with those of transport by road; consequently it was not adopted and no further proposal of this nature is expected. The UK view, after what is undoubtedly the most thorough study of the subject, is that bulk transport by road presents no more hazard than bulk transport by rail and, as has been noted, both have been carried out in this country for about 50 years without incident.

* ADR - Accord European Relatif au Transport International des Merchandises Dangereuses par Route.

\+ RID - Reglament International concernant au Transport des Merchandises Dangereuses par Chemin de Fer.

THE CHOICE

In comparing the merits of small scale 'on site' generation with those of larger scale 'central' generation it is apparent that the consumer most likely to benefit from 'on-site' generation would be one whose requirement was for sodium hypochlorite solution, preferably diluted to about 7% or less. However if all the factors mentioned above are properly taken into account it is evident that the chlorine industry can manufacture 15% Av Cl_2 sodium hypochlorite solution centrally and deliver it to the vast majority of UK customers cheaper than it can be generated by a small scale unit on site, unless the customer has access to abnormally cheap electricity.

Few customers have chlorine and caustic soda requirements that are even approximately in balance but even here, where credit can be given for the value of the caustic soda, the cost advantage lies with efficient central production. In this latter respect it is worth noting a difference between the North American pattern of usage and that of the UK and Western Europe shown in Table III. The relatively large outlet for chlorine required to bleach pulp and paper does not exist in the UK and amounts to very little in Europe as a whole. Furthermore the demand of the North American Pulp & Paper Bleaching Industry for chlorine (14%) is almost exactly matched by its demand for caustic soda (15%). These circumstances, combined with the distances involved, could well outweigh the uncertainties and disadvantages of 'on site' generation in North America and thus provide a market *for small scale units there. However, there is no corresponding* demand from the pulp and paper industry in the UK.

TABLE III

	UK %	Western Europe	North America
Plastics, solvents and other Organic Chemicals	87	81	68
Inorganic Chemicals	9	10	12
Pulp & Paper Bleaching	<1	9	14
Potable & Waste Water	1.5		6
Miscellaneous	1.5		-

Where chlorine alone is required the costs favour large scale central production even more convincingly.

Thus it would appear that any advantage of 'on-site' generation to UK industry in general is likely to be rather limited.

FUTURE DEVELOPMENT OF THE MARKET

The use of chlorine now covers such a broad cross section of industrial uses in this country that the external market is expected to follow a general growth trend probably lying between the industrial production trend line and the slightly higher chemical industry trend line.

As has been indicated earlier, legislation poses no threat to continued development provided the high standards of safety achieved in the past are maintained.

Because of the manifest advantage of large scale production on a few major sites and the minimal transport penalties incurred in the UK, it is not thought that small scale local generation will have any significant cost advantage over the present pattern of production.

FOOTNOTE:

The author is indebted to the Bureau Internationale Technique du Chlor and the Chlorine Institute for permission to publish the figures used in Table III, and to Messrs AOC, BPCL and SCL for assistance in compiling Tables I and II.

PRODUCT HANDLING AND DISTRIBUTION OF CHLORINE AND HYPOCHLORITE

INTRODUCTION

The previous paper described the way in which the chlorine industry has developed and how the usage of chlorine has diversified. Much of this became possible with the ability to fill liquid chlorine into cylinders and later into larger containers and then to transport it safely to locations far distant from the place of manufacture. Prior to 1909 chlorine could only be transported in a "fixed" form, as for instance in bleaching powder but when liquefaction of chlorine commenced in 1909, storage in small tanks and transport in cylinders became possible. Later rail tank transport was introduced, as were drums and road tanks. This ability to transport chlorine easily, and safely, has led to a very large number of chlorine users being supplied from a limited number of chlorine manufacturing plants, thus the economies which can be achieved by scale of production are available to the whole of the chlorine market. This is essential for the large number of smaller users whose demand is limited to say a few cylinders each year. It is also important for larger users who are not basically part of the chemical industry since they are freed from the responsibility of operating a sophisticated and expensive chlorine manufacturing plant, and need only service a much simpler storage installation.

As an alternative to chlorine in the many applications where water chlorination is the objective, use can be made of sodium hypochlorite, which contains typically about 15% available chlorine w/w. In this case very simple storage and dosing plant is all that is required.

This paper describes the advantages and problems involved in the various ways in which chlorine can be handled and used.

CHLORINE SAFETY

To very many people the slight smell of chlorine is quite familiar and characteristic from its release in very low concentration when domestic bleach is used. The smell threshold itself varies according to the individual but is usually below 1 ppm, and it becomes unpleasant at around 5 ppm.

The Threshold Limit Value produced by ACGIH and used in many other countries is 1 ppm - the average concentration deemed safe for a working day. At higher concentrations injuries may result, but the data available for humans relating time, concentration and physiological effect are very limited at these levels. Examination of the data published, and interpretation by experts has led to bands being proposed to describe the conditions to be expected in the average person, ie. someone who is not suffering from respiratory disease. They are reproduced in a paper by Dicken (ref 1) which also describes a suitable method for examining the potential sources of release from an installation and allotting them to three catagories of emission of increasing potential severity, for which acceptable frequencies are also suggested.

By means of hazard and operability analysis, it is possible for all plant and equipment to estimate with reasonable confidence the frequency of leakage and the corresponding rate of leakage. Not only does this provide vital information to supplement accident reports, but it enables effort to be directed towards ways of eliminating or reducing the frequency or rate of leakage.

Using these calculated leakage rates of chlorine into the atmosphere, it is then possible to estimate the likely dispersion under different wind and weather conditions. The results will indicate the distance at which different effects might be experienced. Clearly the smaller gaseous releases can only have short range effects, but if the source were to be in or close to public areas, the effects could be more serious. Larger concentrations can generally only be derived from leakage of liquid chlorine.

HANDLING OF HYPOCHLORITE SOLUTIONS

Many years ago sodium hypochlorite solutions were manufactured mainly to absorb safely low strength chlorine streams, produced largely as by product or vents. Nowadays, however, the growing demand for a high quality product has resulted in a change to manufacture on specialised, larger scale plants producing material to high specifications.

Hypochlorite solutions are among the safest in the chlorination and disinfection industries. Containing up to 1% NaOH, they are alkaline, and hence must be handled with normal care. Otherwise an unlikely but occasional type of incident is that caused by overpressure due to decomposition of the solution and the release of oxygen. This can happen in three ways. Overheating, over-agitation, and contamination particularly by heavy metals. It is therefore important to design packages from which pressure can be safely relieved, and also by good operation to ensure that it is neither overheated, over-agitated nor becomes contaminated. Bulk storage containers are now of PVC/fibre glass or HDPE construction in order to provide vessels which do not contaminate the product and which are not themselves damaged by the solutions. Decomposition from contamination is now less likely as quality has risen, but no new contaminent must be allowed to reach the solution. In the case of the highest quality product made in modern production units, where the solution has been specially polished, storage of product is no longer a problem since decomposition has been largely eliminated.

However there is a risk of decomposition which results from loss of alkalinity. Addition of acid can neutralise the alkali concentration and cause the solution to become acid when it decomposes releasing chlorine as gas with a large increase in volume. Since the cause of this type of accident is so clearly identified it is therefore possible to design both the equipment and the operating system to prevent acid being allowed to come into contact with hypochlorite solutions and so to prevent any hazard occurring. It is recommended that reliance should not be placed entirely on any system based on the human operator, as they can be fallible even in the more obvious operations or constraints. Mixing of hypochlorite type solutions and acid material in plant drains must also be prevented.

HANDLING OF LIQUID CHLORINE IN BULK

By bulk one means the use of storage containers, both static and for transportation of over 1te capacity in the UK, typically in the range 20-400 te for static containers and 15-42te for transport containers. In this system the principle operations of relevance to liquid chlorine handling are:

manufacture ----> storage ----> loading ----> transport ---->
unloading ----> storage ---> vaporisation.

An analysis has been made of the major reported accidents covering the stages from storage to storage (ref 2). It is significant that the most frequent of these are loading and unloading accidents, but their absolute rate is exceedingly low. Indeed the frequency world-wide is lower than say 20 years ago due largely to much stricter operating procedures, despite the larger amounts of chlorine now transported. Worldwide, transport of chlorine in bulk must be of the order of 6m te per year, yet the rate of such accidents is about 2 per year, or approximately 1 per 3 million te shipped. The cause is occasionally failure of the loading connection itself, but more usually it is due to rupture of the transfer line caused by the transport container being moved while connected. Modern practice can ensure that, in the event of a failure, the amount of chlorine escaping is very limited, and any serious hazard is only local to the filling station. A consequence of having few manufacturers in the UK is the limitation of the responsibility for the transport of bulk liquid chlorine to a few companies, thus ensuring that the highest standards can be maintained. These are continually being improved despite the fact that there have been no bulk chlorine transport failures in the UK. The safety standard in the transport of chlorine drums and cylinders has been substantially improved also as a result of hazard analysis.

The history of pressurised chlorine storage tanks is even more satisfactory. Although in the distant past there have been 7 ruptures worldwide the last of these occurred nearly 30 years ago when an old rivetted boiler, unacceptable by present standards for chlorine duty, ruptured. The causes of all these failures are well known and the solutions which prevent their recurrence have long since been identified and implemented. These are reflected in the high standards imposed today by the industry itself and by authorities, as for example described in the UK Code of Practice (ref 3). Modern tanks are safe if properly constructed, tested and operated, are fitted with adequate reliefs of very high reliability, and are kept away from external hazards.

There have been a very few cases reported of tank puncture. These are usually caused by external agents such as explosions, especially if these result in collapse of the tank supports. Such potential causes must be identified by hazard analysis and eliminated as risks before the installation is constructed. Experience exists in the industry to enable this to be done with confidence, so that, with careful attention to siting and high standards of operation and maintenance, a safe system can be installed.

The analysis (ref 2) also indicated that of the fatalities from liquid chlorine accidents that have occurred in the world to date, only two have occurred in the UK, which is a better performancce than that which might be anticipated from the amount of chlorine produced, and far better than for very many other hazardous substances. There is therefore no cause for undue concern, but the maintenance of design and operating standards is of great importance, particularly in the area of ancillary equipment since leakage from the bulk containers is most unlikely.

LOCAL GENERATION OF CHLORINE

For the user who is not consuming chlorine on a large scale, but requires more than that conveniently supplied in cylinders or drums, local generation can appear attractive. There are however several aspects which deserve consideration. If a reliable supply of gas is required on a continuous basis some of the on-site processes only produce gas and, in the absence of the ability to store chlorine as liquid, it may be difficult to maintain a reliable supply. Ensuring this could involve substantial design and operating support and demands on skilled and experienced manpower in a field often outside that of the company's normal area of experience. If a back-up liquid chlorine supply were to be provided to guarantee supply, there is a greater risk of leakage taking place from such an enlarged installation which is only used infrequently. It is therefore most important that the entire logistics of such an operation are adequately thought through and this must include an assessment of the comparable risks and the ability to deal with them. Such an exercise will identify those proposals for local generation which can be undertaken with confidence.

WATER TREATMENT PLANTS

Medically the supply of safe potable water rates high among the priorities of most nations, and failure of an existing chlorination system has occasionally led to the development of small scale epidemics. The techniques of water chlorination are well known, and need not be described further, but handling of the chlorinating agent is the key item of safety.

If liquid chlorine were the agent, it has to be transported to site in cylinders, drums, or bulk containers. As described earlier there are risks associated with faulty connections in the transfer to plant storage or direct to the vaporisers and chlorinators. There must therefore be an appropriate emergency procedure on site and properly trained operators available at all times. Where bulk deliveries are made, the area which is potentially hazardous may extend beyond the plant perimeter, in which case emergency procedures are worked out in conjunction with the relevant authorities, eg. Police and Fire Brigade among others. In addition, industry in the UK provides a specialist emergency service, Chlor-Aid, which is also able to assist at the planning stage. It should also be obvious that adequate separation from members of the public is desirable, and that special attention is given to the likelihood of the occurrence and to size of release when designing the installation. Both of the latter can be reduced by suitable measures, details can be found in reference 3.

SWIMMING POOLS

Liquid chlorine has been used for disinfection of swimming pools for a very long time. The benefits are well known, but often the disadvantages are not fully appreciated. Some of the more obvious ones include the problems of using liquid chlorine for small pools, especially in the domestic area, and in these cases specially developed chemicals are manufactured which are amenable to purchase from hardware shops and to safe storage at home. For public pools, especially the largest sizes, liquid chlorine has been used very successfully, but there have also been a few incidents. It is important to realise that the operating organisation will not be employing trained chemical plant operators but pool attendants to perform the few necessary operations. If conducted carefully and precisely as instructed on the instruction sheet, chlorination can be effectively maintained and be accident free. However a little carelessness, as for instance in the inaccurate insertion of washers into joints, can lead to chlorine escape, the correction of which using a respirator also presents problems and causes delay. Badly sited chlorination rooms have also led to leakages entering the pool area of indoor pools. Consequently liquid chlorine is not acceptable in many countries for swimming pool chlorination. For example, no new chlorine treated pools are allowed in the Netherlands, and all UK pools are required to cease using liquid chlorine by 1 January 1985 unless alternatives are shown to be unacceptable.

The alternatives are hypochlorite treatment, bromine or ozone treatment or the use of speciality chemicals. Of these hypochlorite is the most common in Europe. In order to control the water pH and permit effective disinfection, hydrochloric acid has also to be used. There is a very small risk that the two solutions could be mixed in the storage vessel by accident,but it is possible to design a storage and unloading system which should effectively prevent this happening. It is an aspect which requires careful examination in all installations.

ACKNOWLEDGEMENT

I would like to acknowledge the advice given by many colleagues, and my thanks to ICI Mond Division for permission to publish this paper.

N C HARRIS
Imperial Chemical Industries Limited
Mond Division
Runcorn

References:

1 The Quantitative Assessment of Chlorine Emission Hazards.
A N A Dicken
AIChE Chlorine Bicentennial Symposium, San Francisco, 1974.

2 Analysis of Chlorine Accident Reports.
N C Harris
Chlorine Institute, 21st Plant Manager's Seminar, Houston 1978.

3 Guidelines for Bulk Handling of Chlorine at Customer Installation.
Chemical Industries Association Ltd, 1980.

SOCIETY OF CHEMICAL INDUSTRY

International Conference
on
LOCAL GENERATION AND USE
OF CHLORINE AND HYPOCHLORIDE

London 14th - 16th October 1980

SMALL-SCALE CHLORALKALI PRODUCTION IN DEVELOPING COUNTRIES

Dr M. Burrows, Dr J. Cox
John Cox & Associates

SYNOPSIS

Chloralkali plants have a strategic significance for the chemical industry which makes their installation desireable in developing countries even when on a very small scale. However, the concept of "minimum commercial size" has led some countries to conclude that a chloralkali investment has to be large, and therefore export-orientated, to succeed. This discourages investment or, in some cases, has resulted in the purchase of over-sized plants.

Recent technological advances, notably in membrane technology, have made small-scale chloralkali plants more attractive as a commercial proposition for developing countries. There are, in addition, non-commercial, socio-economic arguments favouring such investments, particularly when the plant can be used, at least in part, as a service unit for a larger complex (for example, a power station, a refinery or a desalination plant).

The design requirements of such plants are not identical in the context of a developing economy to those for small-scale plants in industrialised countries. This paper discusses what features of small-scale plants have utility in developing countries and indicates the specific processing requirements that can be applicable, notably with respect to brine purification.

1. INTRODUCTION

Developing countries, by definition, do not have a developed industrial base. There may be many reasons for this. Some lack natural resources. Others have had their growth stunted by an inappropriate socio-political system or by an unequal relationship with another country. Whatever the historical reasons, all face today a range of similar problems.

Commercial viability is a major problem whilst a country has a low domestic demand for industrial products. The advanced economies have a built-in advantage as their higher domestic demand enables them to operate at higher output levels. Nevertheless, a chloralkali plant may prove commercially viable because of the high costs of imports, especially for liquid chlorine and hydrochloric acid.

Even when the commercial justification is marginal, the project may be worthwhile because of safety factors. On-site generation and use of gaseous chlorine can avoid the need to transport liquid chlorine altogether. This is particularly worthwhile in a country with a labour force inexperienced in the handling of hazardous chemicals.

In practice, in order to make a start on industrialisation and to stimulate domestic demand, a developing country often decides to undertake investments which fail to satisfy either of the above criteria. The 'socio-economic criteria' adopted will vary with local circumstances, including the currently-prevailing ideology, yet there is a growing world consensus on many features which are considered desireable, notably:

(a) Community health. The provision of health services rarely is subjected to cost/benefit analysis. As a corollary, supplies of drinking water, medicines, etc. tend to be compared for relative cost-effectiveness but are not expected to satisfy traditional commercial criteria.

(b) Education and training. Industrial enterprises are used for the development of skills which may have other potential applications. For example, power stations often are used as training bases for new process workers.

(c) Natural resources. It is a prudent long-term objective for any country to seek to reduce its dependance on others, even when the short-term commercial returns are low or, possibly, negative.

Non-commercial criteria of this type can be quantified by economic analysis, using shadow prices and related concepts. For any specific evaluation it is advisable to adopt such procedures, irrespective of the project viability or otherwise in the commercial sense. However, it would be inappropriate to attempt such precision in this paper, which is concerned with general features pertaining to a chloralkali project. Two general comments will suffice at this point to summarise the implications:

(a) Small-scale plants have a wider commercial application in developing countries than often is appreciated.

(b) However, non-commercial criteria, such as those listed above, may be the primary reasons for an investment.

The significance of the investment criteria does not end when a decision is taken to purchase a chloralkali plant. The reasons for a purchase also influence features of the design, construction and operation of the plant, as will be described in later sections.

2. THE MARKET

The market for chloralkali products is partly a reflection of self-generated domestic demand but also, especially in planned economies, a consequence of government policies. In several developing countries, particularly those enjoying large oil revenues, investments are made on the scale considered necessary to make production costs competetive in international markets - without regard for the existing level of domestic demand.

There is nothing wrong in principle with this approach - though few such investments have proved commercially successful in practice. The most common failing has been to apply the concept of 'minimum commercial size', as calculated for industrialised market economies, to the very different situations of the countries we are considering. Moreover, the concept is no more than a generalisation and, for example, fails to explain why there are numerous small-scale chloralkali plants even in the industrialised countries. The detailed economic arguments however do not concern this forum: suffice it to say that, whatever the reasons, this paper is not concerned with large-scale chloralkali plants.

A developing country typically has a small but vital need for water chlorination and bleach, and may have a variety of minor uses for other chloralkali products. If it has begun the process of industrialisation it may require more substantial quantities of chloralkali chemicals, probably including hydrochloric acid. Taking into account population distribution and communication difficulties, there may be a need for 2 - 10 tpd of balanced chloralkali products for each million inhabitants of a newly-developing country.

This is a broad generalisation but appears to be valid for about 20 - 30 countries for which data is available. Three further generalisations can be attempted:

(a) In most cases there will be at least one major user of chlorine for water treatment (a desalination plant, a power station or a refinery), who may be a customer for chlorine or hypochlorite.

(b) By contrast, it will be unusual to find a major domestic customer for caustic soda. Most uses for caustic soda will be as a weak solution - even when transport costs dictate a preference for strong solutions or flake caustic.

(c) Sodium hypochlorite probably can replace imports of TCC or HTH and, though perhaps of only marginal commercial value, its production will improve the operational flexibility of a chloralkali plant.

In presenting this paper we are restricting ourselves to plants of this approximate capacity (2-10 tpd) and will assume that it is sited close to the largest chlorine user. This avoids the need for chlorine liquefaction facilities and liquid chlorine containers, which would add significantly to the cost of a small-scale plant and would impair its commercial performance. For a country with inexperienced chemical plant operators, the extra operating hazard is another major disadvantage of chlorine liquefaction. To maintain operating flexibility, both hypochlorite and gaseous chlorine facilities should be provided for the major chlorine user.

3. RESOURCES

Electricity, salt and labour are the major indigenous resources used by a chloralkali plant. Their price is determined by a combination of objective conditions (e.g. availability) and subjective judgements (e.g. pricing policy). A commercial appraisal has to use the actual prices, whether or not these seem rational, in order to establish whether the investment will prove profitable. A socio-economic appraisal has to take account of the costs to a country's economy, whatever the commercial viability.

As previously explained, it is commonplace for investments in a developing country to be undertaken for non-commercial reasons. For a socio-economic analysis it is convenient to evaluate electricity, salt and labour - and even capital - in terms of the resources used (noting, as we proceed, that the implications of this method of analysis may conflict with the criteria for a commercial venture).

3.1 Fuel

Many developing countries are well-endowed with oil and gas reserves. Their domestic fuel prices often are low, reflecting the actual production costs. It is tempting, but it would be a mistake, to use the domestic fuel price in an economic evaluation. The correct price to employ is the cost to the country's economy arising from the use of this fuel.

Usually this is an alternative to fuel exports at the prevailing world market price. So the value of the fuel is the revenue lost, with minor adjustments for the processing and transport costs. Alternatively, for those countries not possessing indigenous fuel supplies, the fuel value is determined directly by its purchase price, again with the obvious adjustments for handling costs.

In both instances the major determinant is the world market price. There are a few exceptions (countries with non-exportable resources such as hydro-electric power) but, as a general principle, in a socio-economic evaluation developing countries can be expected to employ high-value fuel, whatever its price or origin.

The detailed design of a chloralkali plant therefore should proceed on the assumption that fuel and power costs are high and that savings in electricity usage will be very welcome. The consequences of this conclusion are discussed further in section 4 and apply whatever the commercial price of electricity happens to be. As power costs are the largest single item in the operating costs, this is a major argument for the use of membrane cells that are able to maximise the use of off-peak electricity.

3.2 Salt

Most developing countries possess a climate and coastline which is suitable for the solar evaporation of seawater. If not, they may be only a short distance from a country that does make solar salt. This process uses readily-available natural resources (sea, sun, wind, land, unskilled labour) and normally does not require as much capital investment as any alternative extraction technique. As always there are a few exceptions but, for the purposes of this paper, it is assumed that a reasonably cheap supply of solar salt is to be used by our projected 'typical' chloralkali plant.

The composition of a solar salt depends on each saltfield's specific circumstances: in the worst instances the NaCl content can be as low as 90% and the impurities unacceptably high. This has led some chloralkali producers to conclude that solar salt,per se, is an unsuitable feedstock for a chloralkali plant.

However, merely by improving production methods (with maybe a little redesign), a modern saltworks should be able to produce salt with the following minimum purities (dry basis):

	Washed	Refined
NaCl (min.)	98.5%	99.0%
Ca^{++} (max.)	0.5%	0.1%
Mg^{++} (max.)	0.3%	0.06%
SO_4^{--} (max.)	0.5%	0.5%
Insols. (max.)	0.2%	0.05%
Moisture (app.)	5%	½%

There is scope for further improvements in product quality by tight management control at the saltfield - aided perhaps by some additional equipment. If the chloralkali plant is an important customer this may be the best procedure. But it often happens that the chloralkali plant is the only customer with a use for this higher purity. In such cases the Saltworks' management may not wish to take the trouble to achieve higher product quality. In general it should be assumed for design purposes (though not necessarily in operation) that a solar salt feedstock may have a composition within the range suggested above.

Since salt is a widely-available commodity with limited export potential, its economic value is low - certainly no higher than its domestic selling price. Moreover, exporters rarely can sell as much salt as they could produce (due to transport costs and difficulties). In such circumstances the cost of using salt in a new chloralkali plant will be approximately equivalent to the marginal cost of production and transport - often less than $10/tonne. Although the use of such a relatively impure feedstock has disadvantages, notably with respect to brine purification, from the standpoint of the country's economy the case for solar salt normally is unassailable.

The implications of a solar salt feedstock, with a few exceptions that do not concern this presentation, are:

(a) salt is cheap in the economic sense, even when its price is high,

(b) brine treatment needs a lot of extra attention.

3.3 Labour

Most developing countries have underutilised unskilled labour - sometimes, in the case of the oil-rich countries, encouraged by large-scale immigration. In this situation labour-intensive investments may be welcome - even when governments impose wage levels at a height that makes commercial investments unprofitable.

Whereas the saltfields require essentially unskilled labour (which satisfies this social need), a chloralkali plant demands skilled and trained labour which, invariably, is in short supply. Since the nature of the production process does not allow the skill level to be downgraded, it is realistic to attempt instead to reduce the labour requirements.

The relative simplicity of the membrane cell has made it possible to operate a small-scale plant with only one shift operator - even without indulging in full-scale instrumentation. The requirements for construction labour can be reduced by shipping the plant in compact skid-mounted modules. The remaining labour requirement has proved more difficult to satisfy - that is, the need for a skilled maintenance staff.

Relative to its investment cost, the plant needs many expensive skills (mechanical/electrical/instrument engineers, laboratory technicians, etc). Yet the demands of a well-run small-scale chloralkali plant are insufficient to keep such a labour force fully-occupied. One solution is to locate the chloralkali unit next to a larger plant which employs a similar range of skills. This could be a power plant, a refinery or a desalination plant - most developing countries have at least one. A secondary advantage accrues if this plant is the 'next-door' customer for chlorine as suggested earlier.

If a chloralkali plant is constructed as a service unit of a larger plant, the operating staff levels may be reduced by providing a higher degree of instrumentation. However, the major advantage is that the chloralkali plant enjoys the benefits of shared overheads at minimum cost.

Despite the low labour requirements of membrane cell plants, the equipment supplier still has to provide training as an integral part of the offer. Often it is suggested that training should take place on an existing plant. Unfortunately these plants usually will be in countries enjoying much higher living standards, with a different culture to that previously experienced by the trainees. This can have an unsettling effect and sometimes can tempt trainees to remain abroad. The more consistently successful training programmes take place on-site during the commissioning period and the early months of operation - albeit at some extra cost in ex-patriate labour.

In short, and irrespective of the actual wage level, it is appropriate to treat labour for a chloralkali plant in a developing country exactly as in a high-wage economy - it is a commodity in very short supply whose usage has to be minimised and whose working conditions must be attractive.

3.4 Other consumables

Nearly all the other consumables (water, chemicals, anodes, membranes,etc.) are likely to cost more in a developing country than in an industrial country. For these items there is unlikely to be a divergence between costs in the commercial and in the economic sense.

With regard to chemical usage, it is relevant to note that soda ash and HCl, unless produced locally, may cost very much more than might be expected in a developed industrial country.

3.5 Capital

For the purposes of economic analysis of small-scale chloralkali plants, it is illuminating to employ the academicians' device of treating capital as a natural resource. In this instance there is no alternative but to divide the developing countries into two categories - the money-rich and the money-poor.

The money-rich developing countries enjoy the benefits of large-scale exports of a valuable natural resource (usually oil) and are engaged in the process of converting income into permanent capital assets. For them, cost-minimisation does not have the same significance as for the rest of the world: there is a lot to be said for converting money into assets as quickly as possible, particularly when world inflation rates are high. In their situation the value of money, and cost-minimisation, is less than a conventional commercial appraisal might imply.

Most countries are not in this happy situation: their development is limited by the availability of money - which can have, as foreign currency, a greater worth than its nominal value. In these instances, cost-minimisation (especially of foreign currency) can be more important than cost-effectiveness (for example, with respect to labour productivity).

As it happens, the money-rich developing countries have a tendency to ignore the virtues of small-scale plants and this simplifies our approach. In this presentation we make a further assumption - that our 'typical' developing country does wish to minimise the total capital expenditure and, even when the investment is undertaken primarily for socio-economic reasons, a commercial return will be regarded as a desireable feature of the project.

4. THE PLANT

The foregoing sections have identified a potential need for small-scale chloralkali plants in developing countries, operating within the following typical economic context:

Capacity	2-10 tpd, perhaps higher. No chlorine liquefaction.
Function	Probably a service unit to a larger plant which needs chlorine. Hypochlorite, HCl and caustic soda are sold to balance the chlorine output.
Power/Fuel	Should be considered of high value, even when domestic price is low.
Labour	Skilled labour in short supply.
Salt	Should be considered of low value, even when domestic price is high.
Capital	Cost-minimisation and a commercial return are desireable but not always essential criteria for investment.

4.1 Size and location

As for all other process plant, the design capacity should be sufficient to satisfy predicted demand, plus an allowance for possible growth. For a small plant it is not so easy to reduce infrastructure costs and there is less penalty, relatively-speaking, in oversizing the process equipment. This is especially true of chloralkali plants where the cost of extra cells is relatively low and in any event is partially offset by power savings which accrue from a reduced loading.

The advantages of locating the plant next to a major chlorine user, sharing overheads, have been discussed previously. An additional factor of relevance is the reduction of unit power costs that may be possible by reducing the load when peak demands have to be met by the electricity supply system.

4.2 Design and construction

Although small mercury cell installations are in operation in many countries, it is doubtful whether any more should be constructed. The adverse effects of mercury on the environment, which have become apparent during the past decade, necessitate extra effluent treatment facilities which would be disproportionately expensive for a small-scale plant. In developing countries these problems are exacerbated by the hot climates often prevailing (making atmospheric mercury levels more dangerous) and the generally poor quality of the salt (increasing the quantities of mercury in the solid residues).

Small bipolar diaphragm cells are technologically safer (apart from the environmental hazard from asbestos) but have commercial disadvantages. The capital cost tends to be higher because of the necessity to evaporate the cell liquor to recover the salt. Operation is more complex and the labour requirements can be expected to be greater. Whilst there may be special circumstances which favour diaphragm cells in particular instances, a newly-developing country probably will prefer to make its investment in membrane cell technology which has secure prospects for a long-term future.

The construction costs of chemical plants in developing countries are normally much higher than in industrialised countries, by a factor of 2 or 3. This arises from the lack of experienced construction labour and the shortage of engineering support facilities. The deployment of skid-mounted units reduces the on-site construction work considerably. Ideally all that is required is the supply of services and the interconnections between the modules. This minimises local construction problems and reduces the construction period.

4.3 Brine purification

Conventional brine purification proceeds by the addition of soda ash and caustic soda to precipitate calcium as carbonate and magnesium as hydroxide. After settling, the purified brine is decanted and passed through polishing filters. This technique is able to reduce the total hardness to below 10 ppm (as calcium) - although it is rare for any plant to escape occasional upsets which create much higher impurity levels.

As experience of membrane cell operations grows, it is noticeable that suppliers have advocated lower and lower hardness levels for the brine feed for membrane cells. This means that traditional chemical treatment has to be supplemented or replaced for a membrane cell plant. Three approaches have been suggested:

(a) to accept the necessity for periodic back-flushing to clear precipitates from the membranes,

(b) to employ phosphate addition to improve conventional precipitation to achieve hardness levels below 1 ppm,

(c) to add an ion-exchange purification stage after conventional chemical treatment, to achieve hardness levels below 0.1 ppm.

The third technique has been preferred for large-scale membrane cell plants but, as yet, has not been used for the 2 - 10 tpd scale we are considering. Whatever the reasons for this reluctance in industrialised countries, the simplicity and security of ion-exchange makes it by far the most suitable technique for a small-scale plant in a developing country. The risks of downtime for membrane replacement, quite apart from the cost, make it imperative that brine treatment should be as secure as practicable from operator error.

The use of ion-exchange necessitates the inclusion of a dechlorination unit and provision for regeneration of the resin. The operating procedures for dechlorination and regeneration need to be as simple as possible, in order to maintain the advantages suggested above for the ion-exchange technique. (It should be noted in passing that regeneration requires HCl and that a chloralkali plant without an associated HCl production unit could find ion-exchange unsuitable despite the case argued above).

Finally, although chemical treatment can control sulphate levels in the brine, when salt costs are low it is more appropriate to achieve this by a simple purge. This technique has the added advantage of controlling chlorate levels without requiring additional equipment or operating procedures. With sulphates at 15-30 gpl it is unlikely that current efficiencies will suffer from their presence in the brine.

4.4 Costs

Because of the special conditions in each country, and the current high rate of inflation, it is unwise to quote 'typical' values for capital and operating costs. In the specific instances we have investigated however, we can confirm that small-scale membrane cell plants have been able to generate a conventional commercial return - and that the socio-economic return appears to be even more favourable.

A SURVEY OF PRESENT AND POTENTIAL FUTURE CHLORINE/HYPOCHLORITE PLANT PRACTICE IN THE WATER INDUSTRY.

by

D. G. Stevenson,
Paterson Candy International Limited.

FORWORD

This paper presents the view of a specialist contractor in the Water Treatment Industry, with more current business overseas than at home. Sterilisation by chlorine or hypochlorite is almost always an essential component of the treatment process, sometimes the only treatment.

Electrolytic hypochlorite is a technology which has advanced considerably in recent years and the time would seem right to review its place amongst the alternatives.

INTRODUCTION

Hypochlorite was first used for water disinfection at Lincoln in 1905 and gas chlorine at Reading in 1917. Since that time, which still seems remarkably recent compared with the dramatic impact it has had on public health and the expectation of life, chlorine and hypochlorite have become almost universally adopted as standard disinfectants for potable and industrial water supplies, for swimming pools, as well as controlling growths of mussels, sponges, algae etc., in cooling systems. In some other countries particularly the United States, chlorine is also used widely to disinfect sewage effluents prior to discharge to water courses. In the United Kingdom however such a practice is frowned upon and tends to be regarded as more harmful than beneficial.

One may well ask why chlorine and hypochlorite have become so firmly established, particularly in view of the potential hazards associated with chlorine and its transport. The answer would appear to lie with its relatively low cost (10 p. per kg. in bulk, 25 p per kg. in cylinders - prices given in this draft were those operating in 1978 and will be updated on presentation,) ready availability, lack of competitive alternatives, a fairly simple chemistry and until recently, few significant objections.

contd.

Ozone is more popular in territories which impose restrictions on the transport of chlorine. It requires about four times the amount of power to produce 1 kg. excluding drying and solution of the final product, even though the equivalent weight is only 67% of that of chlorine. It cannot be stored as can chlorine or hypochlorite and in solution it has a half life which varies with pH and impurity level from a few seconds to perhaps an hour or so. On the other hand it is a far more powerful bactericide and leaves no residue in the final water. Like chlorine however, it does not generally oxidise organics to carbon dioxide but forms new (usually colourless) compounds. Chlorine dioxide is also used in special cases for disinfection having a particular advantage in not reacting with ammonia which may be present in polluted rivers etc. Since one part of ammonia in practice reacts with some eight to ten parts of chlorine, the additional cost of chlorine dioxide is soon repaid if the ammonia level exceeds a fraction of 1 mg/l. Secondly, chlorine dioxide destroys certain"T.C.P."tastes which arise when chlorine comes in contact with phenolic compounds. It is prepared in water treatment by the chlorination of sodium chlorite and hence is four to ten times the price of the equivalent weight of chlorine.

Hypochlorites may be regarded as an alternative form of chlorine, but costing about four times the price of bulk chlorine, when purchased on a similar scale. The price ratio falls somewhat at the scale of carboys and small cylinders.

Bromine is used in a few swimming pools but not in potable water treatment. However in seawater,chlorination will convert bromides to bromine, although the reaction is not instantaneous, thus bromine may in fact be the operating agent in seawater cooling systems.

Ultraviolet light is used for specialised purposes where chlorine is not acceptable, such as in some food and drink applications. It leaves no residual disinfecting action and will not protect a distribution system.

Organic disinfecting agents are not economic on any large scale application, neither are they approved for potable use.

contd.

WATERWORKS USE

In the majority of cases chlorine is applied as an aqueous solution as a final disinfectant after the suspended and dissolved impurities have been removed (i.e. after filtration). Bacteria may become occluded in suspended matter and disinfection is more effective in clean water. Furthermore, the chlorine demand is usually less with a clarified water. The disinfection rate is a function of the residual concentration after any reactions have gone to completion, not the applied dose. The difference is described as the chlorine demand.

In many cases Water Authorities also like to prechlorinate at a river intake to maintain a free chlorine residual throughout the settlement tanks and filters. This obviously extends the contact time with chlorine very considerably from perhaps 30 mins. to 2 - 4 hours. The residual chlorine also inhibits algal growth in clarifiers and filters reducing fouling and labour costs for cleaning. It also immobilises many motile species of algae and improves their removal, as well as maintaining filter sand in a cleaner condition.

In recent years concern has been generated in the United States over the formation of haloforms by the reaction of chlorine with organic traces in the water. Haloforms are regarded as potentially carcinogenic. In the U.K. however, this is being viewed as a matter of relative risk. Disinfected water is certainly of much greater importance and the alternatives to chlorine also produce byproducts of unknown characteristics. There may however be modifications to processes to reduce haloform levels. Overall, it is unlikely that this concern will affect the place of chlorine as a primary disinfection agent. The disinfection rate of chlorine is pH sensitive. In fact it appears to be the hypochlorous acid rather than the ionic hypochlorite that is most effective, presumably because this can more readily penetrate the ionised cell walls. Gas chlorine thus offers a marginal advantage not always exploited. The levels of chlorine dosed at the final stage are usually however too small to affect the pH significantly. Prechlorine on the other hand, may be dosed at 5 mg/l or more which is sufficient to be useful at times in adjusting the coagulation pH towards an optimum.

contd.

Before water is finally sent out into supply the pH is corrected to a value at which calcium carbonate is in equilibrium with the water (pHs) so that it has minimum corrosivity but is not supersaturated with respect to calcium carbonate. Ideally such pH correction should take place after the disinfection contact tank so that the latter is kept at a lower and more effective pH value.

The terms breakpoint chlorination and superchlorination are also common in the water industry. The former describes the state of reaction with ammonia, the latter a process of adding an excess to achieve faster and more complete disinfection, followed by partial neutralisation (with sulphur dioxide usually) to leave a low residual (0.2 - 0.5 mg/l) going into supply. When chlorine or hypochlorite are added to water containing ammonia, the monochloramine is first formed.

$$NH_3 + Cl_2 \rightleftharpoons NH_2Cl + HCl$$

This reaction is reversible and the chlorine is still available although described as combined. Additional chlorine forms dichloramine and nitrogen trichloride. However, dichloramine reacts with monochloramine to form nitrogen with the disappearance of the chlorine residual.

$$NH_2Cl + NHCl_2 \longrightarrow N_2 + 3\,HCl.$$

Thus as chlorine is added the detectable residual first rises as chloramine is formed then falls as the chloramine is oxidised to nitrogen and finally rises again as the free chlorine residual builds up.

Monochloramine is a relatively weak disinfection agent and normally a residual of free chlorine is demanded. On the other hand it is more persistent in a distribution system and often ammonia or ammonium salt is added after disinfection to stabilize the residual and maintain clean conditions to the consumer's tap.

There are few situations where it matters whether chlorine of hypochlorite are used, although sometimes the choice can affect a decision as to whether to include a pH correcting chemical or not.

CLOSED CIRCUITS (Swimming Pools and Cooling Systems)
Much of the foregoing is still applicable but the accumulation of dissolved solids and pH control are then more important. Chlorine gas will require a means of dosing an alkali or filtration through

contd.

a pH correcting media such as dolomitic limestone to maintain an acceptable pH. Hypochlorite contains 0.25 percent of free caustic and correction with acid is then needed. Electrolytic hypochlorite from undivided cells is neutral, but the pH can still drift because of other factors (excretion or urea and hydrolysis to ammonia and loss of carbon dioxide in splashing or in cooling towers, all of which tend to increase the pH value.)

GAS CHLORINE PRACTICE

Chlorine as transported in steel cylinders is under a pressure at ambient temperatures of 6 - 7 bar. On rare occasions for plants in remote areas pressure chlorinators are still supplied. These comprise a form of reducing valve supplying gas at a controlled rate to an absorption tower or ejector. The vast majority of chlorine installations however employ a vacuum chlorinator Fig.1 which relies upon an ejector in a motive water line to draw the chlorine from a regulator valve that only opens under vacuum. Thus in the event of power failure or pump breakdown, the chlorine flow ceases automatically. Other control valves are incorporated to prevent backflow of water and to regulate the vacuum within a defined band enabling simple variable area flow meters to be used to measure the gas flow. The ejector provides a simple but effective method of dissolving the chlorine gas into the carrier water. The resultant solution may then be conveyed for several hundred feet, in some cases,to the point of application.

Chlorinators range from free standing cabinet units containing all the control valves and rotameter, together with the ejector,to small cylinder head units.

In all but very small installations it is normal to have the chlorinators in a room separate from the storage room. The latter is normally provided with thermostatically controlled heating to assist evaporation and prevent condensation and corrosion. This is particularly important around the drum connections because steel is widely used for dry chlorine gas and liquid chlorine lines. The presence of moisture would lead to rapid corrosion. Storage rooms are provided with low level ventilators which can be activated by hand or perhaps automatically from a chlorine-in-air detector.

contd.

Small installations rely upon vertical cylinder racks similar to those used for the compressed gas cylinders. (Fig.2) Larger installations employ nominal 1 tonne cylinders supported on stillage rollers with collection manifolds (Fig.3). Since the drum and its contents weigh a total of approximately 1½ tonnes, proper handling equipment such as power operated hoists and a monorail traverse system passing out through double doors to the loading/unloading bay are normal accessories. It is usual to have at least two manifold systems with one or more drums in parallel with an automatic changeover valve to maintain continuity of supply when one set of cylinders becomes exhausted. This operates simply on the falling pressure in the exhausted bank.

Each size of cylinder has a stated maximum rate of evaporation. More cylinders may be coupled in parallel to exceed this rate. A 1 tonne cylinder, for example, will evaporate about 200 kg/day giving a five day exhaustion period. Rather than having large numbers of drums connected for high outputs it is sometimes preferred that liquid chlorine be extracted from the drums and evaporated in an external unit. The drums are provided with pairs of opposing dip pipes and can therefore deliver either gas or liquid from the crown or from the invert as they lie on their stillages.

The evaporator is usually a water jacketed vessel with appropriate controls and alarms and is installed in a chlorine store. The vacuum chlorinators draw from the evaporator whilst the natural vapour pressure in the chlorine drum forces the liquid through to the evaporator.

On an even larger scale, bulk 19 tonne deliveries from road tankers are employed. In many respects the philosophy follows the handling of other bulk liquids. A separate indoor storage area is used with one or more steel tanks supported on load cells. Extreme care is of course exercised in the fabrication of such drums and pipework. All welds are radiographed.

Tanks are not normally run empty like drums but are merely refilled by direct transfer from the road tanker. (Fig.4) Such transfers are effected by the simple expedient of blowing dried air in from a fixed installation in the chlorine store into the head space of

contd.

the mobile tanker to force the liquid chlorine over into the static tank.

Since such transfers are far less frequent than coupling and uncoupling of drums there is arguably far less chance of an accident. However, there is considerable divergence of opinion between nations over the desirability of bulk loads. It is certainly standard U.K. practice and likely to remain so.

Storage tanks are provided with bund walls and often a protein foam blanket facility to retard evaporation of a serious spillage is available. The rooms are designed to contain the absolute minimum of combustible material to avoid fire risks and a sizeable pressure relief tank is provided, separated from the storage tanks by bursting discs, so that over-pressurisation does not lead to release of chlorine to the atmosphere.

Lastly, a scrubber system employing caustic soda or lime is included to deal with venting operations and to dispose of chlorine in the unlikely event of a transfer to the pressure relief vessel.

A bulk chlorine installation complete with buildings would cost in the region of £100,000. It could only be constructed on a site well removed from housing (except employees tied properties), nevertheless an equivalent drum store would occupy even more building space. General water treatment plant cost data analysed by the Water Research Centre suggests that capital charges can add 1 - 5 pence per kg. to the cost of gas chlorine. It is also important to note that such facilities must be designed for peak demand and if under utilized the capital charges continue, thereby increasing the effective price of chlorine added to the water supply. Other factors that have to be taken into account include the essential character of water supplies and the need to store significant quantities to take care of emergency situations such as severe weather or industrial action. All these factors can add significantly to the overall price of a kg. of chlorine applied.

From the above it will be apparent that chlorine facilities are complex, tend to be expensive but are the subject of well established fail safe procedures.

contd.

SODIUM HYPOCHLORITE

By contrast with gas chlorine, facilities are relatively elementary and follow the general practice for other liquid chemicals. A lined bulk storage tank or individual carboys are used, depending upon the size. Storage areas must be bunded to control any leakage or spillage. Facilities are clearly very much cheaper than for gas chlorine. Separate rooms for storage and for chlorinators are not required, neither is the penalty for over-design so severe.

The standard material is 14/15% available chlorine, so that some seven times the weight of material must be moved about compared with chlorine, whereas the drum weighs only about 75% of its contents.

In terms of national resources, it would seem foolish to use power to generate caustic soda and chlorine separately and then recombine when only one component is required. Nevertheless, on small installations or with poor technical back up hypochlorite is a sensible and economic proposition.

Sodium hypochlorite may be dosed by conventional metering pumps and installations vary from purpose made fixed systems to proprietary packages. Gravity dosers or shunt feeders are also used widely on small, particularly rural, overseas plants (Fig.6)

The limitation of sodium hypochlorite arises from its thermal instability. At 65^{o}C a 10% available chlorine solution decays to 5% available chlorine in 3.5 days. Thus it is not suitable for tropical use. It also decomposes in the presence of ultraviolet light.

CALCIUM HYPOCHLORITE

This is available as a 70% available chlorine granular material which is reasonably stable in storage but at about three times the price in the U.K. on the basis of a similar quantity of available chlorine compared with sodium hypochlorite. Its use therefore is restricted to small specialist installations where powdered chemicals are essential or at overseas sites where sodium hypochlorite is not acceptable, either on stability grounds or because of restrictions on transport of corrosive liquids. It can however become economical where shipment costs

contd.

are extremely high, in fact a charge of 20 p. per kilo for transport would balance the price of calcium and sodium hypochlorite.

Calcium hypochlorite is a strong oxidising agent which decomposes to form chlorine monoxide when heated, thus it cannot be carried as general cargo, also traces of insoluble material are common and more specially any free lime will react with bicarbonate alkalinity in the make up water to precipitate chalk. A typical Southern English water for example would precipitate 400-500 mg/l of chalk. It is therefore normal practice to make up the solution in a tank with a floating arm draw off or on a fill and settle basis. Continuous dosing with a dry feeder into a solution tank would lead to the same scaling up problems that are encountered with lime.

The quantities normally dosed (1-3 mg/l of chlorine) to a small water supply are normally too small to have any repercussions in terms of precipitation or pH of the final water.

ELECTROLYTIC HYPOCHLORITE

It is not the purpose of this paper to go into great detail on cell design or cell performance, but rather to concentrate on the processes and economics. Electrolytic hypochlorite may be produced either in a membrane cell along the lines of modern industrial chlorine cells, producing chlorine gas and caustic and recombining them, or direct as sodium hypochlorite in an undivided cell. There may be specific cases such as power stations where chlorine, caustic soda and hydrogen can be used separately, but this is not a general situation. On a waterworks for example, alkali in excess of that equivalent to the chlorine will usually be required, so that a separate facility will be needed.

A membrane cell that produces separate products can do so at high efficiency with very little residual unused sodium chloride in the product. On the other hand, the ion exchange membranes used demand a high quality calcium free brine, perhaps low in iron and manganese and therefore requires separate purification. Furthermore the voltage across the membrane constitutes a

contd.

significant power penalty compared with the undivided cell. Both the membrane and the electrode have a finite life. The current trend in the water treatment industry is to go for utmost simplicity bearing in mind the long life of water treatment plant and the increasing difficulty in obtaining skilled labour prepared to work, often,in remote locations.

In the undivided cell, on the other hand, hypochlorite produced at the anode is reduced at the cathode at a rate proportional to concentration. Thus, the specific power requirement rises with concentration and also with temperature by as much as 1 kW.hr/kg for each 1 g./l of chlorine.

There are many marine applications however where chlorine may be generated insitu in a brine stream such as in antifouling treatments for cooling water systems or disinfection of brines for oil well injection etc. In such cases it is possible to generate at a low concentration at perhaps 250 mg/l to 1000 mg/l only at significantly higher efficiency. In such cases it would be pointless to generate it in higher concentrations and then dilute it back.

Cell designs for sea water electrolysis are governed by a requirement to minimise deposition of magnesium hydroxide. This had led to linear bipolar cell designs and recirculation systems, designed to keep up the liquid velocities and avoid stagnant zones. A selection of available designs is illustrated in Fig.7. Inter-electrode gaps are the outcome of a compromise between requirements for low voltage drop and freedom from blockage or plate distortion, as well as pressure loss. It is also necessary to design out any external current skip which can quickly ruin a simple electrode stack system. Other papers will no doubt go into detail about specific designs.

Electrode materials appear to have stabilised in recent years, partly it would seem because of a deadlock in the patent situation. Titanium is widely used as a cathode but depolarising anodic coatings comprise platinum and platinum alloys, rutheniumoxide based materials and lead dioxide on graphite.

contd.

The ruthenium compositions appear to give the lowest cell voltages followed closely by platinum alloys, platinum and a long way behind, lead dioxide. Since electrode replacement costs constitute a very significant part of the operating cost, particular attention must be focused on their life. Much has been written in the early years of undivided cells, about platinum loss at low temperatures. Once recognised, steps can be taken to combat such effects. There is probably little to worry about if good quality brine prepared from vacuum dried salt is used. However there may be problems with the sun dried salt available in other territories or with on-shore or estuarine sea water perhaps containing traces of sewage contamination or organic metabolic products from marine flora in tropical areas. It would be interesting to have comments of other speakers in this area. Lead dioxide is reputed to be more resistant to organic impurities and one manufacturer sells a deodorizing package for food and sewage works etc., involving a scrubbing tower irrigated with brine electrolysed with a lead dioxide cell which apparently stands up to this sort of fouling.

Although prices will vary widely with the location and size of installation, the following figures were derived from a high conversion evaluation in 1978 in the U.K.

High Conversion Hypochlorite from Brine (1978)

Percentage conversion 47%	
3.5 kg. salt at 2.5 p/kg.	8.7 p/kg. chlorine
5.5 kW/hr. electricity at 1 p.kW/hr.*	5.5 p/kg. chlorine
Electrode replacements (20,000 hrs. life)	2.1 p/kg. chlorine
	16.3 p/kg. chlorine

*Combination of off peak and normal tariff for an industrial user.

This compares with bulk chlorine which at that time was 10 p./kg. or drum chlorine at 13 p/kg. and sodium hypochlorite in bulk at 41 p/kg. The quantity of salt given by another manufacturer is 4.5 kg/kg. chlorine. This would only raise the price to 18.7 p/kg. chlorine.

For low conversion electrolysis of sea water the salt is available free and power costs fall to 4.4 kW/hr./kg. The price then becomes 7.5 p/kg. of chlorine at the same electrode life expectancy.

contd.

It is not surprising therefore that electrolysis of sea water has become firmly established at seaboard power stations. It is however, rather more surprising that high conversion undivided cells have not achieved a wider impact. This is possibly because of the very conservative nature of the water industry at home and overseas and perhaps the unproven reliability of electrodes in primitive surroundings. At 33% conversion 9 mg/l chloride would be added with a typical water disinfection dose of 3 mg/l of chlorine. Most water undertakings endeavour to keep chlorides below the alkalinity figure, to avoid dezincification problems with duplex brass fittings. In very many areas an additional 9 - 10 mg/l of chloride would be of no consequence in a water of T.D.S. of 300 - 400 mg/l.

The extra power demand might also be considered an objection. The majority of waterworks deliver water into supply at high pressure. If, as is often the case, this involves high lift pumps operating at 70% efficiency delivering at 50 m. head, the power demand of 3mg/l. electrolytic hypochlorite would only be 8% of the high lift demand, which would be a negligible extra if included at the outset. Similar calculations can be done on cooling water towers for example.

The ancillary equipment layout for high conversion electrolytic hypochlorite shown in Fig. 8 includes merely a brine saturator and dilution system, recirculation tank, and probably a hypochlorite stock tank according to the method of operation and a hydrogen gas disposal system. It is possible that, on any sizeable installation, a separate room would be required, with flame proof electrical equipment, or else an open area with rain protection. No heating or special ventilation as for a chlorine store would be needed, neither is there a requirement for an equivalent of a chlorinator room. Indeed the antifreeze nature of brine would probably encourage outdoor installations in the same way as some waterworks are now following with large pumps.

Chemical cleaning may occasionally be needed particularly if magnesium brines are used (such as dried sea salt). On a large installation a fully piped up circuit rather than a bucket system may be required.

contd.

The calorific value of the waste hydrogen is not negligible. A 10 million gallon a day works (45 Ml/d) with a 3 mg/l chlorine dose would yield 10 kW. worth of hydrogen which could be burnt in a purpose made boiler, or used for direct combustion space heating to offset some of the running costs.

In contrast to gas chlorine the capital investment in the facility is low with electrolytic hypochlorite. The electrode life is a function of hours run and electrode costs swamp other hardware costs. Hence an installation with a widely fluctuating chlorine demand could prove more economical with electrolytic hypochlorite. A steady demand favours gas chlorine where the standing interest charges are heavier.

There is no reason why in principle, apart from tank size, an electrolytic system should not be made dual purpose, handling sodium hypochlorite or electrolytic material. Typical electrolytic material however is only about 5.7% of the strength of that of commercial liquid hypochlorite so that tank sizes would be hardly compatible.

To the writer's knowledge, there are no examples of high conversion electrolytic plants on a waterworks. Low conversion systems are however being used to disinfect and remineralise distillates both on shore and for marine use. Overseas, the arguments in favour of electrolytic hypochlorite are perhaps stronger in that salt and power are more likely to be available from local sources, whereas gas chlorine or hypochlorite may have to be imported over considerable distances. It is known for example that chlorine drums tend to be stored as deck cargo and are the first to go overboard if conditions get rough leaving shortages both of drums and of chlorine. Even in the U.K. transport over 200 miles can add 1-2p/kg to the price of chemicals.

In the context of swimming pools and cooling water systems, the main concern with undivided cells would be the additional accumulation of sodium chloride. Sea water pools which could be chlorinated direct very economically are rare.

contd.

Taking an average rate of chlorination of say 3 mg/l averaged over a day (peak rates may be very much higher), corresponding to 10 mg/l of chloride or 16 mg/l of sodium chloride from an electrolytic device, a wastage of 3% per day would keep the additional dissolved solids level to 530 mg/l. whereas with hypochlorite the wastage to maintain the same additional solids level would be only 1%.

Consider a flow of 3000 m^3 day.

Hypochlorite at 41 p/kg and 3 mg/l	=	£3.69	per day.
Electrolytic hypochlorite at 18 p/kg.	=	1.62	per day
Saving	=	2.07	" "
Water at 2% extra wastage i.e. 60 m^3 at 12 p/m^3	=	7.20	" "
i.e. net penalty	=	£5.13	" "

To break even the extra wastage would have to be only 0.5%.

If on the other hand a salinity of 1600 mg/l were acceptable the cost saving could be exploited. This however is a grey area where there has been little incentive hitherto to explore. Chlorides at levels of around 1000 mg/l would not be popular however because of potential corrosion problems.

Small membrane cells would eliminate the excess accumulation and salinity but electrode life and their replacement costs as well as power costs and salt purification will have to be taken into consideration.

FUTURE OUTLOOK

Gas chlorine and sodium hypochlorite are very well established in the water industry and it may well take time for any alternatives to gain a foothold. In the absence of any external force such as safety legislation, it is not likely that gas chlorine will be replaced on water treatment works of any reasonable size.

On small installations where smaller cylinders are used or sodium hypochlorite preferred, there appear to be good reasons for considering electrolytic hypochlorite. If safety considerations predominate, for example with larger installations in built up areas, electrolytic hypochlorite could be well worth consideration.

On very small commercial installations, rather than domestic ones, the simplicity of plain hypochlorite is likely to be over-riding.

contd.

On works of any reasonable size in other territories, away from industrial centres where chlorine is produced but where salt and power are readily available, electrolytic hypochlorite would appear very attractive, particularly with the undivided cell. The main problems at the present time would appear to be the general lack of references and experience. Unfortunately, in most technologies one relies heavily on references in the home market. In this case, installations of any representative size are unlikely to be built because of the more favourable economics of gas chlorine. So we have a typical chicken and egg situation to be overcome. Nevertheless this is likely to be resolved in the not too distant future, particularly as experience and confidence builds up in other applications of electrolytic hypochlorite.

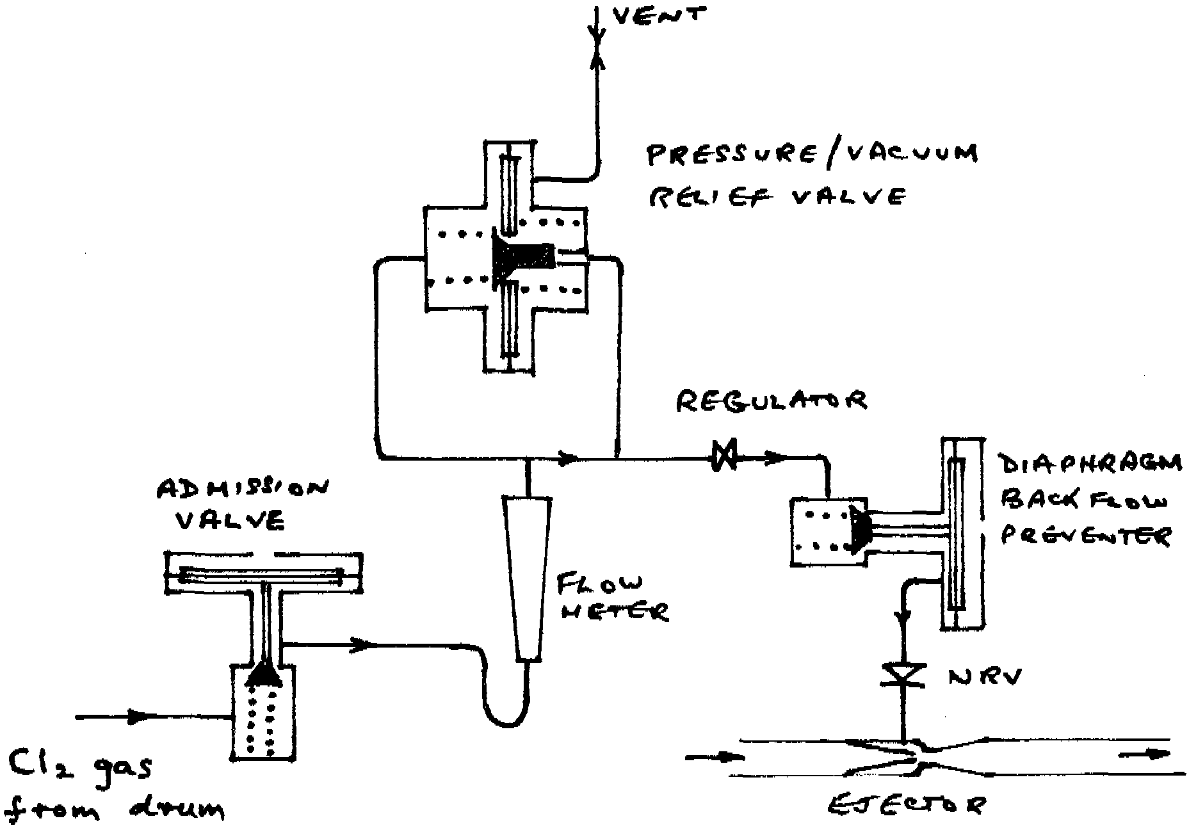


Figure 1 Features of a Vacuum Chlorinator

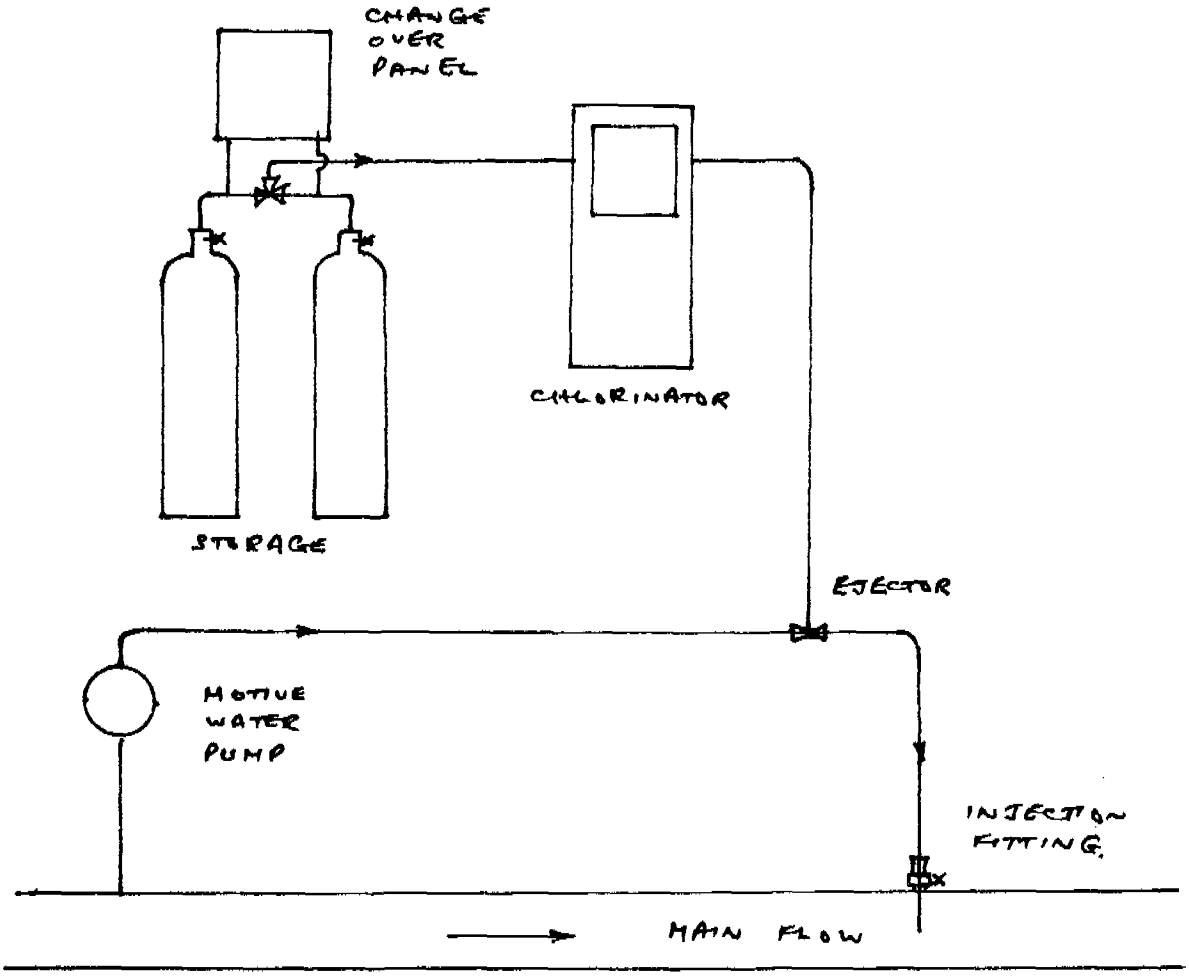


Figure 2 General Arrangement of Gas Chlorination System

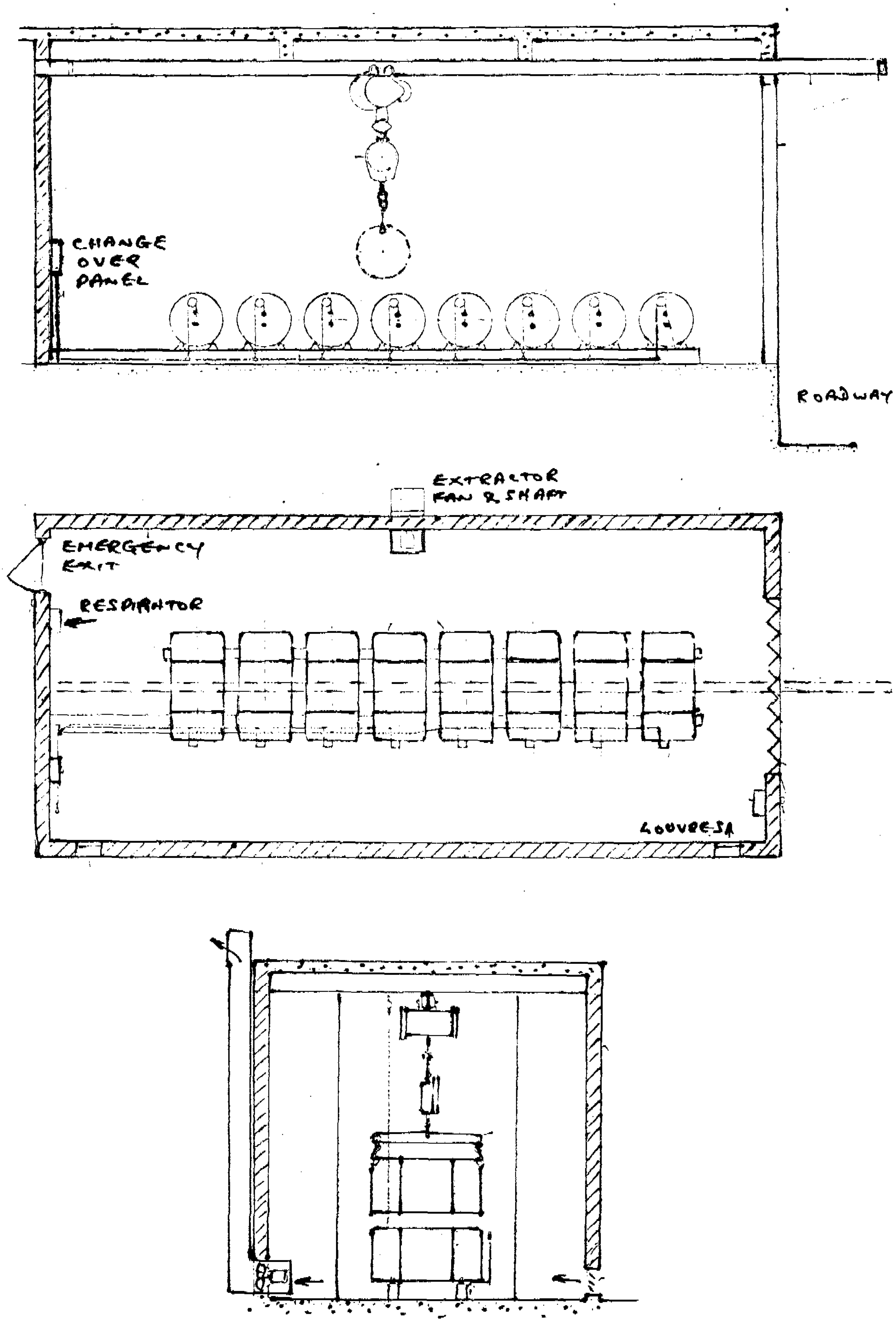


Figure 3 Typical Drum Store Arrangement

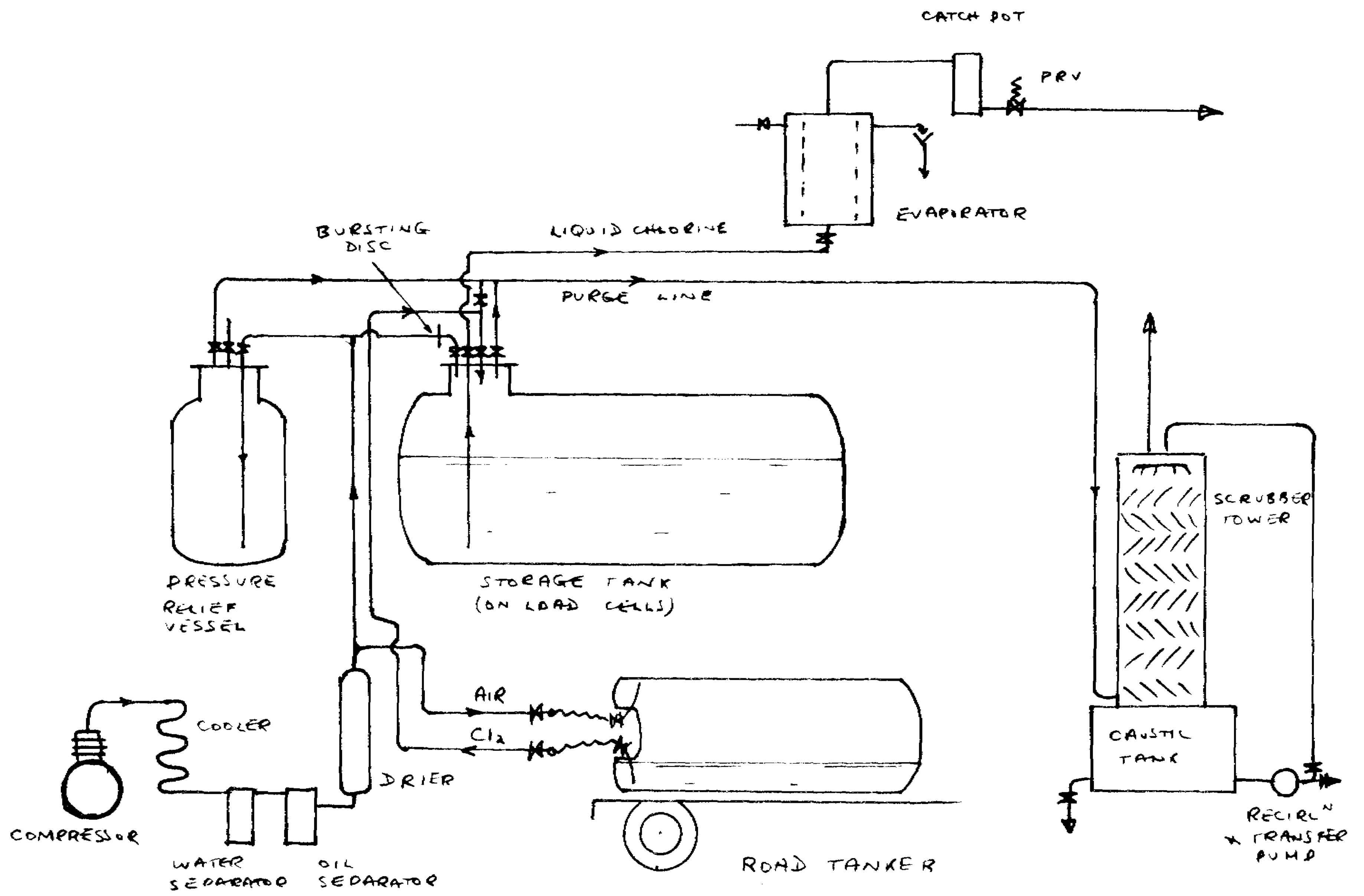


Figure 4 Schematic of bulk chlorine storage and transfer systems

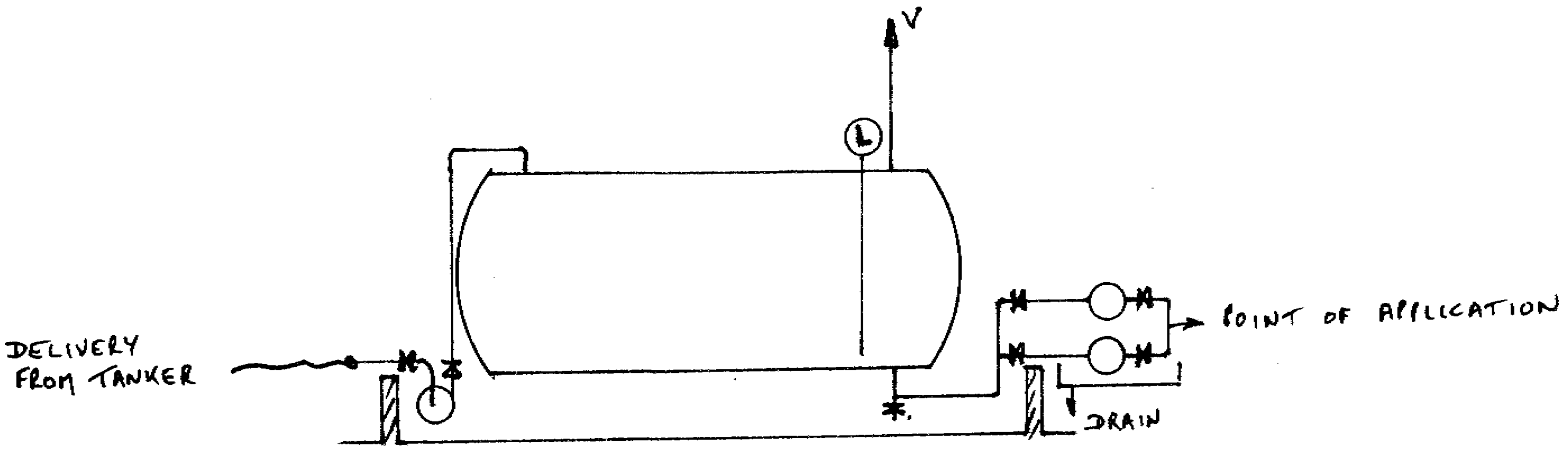


Figure 5 Storage and dosing of sodium hypochlorite

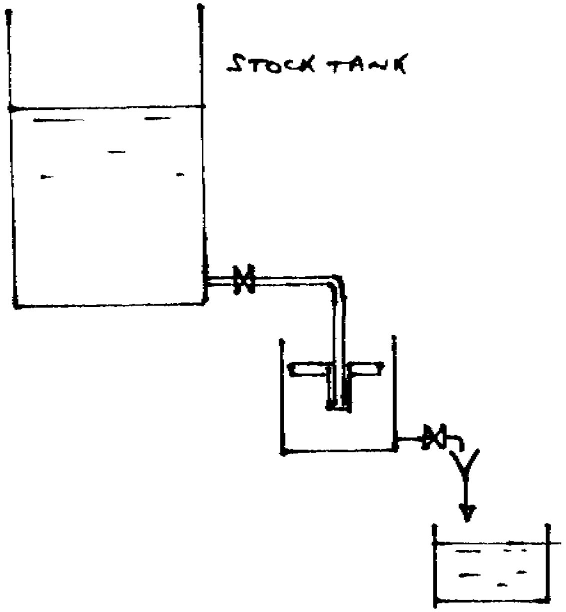


Figure 6a Gravity Doser

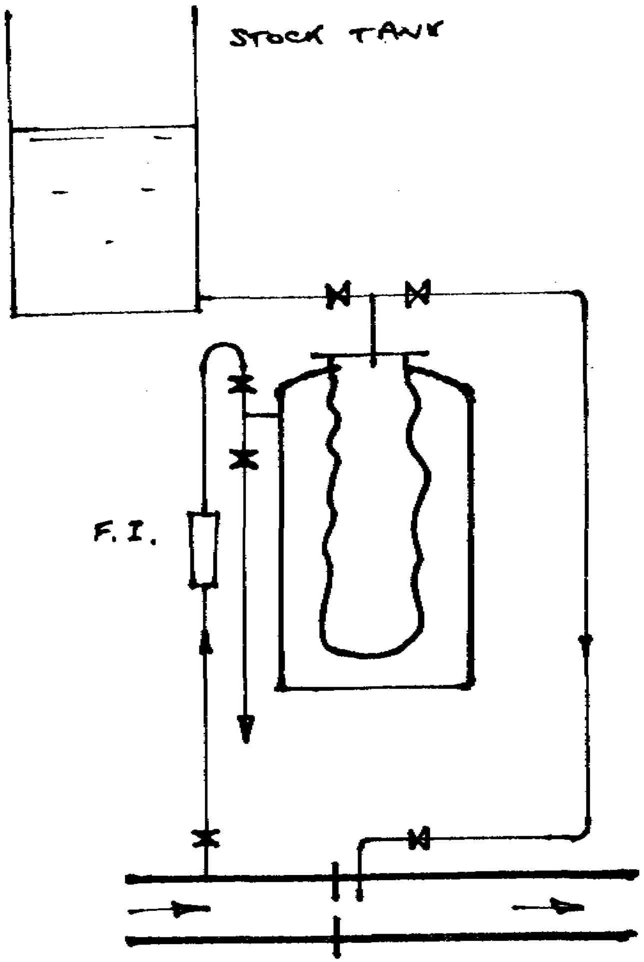


Figure 6b Shunt Feeder

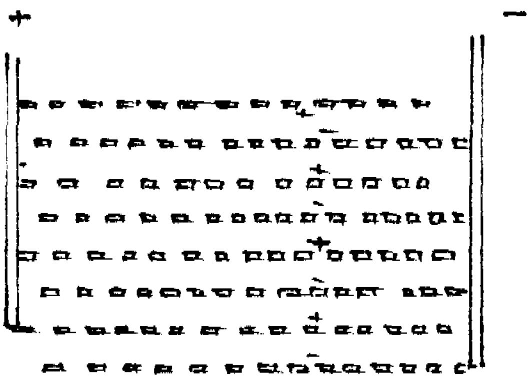


Figure 7a Mono polar mesh electrode

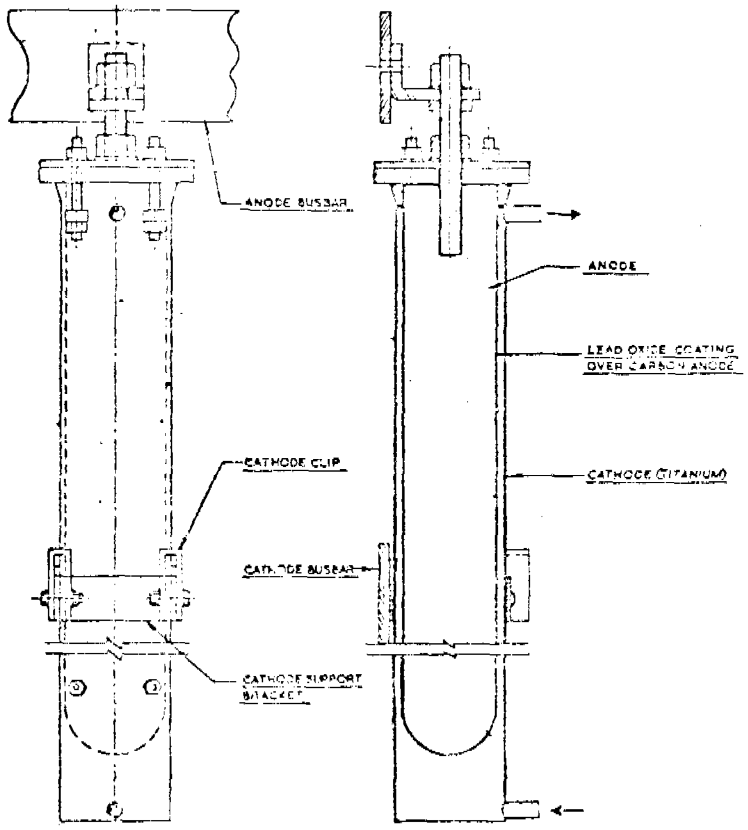


Figure 7b Monopolar tubular (graphite (PbO_2) titanium)

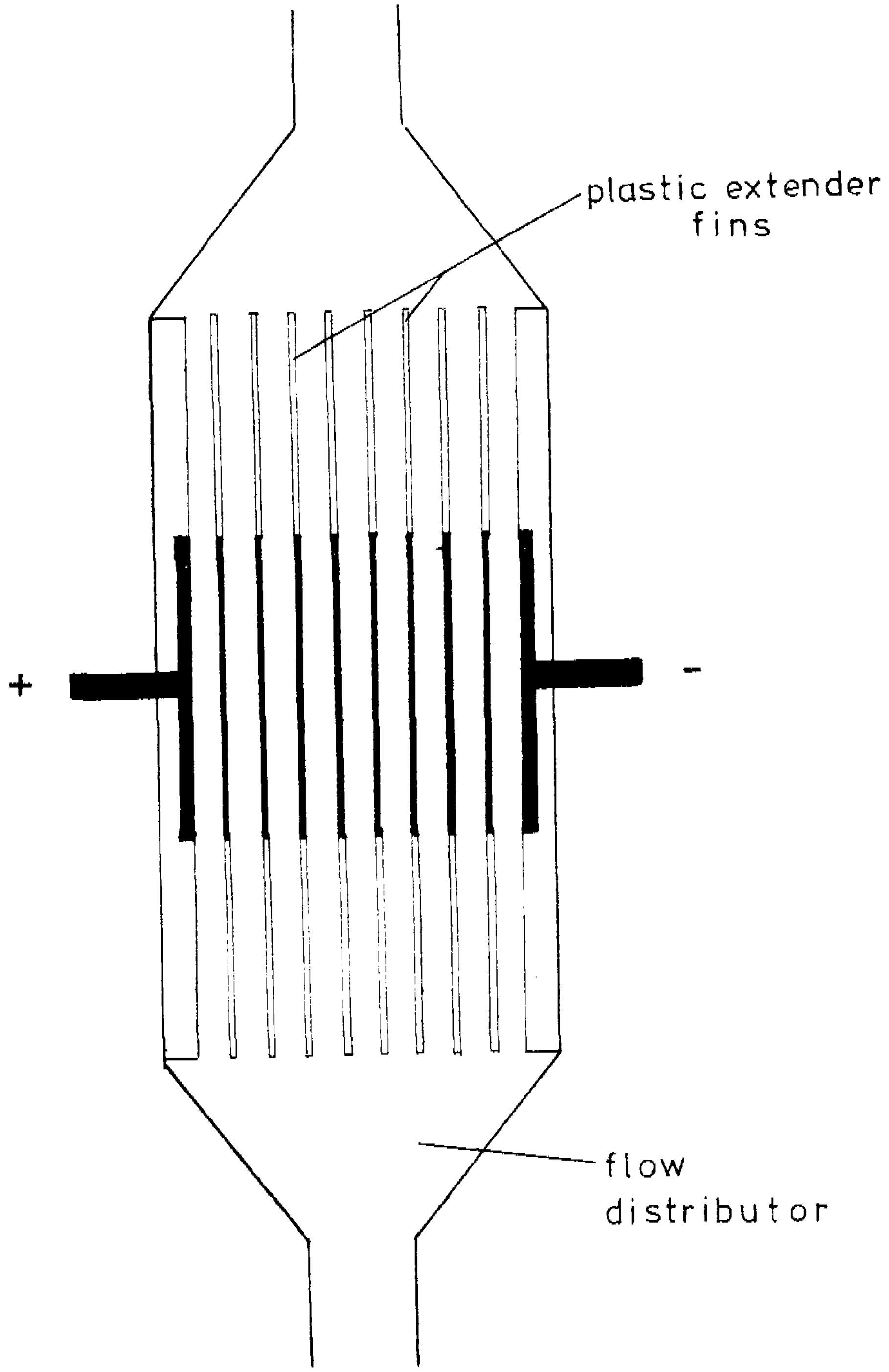


Figure 7c Bipolar parallel flow

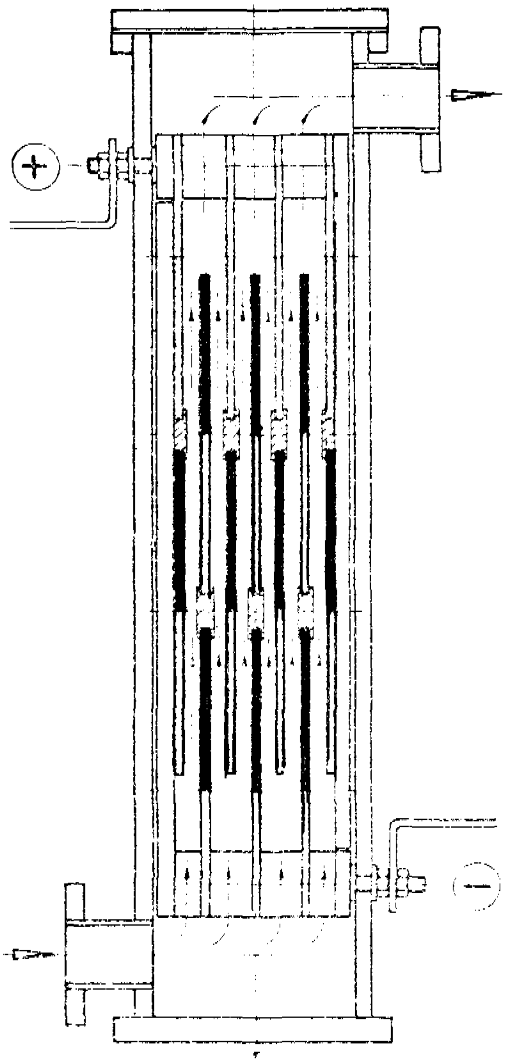


Figure 7d Bipolar plate - series flow

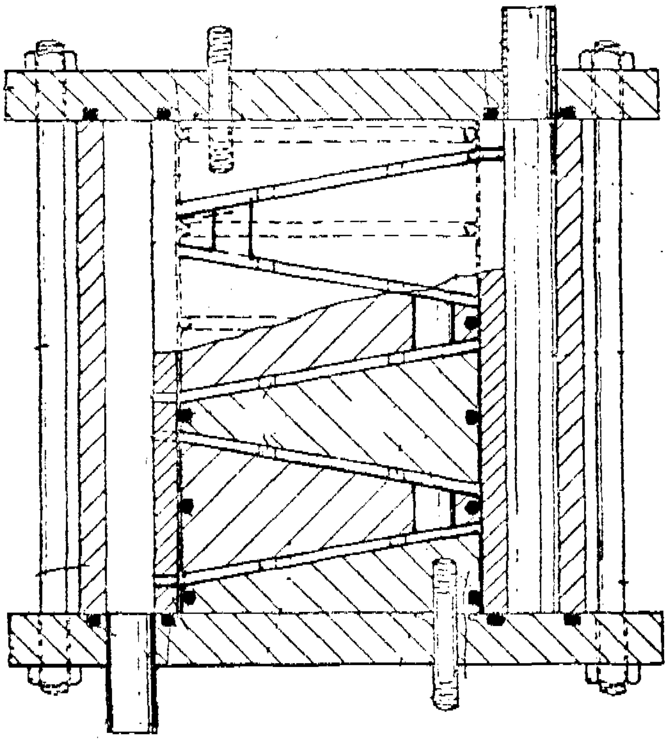


Figure 7e Bipolar wedge - series flow

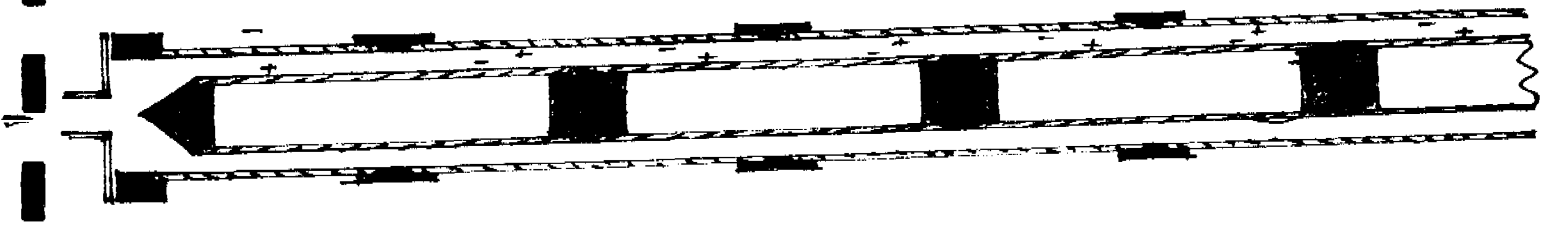


Figure 7f Bipolar tubular series flow

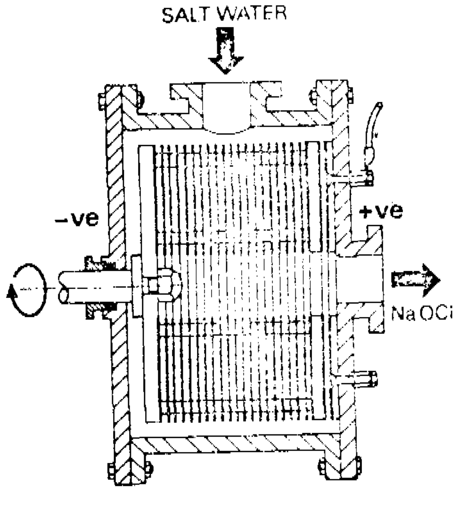


Figure 7g Bipolar parallel flow-rotary

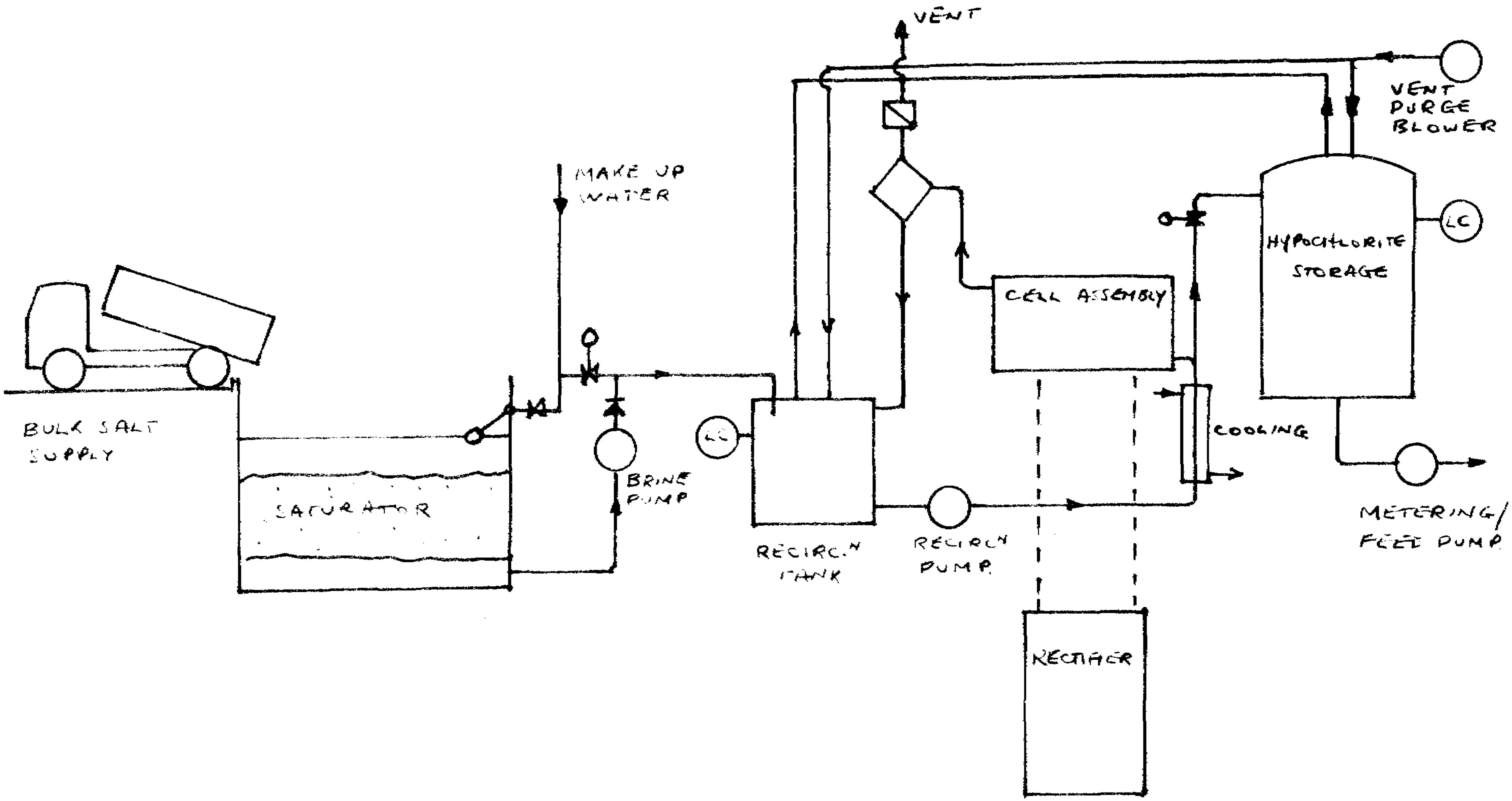


Figure 8 Flow diagram for electrolytic hypochorite plant

CHLORINE/HYPOCHLORITE REQUIREMENTS WITHIN THE CENTRAL ELECTRICITY GENERATING BOARD

by S.I. Ainsworth

SUMMARY

The CEGB's requirement for the use of chlorine in the cooling water systems of its generating stations and its importance to the national economy are described.

The control limits placed on the injection of chlorine into the cooling water systems are indicated. These are necessary to keep heat exchange surfaces clean, to avoid restriction of cooling water flow and to prevent erosion of heat exchanger tubes (with its massive impact on plant availability). The consequences of inadequate control are described.

An indication is provided of the quantity of chlorine required presently and the importance of minimising its ecological impact is stressed.

The Board's long term policy of phasing out the use of liquid chlorine in bulk is outlined and the arrangements made for its implementation described. The stage reached in the necessary investigations of alternatives and the probable continued use of chlorine in the foreseeable future (whilst eliminating its use in bulk) are discussed. The operational problems involved with the various methods of electrochlorination and the use of bulk sodium hypochlorite solution are outlined.

1. THE CEGB NEED FOR CHLORINE

Almost from the start of electricity generation, power stations requiring a significant cooling facility provided by water obtained from a source able to support marine life forms have relied almost exclusively on chlorine or sodium hypochlorite to keep the water swept surfaces of those cooling systems clear of flora and fauna.

It is stressed that the problem is specifically that of surface contamination, so as far as it is practicable, the aim has been to use the biocidal properties of chlorine to prevent animal life and vegetable life from settling in the cooling systems rather than killing it.

A typical installation of a station of 1300 MW output capacity drawing water from the sea and returning it some distance away from the inlet will require as much as $2\frac{1}{2}$ million cubic metres of water per day and this will traverse the installation shown diagramatically in Figure 1. The fact that some 1500 metres of large culvert are involved gives some measure of the magnitude of the problem. In addition a steam condenser for a 660 MW unit has a tube surface area of some 30,000 square metres.

Screening plant is installed at the circulating water inlets and this is designed to remove the maximum amount of solid material from the water, which is compatible with an acceptable pressure drop across the screens. Otherwise our interest is concentrated on three factors, the first two of which are related to the operational heat transfer performance of the main steam condensers and to the continuing availability of the particular generating unit as a whole, whilst the third is not only related to that availability but also to cost of repairing resulting damage to the plant.

Dealing firstly with the two aspects affecting heat transfer: the performance of the main steam condensers is dependent on the cleanliness of their cooling surfaces and the quantity and temperature of the cooling water which passes through them. Obviously the establishment of a vegetable population within the condenser tubes will seriously reduce condenser efficiency, but it is unlikely to have a major effect on the quantity of cooling water passing through. Reduction of cooling water quantity arises mainly from restrictions in the culverts of the system, these stemming from the deposition and growth of animal life and vegetable matter after the screening plant and from deposits of silt.

The initial effect of poor heat transfer in the condenser, whether this arises from dirty surfaces or restrictions in the flow of cooling water, is to reduce the thermodynamic efficiency of the turbo generator and so to cause a significant rise in the cost of the electricity produced by it. If this condition deteriorates progressively, the output that can be taken safely from the turbo generator also decreases, until a point is reached when the machine must be taken off load to avoid damage and to rectify the situation. This is usually carried out by means of an extensive manual operation. The operation will be extensive in itself, but, since the electricity consumers demand continues unaltered, the partial or complete loss of output from the particular machine must be made good by increasing the output of far less efficient turbo generators, which up to then were not needed. Here it is worth stressing that, with the range of ages and thermal efficiencies of the plant the Board must retain in service, it is inevitable that a high efficiency turbo generator can only be replaced by a unit which is very much further down the Board's order of merit, based on thermal efficiency and operating economy.

The second form of impact on the availability of a particular generating unit, in this context, arises from the erosion/corrosion attack which can occur in a condenser tube which is partially blocked at some point. Mussel larvae or spat may pass through the screens and if they become established they grow and develop their shells. Eventually the shells may become dislodged and if they have reached a sufficient size they can lodge inside the condenser tubes causing a highly localised loss of tube metal due to an erosion/corrosion mechanism. Perforation of the tube metal can occur resulting in contamination of the feed water circuits by the cooling water. If the condition is allowed to develop it could ultimately lead to serious contamination of the boiler water producing corrosive conditions and ultimately boiler tube failures. Before this stage is reached the plant must be shut down and the faulty condenser tubes blanked off (and subsequently replaced at an appropriate outage period). However, blanking off a tube, with the reduction in the heat transfer surface it entails, reduces condenser performance itself and so can only be an acceptable palliative whilst the number of blanked off tubes is a small proportion of the total number installed. After that the extensive and costly exercise of retubing these condeners has to be carried out.

It is not within the scope of this paper to consider deeply the thermodynamic effect of poor heat transfer. Suffice to say that the cost of electricity to the consumer would be increased very significantly, if condensers could not be kept in a clean condition by an on load treatment. A mere 1 millibar deterioration in the condenser vacuum of all of the Board's turbo generators (equivalent to a condenser steam temperature increase of about 0.5°C) is estimated to be sufficient to increase the Board's total fuel bill by £1M per year.

The cost of loss of availability of generating plant is equally impressive. For instance, loss of a single 660 MW turbo generator at a seaside nuclear power station can result in an increase in cost for the electricity required by the consumer of as much as £250,000 per day.

Chlorination of the cooling water systems is by far the cheapest, most effective and most generally acceptable method of avoiding the significant problems and resultant costs described.

2. THE CONTROL OF THE INJECTION OF CHLORINE

In establishing control regimes for the injection of chlorine to CEGB cooling systems, the following factors need to be taken into account.

(a) Its effectiveness in keeping the condensers and culverts clear of significant deposits of marine flora and fauna.

(b) Economy in the use of the chlorine itself.

(c) The minimisation of undesirable side effects, the main requirement being to avoid any unacceptable ecological impact within the waterways to which the cooling water is returned.

(d) The avoidance of plant damage due to excessive use of chlorine is also important. This is covered mainly by diluting the pure chlorine with water before it is injected into the main cooling water system.

The form taken by the control method is primarily dependent on the type of station involved. In an inland station, using cooling towers in a closed circulating water system, the problem of biological growths is restricted to the condensers themselves, in that, without treatment, the tubes are likely to become coated with algae. Such organisms appreciate the highly oxygenated nature of the water resulting from the efficient aeration provided in the cooling towers. It is necessary to note that the chlorine may kill but will not remove long established algae coatings, although it may dislodge such coatings which have existed only for short periods of time. Hence, by starting with clean condenser tubes, a satisfactory cleanliness of the condenser can be maintained by an intermittent dosing regime. The injection point chosen will be as close as possible to the condenser inlets, subject to efficient mixing of the chlorine solution and the main water flow.

A typical dosing regime for a 2000 MW (4 x 500 MW) station supplied with river water would be 4 - 6 hours of chlorine injection spread intermittently throughout the day in summer and 2 hours in winter. However this can be optimised by experience for the particular station, as long as care is taken to monitor the thermodynamic performance of the condenser continually during the trial period.

In the case of cooling water systems supplied from estuaries or the sea, the problem of keeping the condensers clear of algae is the same as for the river cooled water systems, but with the additional problem of fouling the culverts. The deterioration of conditions in the culverts may only be detectable when it has reached major proportions, for which an equally major restorative exercise will be required. It is simply not practicable to monitor the deterioration in the culverts progressively within an acceptable band. In addition the main contributor to this deterioration in the condition of the culverts is the mussel, which is capable of remaining closed for long periods thus avoiding exposure to the chlorinated cooling water, with the result that an intermittent dosing regime is unlikely to be effective.

As a result (after some early unfortunate experiences) continuous chlorination is arranged for the sea water cooled systems, the chlorine solution being injected at the inlet to the culverts and the chlorine residual concentration so controlled that a chlorine residual of 0.2 parts per million is maintained at the condenser inlets. When maintained continuously this level has been found to be effective in maintaining the condensers themselves clear of algae. It should also be noted that the figure of 0.2 parts per million also represents a practical level in terms of analysis for the chlorine residual when measured under the conditions met in practice. In view of the chlorine demand of the condensers and the discharge culvert, the chlorine residual in the water returned to the source is considerably below the figure of 0.2 parts per million used for control purposes.

In broad terms winter conditions are not conducive to the growth of marine flora and fauna in the cooling system, so chlorination is confined to the period 1st April - 15th November or whenever the sea water temperature is above 10°C. Any variation from this defined period can only be introduced as a result of a biological monitoring programme. Cognisance must however be taken of the proximity of favourable breeding grounds for mussels, as appears to be the case in Morecambe Bay from which the Heysham nuclear power station, now under construction, takes its cooling water supplies.

With regard to the consequences of loss of control of chlorine injection, which by the nature of the process invariably involves an inadequacy in the use of the gas, mention has already been made of the loss of thermal efficiency and availability of the turbo generators concerned and the resultant increased cost of the electricity to the consumer. Here the intention is to indicate the on site problems which result when manual intervention is necessary to recover the situation.

The manual steps necessary to clean the contaminated condenser tube may include rodding, brushing or internal squeegeeing with rubber bullets propelled by compressed air. With some 17,000 tubes of about 23 metres in length in one of our largest condensers, the operation can be seen to be a major and expensive one and is usually carried out in cramped or unpleasant conditions for the staff concerned. Obviously the water we use for main cooling purposes is always very dirty.

However the most difficulty arises when the cooling water culverts are allowed to become heavily infested with mussels. Clearance of these may involve a lengthy shut down of a whole station whilst the major operation of draining the circulating water culverts is carried out and ton after ton of mussels are removed under conditions which are far from easy or attractive.

3. THE QUANTITY AND DISTRIBUTION OF LIQUID CHLORINE REQUIRED ANNUALLY BY THE CEGB

To meet the problems outlined in the foregoing sections of the paper, the CEGB's consumption of liquid chlorine is now approximately 6,400 tonnes per annum, which will rise as more generating stations are required, with a disproportionately greater rise as the proportion of seaside stations inevitably increases, unless equivalent chlorine compounds are used. Of that quantity approximately 16% is delivered in drums and the remaining 84% is delivered in road tankers. All of the CEGB stations receiving chlorine are shown in Figure 2, with drum delivery points marked with circles and bulk tanker delivery points marked with squares. Without change in our methods, as generating stations throughout the country become fewer and bigger, there would be a progressive move towards more bulk tanker deliveries.

This total pattern of delivery, storage and consumption has to be considered against an increasing sensitivity expressed by society towards large concentrations of dangerous goods in general and towards their dispersion in the air, the ground and waterways generally.

With regard to any significant ecological impact, which may arise from the injection of chlorine into the world's waterways, obviously the users, both from a social and an economic viewpoint, will take action to reduce this to the minimum that is practicable.

On the basis of the foregoing, the Board decided, in the main, to limit its considerations at this stage to the bulk concentrations of liquid chlorine which resulted from its cooling water treatment requirements, whether these bulk concentrations occur in the delivery of the material to the generating stations or in its storage on the station site. It did this against the background of a long history of safe transport, storage and consumption of its liquid chlorine requirements at the many points shown, in which no significant injury has been incurred by any person, whether a member of the public or an employee of the Board. Nonetheless, in common with all human activity, it has to be admitted that certain risks of major releases of chlorine can be postulated and that, no matter how low their probability, it is impossible to guarantee that the postulated events will not come about. Accordingly the Board decided to formulate a long term policy on the subject.

4. THE FORMULATION OF THE CEGB'S LONG TERM POLICY ON BULK LIQUID CHLORINE

Against the background of the use of the most economic commodity for its purpose, admittedly a dangerous material but involving a very low probability of injury to persons, there was little incentive for the Board to change its practices with regard to the transport and storage of liquid chlorine in bulk, until the substance was embraced by the increased sensitivity of world society towards dangerous substances in general.

As must any responsible body, the Board takes cognisance of such changes in the social climate, firstly, to review its existing safety practices to control the postulated risks in the light of any fresh knowledge or experience that may have given rise to the increased sensitivity. Secondly, to reconsider whether the economic balance justifies the continued acceptance of the probable risk involved. Thirdly to review alternatives to the use of the dangerous commodity as to their effectiveness, social and ecological acceptability and cost. The latter has, in fact, been a continuing process throughout the years, but the Board has simply not been able to find an alternative more attractive than chlorine.

With regard to its existing practices for the safe storage of liquid chlorine in bulk, the Board had from the start of such operations adopted a very high standard of design of installation and local practice, in full consultation with the suppliers. In addition it had, in further consultation with the suppliers and with the Factories Inspectorate and an independent plant inspecting authority, established agreed procedures whereby the required standards of construction and operation were maintained and monitored throughout the service lives of all of its bulk storage installations.

Turning to the economic considerations, it quickly became apparent that the use of liquid chlorine in bulk was unquestionably still the cheapest way of satisfying the Board's requirements for clean condensers and cooling water systems. However, whilst there may be minor difficulties introduced in the changeover operations, there are means available whereby the same quantity of chlorine (as chlorine or as sodium hypochlorite) could be provided for the sites, without the need for bulk storage and at a cost increase which would have an insignificant impact on the cost per kWh of electricity produced for the consumer. As a result, in the total circumstances, the Board established as policy the requirement to phase out the use of liquid chlorine in bulk over a period of 10 years, the first part of which time would be spent in determining and developing the most acceptable and economic altneratives, and the second in changing over the installations at the individual stations to the approved arrangement which best suited their particular designs and locations. A Working Group was constituted to co-ordinate and further these activities.

As is indicated, the policy of phasing out the storage of liquid chlorine in bulk will involve the Board in increased expenditure. This may be compared with the expenditure incurred by the Board of amenity considerations including such activities as the landscaping on areas around our installations, the concealment of hydro electric stations inside mountains, the use of underground cables in areas of natural beauty (where overhead lines would be considerably cheaper) and the efforts applied to making more attractive such structures as cannot be concealed, in so far as the basic technology requirements will allow.

5. THE INVESTIGATIONS AND THE STAGE REACHED TO DATE

The Working Group constituted to deal with the subject agreed to consider the alternatives to the use of bulk liquid chlorine under the following headings.

5.1 Methods continuing to use chlorine, subject to there never being a sufficient concentration of the material on a CEGB site, whereby a major accident was even possible. This sub-divided into:-

5.1.1 Some form of electrochlorination of the cooling water in situ.

5.1.2 The injection into the cooling water system of sodium hypochlorite solution delivered to the site.

5.2 Methods involving injection of chemicals other than chlorine or sodium hypochlorite solution.

5.3 Mechanical methods of on load cleaning of condensers. Here it was appreciated that these were unlikely to eliminate chemical treatments altogether at any site, since they could not economically cover auxiliary cooling circuits or the main cooling water culverts themselves. They do have the additional advantage of dealing with mineral deposits in the condensers.

5.4 Thermal treatments, whereby deposits on the condensers could be heat dried when they would flake off the tubes, ready for flushing away, or elevated temperatures would be produced in the cooling water which would kill the flora and fauna present in the culverts so that they would be flushed away. Such methods necessitate a loss of availability of the turbo generators during the treatment, which makes them unattractive for application to the Board's highest merit base load turbo generators. It means that the methods are less likely to be used during the early life of new stations, despite the fact that it is desirable to expend the capital necessary for their installation at the same time as the station is first constructed.

It was not possible to consider seriously methods of treatment which rely on the cladding of all of the internal surfaces of the cooling water culverts. These include such matters as the use of toxic paints, the fixing of toxic panels and the provision of super smooth structures at all points, all of which are intended to prevent adhesion of life forms to the surfaces.

Apart from the fact that such arrangements do not cover the main area of concern, the steam condensers, they are negated by a combination of objections. First and foremost the scale of the construction projects involved, for which a very high quality control would be necessary throughout the whole of the cooling water systems. Secondly the problem of maintaining such installations throughout the lives of the stations without massive outages for draining, inspection and repair alone. Thirdly their cost and, finally, the consequences of their failure in service which may not be obvious for a long time.

However, the most conclusive discounting has applied to the methods involving the use of chemicals other than chlorine or sodium hypochlorite. All other chemicals known or understood to be effective in keeping cooling water systems clear of marine flora and fauna have been adjudged to be unacceptable, for reasons of their safety in handling and/or their ecological impacts and/or their cost.

Mechanical methods of on load cleaning of condensers include the circulation of sponge cleaning balls through the tubes (driven by the water flow) and their return to the tube inlets by means of auxiliary screens, pumps and pipework. When the sponge balls wear to the point of becoming ineffective they escape from the system through the screens designed to trap the sound balls. Make up with fresh sponge balls with the turbo generator remaining on load is relatively easy. In that sense such mechanical methods may be better than those relying on brushes which traverse backwards and forwards through the same tubes, as the direction of flow of the cooling water through the condenser is reversed at intervals by the operator. Rejection and replacement of these brushes would appear to require operator intervention in a major off load operation. It is likely that condenser cleanliness could need to deteriorate significantly, before the condition of the worn brushes was appreciated and action arranged.

All in all, the Working Group decided that mechanical and thermal methods of condenser cleaning were such that they could only apply to existing units where very favourable geometries and designs were present. As such the group's responsibility for dealing with these methods was reduced to ensuring that all of the local managers of the generating stations and the Design Departments were aware of them; when they could assess for themselves their application to their individual installations. Nonetheless, where they are suitable and economic, they have the advantage of reducing the injection of chlorine into the cooling water, which, in whatever chemical form it may take, must appear eventually in the local waterways.

Accordingly the Working Group's further activities were confined to consideration of the injection of sodium hypochlorite solution and the use of the various forms of electrochlorination. These are considered separately in the following two sections.

6. THE USE OF SODIUM HYPOCHLORITE SOLUTION FOR THE CLEANING OF COOLING WATER SYSTEMS

In terms of simplicity, reliability, lack of imponderables involved in the change over and long term acceptability to the local personnel, there is little doubt that the use of sodium hypochlorite solution delivered to site, to take the place of liquid chlorine in bulk, is a very attractive proposition.

Possibly the only objection, as far as the CEGB is concerned, is that the 'bulk' to be handled is some 7 times greater than the liquid chlorine it replaces. Of course, the danger involved is very small indeed, even if a major spillage of the solution took place. However the extra traffic in the vicinity of the generating stations would need consideration to avoid annoying our neighbours. This may only be significant if the stations approach road normally carries little traffic and yet passes close to houses.

Since the first effect of injecting shlorine into water is to form sodium hypochlorite, injection of the solution in the first place does not change the chemistry involved. This is an important point, since it does not involve any new ecological repercussion, or require any new technology for control purposes. Measurement of chlorine residual remains the basic requirement. However, it is this last feature that introduced some of the unexpected cost necessary in a change over to the solution, which disappointed those who were thinking in broad terms of 'pouring in' the solution in large doses as the utmost in injection simplicity.

Unfortunately such an injection method is unsatisfactory, in that it provides poor ecological control. If the rate of the injection of the solution is not continually matched to the chlorine demand of the systems, slugs of chlorinated water may be discharged to the local waterways, and this is quite unacceptable. Hence the use of sodium hypochlorite solution delivered to the site necessitates the installation of precisely controlled metering and dosing equipment. This is inevitably more complex and expensive than the equivalent necessary for the control of the output of an electrochlorination plant, for which a current regulator suffices.

However it may be that, for closed circuit cooling tower stations, sodium hypochlorite solution could be used with a less complicated and expensive metering and dosing equipment. The more precise controls would only need to be placed on the chlorine residual in the water purged from the cooling tower system.

A minor but unfortunate complication arises from the fact that sodium hypochlorite solution, as delivered, deteriorates progressively in store. This restricts the desirable step of building up the stock of the solution during the winter period, and running them down during the summer when treatment of the cooling water systems is required. Apart from that, the phenomenon is only reflected in the quantity of the solution which is required to make good the deterioration.

If sodium hypochlorite solution were to be used, a 2000 MW seaside station would need some 3000 to 6000 tonnes per annum and a cooling tower station around 2000 tonnes per annum. Its adoption will be a matter of a balance of its cost against those of electrochlorination equipment, with transporting distance and the remaining life of the particular station as the prime factors in the assessment. Because of the familiarity of the technology involved, the working group saw little need to arrange any large scale trials in this particular area.

7. THE USE OF ELECTROCHLORINATION FOR THE CLEANING OF COOLING WATER SYSTEMS

Until recently the CEGB had little experience with regard to the use of electrochlorination and what little experience and information from other organisations it had on the subject, were not reassuring. In addition the need to control the safety of the hydrogen, released as a by-product, was something to be avoided if at all possible. Obviously, with the good safety record, the economics and the convenience of liquid chlorine delivered to the sites, there was little incentive to make any change to our arrangements.

A personal and subjective additional view is that, in the area of on site production of chemicals generally the CEGB must regard itself as an amateur. Those holding such a view foresee a risk that activity in these sideline areas, whilst apparently economic in isolation, may divert attention from much more rewarding work.

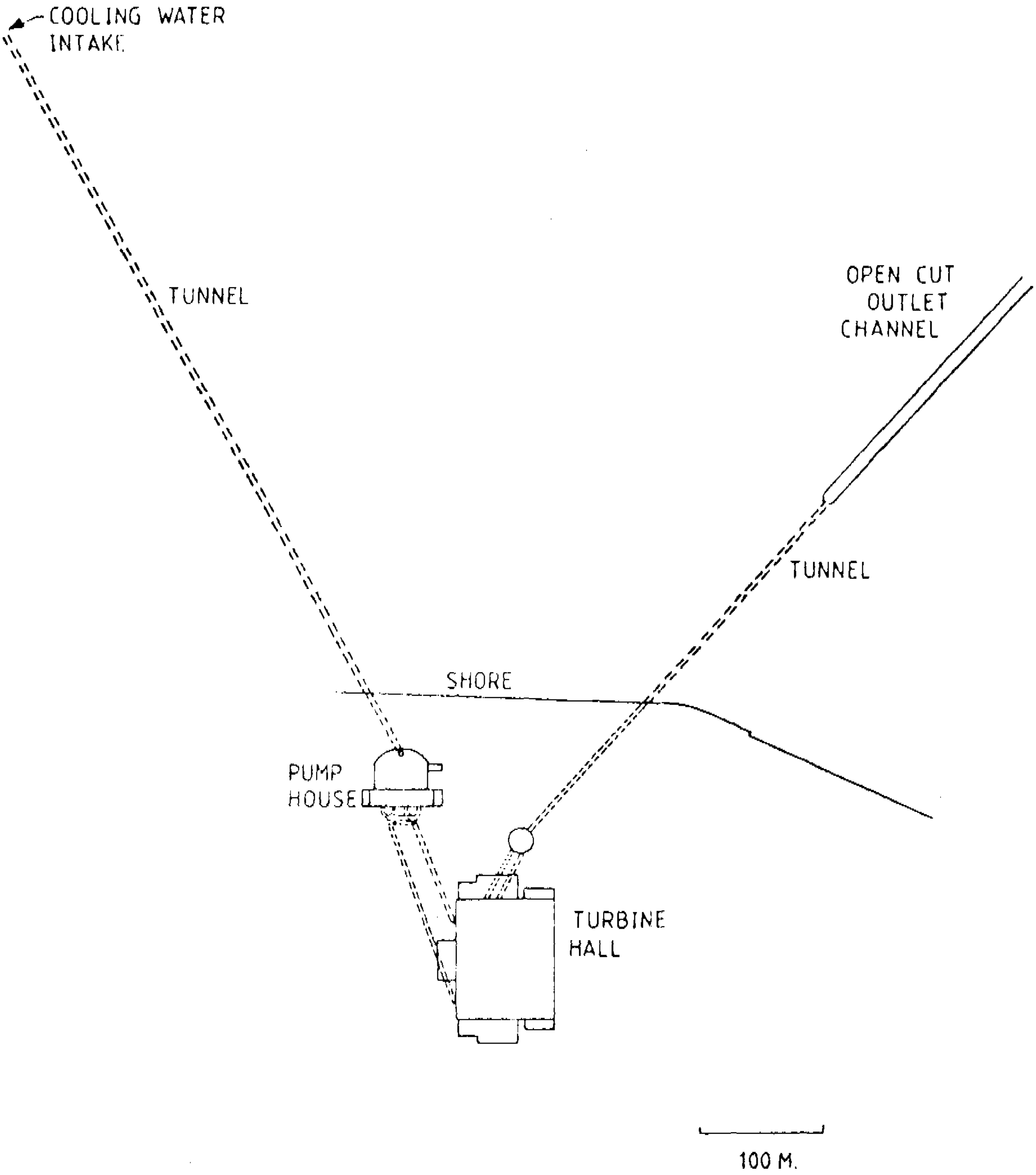
However the on site production of chlorine, if successfully introduced, with the hydrogen explosion danger properly controlled, would satisfy the main policy of eliminating the need for liquid chlorine in bulk. In the present climate obviously the on site production of chlorine had to be taken more seriously and the working group established a sub committee to consider and advise on the subject. The work is proceeding in conjunction with the various manufacturers, for which a number of the other papers to be presented at this Conference are extremely important.

No significant problems are foreseen with regard to the continued operation of these units, but the problems of the routine replacement of electrodes and acid cleaning, must be given attention.

8. CONCLUSION

The conclusions which have been reached about the possible alternatives to the use of bulk chlorine have already been given in the body of this paper. The decision on whether to adopt sodium hypochlorite or electrochlorination, in whatever form, must await the results of the present and proposed trials. These should be completed in 1982 after which the Board foresees a smooth transition from the use of bulk chlorine to the use of one of the two alternatives at each station concerned, over the remainder of the decade.

O(OS)SIA
25th June 1980



EXAMPLE OF SEA-WATER COOLING
SYSTEM FOR A 1320MW POWER STATION

FIG.1

93/154

C.E.G.B. POWER STATIONS RECEIVING CHLORINE

FIG. 2

COOLING WATER ELECTROLYSIS AT COASTAL POWER STATIONS

B Case
W E Heaton

CEGB South Eastern Region, Scientific Services Department

SUMMARY

Power Stations located at coastal and estuarine sites represent about 40% of the CEGB's installed generating capacity but have a much greater need for chlorine or other means of bio-fouling control than inland stations.

An assessment by the Board has indicated that the in-situ production of sodium hypochlorite solution by electrolysis is probably the most practicable and the most economic alternative to the continued use of bulk supplies of chlorine at coastal sites.

Major problems in past CEGB experience of seawater electrolysis systems have been premature electrode failures, fouling of cells with magnesium hydroxide and poor electrochemical efficiency. Substantial development has taken place over the last decade and a number of competitive electrolyser designs is now available.

An appraisal of the electrochemical and engineering aspects of electrochlorination plant is in progress. This includes a comprehensive test programme on the Engelhard and Cumberland Engineering units presently installed at power stations. Consideration is also being given to systems which will need acid cleaning rather than relying on hydrodynamic effects to maintain cells free from scale. Evaluation of a unit with ruthenium dioxide anodes is also a possibility.

This programme should provide experience covering all the major design options for seawater electrolysers and permit the CEGB to make an informed judgement on the system best suited to the requirements of the power generation industry.

1. INTRODUCTION

In accordance with its policy to phase out bulk liquid chlorine installation by the end of the 1980's the CEGB has undertaken a general investigation of alternative approaches and, in particular, to assess the electrochemical and engineering aspects of electrochlorination plant.

It is proposed in this paper to outline the economic and technical factors influencing the Board's choice between various competitive sea water electrolysis systems and to describe the test programme designed to provide information on plant performance and operating costs. The possible advantages of using membrane cell brine electrolysers at power stations will be discussed in a subsequent paper.

2. BIO-FOULING AT COASTAL AND ESTUARINE POWER STATIONS

Approximately 40% of the installed generating capacity of the U.K. power industry uses seawater or saline estuarine cooling water for the steam turbine condensers and auxiliary plant. This figure will have increased to nearer 50% as power stations presently under construction are commissioned in the next few years. Concern with the quality of the environment and efforts to minimise chemical and thermal pollution of inland waters means that much future plant will be sited on the coast.

Seaside and estuarine power stations are prone to mussel infestation of tunnels and culverts and to the formation of organic slimes on condenser tubes. Failure to control this bio-fouling may have undesirable effects such as increasing the power required to pump cooling water, loss of thermal efficiency, and impingement attack on condenser tubes with subsequent boiler corrosion due to sea water contamination of condensate. Inadequate flow of cooling water in the heat exchangers of essential motors or power supplies could possibly reduce the output or shut down one of our very efficient nuclear units.

The most convenient, the least expensive and the best established method of controlling these undesired effects is to maintain a small concentration of chlorine in the sea water while it is in the ducts. The currently recommended CEGB practice is to ensure that a small excess (0.2 ppm) of chlorine (or chlorine as sodium hypochlorite) remains at the inlet to the condenser.

In the context of this paper, "chlorine" and "hypochlorite" are taken to be virtually synonymous in view of the rapid conversion of dissolved chlorine into hydrochloric and hypochlorous acids:

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

The biologically effective agent in sea water may well be derived from the further reaction of the hypochlorous acid with bromide ions.

Chlorine dosing is practised from April to November. The concentrations used, whilst not lethal, prevent mussels settling and also significantly reduce the growth of organic films on condenser tubes.

3. CHLORINE REQUIREMENTS

A simple estimate of the amount of chlorine required can be based on an installed sea-cooled generating capacity of ∿20 GW which uses about 10^5 tonne/hr of cooling water per GW. A demand for 48 tonne of chlorine per day is arrived at by assuming that a 0.2 ppm residual can be achieved by injecting 1 ppm of chlorine into the cooling water intake. Over a 200 day summer period the Board's maximum likely requirement at coastal/estuarine sites would therefore amount to approximately 9,600 tonne. The quantities estimated for individual stations are given in TABLE 1. In practice the amounts of chlorine actually used are rather less than these figures.

4. ON SITE ELECTROLYSIS VS BULK DELIVERED HYPOCHLORITE

An assessment by the CEGB indicates an economic advantage in local production compared with bulk deliveries of sodium hypochlorite solution for those stations which have a long life expectancy-especially if they are remote from a manufacturing source. These stations can write off the capital cost of electrolysis plant over many years and they would incur appreciable transport charges for bulk tankerage (of a product which is mostly water) over long distances. Many of the coastal power stations and certainly the nuclear plants are in this category.

Electrochlorination is also a possibility for high merit estuarine stations if the water salinity at site is high enough. In this case, however, the economic comparison with bulk supplies of sodium hypochlorite is more complex. At Littlebrook 'D', for example, where the chlorine demand will be uncertain until the station operates, the Board has chosen to install a bulk hypochlorite plant. For such estuarine sites where intermittent dosing, in sequence, at a number of points in the cooling water system may be sufficient to control bio-fouling, the complexity of the hypochlorite solution storage and distribution arrangements favours taking bulk deliveries rather than on-site electrolytic production of sodium hypochlorite. Should there prove to be a necessity for continuous chlorination, however, electrolysis appears to be economically competitive even if special measures such as salt spiking of the Thames water feedstock or selective lagooning of water at periods of high salinity were necessary.

5. THE CHOICE OF ELECTROCHLORINATION PLANT

TABLE 2 presents an estimate of the uncertainties in the factors influencing costs of sodium hypochorite production by competitive seawater electrolysis systems for a notional unit capacity of 1000 tonne of chlorine per year. It is inferred from these estimates that it might cost 50% more to operate a poor system than a low priced, efficient unit. To judge from our experience to date the practical electrochemical efficiency (power requirement) is the least certain and most significant variable in the cost equation. The Boards trial programme is therefore primarily concerned with the measurement of power consumption of electrochlorination units under evaluation, as will be explained later in more detail.

The second major uncertainty relates to repayment of the capital and interest. Recent enquiries have indicated differences of ∿ £200,000 for the same capacity of plant. The initial cost may be an over-riding factor in a difficult economic climate and capital charges represent a large fraction of the price of the product.

5.1. PLANT AND INSTALLATION COSTS

Many features such as cell design, electrode type and constructional materials are determined independently by the manufacturer and represent fixed costs. On the other hand economies may be achieved by early consultation between supplier and operator on several factors required of units for use in power stations. These include the selection of power supplies conforming to the Board's specifications, choice of control systems and instrumentation and safety arrangements. In the latter case, for example, methods of hydrogen dispersal vary from natural ventilation from a high-level open top outdoor tank to fan-assisted venting and nitrogen purging. Safety considerations favour the physical separation of electrical supplies and electrolysis cells.

For a power station where a liquid chlorine installation is to be replaced by electrolytic units, compatibility with existing plant is an important consideration. Construction costs may be cut, for example, by the choice of a compact system which can be accommodated within the chlorination house or, alternatively, by selecting plant suitable for outdoor installation. Conventional gas chlorinators produce a solution containing about 3000 ppm of chlorine. Whereas a gas unit might be replaced directly by electrolytic cells which generate sodium hypochlorite solution at relatively high concentration, additional distribution pipework may be needed to eliminate high water velocities for an equivalent dose if a low output concentration electrolysis plant is specified.

5.2 SODIUM HYPOCHLORITE PRODUCTION COSTS

Three factors influence the running costs; power consumption, electrode lifetime and maintenance.

A power consumption of less than 2 kWh/kg of available chlorine is theoretically attainable but practical devices still use from 2 to 4 times this amount of energy. Overpotential losses may be minimised by appropriate choice of electrode materials; resistive power dissipation is reduced by close electrode spacing and efficient hydrogen dispersal within the electrolyte. Current losses are due to both chemical and electrochemical side reactions leading to the destruction of hypochlorite. Coulombic efficiency involves a trade-off between resistive power losses, output hypochlorite concentration and pumping power since the reduction of hypochlorite:

$$OCl^- + H_2O + 2e \rightarrow Cl^- + 2OH^-$$

will be greater the higher the concentration and the faster the mass transfer of hypochlorite ions to the cathode surfaces.

The anodes, which are based on titanium and precious metals, constitute perhaps a quarter of the cost of the electrolysis plant. Electrode lifetimes depend on a wide variety of phenomena. Anode corrosion may be influenced by potential, current density, temperature and pH or may simply be dependent on the total charge passed. Certain electrode types appear to be prone to mechanical problems such as decohesion of coatings or rapid erosive wear. Bipolar electrodes may experience distortion and shorting due to titanium hydride formation at cathodic areas.

Scale formed by precipitation of the magnesium ions in the seawater as alkali is generated in the cells can cause electrode failures and major maintenance problems.

Each cell design, therefore, represents a compromise solution to the problems of producing sodium hypochlorite solution at a reasonable concentration whilst achieving economic electrode lifetimes and low power consumption.

The CEGB was instrumental in developing this technology through the work at Blyth power station in the early 1960's and fundamental studies of cell design and electrode properties are still in progress at the Capenhurst laboratories of the Electricity Council. The variety of designs of seawater electrolysers now available is, however, evidence of substantial research and development on the part of manufacturers over the last decade. Most of the results of this work are, naturally, commercially secret.

In this situation CEGB involvement with electrolyser development is inappropriate. The Board is, nevertheless, intent on a detailed technical assessment before any further decision to order plant is taken. This involves both the evaluation of specifications and performance data provided by manufacturers and a programme of monitoring demonstration units installed at power stations.

6. CEGB EXPERIENCE OF SEA WATER ELECTROLYSERS

6.1. BLYTH

After extensive laboratory evaluations of prototypes by the CEGB a 4 cell commercial system producing 45 kg/hr was installed at Blyth power station in 1964. During a brief period of operation in the winter of 1964/5 there was considerable fall-off in the current efficiency of the bipolar plate cells and after 500 hours with water temperatures between 5 and 6°C sufficient platinum was lost from most of the electrodes to make them unfit for further service. Platinum loss measurements at higher temperatures suggested that this problem would be negligible above 13°C.

Tests on model cells established that the formation of oxygen, chlorate and perchlorate was enhanced at low temperature. At the high current densities (40 - 50 A dm^{-2}) employed the anodes were polarized into a potential region where they were subject to corrosion.

Scaling of the cells with magnesium hydroxide proved especially troublesome. pH values between 11 and 12 were measured near cathode surfaces and after continuous operation for little more than a week accumulations of deposit were sufficient to cause damage to the electrodes and to the P.V.C. cell. Trials showed that the design figure of 0.1 m/sec for the flow rate between the electrodes was far too low and values in excess of 4 m/sec would be required to eliminate scaling. Recirculation of the electrolyte was proposed as a means of achieving high fluid velocity and increased cell temperature.

The measured power consumptions, between 11 and 17 kWh/kg of chlorine made the system quite uneconomic.

6.2 POOLE

Nearly 4000 hours running time was logged during a 10 month trial of an electrolysis unit at Poole Power Station in 1970 during which an average current efficiency of 78% and a power consumption of 6.8 kWh/kg were recorded. With a linear flow through the cell of 1 m/sec magnesium hydroxide deposition was again a problem and acid cleaning was required. Premature failure of the platinum electrodes was experienced due to a series of cell blockages and other mishaps.

6.3 KINGSNORTH

Two 30 kg/hr Cumberland Engineering 'Cychlor' units have been operating reliably since 1975 chlorinating the cooling water supply to a 500 MW turbine steam condenser at Kingsnorth power station. Each unit consists of a pump delivering salt water to a 2 m^3 tank from which another pump supplies water to six cells arranged in parallel. A cell temperature of 14°C is considered to be the lower limit for electrolysis. Originally, water from the condenser outfall was used but this has been discontinued and a minimum influent river water temperature of 10°C is now required.

After recirculating through the cells the hypochlorite solution is bled off to dose the cooling water in a culvert. Hydrogen is vented from the tank to atmosphere. In the early stages of operation there was an explosion when hydrogen was trapped in an organic foam. The risk of this has been reduced by sparging seawater into the top of the tank and by nitrogen purging on start-up and shut-down.

The high velocity of the recycled water has effectively eliminated scaling. Electrode erosion was detected on over-haul in the winter of 1976-7. Examination of failed electrodes after approximately 4000 hours operation suggested that excessive platinum losses were caused by operating with water of low salinity. Deposition of manganese dioxide on the anodes may have been a contributory factor. The Thames at Kingsnorth contains abnormally high concentrations of manganese.

Results of performance monitoring trials carried out by the station staff are given in FIGURE 1. There was a marked difference in the current efficiency and D.C. power consumption of the two units. Pumping and rectification power losses increase the overall power consumption figures to between 8 and 11 kWh/kg of chlorine. However, this design of electrolyser is now obsolete and the new Cumberland 'Rotachlor' design is considerably more efficient.

Periods of operation have been accumulated with experimental electrodes in some of the 'Cyclor' cells.

7. THE CURRENT TEST PROGRAMME

7.1 PARAMETERS TO BE MONITORED

Electrochlorination plant installations at CEGB power stations are listed in TABLE 3. Ideally, competitive electrolysis units should undergo comparative evaluation under the same conditions at the same site which should be typical of the majority of environments where such equipment is to be used. The Board's 'Chloropac' and 'Rotachlor' electrolysers will, however, be operating in quite different locations. It is therefore essential that in these and in any other trials a complete account is kept of all factors affecting their performance so that a valid inter-comparison can be made. It is proposed that the following parameters should be monitored:

conductivity of feedwater
cell temperature
recirculation rate (where appropriate)
individual cell voltages and currents (where appropriate)
hypochlorite production rates
D.C. power consumption
pumping power losses.

It will also be necessary to have analyses of feedwater composition and silt burden to take account of local conditions. As an example of the need for this kind of detail it is possible for two identical cells to show a difference in power consumption of 1 kWh/kg due solely to the difference in solution resistance if one is operating with partly saline water at 10°C and the other with seawater at a cell temperature of 25°C.

7.2 ELECTROCHEMICAL EFFICIENCY

In systems consisting of a number of cells connected hydraulically in series both the concentration and the rate of reduction of the hypochlorite will increase as the seawater flows through the unit. It is, therefore, necessary to test that series combination of cells appropriate to a full scale plant since the efficiency figures for a single cell will be misleadingly high. Small Engelhard units are being tested both at Hartlepool and Fawley but the overall efficiency figures will be determined from the 10-12 cell modules in the large installations at Hinkley and Fawley. It may, however, be possible to correlate single cell results with the multicell system current efficiency data if it is assumed that destruction of hypochlorite in the cell occurs at a rate which is directly proportional to its concentration.

The design of the 'Rotachlor' unit with cells connected hydraulically in parallel makes it possible in principle to monitor the individual cell performance by measuring the hypochlorite concentrations at entry and exit to the cell.

7.3 ASSESSMENT OF SCALING

The degree of cathode scale formation in trial units will be carefully assessed since it has been a major cause of trouble in past CEGB experience and in the operation of seawater electrolysers in other countries such as France and Hong Kong.

Engelhard and Cumberland claim to have tackled the problem of scaling in their electrolysers with two very different designs of cells. Deposition of magnesium hydroxide is prevented in the Engelhard device by the turbulent annular flow between cylindrical electrodes. Scale free operation is achieved in the Cumberland 'Cychlor' units at the expense of high recycle pumping power losses. The new 'Rotachlor' design eliminates scaling with minimal power consumption by feeding the seawater via a high velocity jet which scours any precipitate from the surface of the slowly rotating electrodes.

7.4 ELECTRODE PERFORMANCE

Electrode coatings have frequently failed in power station trials. Both the CEGB and the electrode manufacturers have surface analytical techniques available to assess the condition of electrodes at regular periods during their life. Collaborative investigations on the behaviour of electrodes in both the Engelhard and the Cumberland systems are proposed. The design of the Rotachlor cells makes possible the testing of alternative electrode types.

7.5 LOW TEMPERATURE OPERATION

Certain types of electrodes are now said to be suitable for operation down to 5°C. This is of interest to the CEGB since it has recently been demonstrated that infestation of power station cooling water systems by post-larval mussels can occur between November and March even though sea water temperatures drop to this level or below. Two major coastal stations believe that some chlorination is required during the winter months.

The availability of electrolysis units, even if only working at fractional output with low electrode current densities, would enable at least the auxiliary cooling water supplies to be chlorinated continuously.

7.6 POSSIBLE PROGRAMME EXTENSIONS

Recognising that magnesium hydroxide scaling may occur to a greater or lesser extent in any seawater electrolyser the Board is considering an experimental trial of a system whose manufacturer acknowledges that acid cleaning will be required from time to time. Power station operators would normally prefer to eliminate such maintenance tasks wherever possible. If, however, the necessary pipe connections and acid dosing equipment etc. are properly engineered into the plant and straightforward procedures can be devised no particular problems or hazards are foreseen since these operations will be supervised by highly competent station chemistry staff.

A major omission from current proposals is the evaluation of anode types based on ruthenium dioxide. Reports indicate that units using these anodes have low power consumption due to a correspondingly low overpotential for chlorine evolution. On the other hand there are significant doubts about their wear rates in waters containing abrasive solids, their behaviour at low temperatures and their response to over-polarization. Inclusion of a system incorporating ruthenium dioxide anodes within the CEGB programme is, therefore, under consideration.

CONCLUSION

It is believed that the plant evaluation programme outlined in this paper will provide experience covering all the major design options. This should help the CEGB to form a rational judgement of the system for the production of sodium hypochlorite solution from seawater which best suits the requirements of the power generating industry.

ACKNOWLEDGEMENT

This paper is published by kind permission of the Director General, CEGB, South Eastern Region.

TABLE 1. ESTIMATED CHLORINE REQUIREMENTS AT COASTAL AND ESTUARINE POWER STATIONS.

STATION	COOLING WATER SUPPLY	ANNUAL CHLORINE REQUIREMENT (TONNES)
Dungeness A + B	Sea	500
Kingsnorth	Estuary	1000
Grain	Estuary	1200
Sizewell 'A'	Sea	400
Aberthaw	Sea	400
Carmarthen Bay	Sea	-
Fawley	Sea	1200
Hinkley A + B	Sea	400
Marchwood	Sea	-
Pembroke	Sea	600
Blyth	Sea	1200
Hartlepool	Sea	600
Heysham A	Sea	600
(Heysham B)	Sea	(600)
Wylfa	Sea	1000
TOTAL		9700

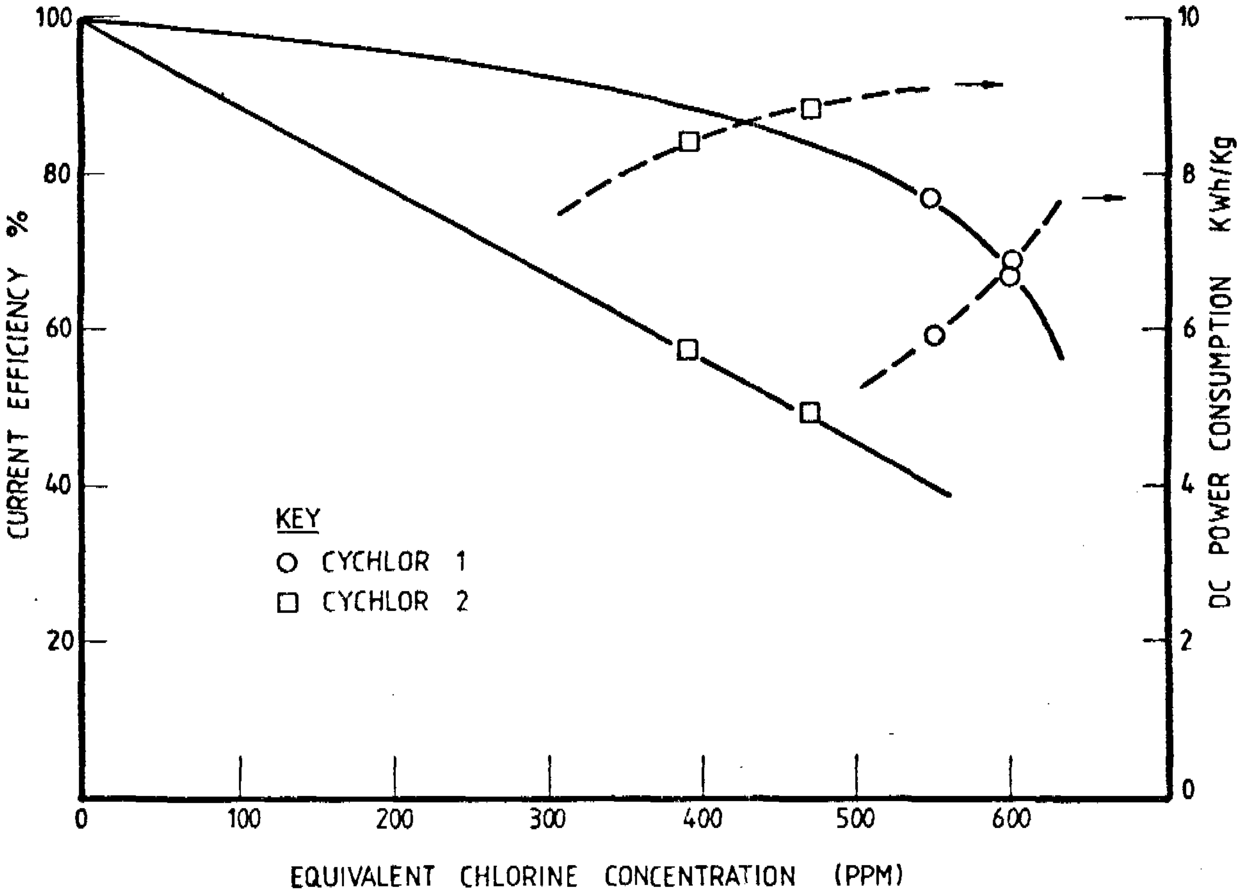
TABLE 2. UNCERTAINTIES IN THE COST OF ELECTROLYTIC HYPOCHLORITE PRODUCTION

(1000 Tonne/Year Plant)

FACTOR	VARIABILITY	ANNUAL COST UNCERTAINTY
Power Consumption	± 2 kWh/kg	£50,000
Plant and Installation	± £200,000	£20,000
Electrode Replacement	2 - 5 year life	£10,000
Maintenance	Uncertain (100 Man-Days)	£ 5,000

TABLE 3. ELECTROCHLORINATION PLANT INSTALLED AT CEGB POWER STATIONS

ENGELHARD			CUMBERLAND ENGINEERING	
Power Station	Experimental Unit	Production Plant	Production Plant	Power Station
HARTLEPOOL	2 cells (0.9 kg/hr) 6 cells (2.7 kg/hr)			
FAWLEY	10 cells (4.5 kg/hr)	4 generators 10 modules/generator 10 cells/module (182 kg/hr)	'Cychlor' 2 units 5 cells/unit (60 kg/hr)	KINGSNORTH
HINKLEY		2 generators 10 modules/generator 12 cells/module (110 kg/hr)	'Rotachlor' 4 units 12 cells/Unit (260 kg/hr)	GRAIN



RESULTS OF TESTS ON THE CUMBERLAND ENGINEERING CYCHLOR UNITS AT KINGSNORTH POWER STATION

FIGURE 1

"Can Membrane Cells Help the CEGB?"

T.P. Smith
Scientific Services Department, CEGB, Harrogate

1. Introduction

During the discussions which led to the C.E.G.B.'s decision to phase out the purchase of liquid chlorine in bulk it was apparent that alternative methods would be expensive. High capital and operating costs are required for seawater electrochlorination, and sodium hypochlorite is considerably more expensive than chlorine. A pioneering experiment in seawater electrochlorination at Blyth during the 1960's was abandoned after some years of concentrated effort had failed to develop a cost effective reliable plant. For these reasons chemists in the C.E.G.B. have asked themselves whether the methods used successfully by the chloralkali industry could also be used to make chlorine on-site. Since the prime concern must be the provision of a safe reliable plant that can operate with minimum supervision the diaphragm and mercury cells are not suitable. Until the advent of the membrane cell the likelihood of on-site chlorine production was ruled out, at any rate in Britain. With this new development however a new appraisal is required to determine whether membrane cell technology can provide a safe, reliable and economically attractive alternative to bulk liquid chlorine.

2. General Requirements for Ancillary Plant

Before discussing the application of membrane cells to power station needs it is appropriate to state briefly some of the factors which are considered when any plant ancillary to the main function of electricity production is proposed. These could be:

(a) how safe will the new plant be?

(b) how reliable will it be?

(c) could there be staffing problems? Will specialist staff be required for operation or maintenance? Do existing staff have spare time and the capability to operate the plant?

(d) how much will the plant cost to install and operate?

(e) where will the plant be sited? Is this location convenient for operation?

(f) are there environmental constraints or benefits?

(g) are there novel or unproven features?

(h) does the proposal provide the best answer?

The relative importance of these factors will vary from one site to another. To some extent a detailed objective assessment can be made but a decision may also depend on factors which cannot easily be quantified as well as on previous experience with comparable systems.

3. Technical Features of the Membrane Cell

A full discussion of the technical features of the membrane cell is both unnecessary on this occasion and beyond the scope of this paper. The essential features which commend its use for local chlorine production appear to be:

(a) a potentiality for low hazard operation;

(b) a capability to produce pure by-product hydrogen and caustic soda as well as chlorine. This feature is attractive to the C.E.G.B. since these commodities are essential to the operation of a modern power station;

(c) environmental acceptability;

(d) the possibility of economic operation on a small scale.

The major disadvantage lies in the membrane's affinity for higher valent cations; this imposes stringent purity requirements on the salt feed to the system.

4. Chlorination at Inland Power Stations

The station chosen for study was a 2000MW baseload station sited inland. The original chlorine plant is of conventional design; water is pumped continuously through the distribution main to each point of application in turn. This water is used:

(i) to 'prove' the flow path through the cooling system;

(ii) to transport the chlorine from the ejector to the required cooler;

(iii) to flush the system after each chlorine injection.

The quantity of chlorine injected can be adjusted independently for main condenser sections and auxiliary coolers. Normally cooling water flow is maintained irrespective of load and is only reduced when a turbine is taken out of service.

The concentration required at the heat transfer surface is obtained by dilution in 2 stages; for stage 1 gaseous chlorine is injected into the water flow at the rate required for the cooler to be treated; the second stage dilution occurs when this chlorine water mixes with main water flow through the cooler. Thus the chlorine concentration in the distribution main varies between zero and high and low values during the chlorination cycle. These variations are so large and so frequent that it would not be possible to match chlorine production to them. A change to continuous chlorination would probably require the use of much larger quantities and would therefore be environmentally unacceptable. Radical modifications to the existing system were also ruled out by the possible need to revert to the use of liquid chlorine if the new plant should prove unreliable.

5. Plant Modifications for On-Site Chlorine Production

A buffer storage tank provides the simplest method of matching chlorine water supply and demand. The low solubility of chlorine in water precludes large volume storage to cover plant breakdown or to allow manufacture using off-peak electricity. Low solubility also implies low absorber efficiency, with high chlorine losses, and a high chlorine partial pressure over the stored solution if a high concentration is required. Fig. 1 shows plots, derived from data by Whitney and Vivian, for chlorine partial pressure over solutions in the range 0.1 - 0.3% by weight between 10 and 25°C. Clearly an optimum concentration could be calculated to minimise the value of chlorine losses and of the caustic soda required for vent gas absorption, as well as the capital cost of the storage tank and chlorine water handling pumps. An arbitrary concentration range of 0.08 - 0.15% was chosen in this instance, as a basis for a simple analysis of the problem.

Chlorine water usage can be spread more uniformly over the chlorine cycle by the alternate treatment of sections of the plant with high and low requirements. If this is done fluctuations in usage could be contained by a 50m^3 tank. If also the start of an injection period is prevented below a preset tank level the rate of use can be controlled by the rate of manufacture; this is preset manually by adjusting the rate of water flow to the absorption system and controlling the concentration by the cell current. Provision could also be made to increase production automatically by 20% when a tank low level setting is reached and reduce it by 20% when the upper operating level is reached.

At this station it is possible to site the storage tank beside the cooling water dock near the main pump intakes. A free-draining bund is required to direct any spillage into this rapidly moving body of water. An obvious advantage of low concentration chlorine water is the low chlorine release into the air from any such leakage.

6. Chlorine Production for Coastal Power Stations

The complexity of the chlorine water handling plant for seawater cooled power stations is much reduced. Since chlorine is required continuously for long periods of time at the seawater intake there is no need for storage or a complex distribution control system. Adequate mussel control depends on continuous low level chlorination and reliable plant is essential. However existing gaseous chlorine plant is never completely reliable and it is unlikely that standby plant would be required, especially if adequate spares are kept and regular maintenance can be carried out during periods when mussel breeding rates are low. To avoid total shutdown on these occasions the plant could be divided into at least two independently operable sections.

7. By-Product Requirements

7.1 Hydrogen

Considerable quantities of hydrogen are used for cooling the large highly rated alternators in modern power stations. Quantities vary widely from one station to another and depend on the gas tightness of the system, the number of alternators, and the frequency of major outages. When maintenance work requires that the alternator be opened the hydrogen must be displaced by CO_2 which is in turn displaced by air. The reverse procedure is required before generation can be restored and large quantities are used rapidly at such times. A typical 2000MW station with 3 x 660MW units would require plant to produce 30m^3/h and use 100,000m^3/y, whereas a similar capacity station with smaller, older units might use over 400,000m^3/y.

Hydrogen purity in the cooling circuit must be kept at a level well above the upper explosive limit at all times, irrespective of whether or not the alternator is on load. Hydrogen humidity must be low and a dew point of less than -40°C at line pressure is usually required, partly to avoid the transfer of moisture into the alternator system, but also to maintain dryness if minor leakage occurs from the water cooled stator conductors. Limits for other trace impurities have not usually been specified in the past. Where hydrogen from a chloralkali cell is to be used for cooling electrical plant grave damage could be caused by traces of chlorine, salt and caustic soda. Caustic could also react with the carbon dioxide used for purging and produce carbonate deposits in the system. Contamination by chlorine and salt could only occur as a result of porosity defects or membrane rupture, both events which it is hoped would be rare. Nevertheless no risk of contamination is acceptable and a water washing system, with on-line instrumentation, is essential to ensure satisfactory hydrogen quality before and after drying.

Whether hydrogen is manufactured on site or not it is normal to store fairly large quantities (500-1000 Nm^3) to provide the high flow necessary during purging after overhauls. Since purchased supplies can usually be obtained to augment the amount stored the reliability of power generation need not be adversely affected by chlorine plant failure.

7.2 Caustic Soda

Caustic soda is an essential commodity at most generating stations where it is used to regenerate anion exchange resin in the water treatment plant. The quantity used depends on the quality of the raw water available and the design of the demineralising plant; for a 2000MW station it could be anything from a few hundred to over 2000 tons of 46% caustic each year.

Demineralisation is usually carried out in stages. Regenerant chemical purity requirements for the first stage anion beds are not exacting and caustic soda containing up to 1% would usually be suitable for a major proportion of the total station requirement. Regeneration is usually carried out at about 40 - 50°C using preheated water to dilute the 46% caustic to the 4% solution required. Thus if caustic is produced at 8% concentration and 80 - 90°C it could be diluted with an equal volume of cold water with a consequent heat saving.

Regeneration of the anion resin from the final polishing stages of mixed bed demineralisers generally requires caustic soda with a lower salt concentration. The production of such caustic in a membrane cell requires a higher catholyte concentration with a consequent need for sophisticated membranes, and a high purity salt feed. The purchase of sufficient high purity caustic for use in those parts of the water treatment plant where it is essential is an obvious alternative, using a membrane cell to supply impure caustic for less exacting processes.

Ion exchange resins are easily damaged by strong oxidising agents. Care will be necessary therefore to ensure that the caustic produced is not contaminated with chlorine, hypochlorite or chlorate, by leakage through the membrane from the anode compartment of the cell. Under normal circumstances damage from this type of contamination should be minimal as the normal routine control tests on the cell should detect membrane damage at an early stage.

8. Salt Purity

It was assumed for the purpose of this study that purified vacuum salt would be used as the basic raw material. PVDS is already purchased for use in many water treatment plants and C.E.G.B. would not wish to install plant for rock salt purification. Fig. 2 shows some typical chemical analysis results. The question of the suitability of this material as a direct cell feed appears to be controversial at present and would seem to depend on the type of membrane to be used and the system designer's operating philosophy. For a small simple plant the spent brine would be added to the chlorine water rather than re-saturated and returned to the cell. A cell design with a high brine depletion rate might therefore be used with an unsophisticated membrane and a low catholyte concentration. For a larger plant greater complexity may be justified to increase salt utilisation, especially if a case can also be made for the production of high strength caustic for distribution to other power stations. An optimisation study would be required to establish the size of plant at which such additional sophistication becomes economic.

9. Current C.E.G.B. Position

The membrane cell is potentially suitable for chlorine production at both inland and coastal sites. A functional specification for a 1t/d plant at an inland power station has been prepared (see Fig.3) in the expection that an installation would yield experience of value at both inland and coastal sites. A decision to seek tenders for this plant was overtaken by a decision to carry out trials with the Taprogge mechanical condenser cleaning system. Although more costly to install than a membrane cell the Taprogge system also removes chemical scale; it should therefore recover its cost quickly and reduce chlorine consumption by over 80%. Similar developments may arise elsewhere since chemical scaling and biological fouling problems are experienced at many inland stations.

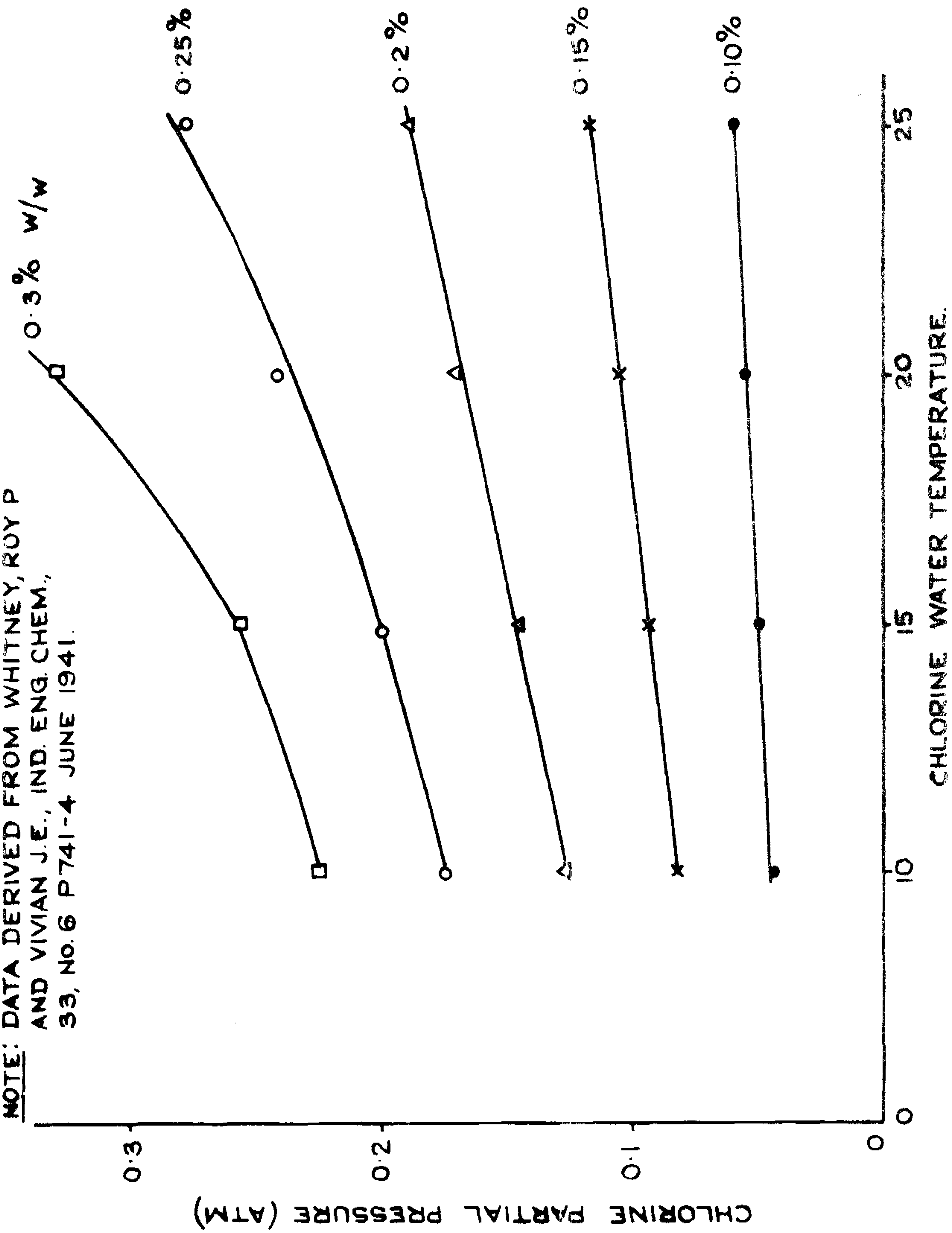
At coastal stations it is essential to prevent mussel fouling in the cooling water culverts as well as the growth of slime in the condenser. Mechanical systems are not capable of protecting the culverts and at most existing British coastal stations it is likely that some form of chlorination will be practised for many years.

A technical appraisal of the processes involved suggests that electrolysis of pure salt in a membrane cell is more inherently reliable than seawater electrochlorination. This is because the electrolyte temperature and concentration in a membrane cell can be closely controlled. Cell output is not therefore subject to variations in ambient temperature or to the dilution by freshwater which occurs with saline water drawn from tidal estuaries. Problems with cell blockage by magnesium hydroxide are also avoided. The advantages of the membrane cell in these respects are offset by a greater requirement for supervision, but at stations where a substantial and reliable supply of chlorine is required throughout the year it remains an option which should be thoroughly investigated.

10. Acknowledgements

The author thanks the Director General, North Eastern Region for permission to publish this paper.

TPS
WP/JK
16.5.80
D23.A22-A28

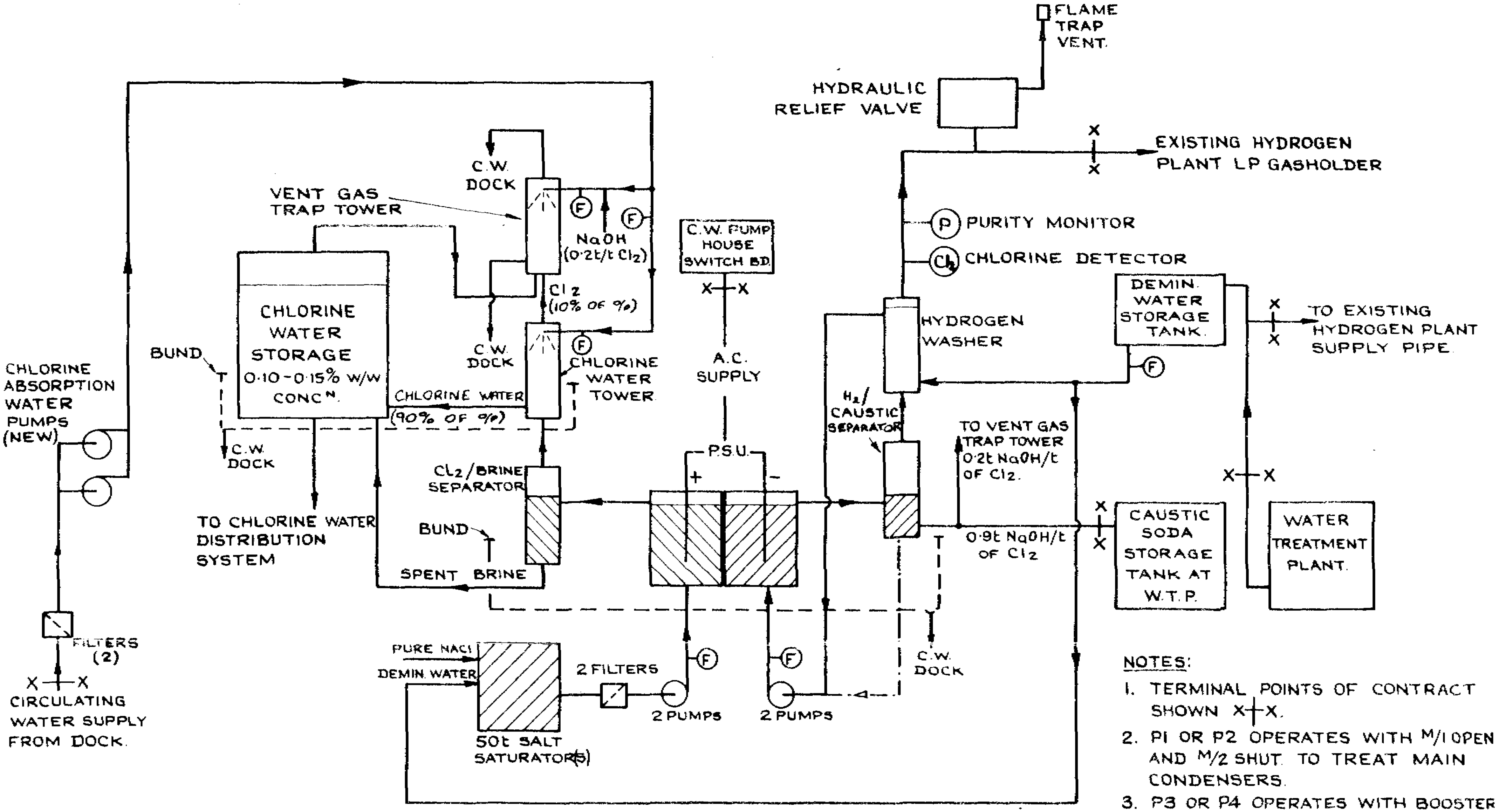


NOTE: DATA DERIVED FROM WHITNEY, ROY P AND VIVIAN J.E., IND. ENG. CHEM., 33, No. 6 P741-4 JUNE 1941.

CHLORINE PARTIAL PRESSURE OVER CHLORINE WATER. FIG. 1

		PURE DRIED VACUUM SALT
CHLORIDE as NaCl (Dry Basis)	%	99.96 - 99.90
MOISTURE Content	%	0.005 - 0.045
SULPHATE as Na_2SO_4	ppm	250 - 800
ALKALINITY as Na_2CO_3	ppm	<10 - 60
IRON as Fe	ppm	0.2 - 3
COPPER as Cu	ppm	<0.1 - 0.1
MAGNESIUM as Mg	ppm	<1
CALCIUM as Ca	ppm	6 - 30
ANTICAKING ADDITIVE (Sodium Ferrocyanide)	ppm	3 - 9

FIGURE 2 CHEMICAL ANALYSES OF VACUUM SALT



NOTES:

1. TERMINAL POINTS OF CONTRACT SHOWN X┼X.
2. P1 OR P2 OPERATES WITH M/1 OPEN AND M/2 SHUT TO TREAT MAIN CONDENSERS.
3. P3 OR P4 OPERATES WITH BOOSTER PUMPS ON, M/1 SHUT AND M/2 OPEN TO TREAT AUXILIARIES.
4. P1 – P4 OFF, M/1 SHUT AND M/2 OPEN TO FLUSH WITH WATER FROM BOOSTER PUMPS.
5. FLOW FAILURE ALARM SENSORS SHOWN ─Ⓕ.

MEMBRANE CELL CHLORALKALI PLANT FOR POWER STATION USE. FIG. 3

STERILIZATION REQUIREMENTS IN OFFSHORE OIL PRODUCTION

Mrs B.A. Crouch and Dr R.W. Mitchell, BP

INTRODUCTION

When the majority of the North Sea Oil Fiels were initially discovered it was predicted that production from the field by simply drilling wells and allowing them to flow would be inefficient. In many cases it was estimated that the pressure in the reservoir would fall substantially if no form of pressure maintenance was practised. When the reservoir pressure falls sufficiently, the wells will no longer flow and the vast majority of the oil will remain in place. Operating experience in many oil fields has confirmed these predictions.

Pressure maintenance can take several forms but in general, in the North Sea, because of the volumes required, sea water has been chosen as the injection fluid.

In most instances an extensive aquifer (water) underlies the oil zone. It is into this aquifer that fluids may be injected to maintain reservoir pressure.

For pressure maintenance, water is normally injected into the aquifer at the outer edges of the reservoir. Injected sea water will push the oil towards producing wells located within the reservoir; as the water moves through the reservoir, it moves oil ahead of it towards the areas of low pressure which are producing oil.

For the injected water to do its job, that is to displace the oil, it must move through the tiny pores or holes which typically make up reservoir rock. To do this it must be pumped at sufficient pressure to overcome the reservoir pressure and maintain production rate. It is important, therefore, that the injection water be sufficiently clean to avoid plugging of the reservoirs by biological slimes and inorganic or organic debris. Sea water is generally filtered, deaerated (oxygen removal) and treated chemically. In respect of the latter, the control of the microorganisms present in the injection water is important as their presence may cause system corrosion, formation plugging and ultimately the souring (H_2S) of a previously 'sweet' (non-H_2S containing) oil reservoir.

This paper discusses the techniques used to control bacteria and monitoring methods in BP's Forties Offshore Water Injection System. A schematic diagram of this system is shown in Figure 2. Details concerning the design and commissioning have been puiblished elsewhere (1).

MICROBIOLOGICAL CONTROL - THE REQUIREMENTS

In the Forties System sea water used for pressure maintenance is taken in from a depth of ≃200 ft below sea level (mid depth). Tests indicated that the quality of North Sea water is optimum at this level with respect to particle size distribution (1). However, it does contain a variety of microorganisms. The growth and accumulation of these microorganisms within the water injection system, and beyond, can cause problems. Such problems can be divided into two main areas relating to the microorganisms concerned:-

- general bacterial growth, aerobic and anaerobic;
- growth of Sulphate Reducing Bacteria.

If bacteria in general are allowed to settle and/or grow significant slimes can accumulate, particularly in static areas. Slimes of this nature can only be removed in one of two ways; physically or chemically. Physical removal in a water injection system is impractical. Consequently extensive chemical treatment would be required to remove those slimes.

Slime build-up in the Forties System would be particularly troublesome in the fine filtration system (5μ). These are of the cartridge type, with back wash facilities. They could become overloaded if excessive microbiological growth was permitted necessitating more frequent filter element changes. Growth of microorganisms (bacteria) within the system will also increase the particle content and could ultimately cause blockage of an injection well.

The second problem area arises from the growth of Sulphate Reducing Bacteria (SRB). These bacteria (the predominant species in the North Sea belong to the genus Desulphovibrio) only grow in environments devoid of oxygen. Their natural marine habitat is in the anoxic region of marine sediments starting about 1 cm below the surface. Although SRB will grow only in anoxic environments, they can survive in oxygenated waters. Therefore these are found throughout the water column, although the in North Sea water (from 200 ft) in low levels, ie less than one per ml. From the deoxygenation towers onwards the environment is anaerobic, thus providing conditions conducive for SRB growth.

The problems associated with the growth of these bacteria originate from their ability to reduce sulphates to sulphides as an essential part of their metabolism. The sulphate is reduced simultaneously as a carbon source is utilised. There are several possible consequences of sulphide generation:

(1) The formation of H_2S gas which can constitute a safety problem.

(2) The formation of insoluble ferrous sulphides which increase the particulate content of the water, thus increasing the chances of blocking in the filter and/or rock formation. Ferrous sulphides are also involved in anaerobic pitting corrosion mechanisms.

(3) The potential growth of SRB in the reservoir itself can lead to the formation of H_2S which can ultimately down-value crude by increasing the sulphur content. Once a reservoir has gone "sour", the problems caused by H_2S will pass along to the transportation, storage and refining systems.

(4) Random, anaerobic pitting corrosion can be attributed directly to the growth of SRB. This corrosion is caused by the cathodic depolarisation of metal surfaces, brought about by the enzymic (hydrogenase) removal of the pacifying hydrogen film.

MICROBIOLOGICAL CONTROL - THE METHODS

Having outlined the possible consequences of bacterial growth, especially SRB, it would seem logical to recommend sterilization of the injection water. However, this is not a viable proposition, because of the energy necessary, the plant size, and hence cost required to handle vast quantities of water (eg 150,000 bbl/day/platform).

The only practical approach is continuous chemical control at the earliest possible stage in the system. However, the selected chemical must meet certain requirements.

(1) Since it will be in continuous use it must be indescriminate in its biocidal action. In this way the development of strains resistant to the chemical can be prevented.

(2) It must control bacterial levels by preventing growth and if possible reducing the numbers passing through the whole injection system.

(3) The dose required to achieve this control must be very low, due to the logistics of the offshore location.

Finally, it must not be toxic to man at the dosage used. This last point is very important since the potable water on these offshore platforms is derived from the distillation of sea water taken off the water injection system.

A biologically active inhibitor which meets these requirements is chlorine. However, as chlorine is extremely corrosive, there is a limitation to the applied dose.

A situation may arise when the chlorination treatment has to be augmented with additional biocide treatments. Additional biocides are necessary when:

(1) Chlorine supply is interrupted for whatever reason.

(2) No chlorine residual exists due to interactions with other chemical additives present in the system (eg oxygen scavengers).

(3) There are indications of microbiological growth within the system.

Such additional treatments are generally of organic biocides applied on a slug basis at a point downstream of the de-aeration towers (Position 4 in Figure 1).

PRACTICAL PROBLEMS

As mentioned earlier two types of microbiological control are practised in Forties:-

- chlorination (ie injection of hypochlorite)
- injection of organic biocides.

Chlorination can be achieved by either direct addition of the concentrated (14 per cent) liquid sodium hypochlorite or in situ electro-chlorination of sea water. From an operational point of view the latter method is preferred. (However, several practical problems still occur.) An electrochlorinator essentially consists of the electrolysis cell which is generally intrinsically safe and robust; and the associated electronics and rectification which is not intrinsically safe and often very susceptible to atmospheric corrosion. This safety problem naturally restricts the positioning of the electrical unit, generally to an environment with a controlled atmosphere. In addition, as hydrogen is also generated in the electrolysis of sea water, it is normal practice to employ a hydrogen removal tank. This unfortunately necessitates additional pumping. A typical schematic diagram of an electrochlorinator system is shown in Figure 2.

Major problems with the system appear to be in establishing the system current/water flow relationship, the formation of magnesium hydroxide scale in the units, and the effect of the corrosive atmospheric conditions found offshore. Whilse the electrochlorinator units are being commissioned on Forties, control (chlorination) is achieved by the direct injection of concentrated sodium hypochlorite. This system has been used during the last four years and has given rise to numerous problems, the major ones being:

- logistics
- design of hypochlorite tanks
- corrosion and pumping problems.

In Forties, hypochlorite is injected at the approximate rate of 110 litres/day on each of the four Forties platforms. Liquid hypochlorite is generally delivered in 1000 litre containers which means each platform requires around 33 containers per month.

This can give rise to several logistical problems during the winter months. At an early stage it was recognised that the typical container in which hypochlorite was supplied (plastic or fibre glass in a steel frame/jacket) was unsuitable for offshore use. The containers were designed for use with fork lift trucks rather than cranes. Consequently containers had to be redesigned and strengthened to allow them to be safely offloaded from the supply boat to the platform by crane and subsequently relocated around the platform.

In the initial stages, considerable problems were encountered with the pumps and associated pipework. Concentrated hypochlorite as used in Forties is highly corrosive to stainless steel with the result that glass pump plungers and plastic tubing had to be employed throughout. Further, as the use of liquid hypochlorite was initially proposed as a temporary measure, the tanks and pumps were located a considerable distance from the injection point. Consequently, continuous pumping was often difficult due to the presence of air and solids in the line.

It has been noted earlier that occasionally chlorine injection is supplemented by the use of organic biocide. This is achieved by using purpose-built chemical injection. Care, however, has to be exercised in handling such materials, and it is sometimes difficult to accurately estimate the dose of biocide per barrel of injected water.

RESULTS

1. Methods of Evaluation

Before presenting data on the chlorination treatment, the microbiological methods by which the treatments are evaluated will be briefly described.

Microbiological monitoring for "general aerobic bacteria" and SRB is routinely carried out. The sampling points are shown on Figure 1. The baseline data for comparison is obtained from sample point (1) upstream of the chlorine injection point.

Until recently, microbiological monitoring was carried out by shore-based personnel. Consequently, due to logistical reasons, the frequency of sampling was not as high as desired. However, the monitoring is only designed to show trends, up or down, in the microbiological population.

2. Results

The results for all four Forties production platforms are in Tables 1-4. Since the number of microbiological tests per sampling point is not consistent, these results have been expressed as percentage increases, decreases, or no change (% constant) compared to the unchlorinated intake water on the same day.

The percentage constant and decrease have also been summed for comparison with percentage increase. The constant results show that there is no detectable proliferation within the system and the decreases indicate that the chlorination is also reducing the intake population.

The following observations can be made from the data presented:

(1) Some of the sampling points are often "not available". This is represented by NO DATA on the tables. The main reason for this being that the sampling points were used for other purposes.

(2) SRB monitoring takes priority over general aerobic bacteria. This is demonstrated by more "anaerobic" data being available.

(3) The individual results show a degree of scatter, in that "increase" results are obtained.

(4) The percentage of tests for constant and degrease together and individually demonstrate that the chlorination treatment is fulfilling its function, ie preventing growth and reducing viability.

(5) There is strong indication of SRB growth occurring across the deoxy tower on FD (Table 4).

CONCLUSIONS

The use of chlorine to maintain biological control in a sea water injection system is now common place in most North Sea oil installations. The majority of injection systems now include electrochlorinators as part of their design specifications. Whilst the injection of liquid hypochlorite is a useful temporary back-up method, the associated logistical problems negate its long term use.

The results found to date in Forties indicate that the chlorination regime is, in general, preventing the proliferation of microorganisms and to some extent is reducing them. The microbiological monitoring regime, whilst not being ideal, does demonstrate the establishment and growth of microorganisms within Water Injection Systems.

REFERENCE

(1) THE FORTIES FIELD SEA WATER INJECTION SYSTEM
R.W. Mitchell
J.P.T., 877, June 1978.

Pages 1 - 11
Tables 1 - 4
Figures 1 - 2

TABLE 1 : MICROBIOLOGICAL DATA RELATING TO PLATFORM FA

PLATFORM/FA		ANAEROBES (SRB)				GENERAL AEROBES			
Sample Point Nos.	Location description	% increase	% constant	% decrease	% constant + decrease	% increase	% constant	% decrease	% constant + decrease
1-2	Water Winning Pump → U/S Deoxygenation Towers	5	25	70	95	18	9	73	82
2-3	U/S Deoxygenation Towers → D/S Deoxygenation Towers	—	—	—		—	—	—	
3-4	D/S Deoxygenation Towers → U/S Fine Filters	—	—	—		—	—	—	
4-5	U/S Fine Filters → Water Injection Header	19	43	39	82	—	—	—	
1-4	Water Winning Pump → U/S Fine Filters	32	26	42	68	26	17	57	74
1-5	Water Winning Pump → Water Injection Header	14	29	57	86	—	—	—	

U/S = Upstream

D/S = Down Stream

—— = No Data

TABLE 2 : MICROBIOLOGICAL DATA RELATING TO PLATFORM FB

PLATFORM/FB		ANAEROBES (SRB)				GENERAL AEROBES			
Sample Point Nos.	location description	% increase	% constant	% decrease	% constant + decrease	% increase	% constant	% decrease	% constant + decrease
1-2	Water Winning Pump → U/S Deoxygenation Towers	14	18	68	86	8	8	83	91
2-3	U/S Deoxygenation Towers → D/S Deoxygenation Towers	———	———	———		———	———	———	
3-4	D/S Deoxygenation Towers → U/S Fine Filters	———	———	———		———	———	———	
4-5	U/S Fine Filters → Water Injection Header	21	48	30	78	———	———	———	
1-4	Water Winning Pump → U/S Fine Filters	29	21	50	71	21	13	67	80
1-5	Water Winning Pump → Water Injection Header	21	25	54	79	———	———	———	

U/S = Upstream, ——— = No Data

D/S = Down Stream

TABLE 3 : MICROBIOLOGICAL DATA RELATING TO PLATFORM FC

PLATFORM/FC		ANAEROBES (SRB)				GENERAL AEROBES			
Sample Point Nos.	location description	% increase	% constant	% decrease	% constant + decrease	% increase	% constant	% decrease	% constant + decrease
1-2	Water Winning Pump → U/S Deoxygenation Towers	10	30	60	90	45	18	36	54
2-3	U/S Deoxygenation Towers → D/S Deoxygenation Towers	33	33	33	66	0	0	100	100
3-4	D/S Deoxygenation Towers → U/S Fine Filters	20	20	60	80	29	71	0	71
4-5	U/S Fine Filters → Water Injection Header	17	54	29	83	———	———	———	
1-4	Water Winning Pump → U/S Fine Filters	23	15	62	77	19	27	54	81
1-5	Water Winning Pump → Water Injection Header	12	28	60	88	———	———	———	

U/S = Upstream ——— = No Data ,

D/S = Down Stream

TABLE 4 : MICROBIOLOGICAL DATA RELATING TO PLATFORM FD

PLATFORM/FD.		ANAEROBES (SRB)				GENERAL AEROBES			
Sample Point Nos.	Location description	% increase	% constant	% decrease	% constant + decrease	% increase	% constant	% decrease	% constant + decrease
1-2	Water Winning Pump -> U/S Deoxygenation Towers	5	24	71	95	4	4	92	96
2-3	U/S Deoxygenation Towers-> D/S Deoxygenation Towers	94	6	0	6	67	29	24	33
3-4	[illegible] Towers->U/S Fine Filters	0	17	83	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]				
1-4	Water Winning Pump ->U/S Fine Filters	[illegible]	19	58	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1-5	Water Winning Pump ->Water Injection Header	33	14	53	67				

U/S = Upstream
D/S = Down Stream

——— : No Data

THE FORTIES FIELD PLATFORMS WATER INJECTION SYSTEM

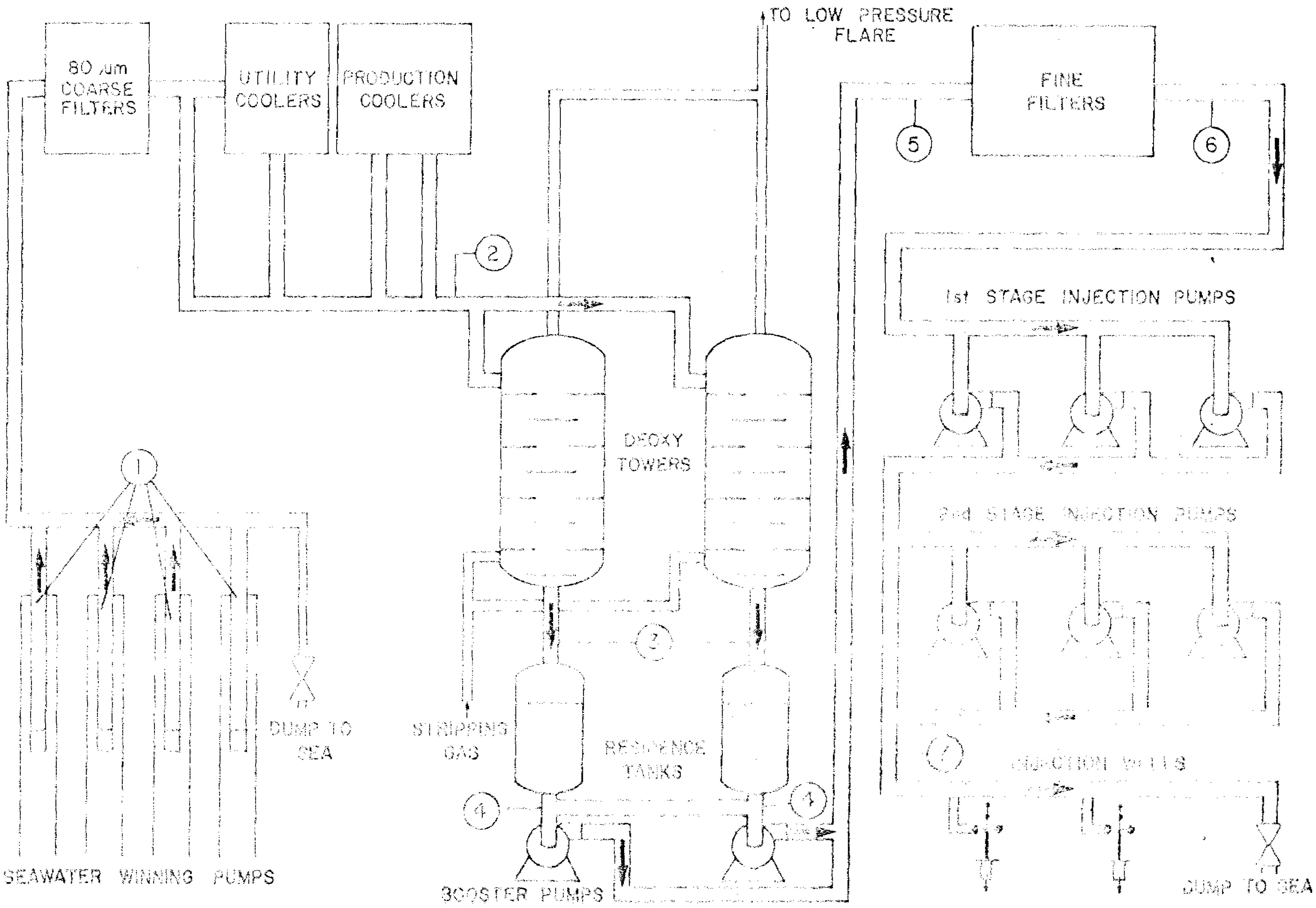
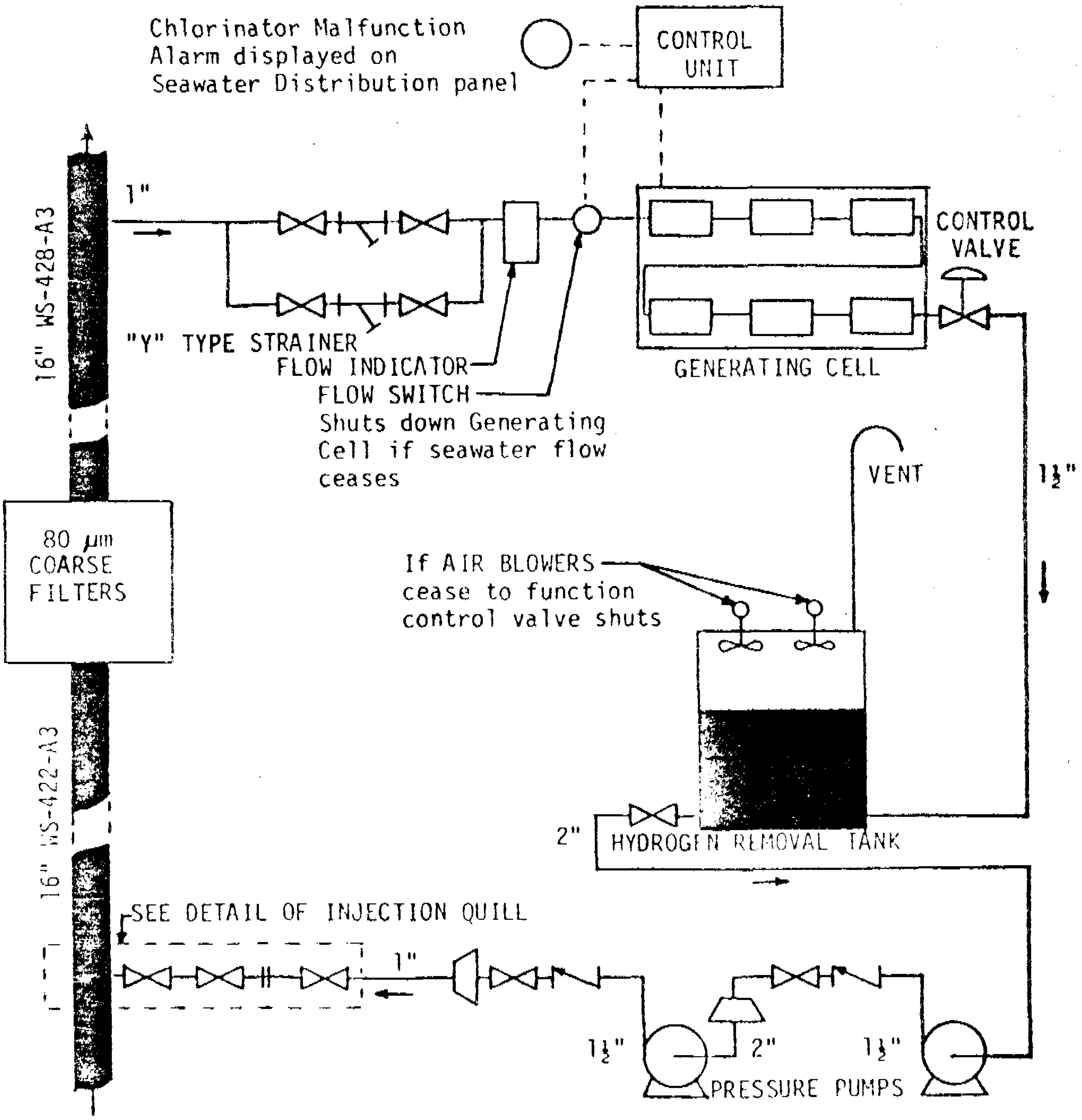


FIG. 1

BP PETROLEUM DEVELOPMENT LTD

Author

NPE/BR/212



DETAIL OF INJECTION QUILL

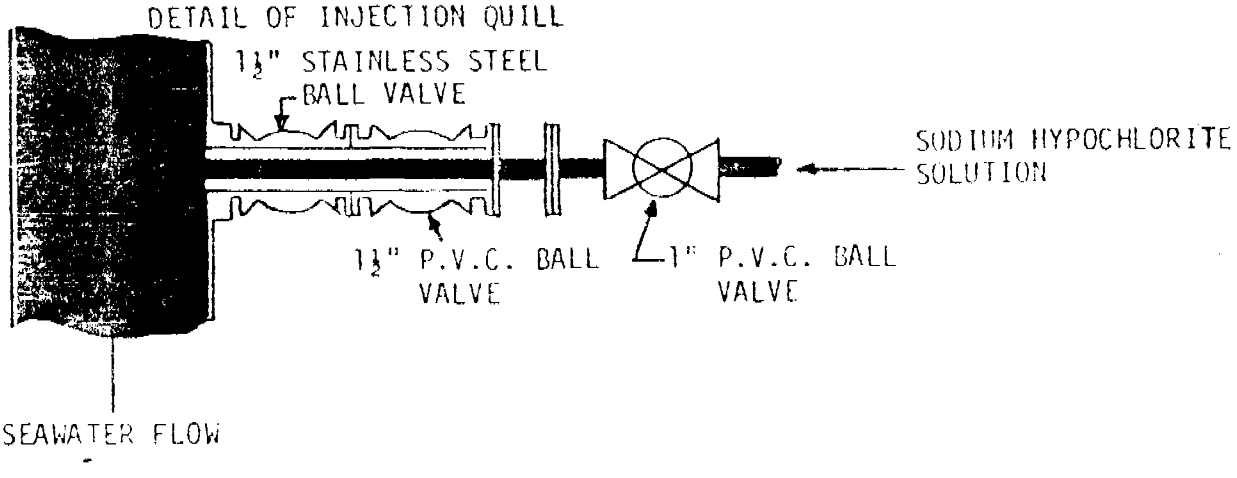


Fig. 2 THE ELECTROCHLORINATOR SYSTEM

TREATMENT OF POTABLE WATER

J.W. Atkinson

Introduction

The statutory duty of water authorities and water companies is to supply the public with a water which is rather vaguely described as "wholesome". This term is usually understood to mean that the water is free from harmful bacteria, it contains no undesirable chemicals, it is clear and colourless and has no taste or odour.

It is rare for any natural sources of water to satisfy all these requirements and some form of treatment is required before the water enters the distribution systems. This treatment varies from simple chlorination to a rather complicated system involving several stages of chemical and mechanical processes. There may be some value in considering briefly the development of water treatment processes.

Water Treatment

Our forefathers built reservoirs in the more hilly parts of the country (and usually remote from the population to be served,) to ensure an adequate supply of clean water to the local communities but it was not until the early 1900's that it was realised that storage of water itself produced improvements in water quality - natural settlement took place, bacterial counts were reduced and, in those areas where the sun shone, colour could be reduced. The next process developed was slow sand filtration, an apparently simple straining process but actually a rather complicated biological process which produces marked improvements in water quality, both chemically and bacteriologically. At the beginning of this century, chlorination of waters for potable supply was introduced but on only a limited scale. In the meantime, in order to satisfy the increasing demand for water, other sources had to be found and eyes were turned to the more doubtful sources such as rivers. As is known, rivers also are the receivers of unwanted wastes so that more complicated treatment processes are necessary. Such processes can include microstraining, aeration, chemical coagulation and sedimentation (or flotation), rapid sand filtration, pH correction, disinfection, softening and activated carbon dosing and the control of such systems presents many problems, especially if the raw water source is of varying quality.

Straining is a purely mechanical means of separating larger solids from liquids, thus reducing the load on ensuing treatment stages but chemical coagulation is the process by which colour and turbidity can be removed. This process utilises the effects of the chemical reaction of trivalent metals, such as aluminium and iron, with the bicarbonates in the water to form flocculant trivalent hydroxides which are capable of adsorbing colour and turbidity. "Alum' is the most common material used and sometimes ferric sulphate, though ferrous sulphate, oxidised with chlorine to produce a mixture of ferric chloride and ferric sulphate (and then known as 'chlorinated copperas') is used with some waters, particularly those naturally rich in iron.

As will be appreciated, in any chemical process pH control is very important, and this is especially so when dealing with thin, highly coloured unbuffered waters; pH adjustment can be up or down according to the nature of the water being treated and the coagulant used. The optimum pH for colour removal may not coincide with that for turbidity removal.

If the above conditions are correct, then the solid particles formed during coagulation (or precipitation) stages unite to form a 'floc'. This may be quite dense and tough but sometimes a coagulant aid may be added to improve the quality of the floc and make it more handleable.

The separation of the floc from the now colourless liquid can be performed in one of two ways : either by direct filtration or, as a two stage process involving sedimentation or flotation followed by rapid sand filters. The choice depends on the overall treatment requirements of the water but two stage treatments offer greater flexibility and control. Further polishing of the water may be effected by using activated carbon, either in powder form as a prefiltration additive or as granules in a separate stage post filtration. Usually the final stage of treatment is disinfection but this is not always the case; lime treatment, again for pH correction and corrosion control, sometimes follows final disinfection though pre-chlorination lime dosing is preferred since chlorination is more effective at low or pH values. It must be remembered that pH correction can be applied at any required stage, eg,with some water containing naturally occurring iron and manganese, pH adjustment may be necessary at several stages in the overall treatment. Using chlorinated copperas as a coagulant, the lower reaction pH enables Fe to be removed and pH adjustment to ~ 8.5 before filtration then precipitates the manganese on the filter sand. This latter reaction is aided by also having an oxidant, such as chlorine or potassium permanganate, present.

Disinfection (1) Chlorine

Chlorine is by far the most widely used disinfectant in the water industry, partly because it is relatively cheap and, with due care, easy to handle but it does have some disadvantages and these will be discussed later.

Basically there are three common methods of chlorination practised in potable water supply treatment, viz:-

(a) marginal chlorination

(b) chloramination (an ammonia-chlorine treatment).

& (c) superchlorination, including breakpoint chlorination.

(a) Marginal chlorination consists simply of the additon of chlorine to water at a controlled dose. This is the process most often adopted with exceedingly pure waters, such as those from boreholes, and the dose is usually very small, of the order of 0.1 - 0.3 mg/ℓ. There are several disadvantages with this process, including; the residual will not persist very far into the distribution system (thus offering no safety factor should there be any disturbance caused by leaks, bursts, etc), it offers no control over taste and odour in the water and, indeed, it may be the cause of complaints of tastes should any phenolic material be present in the water. Some consumers are able to taste pre chlorine levels at levels even as low as 0.05 mg/ℓ

(b) Chloramination

It is well known that chlorine dissociates in water to give HCl & OCl^-, the proportions depending on pH.

Chlorine reacts readily with ammonia in aqueous solution on the intermediary pH range, ie the range in which most of water treatment take place, and may be summarised as :-

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O \qquad \text{(monochloramine)}$$

$$NH_3 + 2HOCl \longrightarrow NHCl_2 + 2H_2O \qquad \text{(dichloramine)}$$

$$NH_3 + 3HOCl \longrightarrow NCl_3 + 3H_2O \qquad \text{(trichloramine or nitrogen trichloride)}$$

Mono - and dichloramine are favoured by the presence of excess ammonia ion but NCl_3 is favoured by excess chlorine. However, pH is also important and, as a general rule, low pH and high initial Cl_2/N_2 level favour the formation of the more highly chlorinated derivatives.

In addition to the effects of pH and concentration of reactants, the contact time and temperature can also have a marked effect on the end products. It has been demonstrated that the lower the temperature, the slower is the bactericidal action. For example, it is reported that "to obtain 100% destruction of E.Coli at 2^{O}-5^{O}C requires three times longer contact time when free chlorine is used at a given residual than is required at 20-25^{O}C while, with chloramines, nine times longer contact is required at the lower temperature or, for a given period, it requires four times as much chlorine or 2½ times as much chloramine to obtain the same bacteriological effect at 2-5^{O}C or at 20-25^{O}C." (Public Health Bulletin 1946).

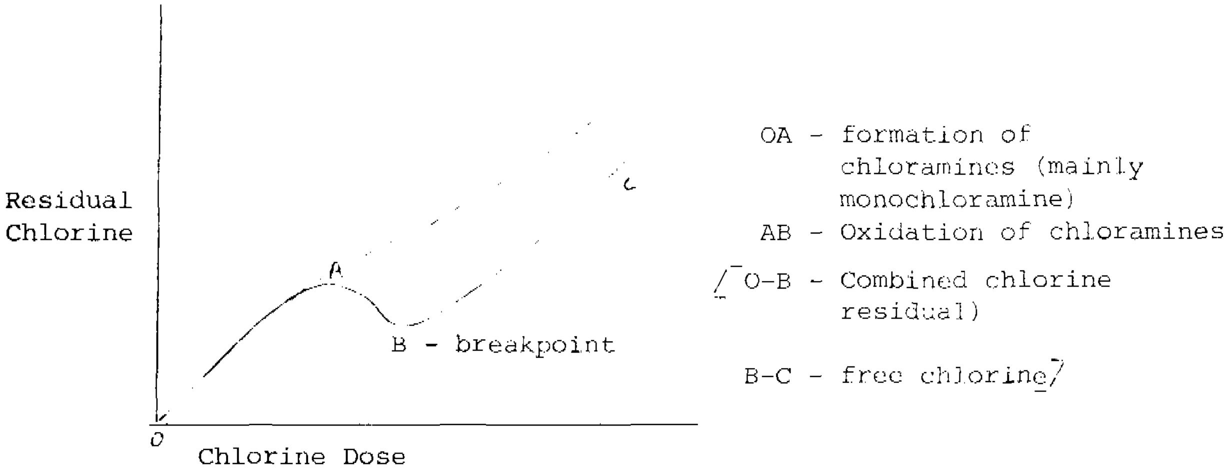
In the chloramination process carried out in potable water treatment, by careful control of chemical doses and with the knowledge of the chemical analysis of the water, only the first two derivatives are formed. Theoretically, for monochloramine, the chlorine/ammonia ratio is 4/1 but, in practice, this naturally varies according to several factors and the usual procedure for chloramination treatment is to add chlorine first so that rapid disinfection can take place and then to 'fix' the residual chlorine with the added ammonia. This procedure is only possible where taste/odour cause no concern: if there are problems, then ammonia may be added first but the bactericidal effects are then somewhat reduced. There are several benefits from this treatment: chloramine residuals are more persistent within the distribution system, thus offering an added microbiological safeguard to water supplies and higher residuals - without accompanying taste complaints - are possible than with free chlorine. The major disadvantage is that the reduced bactericidal effect necessitates longer contact times when compared to straight chlorination.

(c) Super Chlorination

As mentioned earlier, effective disinfection depends on both the agent used and the contact time and, in ideal practice, enough chlorine is added to give a free residual of 0.1-0.3 mg/ℓ after thirty minutes contact. With many badly polluted waters, it is often desirable to add sufficient chlorine to give a much higher residual and then, after contact, to reduce the excess chlorine by sulphur dioxide additions to give the desired chlorine residual to pass into supply.

This method of chlorination is useful for treating waters which are liable to large and sudden variations in chlorine demand. Sometimes, this heavy chlorination is applied to the incoming raw water as the first stage of treatment, thus keeping the sedimentation tanks and filters clear of algal growths and, ideally, giving the desired final chlorine residual in the water leaving the plant - this rarely occurs! Prechlorination can often control the development of objectionable taste and odours but, naturally, this depends on the overall quality of the water being treated.

A more controlled type of superchlorination is known as breakpoint chlorination or, in America, as free residual chlorination.
In this process, sufficient chlorine is added to the water to oxidise all the ammonia present, to satisfy the organic demand of the water and, after an appropriate contact period, to leave a residual of free chlorine. The reactions of chlorine and ammonia were mentioned in (b) but it is necessary to discuss this topic a little further. Assuming the chloramine reaction is the only action taking place, ie, the only reactants are chlorine and ammonia, then the maximum chloramine occurs when the chlorine/nitrogen ratio is about 5:1. The addition of further chlorine oxidises the chloramines until, ultimately (and in theory), the residual reaches zero. (This does not occur in practice since in natural waters the pollutant is not simply pure ammonia) and the chlorine/nitrogen ratio is then about 10:1. The actual ratio is dependent on pH but the addition of yet more chlorine produces what is known as free chlorine.
Fig 1 below summarises this reaction



OA - formation of chloramines (mainly monochloramine)
AB - Oxidation of chloramines
[O-B - Combined chlorine residual)

B-C - free chlorine]

Fig. 1

The breakdown of the chloramines is assumed to take place by the following routes.

$2NH_2Cl + HOCl \longrightarrow N_2 + 3HCl + H_2O$

$2NHCl_2 \longrightarrow N_2 + 2HCl + Cl_2$

$NH_2Cl + NHCl_2 \longrightarrow N_2 + 3HCl$

As indicated above, natural waters contain materials other than ammonia having a chlorine demand so that, in practice, point B of the curve never reaches zero residual but the longer the contact period of the chlorine, the nearer B approaches zero. Interpretation of such results should be based on a working knowledge of the appropriate water treatment process.

It is interesting to note that many Pennine type waters, having high colour and low ammonia, do not exhibit the typical hump and dip breakpoint curve. The residual/dose curve only shows a point of inflexion as indicated by the dotted line in Fig 1.

Superchlorination has some benefits and among these are improved bacteriological quality of the water, improved colour removal, improved cleanliness of plant and control of some tastes and odours. However, it should be remembered that, apart from the increased costs of chemicals and maintenance, other obnoxious tastes and odours can still be produced and, more recently, the demonstration that prechlorination processes can induce trihalomethane production encourages a more careful look at all disinfection, and in particular chlorination, processes.

The ultimate decision on what type of chlorination to use on a particular plant depends primarily on the water quality and the overall water treatment processes necessary. For example, while controlled superchlorination may be highly desirable under certain circumstances, it may prove to be completely uneconomic. Indeed, with some raw waters which may vary markedly and rapidly in quality, it may be impossible to instal equipment suitable for all ranges of doses required. Flexibility on treatment is more important.

Mention has already been made of chlorine reacting with phenolic materials which may be present in the water source to produce the highly objectionable chlorophenol or TCP taste. The options available to potable water suppliers to overcome this difficulty are by treating the water with activated carbon to remove undesirable organics before chlorination, (a method which, apart from expense, may cause other problems, not least on sludge disposal), by altering the existing treatment processes, eg, changing point of chlorine injection, or by changing to other chemical methods of disinfection. The last option is worthy of further consideration.

(2) Other Disinfectants

A simple way of overcoming the formation of TCP is to change from chlorination to chlorine dioxide treatment. Chlorine dioxide being very unstable is produced in situ by reacting chlorine solution with sodium chlorite solution, the resulting solution containing the ClO_2 then being fed direct into the water treatment process. The reaction needs a chlorine solution of not less than 500 mg/ℓ Cl_2 and with a pH not greater than 2.5 and, although the reaction is virtually instantaneous, a mixing time of several minutes is usually allowed.

The chemical reaction is normally represented by

$$2NaClO_2 + Cl_2 \longrightarrow 2NaCl + 2ClO_2$$

In practice, a small excess of chlorine is used.

Apart from its excellent bactericidal properties and the fact that it reacts with phenols, giving no organoleptic intermediates, it has been found useful as an aid to iron and manganese removal. It is also stated to be effective in colour removal, though not as effective as Cl_2, and another benefit is its persistent residual without taste within distribution systems. There appears to be no 'chlorine demand' with water of high ammonia content but, as with other processes, it works best when used on waters after appropriate pretreatment to remove suspended and other undesirable matter. As is expected, ClO_2 is more expensive than Cl_2 but it can satisfy a need. Some concern has been expressed over its use on water treatment and in the food industry for it has been claimed that levels of 0.7 mg/ℓ caused gastro intestinal troubles in laboratory workers. Some investigators have recommended that the residual of chlorite ion should be nil, mainly because of its possible blocking effect on the oxidation of haemoglobin and that effect on young babies - similar to the nitrate/nitrite effects. Despite these reservations, another investigation has recommended its use up to 8 mg/ℓ for controlling actinomycetes in distribution systems! This country has no fixed limit for dose but Western Germany limits its maximum applied dose to 0.3 mg/ℓ.

Ozone is another beneficial disinfectant used in the industry and is invariably produced in situ by passing a high voltage silent electrical discharge through dry air. Because of its corrosive properties, the apparatus used for its production is constructed mainly of stainless steel and glass.

It is very unstable - and therefore highly reactive - and only sparingly - soluble in water, so that difficulties can arise in designing an efficient ozone injection system. There are three main methods :-

(a) using an injection system similar to a laboratory water pump.

(b) using the Kerag system in which ozonised air is injected into the vortex created by a mechanical mixer at the base of a contact column

& (c) using diffusers in the base of a 'contraflow' contact column.

Adequate contact time between ozonised air and the receiving water is essential although the reactions with ozone appear to suggest an 'all or nothing' bacteriocidal effect.

The advantages of ozone use are its extremely good oxidation and bactericidal powers, it is excellent for colour removal and for taste and odour control and the fact that, eventually, the only waste product is oxygen. The disadvantages include the costs of power and equipment.

In this survey of water treatment, mention must be made of the use of UV irradiation for water disinfection. This process can be most effectively used on waters which are free from colour and turbidity but because of limitations of the equipment, it is generally only used for small supplies. Its main advantage to the water industry is that, provided there is a power supply available, attention and running costs are very small.

A more recent innovation has been an attempt to couple UV irradiation with ozone treatment. The process is claimed to be highly effective for colour removal and more economical than the two separate processes though experiments on some waters and effluents in the North of England have not proved successful in the time available to carry out that experimental work.

Summary

This paper has briefly considered aspects of disinfection in present day water treatment but it would be wrong to give the impression that no other work has been or is being done. For example, several years ago, in the days of Civil Defence, a former water undertaking in the North of England performed some work using a manufactured piece of equipment to be run from a car battery for producing chlorine from brine by electrolysis, the resultant chlorine solution (cocktail) being injected direct into small emergency water supplies. The work was reasonably satisfactory but the equipment, being a prototype instrument, suffered from a few minor ailments, not least a suspicion that ozone was being formed along with the chlorine.

Since then, large steps have been made in this field of work and electrolysis of sea water is being utilised for Cl_2 production at power stations. Indeed, one water authority is currently considering the possibility of applying such a process to the chlorination of a long sea sewage outfall:

No reference has been made in this paper to the use of sodium or calcium hypochlorite for, from the author's knowledge, these materials are not widely used on large scale potable water treatment operations in the UK. Sodium hypochlorite is certainly used on some small supplies and apparently will soon become compulsory for treating swimming pools in the near future but, unless new legislation is enacted, the water industry has no intention of utilising swimming pools as sources of water.

A REVIEW OF METHODS FOR DETERMINING LOW LEVELS OF RESIDUAL CHLORINE IN FRESH WATER AND SEA WATER

Dr D. Midgley

Central Electricity Research Laboratories, Kelvin Avenue,
Leatherhead, Surrey

Analytical methods for residual chlorine have mainly been developed so that the concentration of chlorine added as a biocide to drinking water, swimming pools and industrial cooling water can be controlled at an effective level without wasting reagent. Concern for the environment has led to a demand for more sensitive methods that are suitable for analysing discharges and receiving waters, since levels of 50 $\mu g\ l^{-1}$ or less are still toxic to some organisms, depending on the duration of exposure. Methods for determining 5 $\mu g\ l^{-1}$ are needed.

Before discussing the performance of different analytical methods for determining residual chlorine, it is necessary to establish which are the chemical species whose concentrations we wish to measure. A reaction scheme is shown in Fig. 1.

Gaseous chlorine, on addition to water, hydrolyses to hypochlorous acid and hypochlorite.

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl \rightleftarrows OCl^- + H^+$$

Unless the pH is below 3, the concentration of molecular chlorine is negligible and the active oxidizing agent or biocide is HOCl.

Hypochlorous acid can react with ammonia to give a series of chloramines (NH_2Cl, $NHCl_2$, NCl_3) which also have oxidising and biocidal properties but react more slowly than HOCl or Cl_2.

In fresh waters it is usual to classify the oxidising species as "free residual chlorine" (Cl_2 + HOCl + OCl^-), and "combined residual chlorine" (NH_2Cl + $NHCl_2$ + NCl_3 + organic N-chloramino compounds). The "total residual chlorine" is the sum of the two.

Except in direct amperometry, free residual chlorine is found by measuring the extent of oxidation of a specified reagent in a specified time. Combined residual chlorine oxidizes the same reagents, but more slowly, and will generally interfere to some extent with measurements of the free residual. Both free and combined residual chlorine oxidize iodide to iodine: thus adding an excess of iodide to the sample and measuring the concentration of iodine formed gives the total residual chlorine, leaving the combined residual to be calculated by difference. (One of the amperometric membrane probes (see below) is intended to determine combined residuals directly, but its utility remains to be confirmed in practice.) The presence of other substances that oxidize iodide will result in an overestimate of the total residual chlorine whatever the method of detection. The most common interferents are Cu^{2+}, Fe^{3+}, Mn^{3+}, MnO_4^- and IO_3^-; some of these also interfere in some methods for determining free residuals.

While categories of free and combined residuals have been found useful in fresh waters, the chemistry is more complicated in sea water and estuarine waters. The bromide in sea water (∿70 μg ml^{-1}) is oxidized by chlorine and hypochlorous acid to bromine and hypobromous acid, which react with ammonia to form bromamines.

In the low-level chlorination of sea water, therefore, the "residual chlorine" consists of bromine-containing species and the term "residual oxidants" would be less misleading. Moreover, the bromamines are more active oxidizing agents and biocides than the chloramines and the "combined residual" category is of doubtful utility in sea water chlorination.

The high halide ion concentration in sea water enables complexes such as Br_2Cl^- and $BrCl_2^-$ to be formed: in electrochemical methods of analysis the existence of these complexes can greatly complicate the interpretation of measurements in sea water and even more so in estuarine waters, where the halide concentration and, hence the extent of complex formation, is subject to tidal variation.

In considering methods for determining residual oxidants, we should take into account their discrimination between free and combined residuals, their performance with fresh and saline samples and their applicability to measurements in situ (with either portable or permanently installed and continuously operating apparatus). The last feature is important because in the time taken to carry a sample back to the laboratory the level of residual chlorine may fall (at a rate dependent on the nature of the sample). The methods are divided between colorimetric and electrochemical techniques.

COLORIMETRIC METHODS

In colorimetry the residual chlorine oxidizes an organic reagent (usually an amino-substituted aromatic compound) to give a coloured product, the intensity of the colour produced being proportional to the concentration of oxidant originally present. Colorimetric methods have been described in standard analytical texts[1] and reviewed by Palin[2]. Extensive comparative studies of methods for determining free residual chlorine in fresh waters have been carried out[3,4]. The most commonly used reagents are o-tolidine (OT or SNORT), N,N-diethyl-p-phenylenediamine (DPD), leuco crystal violet (LCV) and syringaldazine (FACTS). o-tolidine has the longest history of use, but it is now known to be carcinogenic and is no longer used in the United Kingdom. Tests[1,3,4] show that the newer reagents are at least as good as o-tolidine. LCV and FACTS have not been used as extensively as DPD, which is now established as the most commonly used reagent for residual chlorine. DPD can be bought as the sulphate salt (B.D.H.) and prepared as a reagent solution for colorimetric or spectrophotometric methods. In a buffer at pH 7, DPD reacts with free residual chlorine and after addition of potassium iodide and a lowering of the pH to 4 DPD reacts also with the combined residual. All the reagents for the DPD methods are available in tablet form (B.D.H., Wilkinson and Simpson Ltd.) for addition to a standard volume of sample. The method has been adapted for use with colour comparators, in which the residual chlorine concentration is estimated to within 0.1 μg ml^{-1} by visual comparison of the colour of the solution with a series of standard coloured glass discs (B.D.H., Gallenkamp, Tintometer, Wallace and Tiernan).

Although the comparator is not capable of the precision and accuracy of a colorimeter or spectrophotometer, its portability makes it suitable for field work, so that samples can be analysed almost immediately and, therefore, without significant decay of the chlorine residual. The comparator also has the advantage of being simple and inexpensive (less than £50).

Reports of the performance characteristics of continuous colorimetric analysis of chlorinated water have not been found in the literature, although at least one company (Bran and Luebbe) make a water analyzer using colorimetric reagents for determining chlorine. With turbid waters, fouling of the optical cell may cause errors in such systems. Another problem is the instability of the organic reagents in solution, but sufficiently regular servicing of the system would ensure that errors from this source were kept within tolerable limits. Reports[3,5] of the stability of DPD solutions are variable, but solutions should be usable for 7 days at least. There is also a continuous colorimetric system for determining chlorine in air (Telsec Process Analysers); this measures the extent of bleaching of a methyl orange solution and it seems possible that it might be adapted to water analysis.

The discrimination between free and combined residuals which is observed in fresh waters is often reduced in saline waters, thus with DPD 90% of monochloramine added to sea water appeared in the free residual fraction[6] and the high selectivity[4] of syringaldazine for free residual chlorine is lost in sea water[5].

Although Nicolson[3] reported very low limits of detection for various colorimetric systems in laboratory conditions, a more realistic[5,6] limit is probably about 50-100 μg l^{-1}. With this limit the methods would usually be adequate for monitoring chlorine dosing but not for montoring levels that may be set to meet environmental requirements[7,8].

ELECTROCHEMICAL METHODS

Amperometric methods have been in use since the 1950s, but recently they have been considerably improved and two new techniques, potentiometry and differential pulse polarography, have been introduced.

Amperometric Titration

Amperometric titration[3,5,9-15] is accepted as the best method because of its ability to discriminate between free and combined residuals (in fresh waters) and because it is sensitive enough to detect low levels of residual chlorine (∿2 μg l^{-1}). More skill and experience is needed in this method than in the others discussed, since, even though it is possible to carry out the titration automatically[5], the titration curve still has to be interpreted by the analyst.

Titrimetry gives more precise results than direct-reading methods such as amperometry and potentiometry, but is more time-consuming and cannot be used for continuous analysis.

Simple amperometric titrators have been available for over 20 years and consist of a platinum electrode in series with a reference electrode and a microammeter. The chlorine residual diffuses to the platinum electrode (as HOCl or I_2 depending on whether the free or total residual is being determined), is reduced and thereby produces a current. As phenylarsenoxide titrant is added, the chlorine residual is consumed and the current falls. When the microammeter reading stops falling, the end-point is assumed to have been reached. At concentrations greater than about 100 $\mu g\ l^{-1}$ this dead-stop end-point is distinct, but as the concentration decreases the end-point becomes harder to detect. This is shown by plotting the current against the volume of titrant as in Fig. 2. Extrapolating the two linear portions of the titration curve gives the end-point as the intersection of the two straight lines. Connecting the apparatus to a chart recorder is a help in detecting the end-point, but this is not always possible with the simpler titrators. More recently, polarographs have been used with stationary platinum electrodes[9-11,15], but no increase in sensitivity has been demonstrated with this expensive apparatus over that achieved with simple apparatus connected to a chart recorder[12]. Metals such as Cu^{2+} and Fe^{3+} interfere, but can be masked by the addition of pyrophosphate[15].

In sea water the distribution between free and combined residuals is not maintained[5] because bromamines react partially as free residual chlorine.

Simple portable titrators[14] are available from Fischer and Porter and Wallace and Tiernan, making field-work possible, if inconvenient compared with direct-reading methods. Some types of more advanced apparatus can be run off a 12 V battery[5] but, with the additional weight and bulk of chart recorders, piston burettes and other items, portability is likely to be restricted. Since PAO is stable in solution[5], it should be possible to add a known quantity (in excess) at the time of sampling and then determine the unreacted PAO in the laboratory by titration with standard iodine solution. This gives the total residual chlorine by back-titration.

Direct-reading Amperometric Monitors

Amperometric instruments have been used for continuous on-line monitoring for over 20 years, but measurements in sea water have usually been unsatisfactory. Instruments are available from Wallace and Tiernan, Fischer and Porter, Capital Controls, Portacel Ltd. and Delta Scientific.

The simplest form of apparatus is galvanic, i.e. it generates a current without an external e.m.f. being imposed. A gold or platinum cathode and a copper anode are immersed in the chlorinated solution, HOCl diffuses to the cathode and is reduced, the resultant current being proportional to the HOCl concentration. Hypochlorite ion is not reduced at the cathode and in order to relate the current to the free residual chlorine a buffer is added to keep the pH constant. Metals such as Cu^{2+}, Fe^{3+} and Mn^{3+} interfere, but these could probably be masked by pyrophosphate[15]. In sea water, oxygen causes a corrosion current and the results are useless.

By imposing a potential on the electrodes and adding a buffered solution of potassium bromide so that HOBr was formed from the HOCl, Morrow and Roop[16] measured free residual chlorine in sea water. At a different applied potential and with the addition of potassium iodide instead of bromide, total residual chlorine can be determined. These features are incorporated in industrial on-line monitors made by Fischer and Porter.

The latest development in amperometric sensors is the membrane probe developed by Johnson[17] and made by Delta Scientific. This has a gold cathode covered by a microporous PTFE membrane which separates the electrode from the sample solution. Between the electrode and the membrane is a thin film of solution containing potassium chloride (for a high conductivity) and a pH buffer. The membrane only allows non-ionic species to pass, so metal ions cannot interfere. Johnson's intention was that the probe could be immersed directly in the chlorinated water, where it would respond only to HOCl because hypochlorite ion cannot cross the membrane. The probe would then give a measure of effective disinfectant power, because OCl^- is scarcely an effective biocide.

In order that the output of the probe can be related to the conventional free residual chlorine, the sample is treated with a buffer so that the HOCl is a constant proportion of the free residual chlorine. The probe is, however, more sensitive to hypobromous acid than to hypochlorous acid[18] and therefore has different calibrations in fresh and sea water. Moreover, the probe's response also depends on salinity[18], which means that in estuarine waters frequent recalibration would be necessary.

The performance has been improved by adding an excess of bromide to the sample and changing the filling solution inside the probe[19]. With these modifications, the probe's response is almost independent of salinity and gives a limit of detection of 20 $\mu g\ l^{-1}$ free residual chlorine. Combined residual chlorine does, however, interfere with these measurements. With iodide added to the sample and an iodide-containing filling solution, a probe is obtained that responds to total residual chlorine with a limit of detection of 20-30 $\mu g\ l^{-1}$. Delta Scientific also make a probe responding to combined residual chlorine, but so far experience has shown that its response is very slow.

The probe can be used with both portable and on-line instrumentation and in one application in fresh water with a high suspended solids content continued to work when other instruments had become fouled. In comparative tests on inland waters[15], the probe agreed closely with the amperometric titration method and was preferred to an amperometric analyzer without a membrane and to the potentiometric electrode.

While the probe needs a more effective means of temperature compensation[18,20], it has promise for many applications because of its comparative freedom from fouling, its portability and its ability to work in sea water, although modifications to the commercial form of the probe would improve the performance, as discussed above.

Potentiometry

A new ion-selective electrode (Orion 97-70) consists of a platinum electrode and an iodide-selective membrane electrode mounted on a common stem, like a combination pH electrode. The electrode is connected to a pH or specific-ion meter. The electrode potential is proportional to the logarithm of the concentration of iodine produced when an excess of iodide is added to the chlorinated water.

$$E = \text{Constant} + k \log [I_2]$$

where k ≃ 30 mV for a tenfold change in concentration is a constant at a given temperature.

Almost theoretical responses have been reported[9,21] in fresh and sea waters at levels below 10 $\mu g\ l^{-1}$, while the manufacturers claim that this response extends to 1 $\mu g\ l^{-1}$ in a continuous flow-through apparatus for industrial use (Orion Chlorine SLeD). In tests at the Tennessee Valley Authority, the Orion continuous system gave low results.

The present system for dosing the sample with iodide may be prone to fouling in hard waters or sea water, but ways of avoiding this could be found and there should be no problem in the analysis of discrete samples. In waste water analysis[22], the electrode agreed closely with the amperometric titration above 1 $\mu g\ ml^{-1}$ and was preferred at lower concentrations. The electrode can be used with portable pH meters that are available from many sources and is, therefore, particularly promising as a means of determining low levels of total residual chlorine in the field. The method does not permit the discrimination of free and combined residuals.

Differential Pulse Polarography

If an excess of phenylarsenoxide (PAO) is added to a portion of chlorinated water, the unreacted PAO can be determined by differential pulse polarography at the hanging mercury drop electrode[23]. Reaction at pH 7 gives the free residual and reaction at pH 4 in the presence of iodide, the total residual. The difference in peak current between the sample solution and a blank solution indicates the quantity of PAO consumed and, hence, the residual chlorine.

The method is very sensitive, having a limit of detection of 2 $\mu g\ l^{-1}$, but is neither portable nor readily adapted to continuous monitoring. The excess of PAO is stable for at least 24 h in tap[23] and brackish[5] waters; if the PAO is added at the time of sampling, analysis may be deferred until a return to the laboratory.

Results have been reported[23] for drinking water and sewage effluent, but tests are needed in sea water.

DISCUSSION

There are several methods capable of determining free and total residual chlorine in fresh waters in the concentration range expected of the treated water (0.1-5 $\mu g\ ml^{-1}$). Except for differential pulse polarography, all the methods can be made portable. Amperometry and potentiometry are the two most suitable methods for on-line analysis.

Environmental monitoring[7,8] may involve levels down to 5 $\mu g\ l^{-1}$. Measurements at such levels have been claimed for amperometric titration, differential pulse polarography and potentiometry (for total residual chlorine only); amperometric titration is the best-documented of the methods at this level.

There is little to suggest that any method can accurately discriminate between free and combined residual in sea water and the need for such discrimination is uncertain in view of the high activity of the bromamines compared with the chloramines obtained in fresh water.

Total residual chlorine seems to be the least ambiguous measure of oxidant concentration in sea water, but its determination is subject to systematic error from the iodate naturally present in sea water at levels of about 50 $\mu g\ l^{-1}$ (equivalent to about 60 $\mu g\ l^{-1}$ chlorine). When iodide is added to the sea water in the procedure for the determination of total residual chlorine, it is oxidized by iodate to iodine.

$$IO_3^- + I^- + 6H^+ \rightarrow 3I_2 + 2H_2O$$

Although the reaction may not go to completion during the analysis for total residual chlorine, enough iodine is likely to be produced to bias measurements below 100 $\mu g\ l^{-1}$. Wong[24] recommends adding iodide to the sample first, followed by the pH 4 buffer no more than 1 min later, so that the error is minimized.

REFERENCES

1. "Standard Methods for the Examination of Water and Waste Water", 14th edn., American Public Health Association, Washington D.C., 1975.

2. A.T. Palin, 'Water Disinfection - Chemical Aspects and Analytical Control' in "Disinfection, Water and Wastewater", (J.D. Johnson, ed.), Ann Arbor Science Publishers, Ann Arbor, 1975, p.67.

3. N.J. Nicolson, Analyst, 1965, 90, 187. 'An Evaluation of the Methods for Determining Residual Chlorine in Water'.

4. C. Sorber, W. Cooper and E. Meier, 'Selection of a Field Method for Free Available Chlorine' in "Disinfection, Water and Wastewater", (J.D. Johnson, ed.), Ann Arbor Science Publishers, Ann Arbor, 1975, p.91.

5. G.R. Helz, J.W. Gretz, P. Higgins, J.C. Peterson, A.C. Siglio and R. Sugam, EPRI EA-929, 'Survey of Chlorine Analytical Methods Suitable for the Power Industry', Electric Power Research Institute, Palo Alto, 1978.

6. N.A. Dimmock and G.I. Goodfellow (Central Electricity Research Laboratories, Leatherhead), unpublished work.

7. Official Journal of the European Communities No. L222 (14.8.78). 'Council Directive of 18 July 1978 on the Quality of Fresh Waters Needing Protection or Improvement in order to Support Fish Life'.

8. R.N. Roop, 'Chlorination Residual Measurement and Control of Dechlorination Processes', Proc. 3rd Annu. Pollut. Control Conf., 1-4 April 1975, Ann Arbor Science Publishers, Ann Arbor, 1975, p.607.

9. G. Scarano and M.G. Saroglia, 'Residual Chlorine Analysis: a Comparison between Amperometric and Potentiometric Methods', Condenser Biofouling Control Symposium, Atlanta, Ga., 1979.

10. J.A. Grieve, L.E. Johnston, T.G. Dunstall and J. Minor, 'A Program to Introduce Site-specific Chlorination Regimes at Ontario Hydro Generating Stations' in "Water Chlorination, Environmental Impact and Health Effects, Vol. 2", (R.L. Jolley, H. Gorchev and D.H. Hamilton, eds.), Ann Arbor Science Publishers, Ann Arbor, 1978, p.77.

11. A.S. Brooks and G.L. Seegert, *J. Water Pollut. Control Fed.*, 1979, *51*, 2636. 'Low-level Chlorine Analysis by Amperometric Titration'.

12. J.T. Payne, *J. Water Pollut. Control Fed.*, 1979, *51*, 2540. 'Performance Characteristics of an Amperometric Titrator'.

13. R.M. Manabe, EPA-660/2-73-039, 'Measurement of Residual Chlorine Levels in Cooling Water - Amperometric Method', U.S. Government Printing Office, Washington, D.C., 1974.

14. J.J. Morrow, *J. Am. Water Works Assoc.*, 1966, *58*, 363. 'Residual-Chlorine Determination with Dual Polarizable Electrodes'.

15. C.V. Seaman, H.B. Flora and R.A. Hiltunen (Tennessee Valley Authority, Chattanooga), unpublished work.

16. J.J. Morrow and R.N. Roop, *J. Am. Water Works Assoc.*, 1975, *67*, 184. 'Advances in Chlorine-Residual Analysis'.

17. J.D. Johnson, J.W. Edwards and F. Keeslar, *J. Am. Water Works Assoc.*, 1978, *70*, 341. 'Chlorine Residual Measurement Cell: the HOCl Membrane Electrode'.

18. N.A. Dimmock and D. Midgley, *Water Res.*, 1979, *13*, 1101. 'Assessment of an Amperometric Membrane Probe for Determining Free Residual Chlorine in Saline Cooling Waters'.

19. N.A. Dimmock and D. Midgley, *Water Res.*, 1979, *13*, 1317. 'Modified Amperometric Membrane Probes for Determining Free and Total Residual Chlorine in Saline Cooling Waters'.

20. P. Fischer and E. Thofern, Zbl. Bakt. Hyg., 1977, B164, 549. 'Zur Chlorbestimmung mit einer polarographischen Sonde'.

21. L.P. Rigdon, G.J. Moody and J.W. Frazer, Anal. Chem., 1978, 50, 465. 'Determination of Residual Chlorine in Water with Computer Automation and a Residual-Chlorine Electrode'.

22. R.L. Jenkins and R.B. Baird, Anal. Lett., 1979, 12, 125. 'Determination of Total Chlorine Residual in Treated Wastewaters by Electrode'.

23. R.B. Smart, J.H. Lowry and K.H. Mancy, Environ. Sci. Technol., 1979, 13, 89. 'Analysis for Ozone and Residual Chlorine by Differential Pulse Polarography of Phenylarsine Oxide'.

24. G.T.F. Wong, Water Res., 1980, 14, 51. 'Some Problems in the Determination of Total Residual "Chlorine" in Chlorinated Sea-water'.

ACKNOWLEDGEMENT

Published with the permission of the Central Electricity Generating Board.

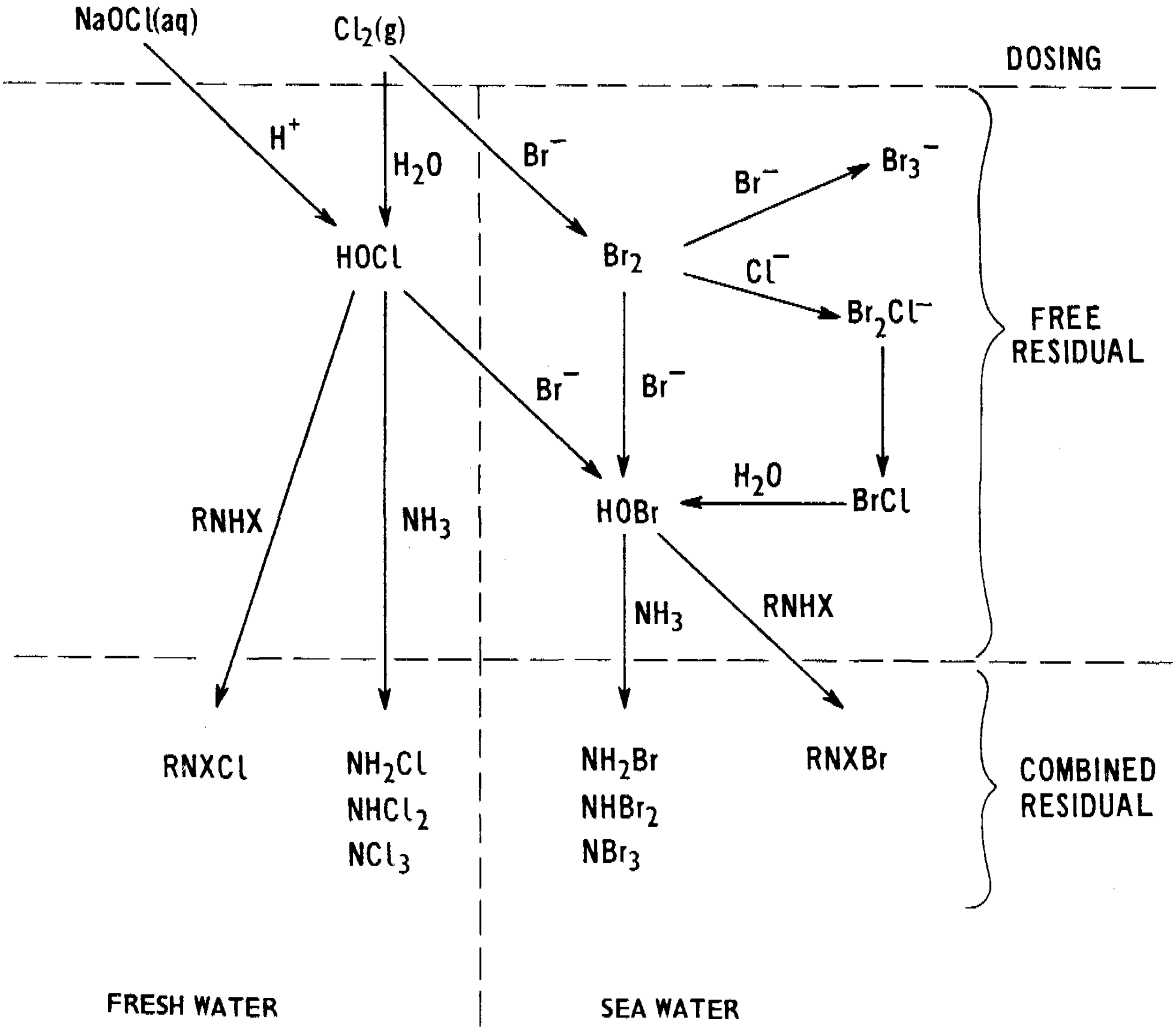


FIG. 1 REACTION SCHEME FOR CHLORINATION OF FRESH AND SEA WATER

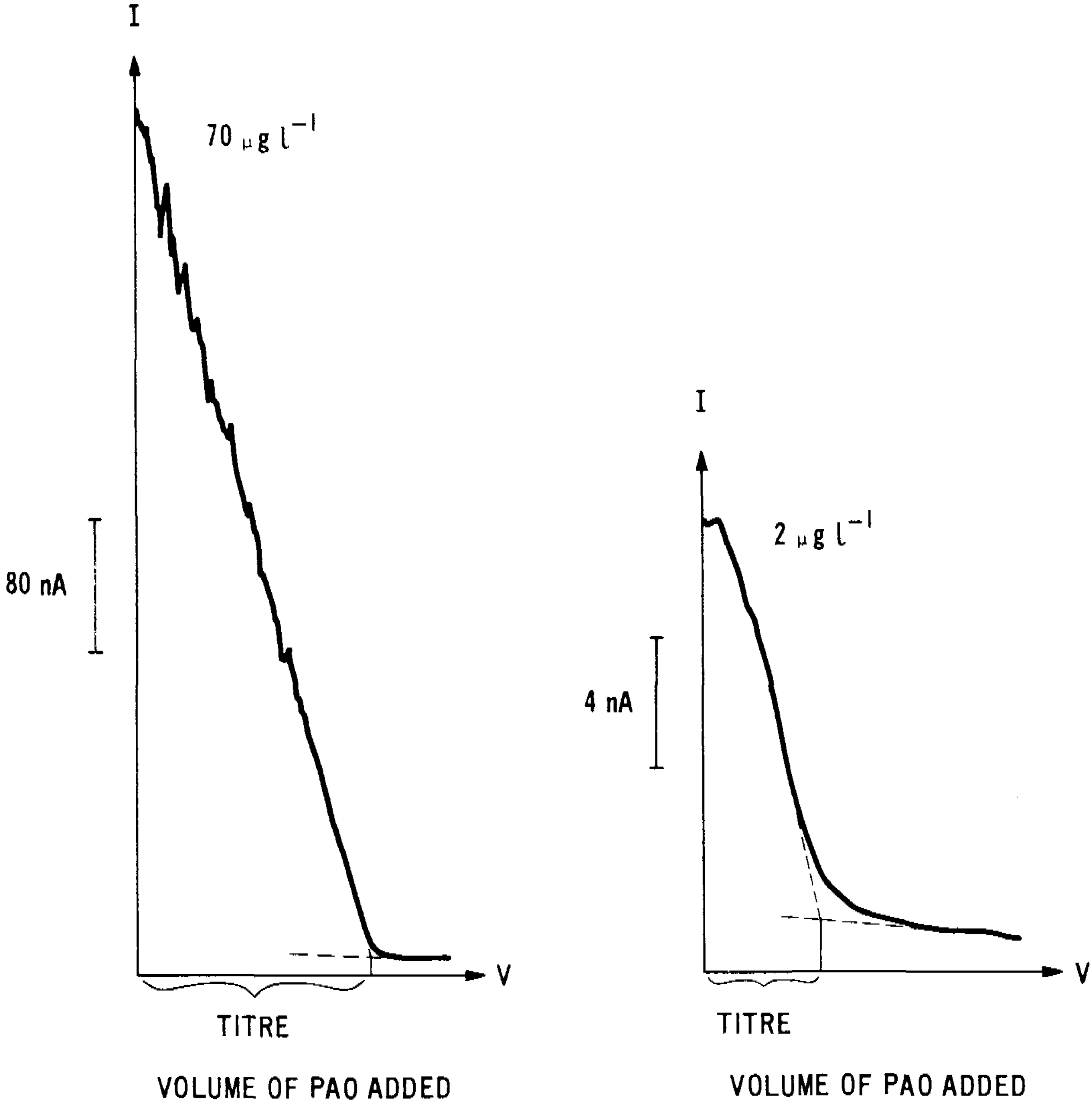


FIG. 2 AMPEROMETRIC TITRATION CURVES

APPENDIX

Addresses of Manufacturers and Suppliers of Chlorine Analytical Instruments.

B.D.H. Chemicals Ltd., Broom Road, Poole, Dorset BH12 4NN,
Tel. Parkstone (0202) 745520.

Bran and Luebbe (GB) Ltd., Scaldwell Road, Brixworth, Northants NN6 9EN,
Tel. (0604) 880751.

Capital Controls, Sittingbourne Industrial Park, Crown Quay Lane,
Sittingbourne, Kent ME10 3JG, Tel. Sittingbourne (0795) 76241.

Delta Scientific, Hauppauge, New York. Agents: Centronic Sales Ltd.,
Centronic House, King Henry's Drive, New Addington, Croydon CR9 0BG,
Tel. Lodge Hill (0689) 47021.

Fischer and Porter Ltd., Salterbeck Trading Estate, Workington,
Cumbria CA14 5DS, Tel. Harrington (0946) 830 611.

Gallenkamp and Co. Ltd., P.O. Box 290, Technico House, Christopher Street,
London EC2P 2ER, Tel. 01-247 3211.

Orion Research Inc., Cambridge, Mass. Agents: Serck Glocon, Eastern
Avenue, Gloucester GL4 7BZ, Tel. 0452 28631.

Portacel Ltd., Cannon Lane, Tonbridge, Kent TN9 1PP, Tel. Tonbridge
(07322) 64411.

Telsec Process Analysers Ltd., Orton Southgate Industrial Estate,
P.O. Box 41, Peterborough, PE2 0SE, Tel. Peterborough (0733) 235500.

The Tintometer Ltd., Waterloo Road, Salisbury SP1 2JY, Tel. Salisbury
27242.

Wallace and Tiernan Ltd., Priory Works, Tonbridge, Kent TN11 0QL,
Tel. Tonbridge (07322) 4481

Wilkinson and Simpson Ltd., 57 Queensway, Team Valley Trading Estate,
Gateshead, NE11 0NS, Tel. (0632) 872164.

ANODE MATERIALS FOR USE IN THE GENERATION OF SODIUM HYPOCHLORITE

P N Richards : IMI Research and Development Dept.
P C S Hayfield : " " " " "
W R Jacob : IMI Marston Ltd

INTRODUCTION

The present paper is concerned with experience gained in electrochlorinators using two particular anode coatings, platinum electroplate and thermally-formed 70/30 platinum/iridium. It is well known that ruthenium dioxide-type electrodes also find use in electrochlorinators but such types fall outside the scope of the present paper.

Platinum electroplated titanium was first described in 1957 by Cotton et al (1). The technology of manufacture was based upon electrodeposition of platinum from a hexa-hydroxyplatinate bath onto a titanium surface which had been etched in hydrochloric acid at room temperature. This is one of several platinum electroplating solutions known (2) and used for electrode manufacture. The early material found immediate use in cathodic protection duties, and over the next 5 years was introduced into small capacity electrochlorinators of up to ½ kg/hr equivalent chlorine capacity. Such a device is illustrated in Cotton and Wood's paper of 1963 (3).

In the early 1960's extensive trials were undertaken with a 45 kg/hr capacity unit, using platinum electroplated titanium anodes, for disinfecting cooling water for a power station. The electrolyser was of bipolar construction, with the platinum applied to the anode side and the cathode remaining 'bare' titanium. This electrochlorinator plant was not maintained in commercial operation, but a great deal of valuable practical experience was accumulated over its working life. This included :

i) The necessity to prevent excessive build-up of calcium and magnesium deposits on cathodes, which otherwise could cause restricted flow of electrolyte, inter cell blockages and consequent serious damage to anode coatings.

ii) Warping of bipolar titanium electrodes due to hydriding of the cathode face.

iii) Evidence for increased platinum coating loss with decreasing seawater temperature.

Coatings of 70/30 platinum/iridium, both electroplated and thermally produced, were also tested over short periods at that time; ruthenium dioxide-based coatings were not then available.

It is a widely held view that the early operating problems experienced with this large scale electrochlorinator, although eventually overcome, did much to set back wide scale exploitation of seawater electrochlorination for at least a decade.

In the ensuing years there appeared, principally in the UK, a range of different designs of mainly small capacity systems. Most of these used platinum electroplated titanium anodes and, apart from swimming pool electrolysers, were of bipolar construction. The primary aim of the designs was to produce an economically viable, maintenance-free, 'clean' cell. It is interesting to list the various approaches adopted to achieve this end, which included :

i Pretreatment of seawater to remove calcium and magnesium.

ii Use of fast linear electrolyte flow (6 m/sec or higher).

iii Promotion of electrolyte turbulence.

iv Introduction of periodic cleaning by either mechanical or chemical methods, or a combination of both.

v Use of current reversal.

vi Doing nothing .... as with some swimming pool electrolysers.

Within the last 5 to 7 years, and especially as hypochlorite demand for disinfection purposes has increased and bans or restrictions have seemed likely on the transport of bulk liquid chlorine, a range of new criteria for cell operation has appeared, over and above the need to keep cells 'clean'. These include :

1 A need to operate without restriction on minimum seawater temperature.

2 A need to tolerate seawater dilution in estuarine conditions.

3 An ability to run discontinuously.

4 High current efficiency for hypochlorite generation.

5 Low operating (power) costs.

6 Low capital cost.

It is against the aforementioned background that this paper discusses the characteristics of two forms of anode coating, namely platinum electroplate and thermally-formed 70/30 platinum/iridium.

PLATINUM ELECTROPLATED TITANIUM

This is now such an established anode material that it might seem unnecessary to provide any description. Basically, titanium, like aluminium, is difficult to electroplate. Since platinised titanium was first made over 20 years ago, the method of platinising has undergone some important changes, so that the material marketed today does not bear much resemblance to that available in the early 1960's. The coating is still high purity platinum deposited electrolytically, containing some dissolved hydrogen. Attention to plating techniques now ensures high levels of adhesion, minimum porosity and uniformity of deposition for a variety of shapes. Methods developed and now used by IMI Marston (4) involve the production of an electrically conductive surface on the titanium prior to platinum deposition. This ensures uniformity of plating right from the start of the process and hence minimises porosity for a given thickness of platinum. These improvements are reflected in the scanning electron micrographs of Figs 1 and 2. An additional benefit from the pre-treatment of the titanium is superior resistance to acid attack of the substrate leading to undermining and premature loss of the platinum, see Fig 3.

THERMALLY PRODUCED 70/30 PLATINUM/IRIDIUM ON TITANIUM

The most commonly used 70/30 Pt/Ir coating is deposited from an organo-metallic compound. Coatings of the same composition can be deposited by other thermal decomposition routes and have significantly different characteristics.

The exact method of application and thermal decomposition of the Pt/Ir paint by our own Company is proprietary, but the principal features are the preparation of coatings by a series of paint applications, each of which is separately stoved. Thermally-formed coatings are made more adherent by applying to a chemically etched titanium substrate rather than to the relatively smooth surface of rolled, annealed and chemically descaled (pickled) titanium sheet.

COATING THICKNESS

Historically, platinum electroplate coatings have been described in terms of thickness, microinches or microns, assuming a flat surface ie plan surface area. The fact that coatings are always applied to roughened surfaces means that the true thickness is always less than that calculated on the basis of geometric surface area.

Thermally decomposed coatings, due to their high active surface area, are best defined in terms of noble metal loading expressed as g/m^2 of geometric surface area. To assist comparison of the two types of coating, thicknesses and loadings of typical electrochlorinator anodes are given in Table I below :

Coating	Thickness per plan surface area		Loading, g/m^2 plan surface area
	Imperial units (microinches)	Metric units (microns)	
Platinum electroplate	100	2.5	55
Thermally-formed 70/30 platinum/iridium	55*	1.4*	30

*Actual thickness greater due to the porous nature of the coating.

Platinum electroplate can be applied up to a thickness of 300 micro-inches (7½ microns) by conventional means or to 10 to 15 microns by special processes. Thermally decomposed 70/30 Pt/Ir has been manufactured at up to 100 g/m^2 loading. Even at such very high loading the coating is still strongly adherent, but the process is time consuming and therefore costly.

ELECTROCHEMICAL PROPERTIES

Overpotential characteristics

At current densities up to 10 KA/m^2 the chlorine overpotential is high for platinum electroplate and very low for 70/30 platinum/iridium, see Fig 4. At 2 kA/m^2 current density, for example, the respective values are approximately 700 and 80 millivolts.

A commonly used criterion in the application of anodes is the difference in electrode potential between operation in chlorine and oxygen evolving situations, because this provides an indication of likely behaviour in service. Arbitrarily we take this as the difference in electrode potential, both expressed with respect to nHE, between the following conditions :

1 M sulphuric acid at 25 to 30°C and 1.5 kA/m^2 current density.

Saturated brine at 70°C, and also 1.5 KA/m^2 current density.

The quantity provides a convenient assessment of the relative propensity of an electrode to evolve oxygen in a chloride environment, see Fig 5. Pure ruthenium dioxide, for example, has a very low oxygen overpotential as well as a low chlorine value, and hence the O_2-Cl_2 value is low - less than 300 mV. Both Pt and Pt/Ir have high oxygen overpotentials, and generally the O_2-Cl_2 values are considerably higher than for pure ruthenium dioxide. Some quantitative data for samples in brine at different temperatures and concentrations are given in Table II. High values of this parameter lead to good operating current efficiencies in hypochlorite generation which can assume considerable importance with diluted seawater, as in estuary applications.

LABORATORY EVALUATION OF COATINGS FOR ELECTROCHLORINATOR APPLICATION

Experimental arrangements

A The simplest, least controlled of tests consisted of samples held between two perspex plates, and suspended as an undivided cell in a large tank of brine, hydrogen evolution from the cathode provided gas lift to give a measure of liquor circulation.

B A second experimental arrangement involved two plate electrodes, 15 mm wide by 40 mm high, set 1 to 2 mm apart in the flow path of a gas lift circulation system. Temperature could be controlled by immersing the electrolyte reservoir in a freezer cabinet. Electrolyte, usually 3% sodium chloride, could be adjusted to circa pH 7 to 8 by acid dosing via a dripping funnel set into a gas separating part of the apparatus, see Fig 6. Air was used for the gas lift.

C In the third apparatus, see Fig 7, liquor from a reservoir was pumped through mono or bipolar cells at rates that could be controlled and measured. Variables included brine strength, temperature and pH. Measurements were made of cell voltage and current, electrolyte flow rate, temperature and available chlorine content. Evolved gases were also analysed. Brine flow could be either single pass or recirculated.

Influence of temperature

Using experimental test A, wear rate data were obtained for MA platinum electroplate and K-type 70/30 platinum/iridium in 3% sodium chloride at 5°C, results being summarised in Fig 8. The platinum coating wore uniformly at a corrosion rate of ~ 1 micro-gram/Amp hr. In marked contrast the 70/30 Pt/Ir coating began with a slow corrosion rate, which increased dramatically later in the experiment. This deterioration proved to be mechanical loss of coating due to corrosion of the titanium substrate and subsequent loss of coating adhesion.

More extensive experimental results were obtained using experimental test B, some with electrolyte at 20°C and others in the range 1 to 5°C, for periods of up to 2 months. A variety of substrates was investigated, including titanium, titanium-15% molybdenum, niobium and tantalum, coated with either platinum electroplate or thermally formed 70/30 Pt/Ir. Samples of solid platinum and the alloy 70/30 Pt/Ir were also investigated. Principal findings were :

i) As coating of either type corroded, substrate became exposed and in the latter stages of anode life corrosion of the substrate lead to coating loss by undermining. Titanium-molybdenum (15%, IMI Ti 205) and niobium were superior to titanium but not devoid of a slow loss of coating adhesion. Only coatings applied to tantalum remained fully adherent during long term electrolysis.

ii) Of the solid noble metals evaluated, the lowest anodic corrosion rates were obtained with pure platinum. This may have in part been due to the better metallurgical condition of the platinum; the Pt/Ir alloy showed metallurgical defects which may have been due to processing of a very small ingot of starting material. The anodic corrosion rate of solid platinum at 3°C was 2.2 micrograms/Amp hr, see Fig 9, which is little higher than the levels of 1 to 2 micrograms/Amp hr, measured in electrolyte at circa 20°C.

iii) The platinum plated coatings were thicker and less porous than the thermally produced coatings.

Using a cell of five bipolar electrodes in experimental test type C, shorter-term experiments were conducted using both types of coated titanium anode. Corrosion rate data for simulated seawater at 8°C and 22°C are contained in Figs 10 and 11, providing a clear indication that durability of the platinum electroplate coating is relatively insensitive to temperature, whereas there is a greater dependency with the thermally deposited Pt/Ir coating.

Cell chemistry effects

Other experimental data collected included :

i) Influence of brine inlet temperature and flow rate on evolved oxygen for a constant current density of 2.5 kA/m^2 (250 Amp/ft^2), see Fig 12.

ii) Relative electrode potentials under conditions of oxygen and chlorine evolution for platinum electroplate coatings in a standard overpotential measurement cell, see Fig 13.

iii) Relative electrode potentials under conditions of oxygen and chlorine evolution for platinum electroplate coatings but taken insitu in an electrochlorinator cell with narrow anode/cathode spacing, see Fig 14.

iv) Relative increase in concentration of hypochlorite and chlorate with time at 5°C and 15°C, see Fig 15.

Data illustrated in Fig 12 provides evidence for increased oxygen evolution from electrochlorinator cells with decreasing inlet temperature, leading to lower current efficiency for the conversion to useful sodium hypochlorite product. This finding is not mirrored by any dramatic increase in electrode potential as electrolyte temperature falls towards 0°C, or in the oxygen-chlorine potential characteristic as determined by measurements on samples in standard overpotential measurement apparatus. However, when electrode potentials were measured insitu in simulated electrochlorinators, the results were indicative of the O_2-Cl_2 potential difference decreasing as temperature decreased, ie conditions developed that facilitated oxygen release. Concurrent with increased oxygen evolution was a decrease rather than increase in chlorate levels, see Fig 15. The latter result is suggestive of oxygen generation not arising from oxidation of hypochlorite to chlorate and oxygen, the more likely source being direct electrolysis of water.

INFLUENCE OF BRINE SALINITY

Using experimental test A, long term assessments were determined of the relative anodic corrosion rate of platinum electroplate and 70/30 Pt/Ir in 1% brine at 20°C. The dissolution rate of 70/30 Pt/Ir is substantially lower than that of platinum electroplate, see Fig 16. The difference in characteristics between the two types of coating was investigated in more detail over a range of brine strengths, see Fig 17, highlighting strongly the greater durability of 70/30 Pt/Ir at low brine dilutions compared with platinum electroplate. Less dramatic differences in corrosion rate have been observed in long term evaluation of materials in cathodic protection situations (the essential difference is anode/cathode gap is much greater than in hypochlorite cells), see Tables III and IV.

Influence of anode type on current efficiency

Comparative data using 3% sodium chloride at 20°C and current density 2.5 kA/m^2 in test C is given in Table V. The 70/30 Pt/Ir operates at a significantly higher current efficiency.

EXPERIENCE IN COMMERCIAL ELECTROCHLORINATORS

Data on operation in commercial plants are difficult for an anode supplier to obtain, and if available are usually proprietary to a particular cell manufacturer.

Following the introduction of later versions of platinum electroplate (ie MA), no basic anodic corrosion problems have arisen in service. A 100 microinch (2.24 micron) coating has a service life of about 2 years at circa 3 kA/m^2 (300 Amp/ft^2) current density, corresponding to a wear rate of circa 1 microgram / Amp hr. This is similar to the rate for platinised titanium in cathodic protection applications $^{(3)}$.

K-type 70/30 Pt/Ir has only recently been re-introduced into commercial electrochlorinators. Fig 18 shows the anodic corrosion rate obtained in a proto-type commercial unit, the results being indicative of a substantially lower anodic corrosion rate of the coating compared with platinum electroplate. However, as indicated earlier in this paper, premature loss of this type of coating has been encountered due to undermining when electrolyte temperature falls significantly lower than 10°C.

DISCUSSION

The electrolysis of seawater to form sodium hypochlorite has been extensively studied and comprehensive reviews have been provided by Regner $^{(5)}$, Kuhn $^{(7)}$ and Kuhn and Lartey $^{(8)}$. A predominating aim has been to achieve an understanding of the electrochemistry/chemistry of reactions occurring. Cell design and method of operation have also been considered. Less documentation exists on choice of electrode material, even though anode characteristics are important in determining current and power efficiency, and both initial and any recoating costs are a very significant proportion of both initial capital and running costs.

The two materials considered in this paper have been described previously $^{(4)(9)}$ though not in detail in respect of electrochlorinator operation. Both have intrinsically low anodic corrosion rates in full strength natural seawater, the level being 1 to 2 micrograms/Amps hr for MA platinum electroplate and an order of magnitude lower for K-type 70/30 Pt/Ir. The operating electrode potential of the 70/30 Pt/Ir is lower than that for platinum electroplate at an equivalent current density, and furthermore the former coating leads to substantially higher current efficiency for the formation of sodium hypochlorite. 70/30 Pt/Ir is a better coating for operation of electrochlorinators in diluted seawater compared with platinum electroplate. In spite of its apparent advantages 70/30 Pt/Ir is more difficult to produce in thick coatings, is porous and hence susceptible to undermining attack on the substrate titanium at low temperatures, and has a lower resistance to mechanical abrasion compared with hard platinum electroplate.

Seawater below circa $10^{o}C$

Since the practical experience accumulated more than a decade ago with platinum electroplated titanium in a 45 kg/hr unit for disinfecting power station cooling water, in which evidence was found for enhanced anodic corrosion rate with low inlet seawater temperatures, there has in general been a reluctance to operate further equipment under similar conditions. However, it should be noted that this initial data was inferred from assessment of coatings by the non-destruction monitoring technique of beta-backscatter, whereby it is not possible to resolve between electrochemical or chemical dissolution of coatings and localised coating underminining.

Results accumulating over several years of evaluation using the different experimental arrangements described in this paper, show that, with either bulk pure platinum, or platinum electroplated titanium, decreasing the inlet electrolyte temperature to electrochlorinators from 15 to $20^{o}C$ down to 0 to $5^{o}C$, does not cause an increase in anodic dissolution rate of more than a factor of X2 or X3 (from circa 1 to 2 - 3 micrograms/Amp hr). In addition to such enhancement of anodic wear of the coating by dissolution, an additional method of degradation has been identified, namely coating undermining. This is deduced from such observations as

i) Initially adherent but porous coatings fail by this mechanism.

ii) Platinum electroplated to a given thickness behaves differently on different substrates when operated with electrolyte at $5^{o}C$. Coatings applied to tantalum have not been found susceptible to degradation whereas those applied to titanium evenutally degrade by an undermining mechanism.

The undermining mode of failure is unexpected in view of the apparently inoccuous nature of cold natural seawater, this in part explaining the long period over which experimentation has been continued before publication of findings. It is known that titanium is susceptible to superficial dissolution in both strongly reducing acid and alkali media, and sufficient to impair adhesion of applied noble metal coatings. Merely anodically polarising titanium in low temperature neutral seawater does not produce measurable corrosion. Hence it seems likely that any explanation is associated with the formation of extremes of pH in boundary layers which are perhaps more readily formed at the lower diffusion rates encountered at low temperatures, coupled with porosity of the coating.

Diluted seawater

With platinum electroplated titanium, both in hypochlorite and cathodic protection environments, there is firm experimental evidence to associate increased anodic dissolution of platinum with decreasing chloride concentration, see Table III. This effect, clearly not associated with substrate characteristics,is much more accentuated with platinum electroplate than it is with 70/30 Pt/Ir, see Fig 16. Further, it can be seen from Fig 5 that both platinum and platinum/iridium coated titanium electrodes have high oxygen overpotentials .... hence high O_2-Cl_2 electrode potential differences - in comparison with other permanent anode materials. Thus in the electrolysis of dilute brine such coating will continue to operate with high hypochlorite generating efficiency with decrease in chloride concentration compared with other permanent anode materials.

FUTURE TRENDS IN ELECTROCHLORINATOR ANODE MATERIALS

Present-day contender materials for use in electrochlorinators include graphite, lead dioxide coated titanium and titanium coated with noble metals or noble metal oxides. The majority of modern units incorporate titanium coated with noble metals or noble metal oxides. Important characteristics are cost, life, electrochemical performance, together with overall performance in a particular design of cell for use in particular environmental conditions.

Platinum electroplate has long been a 'workhorse' type of coating, with the MA platinum variety particularly suited for small to modest size units, for example on ships and on oil platforms where reliability and freedom from maintenance are paramount. Our studies suggest that non-porous platinum electroplate coating will tolerate seawater inlet temperatures falling below 10°C. The corrosion rate of this type of coating is, however, increased by significant dilution of seawater with fresh water. The platinum electroplate coating has a virtue in being particularly hard, 600 VPN, and hence it resists attrition from particulate matter in fast flowing seawater, and in abrasive methods of cell cleaning.

To meet the needs of large capacity plant, for example for disinfecting power station cooling water, then particular importance attaches to attaining high current efficiency combined with low running costs and anodes with low chlorine overpotential become essential. Of candidate materials, the 70/30 Pt/Ir coating described in this paper is particularly suitable, especially where seawater is likely to be diluted by fresh water. This is thought to be associated with its intrinsically high O_2-Cl_2 electrode potential characteristic .... the highest of any electrode material of which we are aware .... which not only contributes to a high current efficiency for hypochlorite formation compared with platinum electroplate, but maintains a high efficiency even at decreased salinity. Associated with this characteristic is a lower anodic corrosion rate than for MA platinum electroplate.

Disadvantages of the Pt/Ir coating are its intrinsically higher cost compared with RuO_2-based coatings, its inherent porosity at low applied loadings compared with MA platinum electroplate and its lower hardness and hence resistance to abrasion with respect to platinum electroplate. Very little can be done to change the first characteristic but we are making positive progress towards alleviating the problems caused by the coating porosity and lack of hardness by either pretreating the titanium or selection of alternative substrates to titanium, both of which have been shown to reduce the undermining mode of failure at low temperatures.

CONCLUSION

MA platinum electroplated titanium has a low anodic corrosion rate when used in most present-day designs of electrochlorinator cell. The coating shows more tolerance to use with seawater below 10°C than other contender material, and being very hard is resistant to abrasive cleaning actions. Platinum electroplate shows an increase in anodic corrosion rate as seawater dilution falls to circa 1 gpl, and it is a high chlorine overpotential surface.

In contrast, thermally deposited 70/30 Pt/Ir possesses a very low chlorine overpotential, and in seawater at 15°C exhibits an anodic dissolution rate about an order of magnitude lower than for platinum electroplate. On account of the very high O_2-Cl_2 electrode potential characteristic of the material, the current efficiency for hypochlorite generation at ~85% is substantially higher than for platinum electroplate at nearer 60%. Additionally the current efficiency for hypochlorite formation remains high with decreasing seawater dilution, and the anodic corrosion rate remains low. K-type 70/30 Pt/Ir coating in its present form on titanium is susceptible to degradation by undermining if seawater temperature falls below about 10°C, and it is less resistant to mechanical abrasion than MA platinum electroplate. Techniques are being developed to overcome the latter problems.

ACKNOWLEDGEMENT

The authors acknowledge with thanks the many experimentalists who have, over the past 13 years, been engaged in research from which data has been culled for presentation in this paper. They also thank the directors of IMI Marston Ltd for permission to publish the accumulated findings.

REFERENCES

1 British patent 877,901 11 July 1958

2 Reid F H. Metallurgical Reviews 1963 8 167

3 Cotton J B, Wood A C. Trans. Inst. Chem. Eng. 1963 41 354

4 British patent 1351,741 1 May 1974

5 Warne M A, Hayfield P C S. Materials Performance 1967 15 39

6 Regner A. "Electrochemical Processes in Chemical Industries" Artia, Prague 1957

7 Kuhn A T. Chem Processing 1975 March/April

8 Kuhn A T, Lartey R B. Chemie-Ing Tech 1975 47, 129

9 Faita C, Fiori G, and Augustynski J W. J Electrochem Soc 1969 116(7) 928

TABLE II

O_2-Cl_2 ELECTRODE POTENTIAL DIFFERENCE AT 1.5 kA/m^2 FOR ANODE SURFACES IN BRINE SOLUTIONS OF VARIOUS DILUTION

Electrolyte	MA Platinum Electroplate		K-type Pt/Ir Surface	
	Electrode potential volts hydrogen scale	O_2-Cl_2 millivolts	Electrode potential volts hydrogen scale	O_2-Cl_2
250 g/l brine at 70°C	1.602	479	1.255	534
30 g/l brine at 20°C	2.086	-5	1.363	426
10 g/l brine at 20°C	2.106	-25	1.447	342
1M sulphuric acid at 20°C	2.081	-	1.789	-

TABLE III

INFLUENCE OF SEAWATER DILUTION ON THE CORROSION RATE OF MA PLATINUM ELECTROPLATE UNDER CATHODIC PROTECTION CONDITIONS

Sea water concentration	Working current density kA/m^2	Temp range of seawater °C	Period of test (weeks)	Wear rate (micrograms / Amp /hr)
Normal	3.5	7-18	23	0.83
Normal	3.2	7-18	23	0.75
3 Fresh 1 Sea	1.0	4-18	23	1.7
3 Fresh 1 Sea	0.4	4-18	23	2.3

Initial thickness of platinum electroplate ~100 microinches

TABLE IV

INFLUENCE OF SEAWATER DILUTION ON THE CORROSION RATE OF K-TYPE 70/30 PLATINUM IRIDIUM COATED TITANIUM UNDER CATHODIC PROTECTION CONDITIONS

Seawater concentration	Working current density kA/m^2	Temp range of seawater °C	Period of test (weeks)	Wear rate (micrograms / Amp /hr)
Normal	1.7	7-18	27	0.1
Normal	1.2	7-18	27	0.2
3 Fresh 1 Sea	0.85	8-15	19	1.2
3 Fresh 1 Sea	0.4	4-17	27	0.3

Initial loading of Pt/Ir ~ 10 g/m^2

TABLE V

RELATIVE POWER EFFICIENCY OBTAINABLE WITH PLATINUM ELECTROPLATED AND 70/30 PLATINUM/IRIDIUM COATED TITANIUM ANODES IN HYPOCHLORITE GENERATION FROM 3% SODIUM CHLORIDE (TEST APPARATUS C)

Surface	Vol % oxygen in hydrogen (fresh brine)	Percentage current efficiency	Power efficiency kWh/Kg of chlorine
MA platinum electroplate	11.3	67.9	6.2
K-type 70/30 Pt/Ir	8.3	84.6	3.9

CONDITIONS

Electrode gap 3mm
Brine strength 3%
Temperature 20°C
Brine flow rate 33 cm/sec
Current density 2.5 kA/m^2

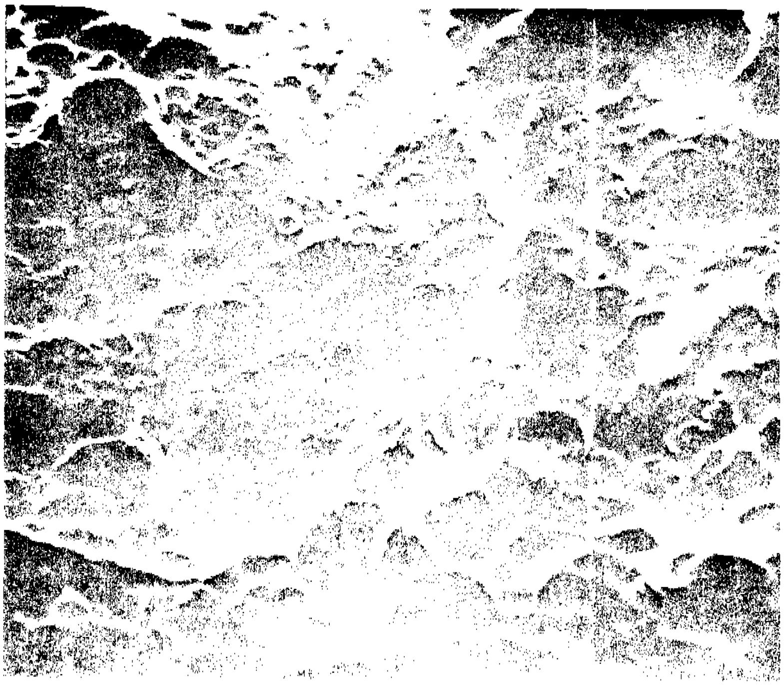


FIG 1 EARLY 'A' TYPE PLATINUM ELECTROPLATED TITANIUM (X3000)

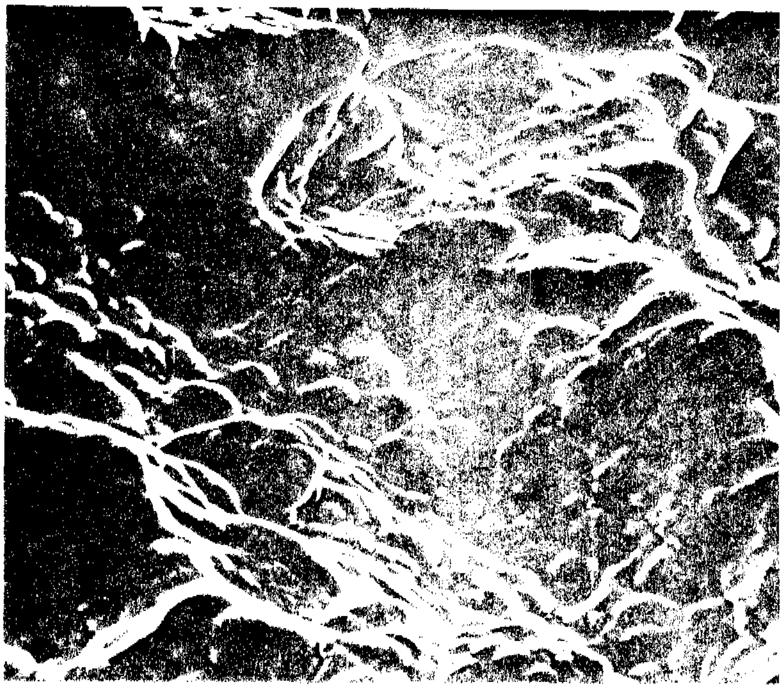


FIG 2 'MA' TYPE PLATINUM ELECTROPLATED TITANIUM (X3000)

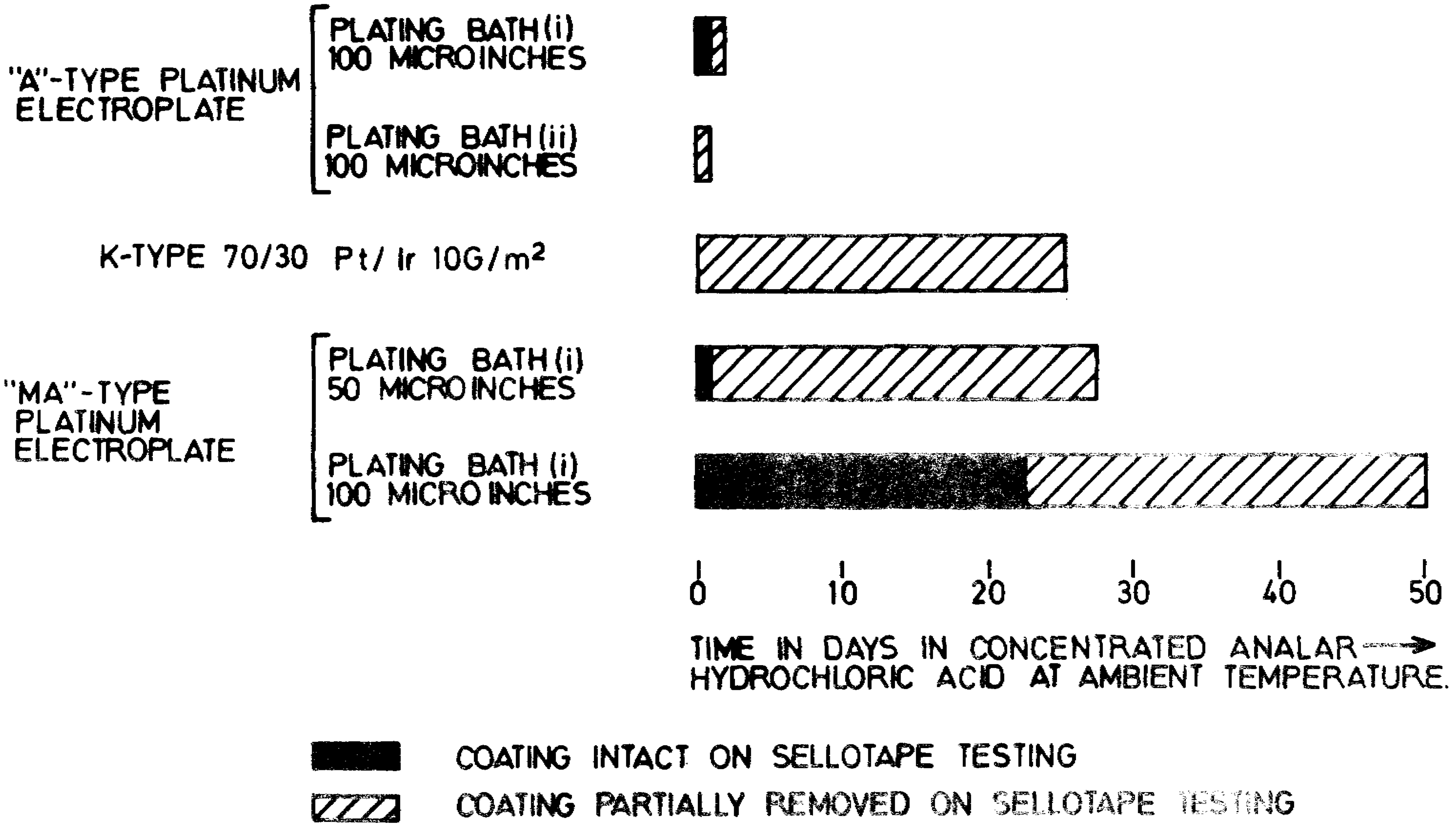


FIG. 3. RELATIVE RESISTANCE OF VARIOUS NMT ANODES TO COATING UNDERMINING ON IMMERSION IN CONCENTRATED HYDROCHLORIC ACID AT RT.

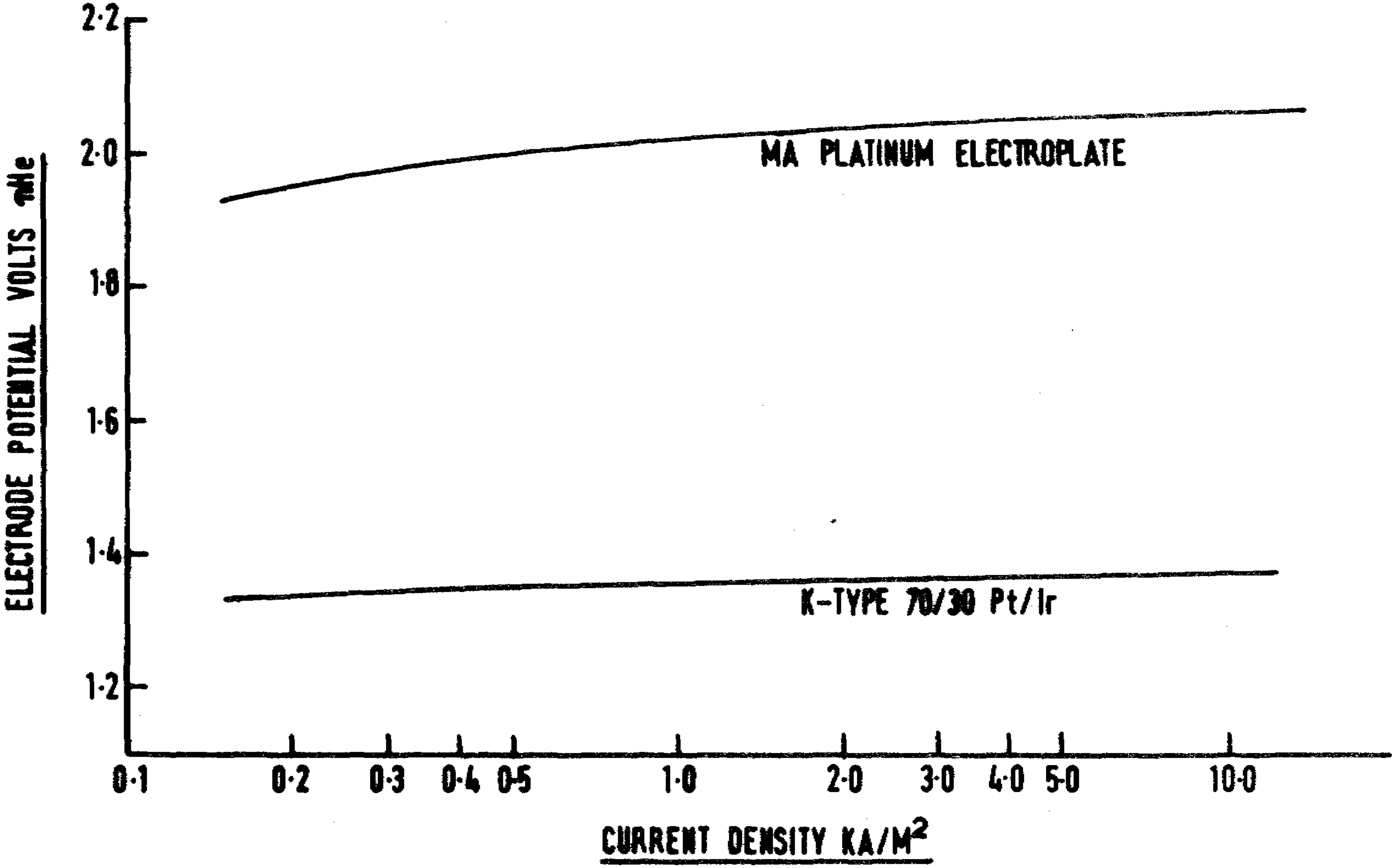


FIG. 4. ELECTRODE POTENTIAL/CURRENT DENSITY RELATIONSHIPS FOR MA PLATINUM ELECTROPLATED AND K-TYPE 70/30 PLATINUM/IRIDIUM COATED TITANIUM IN SEAWATER AT 23°C

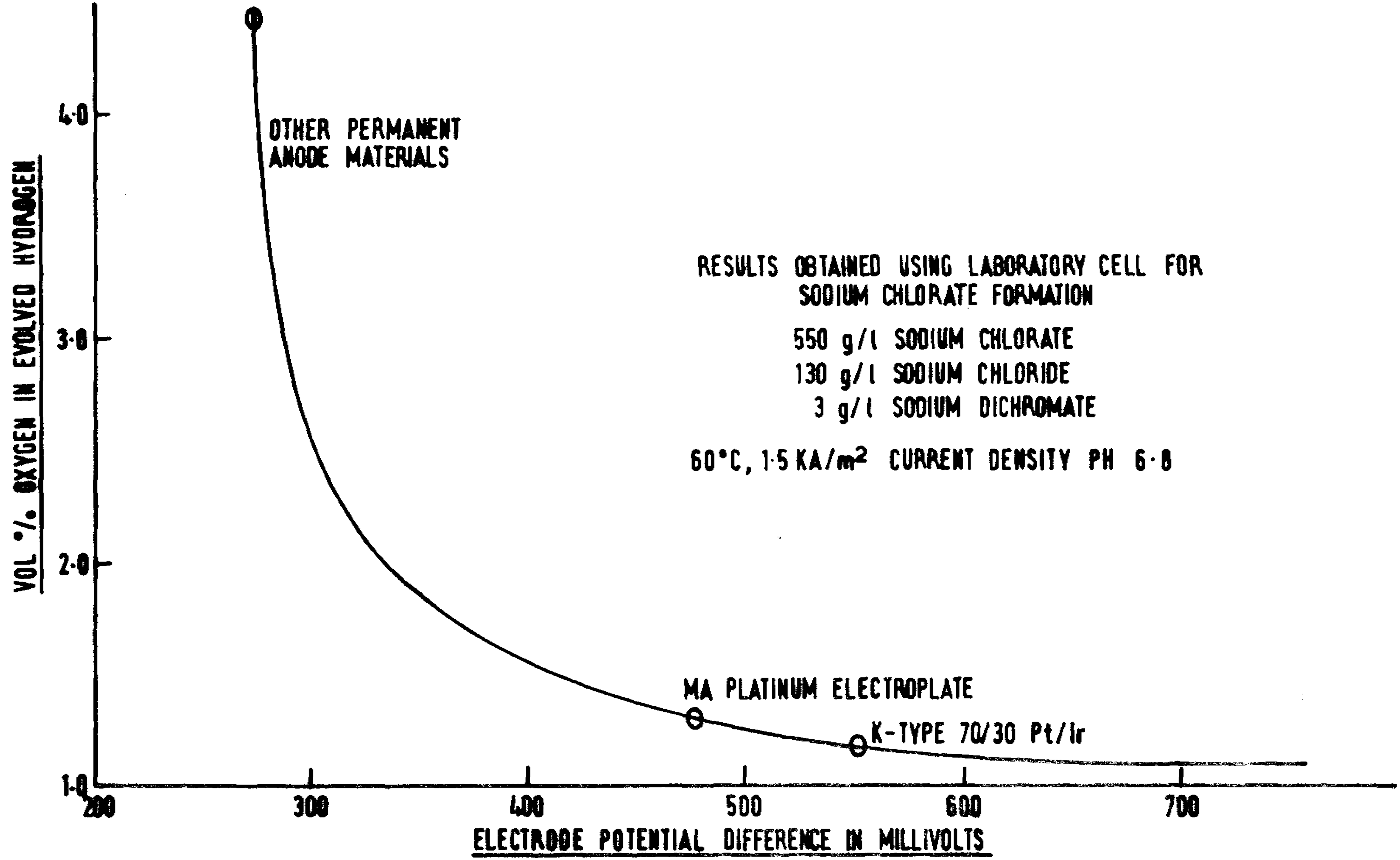
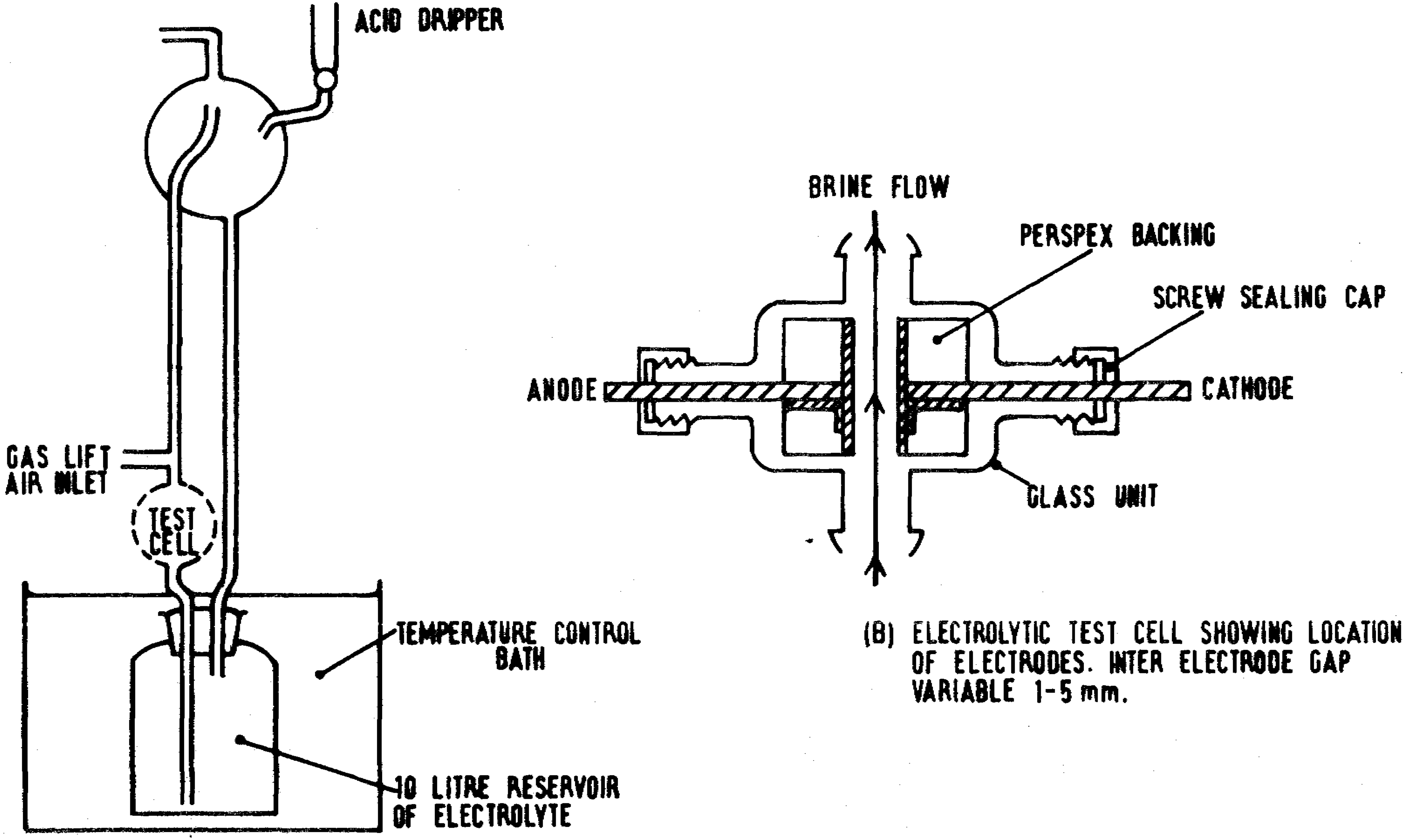


FIG. 5. VOL % OXYGEN IN EVOLVED HYDROGEN AS A FUNCTION OF ANODE SURFACE '$O_2 - Cl_2$' ELECTRODE POTENTIAL DIFFERENCE



(A) ELECTROLYTE CIRCULATION ASSEMBLY SHOWING LOCATION OF TEST CELL.

(B) ELECTROLYTIC TEST CELL SHOWING LOCATION OF ELECTRODES. INTER ELECTRODE GAP VARIABLE 1-5 mm.

FIG. 6. EXPERIMENTAL HYPOCHLORITE CELL (ARRANGEMENT B) USING GAS LIFT FLOW AND TEMPERATURE CONTROL

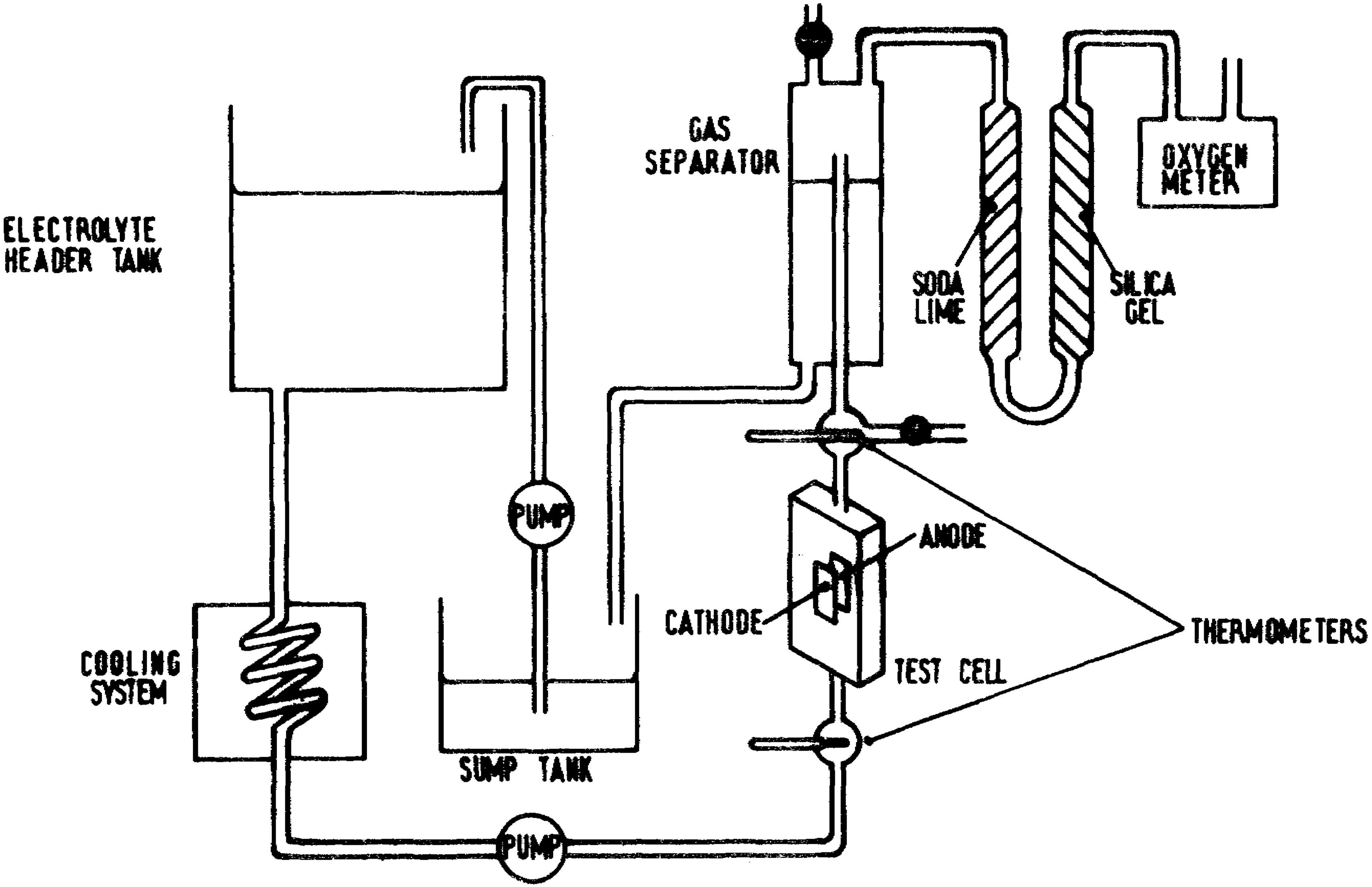


FIG. 7. LAYOUT OF LABORATORY HYPOCHLORITE TEST CELL

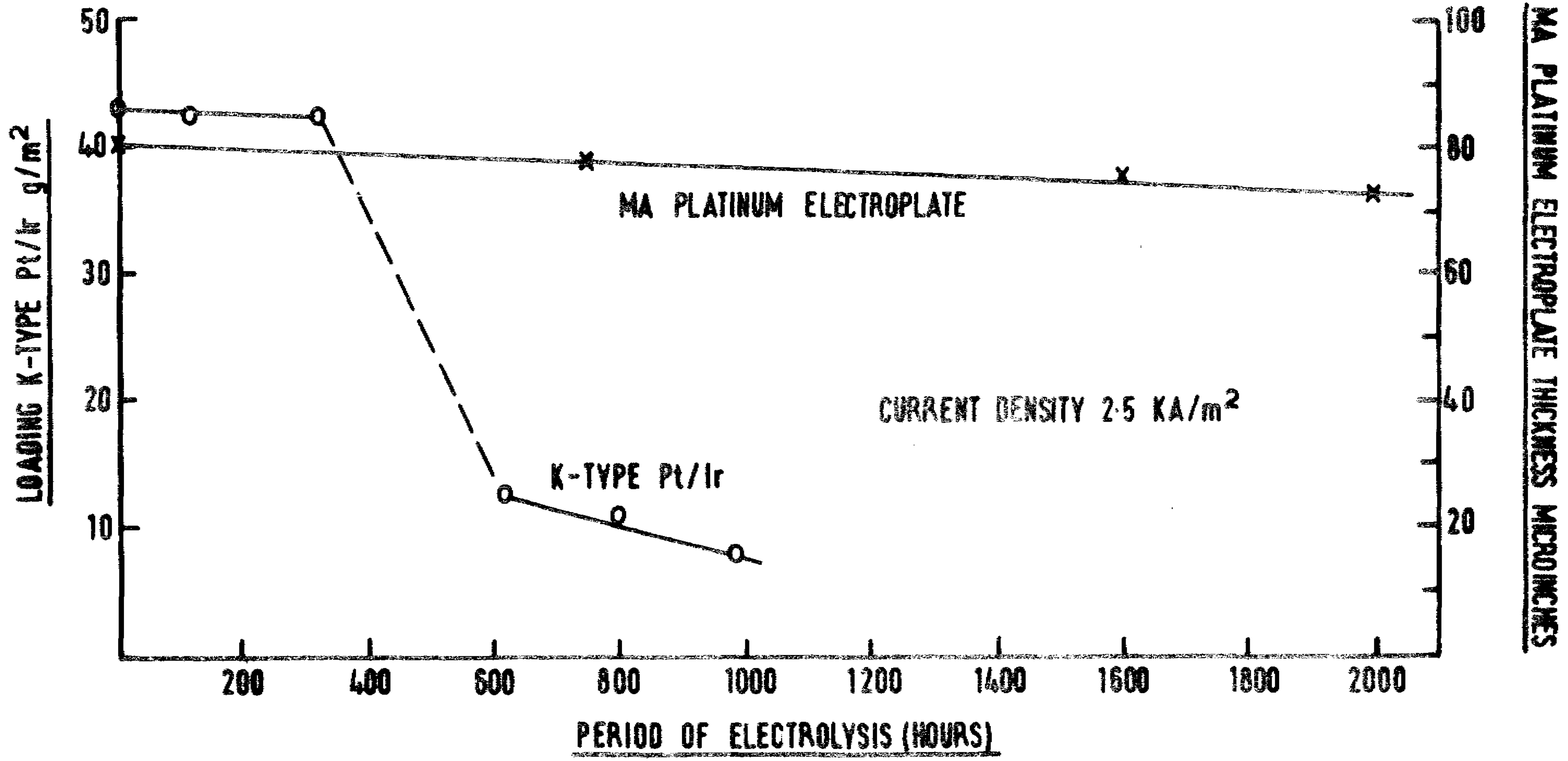


FIG. 8. CORROSION RATE OF MA PLATINUM ELECTROPLATE AND K-TYPE Pt/Ir COATED TITANIUM ANODES IN THE ELECTROCHLORINATION OF 3% SODIUM CHLORIDE AT 5°C

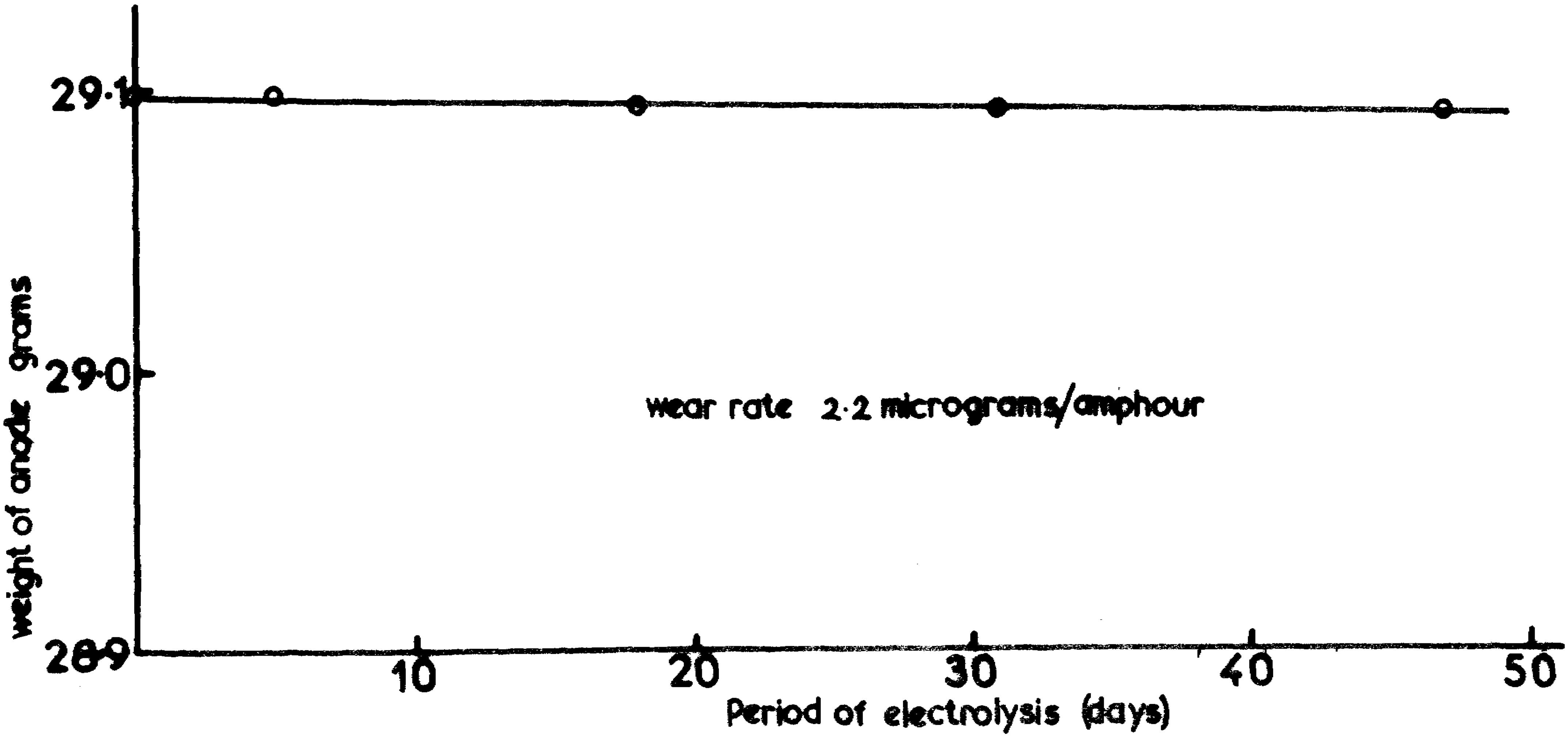


FIG9 CORROSION RATE OF A PLATINUM FOIL ANODE IN 3% SODIUM CHLORIDE AT 3°C AND A CURRENT DENSITY 5KA/M².

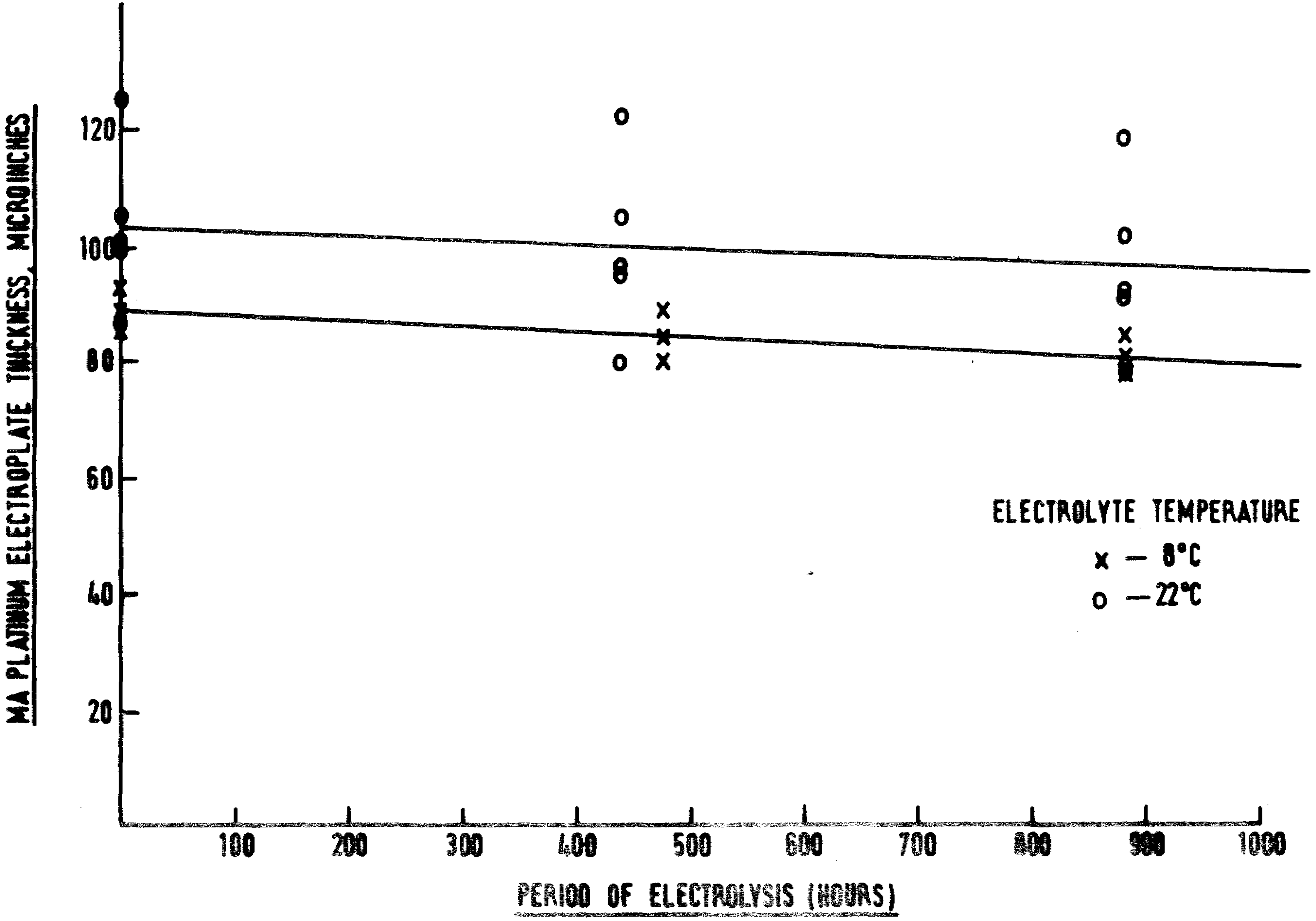


FIG. 10. INFLUENCE OF TEMPERATURE OF 3% SODIUM CHLORIDE ON CORROSION OF PLATINUM ELECTROPLATED TITANIUM ANODES IN A BIPOLAR LABORATORY SODIUM HYPOCHLORITE CELL

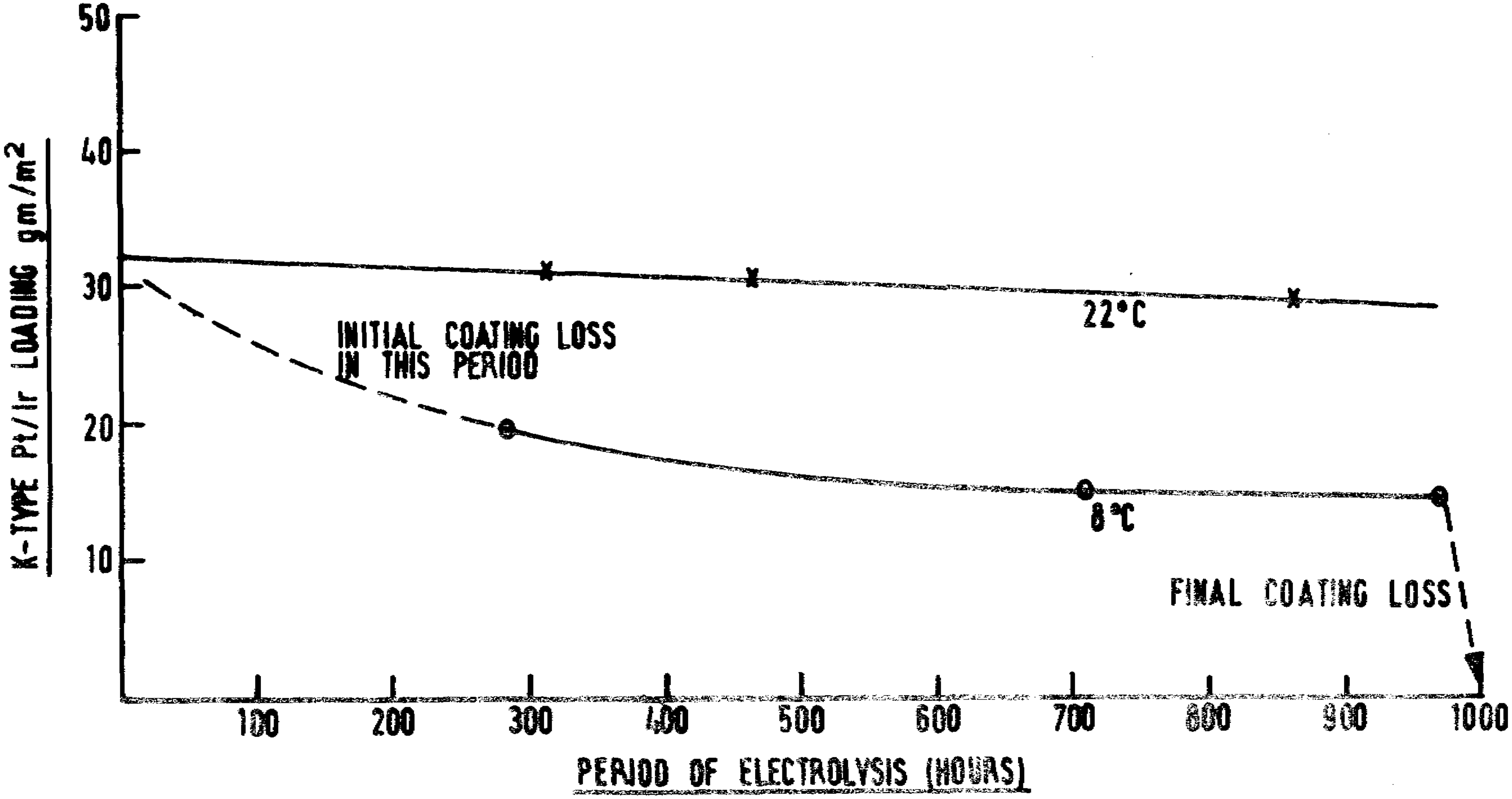


FIG. 11. INFLUENCE OF TEMPERATURE OF 3% SODIUM CHLORIDE ON CORROSION OF K-TYPE 70/30 Pt/Ir COATED TITANIUM ANODES IN A BIPOLAR LABORATORY SODIUM HYPOCHLORITE CELL

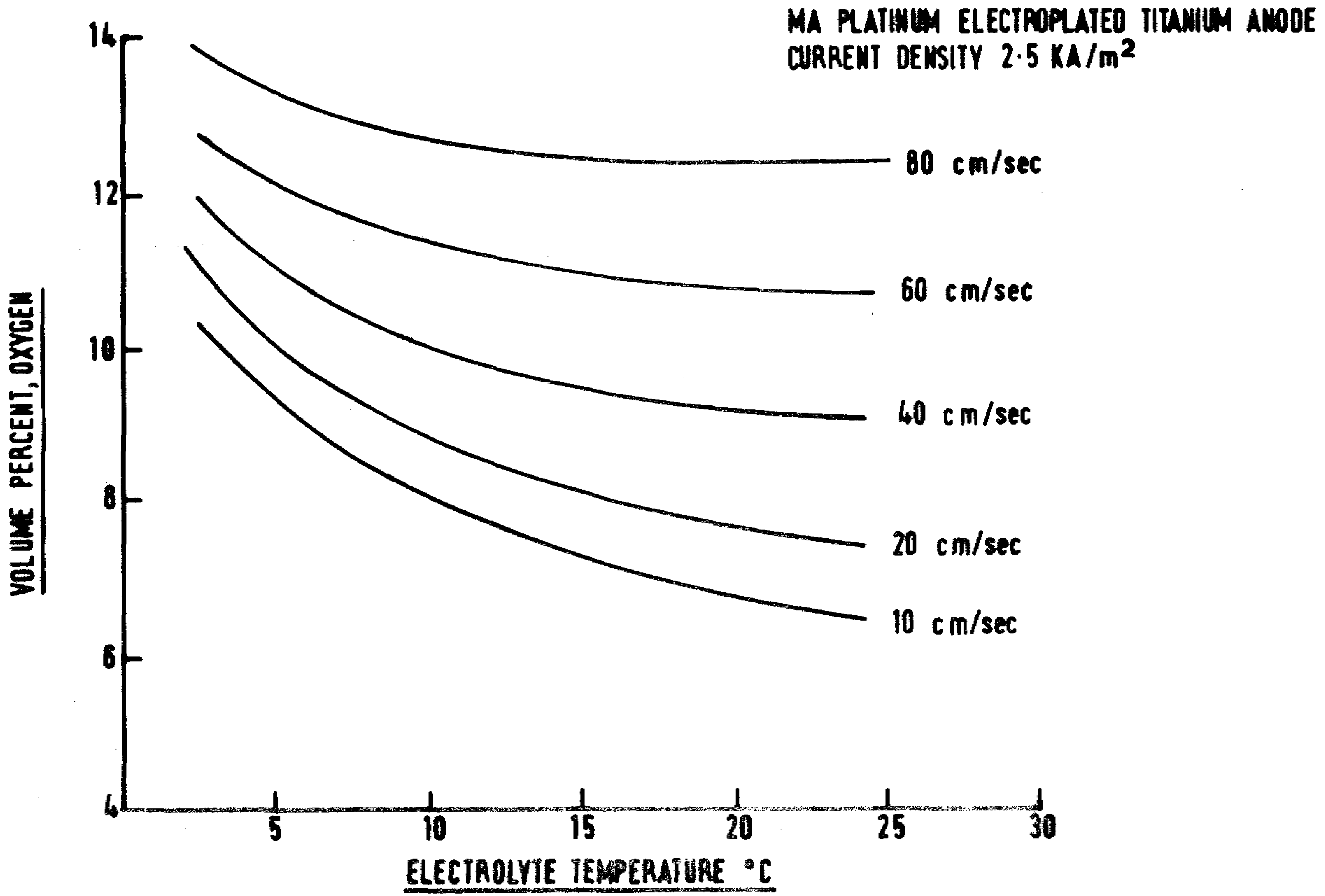


FIG.12. OXYGEN EVOLUTION VERSUS ELECTROLYTE TEMPERATURE FOR VARIOUS FLOW RATES OF 3% SODIUM CHLORIDE IN A LABORATORY ELECTROCHLORINATOR

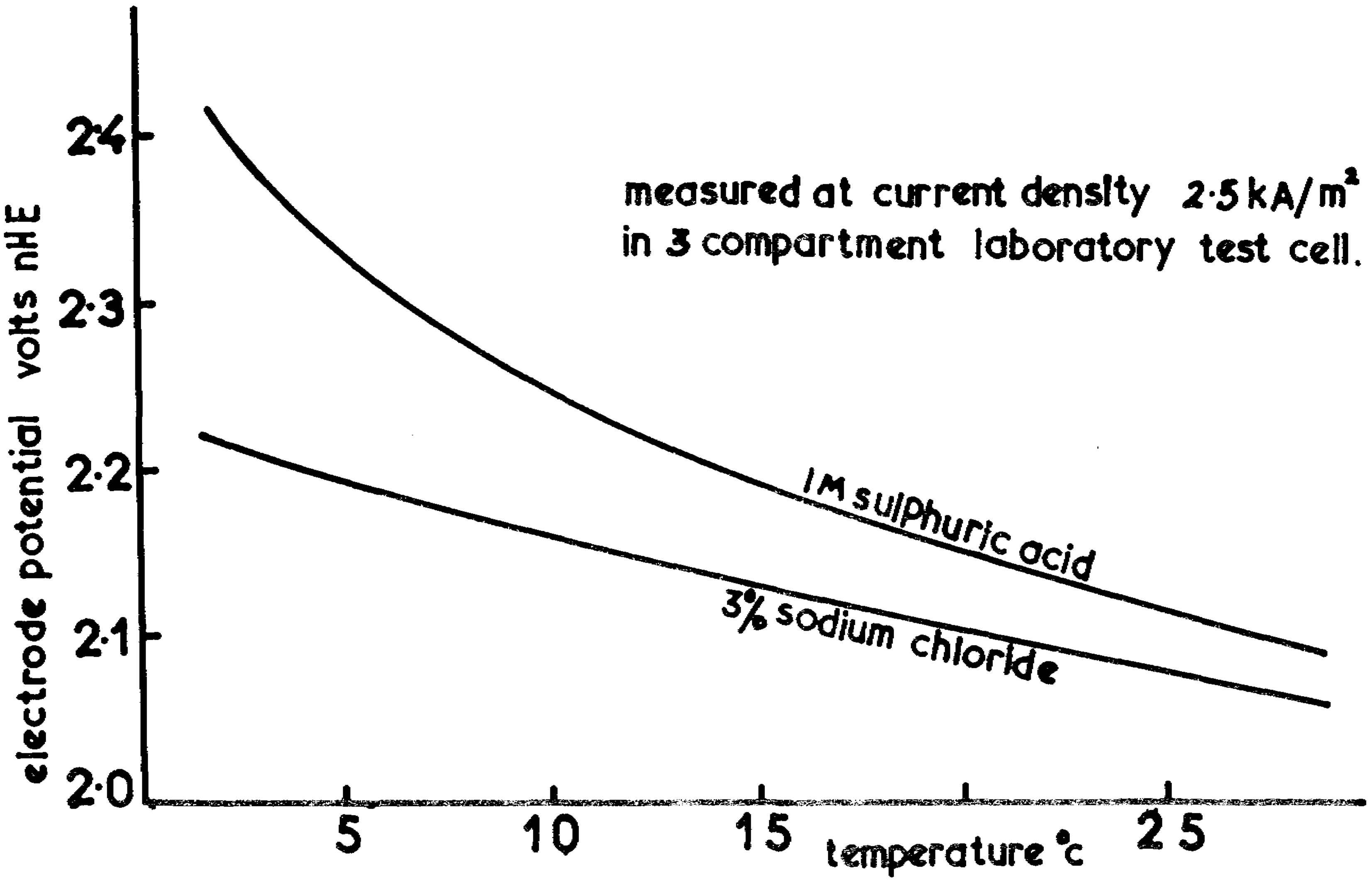


FIG.13 ELECTRODE POTENTIAL OF MA PLATINUM PLATE IN 3% SODIUM CHLORIDE AND 1M SULPHURIC ACID AT VARIOUS TEMPERATURES.

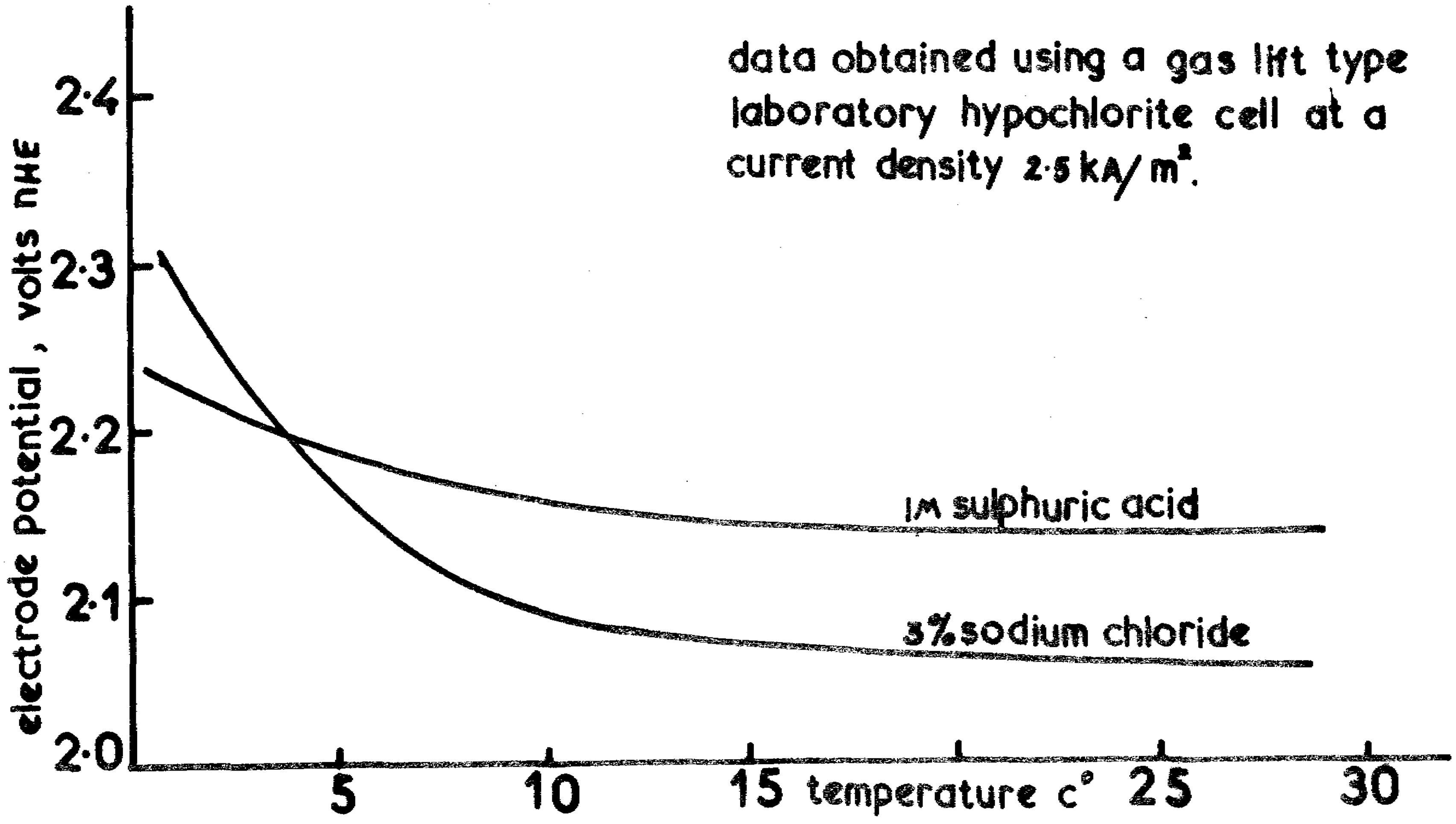


FIG.14 ELECTRODE POTENTIAL OF MA PLATINUM PLATE IN 3% SODIUM CHLORIDE AND 1M SULPHURIC ACID AT VARIOUS TEMPERATURES.

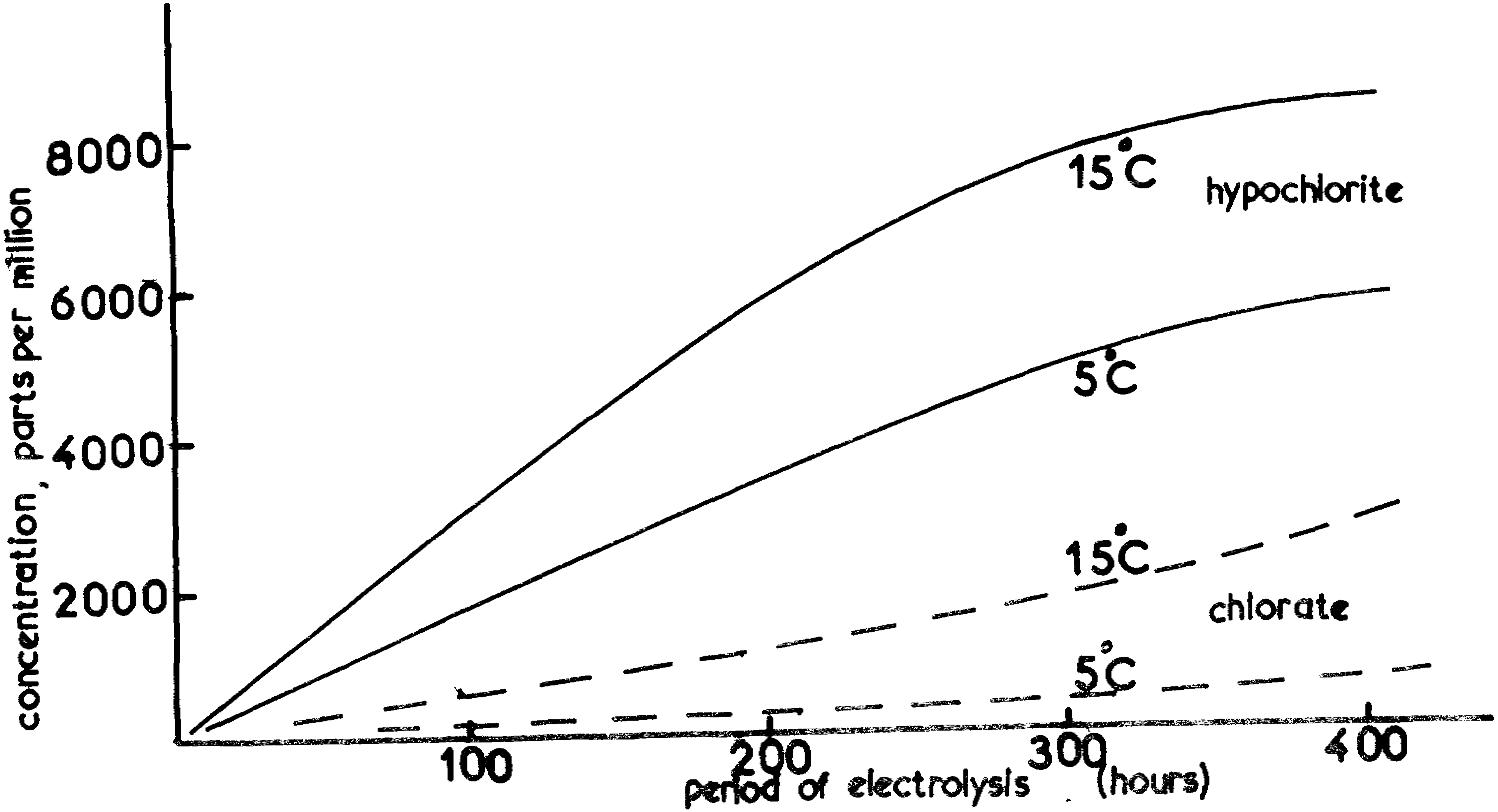


FIG.15 THE INFLUENCE OF TEMPERATURE ON HYPOCHLORITE AND CHLORATE FORMATION RATE.

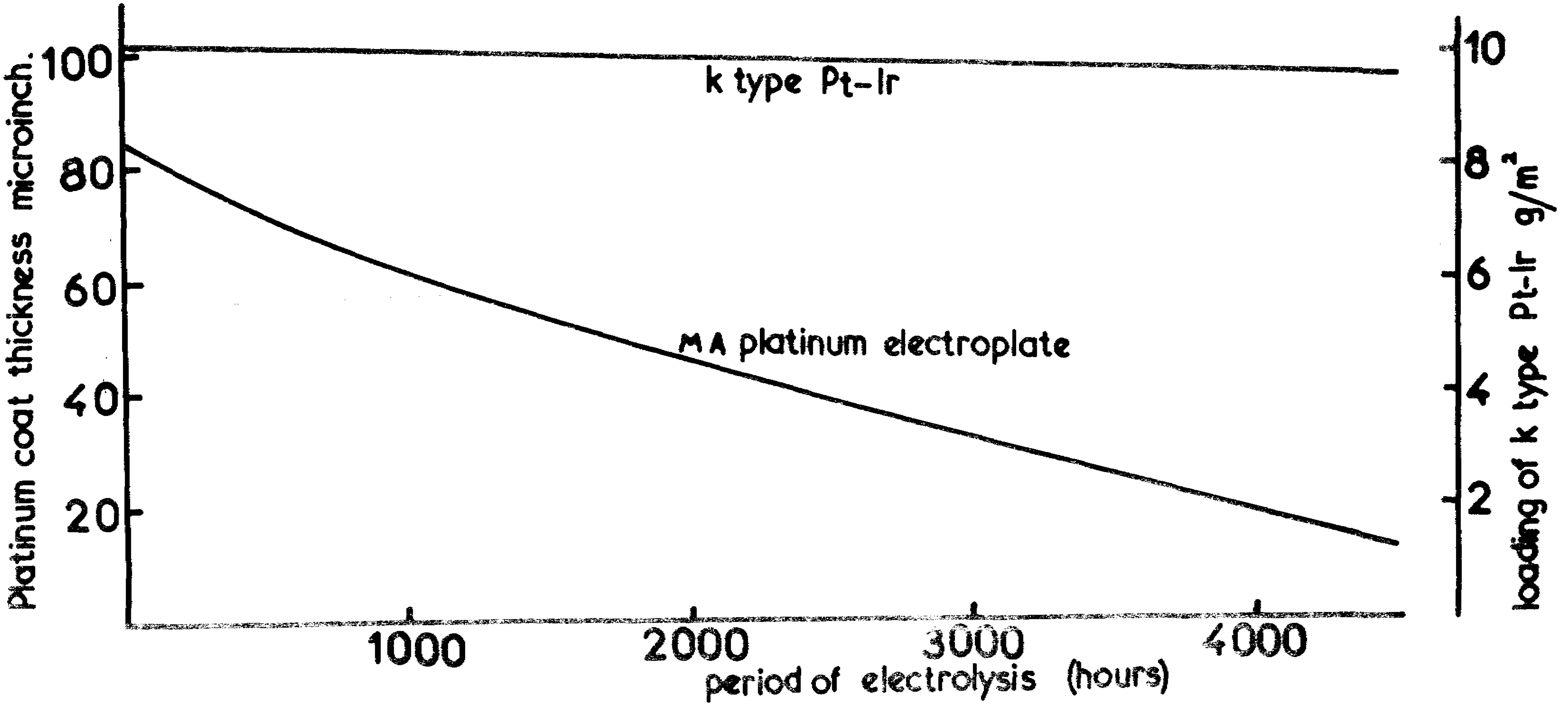


FIG.16 CORROSION OF MA PLATINUM PLATE AND K TYPE Pt-Ir ANODE COATINGS IN 1% SODIUM CHLORIDE AT 20°C IN A LABORATORY HYPOCHLORITE CELL.

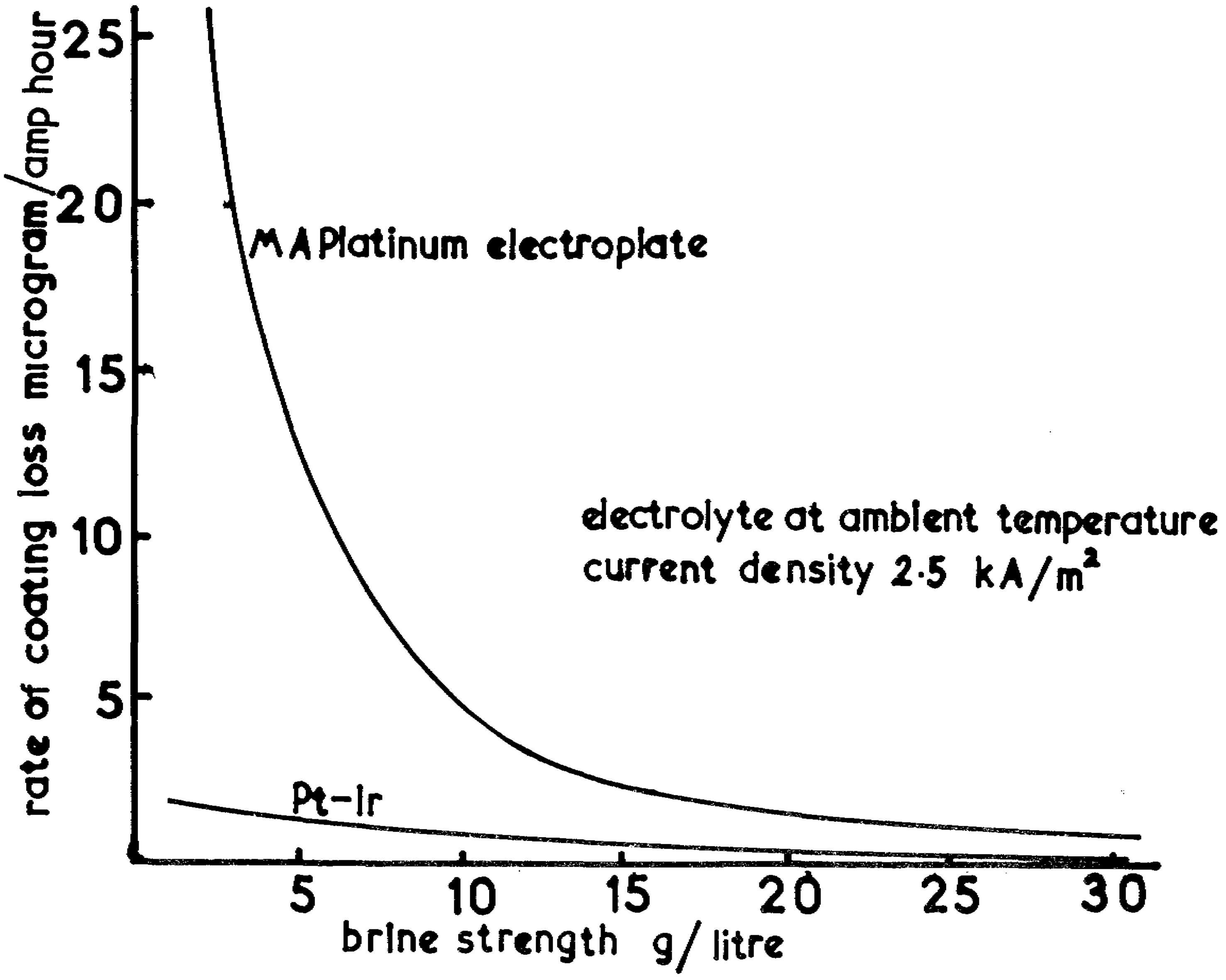


FIG.17 THE CORROSION RATE OF ANODE COATINGS AS A FUNCTION OF BRINE CONCENTRATION.

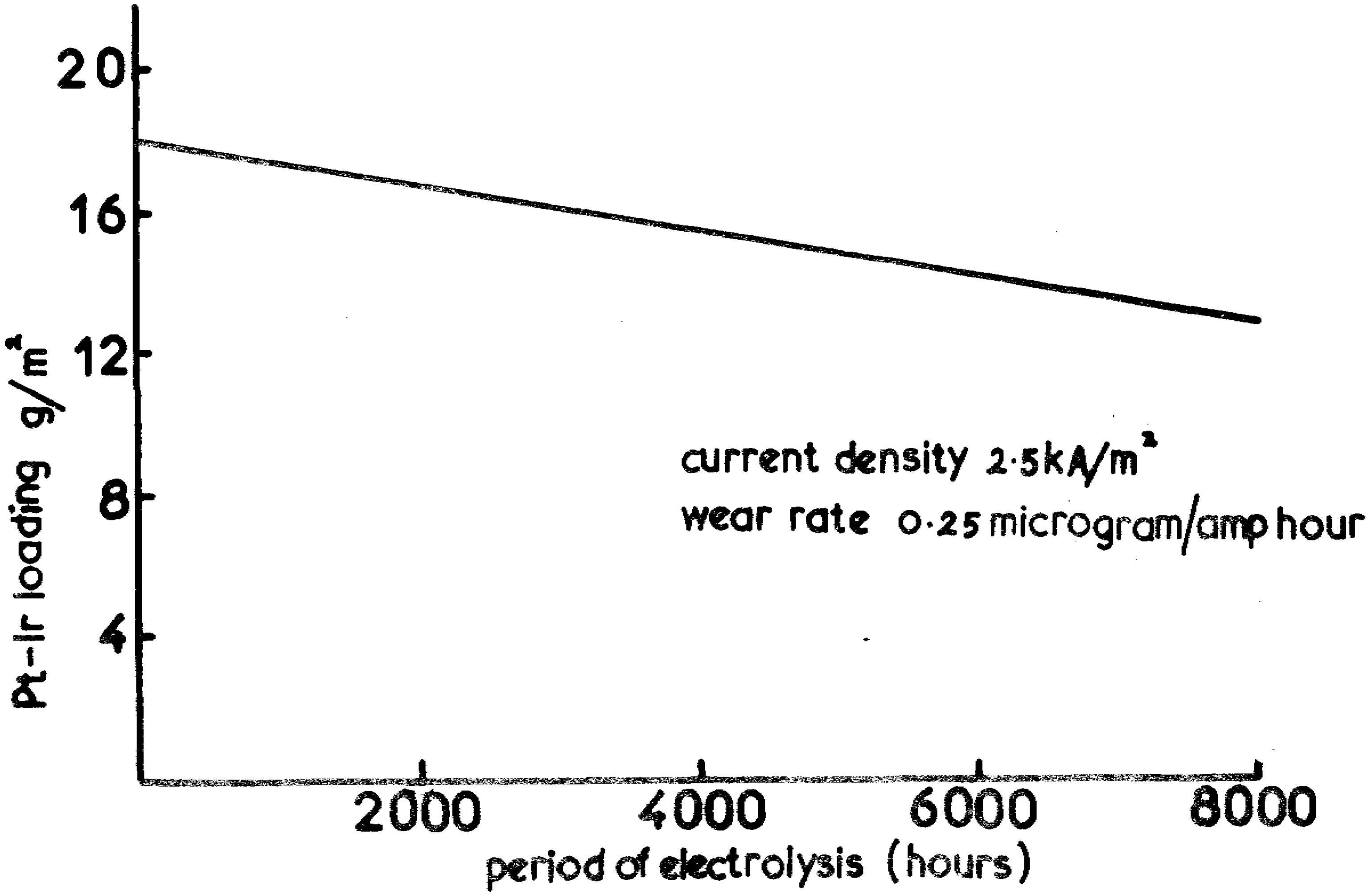


FIG.18 CORROSION OF 70/30 Pt-Ir COATED TITANIUM ANODES IN A COMMERCIAL CELL FOR THE FORMATION OF HYPOCHLORITE FROM SEA WATER.

SOCIETY OF CHEMICAL INDUSTRY CONFERENCE
14TH-16TH OCTOBER 1980

PAPER TITLE:

ELECTROCHLORINATION REQUIREMENTS OF THE OIL SHIPPING INDUSTRY

AUTHOR G.C. GRIM M.Sc CEng MIM MICorrT.

INTRODUCTION

Marine fouling in the sea water systems of ships has presented a problem to shipowners throughout history. Such fouling can eventually cause blockage with accompanying reduced equipment performance and can lead to failure by leakage.

Various measures have been taken to combat the problem including careful screening of sea inlets to prevent larger objects being drawn into systems and injection of toxins, chlorine and hypochlorite to produce a hostile environment which will either discourage fouling settlement and growth or remove existing fouling. The shipboard use of toxins has various disadvantages including handling, supply, storage, toxicity to humans, injection equipment requirements and environmental considerations. Concern also exists regarding their addition to sea water to be evaporated for drinking water. Toxins have been widely used on Shell Vessels in the past but their popularity and use has decreased for the various reasons given. Experience has indicated that success in their application invariably required heavy dosage with accompanying high chemical costs.

Shell, from experience, considers electrochlorination possesses the best potential for maintaining shipboard systems free of fouling as well as being the most cost effective. In addition to requiring no regular chemical handling, storage or charging, the system has the potential to be compact, should require little attention during service and be cheap to operate. Unfortunately these features do not always exist in practice. This paper is an attempt to summarise the shipboard fouling problem and the problem associated with, and requirements for, shipboard electrochlorination based on Shell's experience to date.

SYSTEM AND FOULING PROBLEM

Shipboard sea water systems consist of a number of sea intakes supplying such equipment as main engine condensers, lub. oil coolers and other sea water services. The systems are normally of the once through type, the effluent sea water being collected and discharged via the main overboard discharge line. With such an array of equipment dependent on sea water for cooling, the potential problem that exists from fouling is clear.

The three main types of marine fouling found in ships sea water circuits are:-

1. Hard and soft fouling, e.g. mussels, barnacles and hydroids.
2. Sand and silt from shallow water areas.
3. Plastic bags, fish etc.

Of these three types, 1 is probably the most common. There is little that can be done to prevent 2 and 3 apart from utilising fine intake screens to reduce the ingress of larger objects and ensuring water inlets are mounted as high as possible in an attempt to reduce silt intake.

The hard and soft forms of fouling commonly referred to as "shell and weed" are frequently found in water boxes, scoops, main condensers and other cooled equipment plus their associated pipework. It is difficult to suggest sea areas which represent the greatest fouling risk except that coastal waters are more favourable for the growth of fouling, fouling population also varying from place to place. Increase in water temperatures, as in tropical areas, produce greater speed of fouling growth. The problem is further increased by reduced water velocities through sea water systems due to vessels being on standby or at a stand-still in harbour allowing fouling settlement. It is perhaps opportune at this point to mention that ships' sea water systems are ideal for many types of marine growth,being free of predators and warm from equipment cooling. This warmth has been known to produce very high growth rates in at least one ship where mollusc fouling occurred in 9 months to a size normally expected in 4-5 years.

The hard shelled types of fouling are typically, but not exclusively, mussels, oysters and barnacles. These commence life as free swimming minute embryo which, under conditions of favourable water velocity and temperature etc., will settle and commence to grow; the mussels to a length of 75 mm or more and the barnacles to a diameter and height of up to 50 - 70 mm. Such fouling can obviously cause serious blockage of piping and associated equipment especially where water transport is via small tubes which, in contrast to larger piping that can often tolerate quite heavy fouling, may be significantly affected by very modest growth. Some copper alloys possess a certain degree of antifouling ability but not all are capable of sustained long term fouling resistance and hence cannot be relied upon to maintain systems free of growth. The more important equipment, such as main engine condensers, usually receive most antifouling attention, as a fouling problem here can require plant shut down for equipment cleaning with accompanying operational delays. Fouling of such condensers can cause other problems. Erosion may occur if shell fouling becomes lodged or grows in tubes, and, should the obstruction be a barnacle, degradation may also occur beneath its point of attachment. Fig. 1 indicates such a barnacle attachment to a copper-nickel main condenser tube and Fig. 2 shows the same tube with the barnacle removed. The tube surface is clearly active beneath and downstream of the barnacle, flow being from left to right. Thicker materials ensure longer equipment service life under such circumstances, but of course entail additional costs and may reduce equipment performance i.e. thicker condenser tubes reducing cooling efficiency. Fouling of less important equipment i.e. that run intermittently does not normally present a significant problem, the opportunity being available to carry out cleaning when such equipment is not in use. Fortunately, condensers etc. are normally oversized to the extent that they can tolerate the occasional local blockage and still ensure adequate cooling. This fouling tolerance is further enhanced at present with ships slow steaming when equipment loads are light. However, this tolerance must not be abused and every effort made to ensure systems free of growth to avoid operational embarrassments upon full load requirements.

Of the two consequences of fouling i.e. blockage or leakage, the latter has probably the most significant effect on ship operation, causing unplanned maintenance and trading delays. Such occurrences are unacceptable to efficient ship operation and more than justify the cost of an antifouling system.

CHLORINATION

The objective of chlorination, as other antifouling measures, is to discourage the settlement and growth of hard and soft fouling embryo. Experience suggests this can be achieved, dependent on ship trading pattern, by intermittent introduction; established soft fouling being treated in a similar manner. However, in systems where hard shelled fouling is well established, continuous chlorination is necessary. The organisms swiftly detect the change in chlorine concentration and quickly close and remain so for long periods. The overall effect of chlorination on a fouling community is therefore a combination of poisoning, starvation and a general discouragement of growth. A point to be highlighted here is that when chlorinating established fouling, accumulations of detached dead marine growth at local restrictions such as condensers may occur and necessary remedial action taken to avoid catastrophic blockage.

From Shell's world-wide shipping experience it has been confirmed that chlorine injection producing a feedwater concentration of 0.5 ppm free chlorine will maintain seawater cooling systems free of fouling. In practice, this usually produces a chlorine residual at main condenser outlets of approximately 0.1 ppm. During deep sea operation, for example when trading between the Persian Gulf and Europe, such levels of chlorine injection may be limited to 4 hours per day whilst continuous additions are effected for 12 hours prior to entering harbour and maintained until 12 hours out of inshore waters.

Various types of electrochlorination system are available, marked design differences existing between each, but with 3 basic forms of installation; Fig. 3 indicating the three systems. System (a) is considered the most suitable, the chlorine generation unit being readily isolated for routine maintenance and also completely separate from electrical components. (b) although allowing easy isolation of the chlorine unit has the disadvantage of possible flooding of the electrical cabinet with highly corrosive products of electrolysis, should cell or pipe leakage occur. The use of electrodes in sea chests as indicated in (c) is not particularly desirable since any problems with them may necessitate ship delays to allow rectification. A type (a) system is illustrated in Fig. 4. Water is taken from the service pumps to the chlorination cell and thence via a distribution manifold to all sea water intakes. Drilled manifolds are fitted in the larger intakes to ensure good chlorine distribution.

Wherever possible, as illustrated in Fig. 4, chlorine injection should occur as far outboard as possible to prevent fouling growth upstream of introduction points.

REQUIREMENTS

Modern efficient ship management requires that shipboard equipment operates reliably for extended periods, necessitating, at most, daily adjustment to maintain correct operation. This efficiency requirement is of paramount importance and one that manufacturers must appreciate and seek to achieve if their equipment is to stand any chance of widespread, long term utilisation. Ships do not enjoy the same benefits of land based installations whereby service engineers and spares are often readily available. Dependent on a ship's position and trade, an extended period may elapse before spares can be made available and fitted; by which time a fouling problem may have developed. Preferably, manufacturers should provide world-wide service facilities, at least in the principle trading locations, to allow an efficient after sales service when required. Equipment should be simple in design, allowing ease of maintenance and component replacement when necessary by ship's staff. As the products of electrolysis are very corrosive, corrosion resistant materials such as plastic coated steel, reinforced plastic, certain types of stainless steel or titanium must be utilised between cells and injection points.

Various problems have occurred in chlorination systems including platinum loss from electrodes, flow switch malfunctions, cell and pipework leakage, cell blockage by calcerous deposits and complicated interactions of each. Platinum loss has been experienced to a greater or lesser degree with several systems and has been a subject of investigation for a considerable period. This platinum loss is promoted by increased anode potentials which under operating conditions are influenced by sea water salinity and temperature. To prevent excessive platinum loss, cells may be fitted with a thermostat that operates to reduce anode current densities, and hence anode voltages, when sea water of less than 10°C passes through the chlorination unit. Equipment does exist, which it is claimed does not have a sea water temperature limitation; here voltage is prevented from rising above a certain level by electrical circuit design, again the result is reduced anode current and hence reduced chlorine production. Other units are protected by a manufacturers warning that systems should not be operated in sea waters below 10 - 14°C.

The explanation sometimes advanced by cell manufacturers to customers to reassure them that this reduction in cell output will not be detrimental in fouling control is that less chlorine is needed for cold water fouling control. This may or may not be true, but what must be remembered is that actual water temperatures within hot condensers are often sufficiently elevated, as mentioned earlier, to enhance fouling growth which will require sufficient chlorine for control; a quantity which may not be available under cell low temperature current density control. These temperature constraints supplied to electrochlorination units are undesirable and must be taken into account by ships trading in colder waters. It is hoped advances will be made in future plating techniques and/or anode design to reduce this problem to a minimum. An alternative that may be worth considering is to utilise a warmed water supply to chlorinators, tapped downstream of a condenser, to avoid subjecting cells to cold water conditions and accompanying problems.

In general, few electrical difficulties have been experienced with electrochlorinators; problems in the main having been a consequence of cell leakage. Several instances of anode insulation failure have occurred; the result of one such failure is indicated in Fig. 5. Here, catastrophic corrosion occurred to a titanium valve, situated at a main condenser chlorine injection point, following its polarisation by a cell anode. The result is clearly evident.

Flow switches are important components in preventing cell operation under low flow conditions producing amongst other things overheating and calcareous scale deposits. Entrained air in sea water passing through a tubular type of flow switch has caused erroneous effects to occur, i.e. indicated a higher flow rate than actually existed. Fouling within the same flow switch can also lead to incorrect readings. Flow switches should thus be designed to avoid such problems as air entrainment and allow easy dismantling for cleaning.

The occurrence of cell leakage invariably causes an unpleasant mess that usually requires immediate action to prevent further problems. Superior design and of course care in assembly would reduce the incidence of this type of failure. It is perhaps opportune at this moment to highlight the point that ships and of course their equipment are subject to high levels of vibration, far higher than most land based installations. These levels of vibration must contribute to system leakage plus other forms of failure; it is hoped manufacturers take this feature into consideration when designing and fitting chlorination units onboard ship.

Pipeline leakage between cell and sea water main invariably occurs where sub-standard materials have been utilised or materials have not been correctly protected. Preferably pipework and fittings conveying products of electrolysis from cells should be kept to a minimum to reduce the likelihood of such failure. Care in installation design and cell positioning will keep such plumbing to a minimum.

The problem of calcerous deposit formation on anodes can be particularly troublesome, neccessitating cell dismantling for cleaning, low water flows often being the cause of the problem. Whether units passing greater quantities of water are superior in combating these deposits is of course open to argument but superior cell design may reduce the likelihood of this time consuming problem.

From the foregoing it is clear that successful chlorination equipment for shipboard use must be robust, of good design, manufactured to a high standard and correctly installed. No matter how excellent the equipment may be, much benefit can be lost by poor installation onboard ship, resulting in a perfectly good piece of equipment acquiring an unwarranted rogue reputation. Often, unless otherwise requested, only installation guidelines are provided by chlorination unit manufacturers. For best results, close liaison should occur between shipowner and unit manufacturers, studying sea water systems carefully to ensure best water take off and injection positions. One of the most common fitting mistakes is incorrect water take off to cells both in location and geometry i.e. pressures being occasionally or constantly insufficient to provide an adequate quantity of water through cells and/or stub-in connections made in tops of pipes often allowing excessive ingress of entrained air to cells. It may well be that, for certain systems, a separate water pump should be utilised purely to supply the chlorination unit to prevent low water flows and their accompanying problems.

There is no doubt that improvements are possible to all chlorination equipment at present marketed. It is hoped that the foregoing comments may prompt or contribute to such improvements.

CONCLUSIONS

The problem of marine fouling in shipboard sea water systems has been summarised.

From experience, Shell consider electrochlorination is potentially capable of maintaining such systems free of marine growth.

Preferred systems are those with chlorination cells completely separate from electrical components, external to the main sea water system allowing injection at various locations.

Electrochlorination units should be:

1. Capable of supplying sufficient chlorine under all sea water temperature conditions.
2. Reliable and durable i.e. corrosion resistant, robust, vibration resistant, electrically reliable etc.
3. Correctly fitted.
4. Designed to allow ease of repair by ship's personnel.
5. Ideally, capable of providing a minimum of 5 years trouble free service, apart from minor maintenance, before any major replacements or servicing is necessary i.e. replatinising of anodes.

Acknowledgements

The author wishes to extend his appreciation to Dr. G.G. Summers and Dr. M.B. Levens for their assistance in the compilation of this paper.

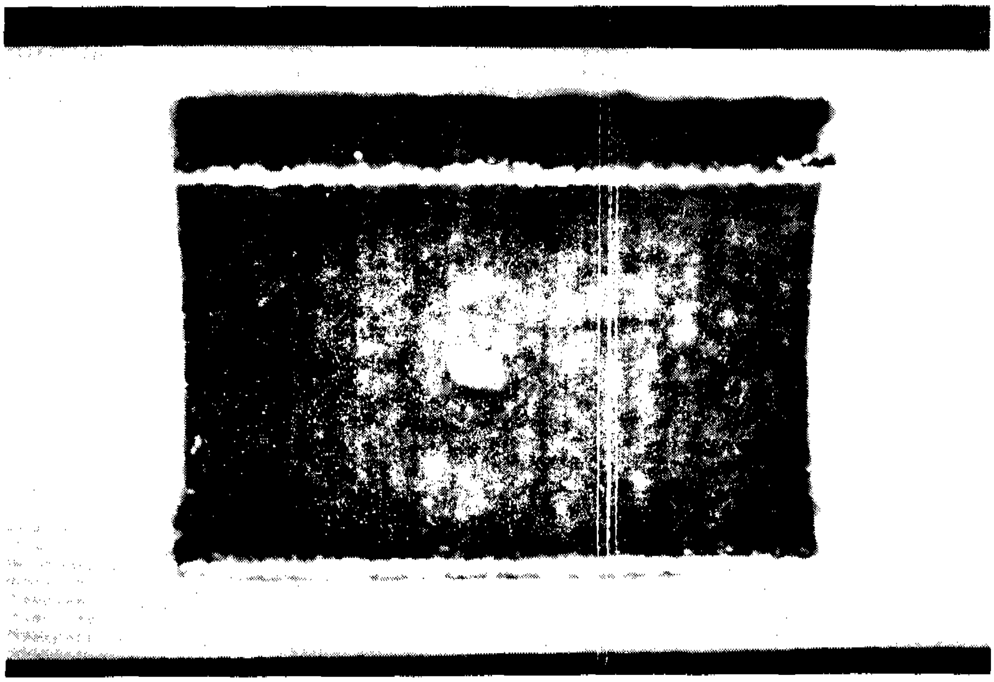


Fig. 1 Showing a section of copper/nickel condenser tube containing an acorn barnacle attachment.

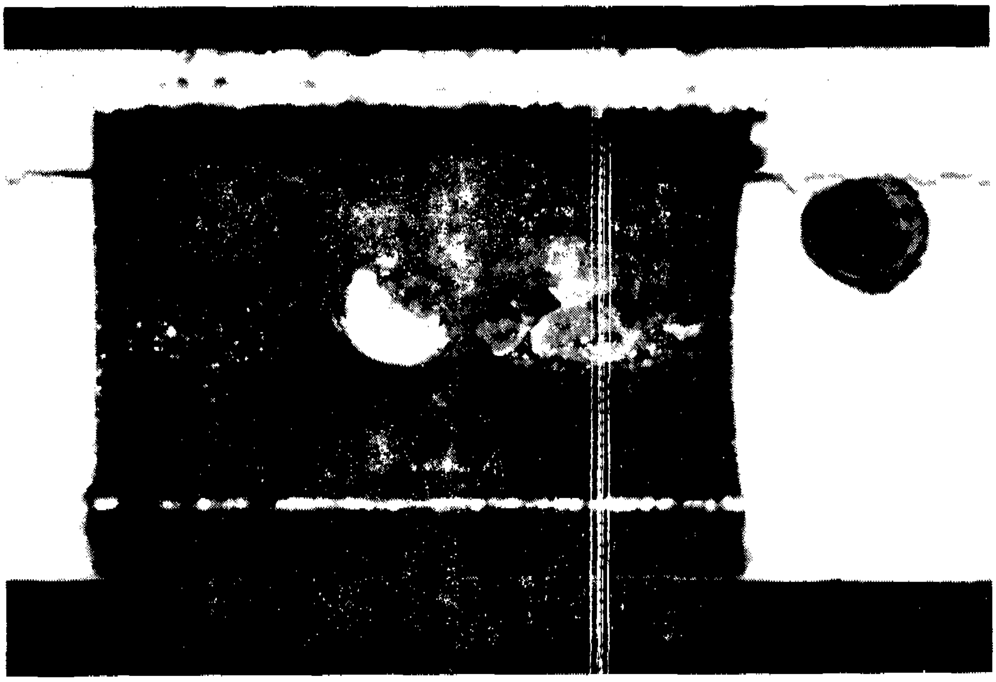


Fig. 2 Indicating the section of tube in Fig. 1 following barnacle removal and cleaning. Active corrosion is clearly evident both beneath and alongside the barnacles attachment point, flow being from left to right.

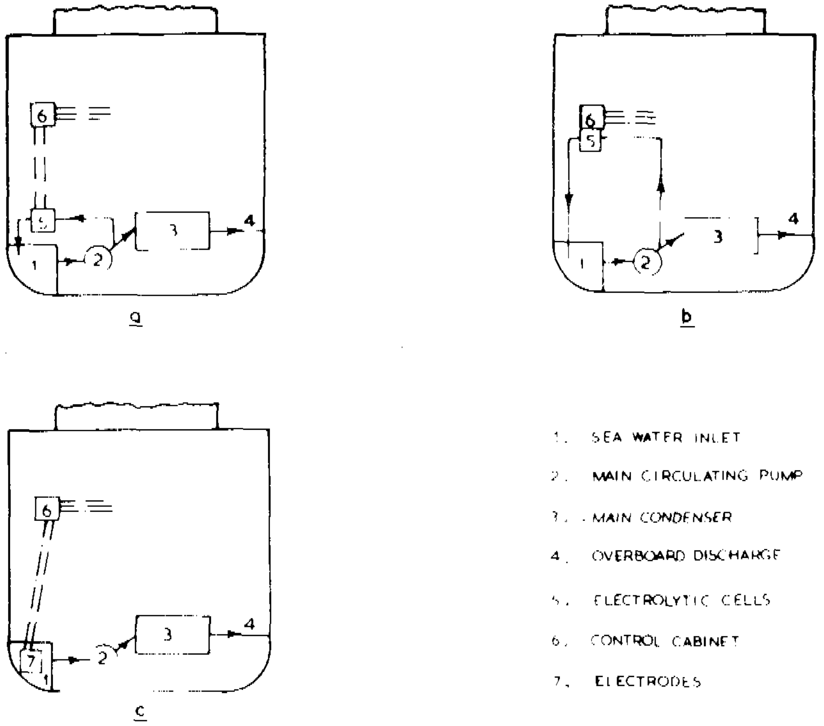


Figure 3

THREE BASIC FORMS OF SHIPBOARD ELECTRO-CHLORINATION SYSTEM

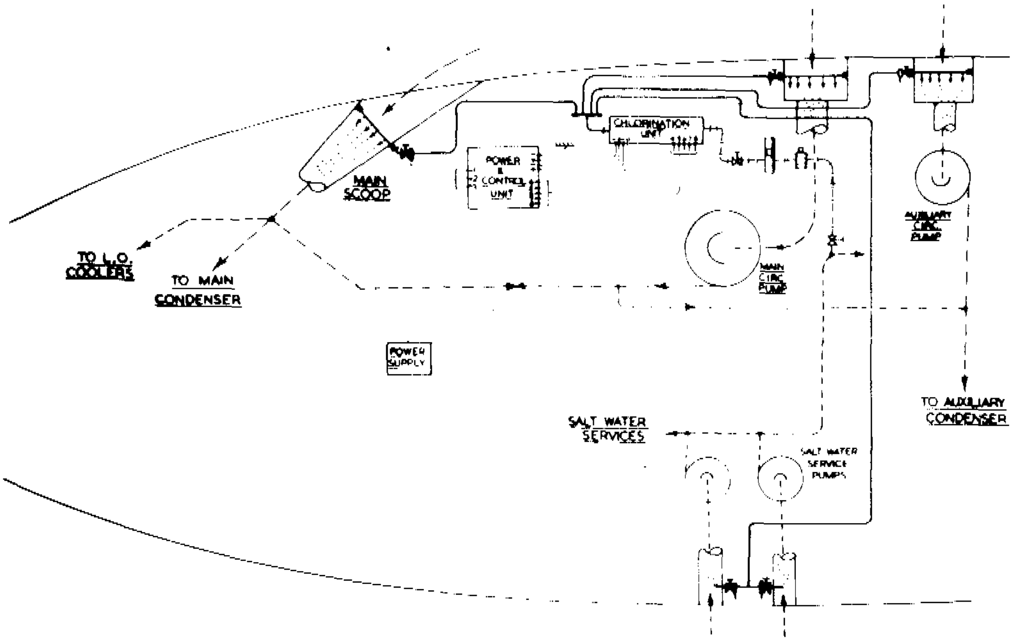


Figure 4

SIMPLIFIED DIAGRAM OF AN ELECTRO-CHLORINATION SYSTEM AS FITTED TO A $75000m^3$ SHELL L.N.G. SHIP

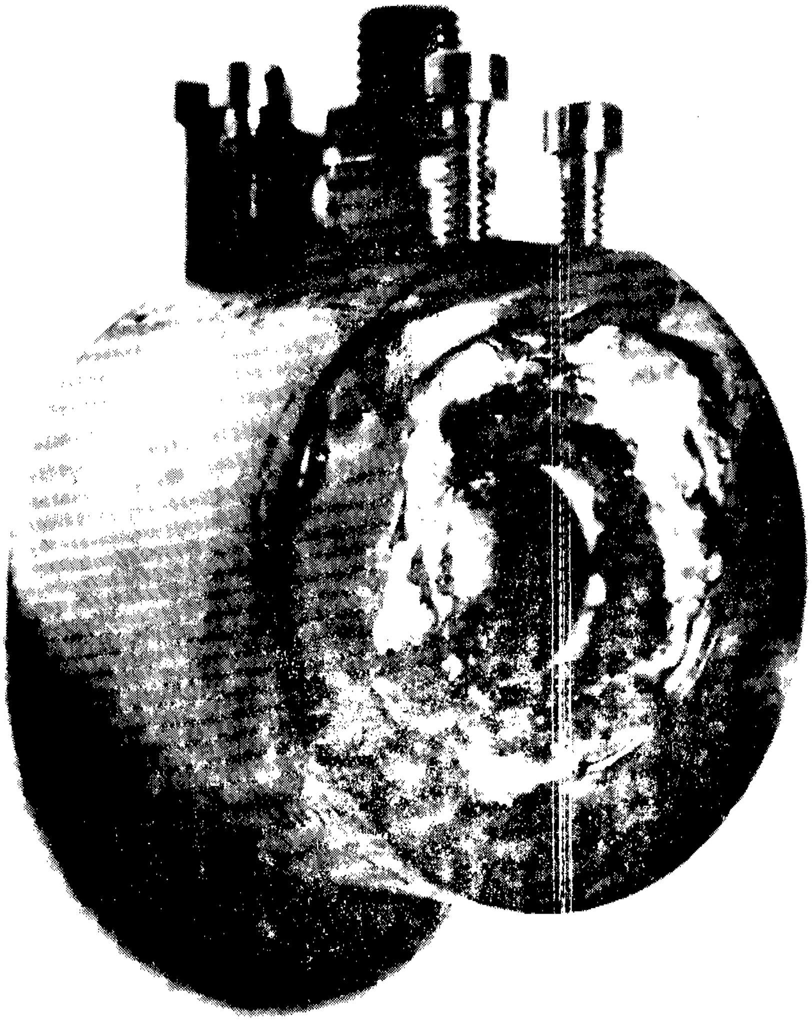


Fig. 5 Corrosion damage of a titanium ball valve following polarisation by a chlorination cell.

Society of Chemical Industry Conference, October 1980

Fouling Control in Circulating Water Systems using the Engelhard 'Chloropac'(R) Electrochlorinator

by B.J. Connolly,
Engelhard Industries Limited.

1. Introduction

Traditionally, control of marine fouling in land-based seawater cooling and other circulating systems has been mainly by the use of chlorine, either in gaseous form or as liquid sodium hypochlorite. However, the ever-increasing quantity of this chemical used over the past year or two has caused concern due to the hazards involved in transportation and storage, particularly of liquid chlorine. Several recent major disasters accompanied by fatalities, particularly in the U.S.A., have caused power station and other land-based installation operators to seek a safer alternative such as electrochlorination, which uses only seawater and electric power as the raw materials for producing the requisite active chlorine in situ. In certain European countries, notably Italy and France, electrochlorination has already been in use for several years, replacing gas chlorination in coastal power stations. Other countries such as Holland and Denmark are likely to follow suit, and in the U.K. there is now also a trend towards electrochlorination.

2. Electrochlorinator Design

Considerable improvements in cell design and efficiency in recent years have restored end-user confidence in electrochlorination as a reliable method of fouling control, and in particular the unique tubular design of 'Chloropac' (R), with its ability to operate in remote areas without supervision, has contributed to this situation.

Over the last eight years, Engelhard has developed the Chloropac system which is specifically designed to overcome the various problems encountered with other electrochlorination systems in the past, notably poor adhesion of the platinum to the titanium anode surfaces and inability to operate in

(R) Registered trademark.

cold seawater. There are no low temperature limitations on the operation of Chloropac anodes in seawater and hence no necessity to use water heaters as with certain other systems. Operational experience in ships, on off-shore platforms and in land-based installations, where the temperature of the seawater feed to the Chlorpac unit is less than 4°C, has confirmed this latter point. The anode surfaces in the Chlorpac cell are designed for a minimum life of seven years on continuous operation at maximum rated output.

3. Operating Parameters for the Chlorpac System, Power Consumption etc.

The basic Chlorpac cell unit, an exploded view of which is shown in Fig. 1, consists of two concentric titanium tubes with seawater flowing in the annular space between the inner and outer tubes. The inner tube is a continuous bi-polar electrode whereas the outer tube is in two halves which are insulated from each other. The anode surfaces are platinised by a proven technique which was specially developed by Engelhard and which has been used for more than twenty years for electrodes employed in various applications, such as anodes for cathodic protection, electrodialysis and electroplating. Engelhard, therefore, has a great many years of experience and expertise in the manufacture and use of precious metal-coated titanium electrodes.

The Chlorpac system is designed to operate on a once-through basis using seawater, brine or other made-up saline solutions of resistivity 20-40 ohm cm approximately (50,000-25,000 micromhos per cm conductivity), corresponding to seawater with 3.0 - 3.5% sodium chloride content. Within this range of resistivity the system is self-adjusting to maintain a constant chlorine output with change in water salinity and/or temperature.

At a normal design water flow through the Chloropac cells of approximately 5 m^3/hr, each standard cell of 0.45 kg/hr output capacity, that is 0.45 kg/hr available chlorine expressed as sodium hypochlorite, typically produces a concentration of 100 mg/litre of hypochlorite in the seawater coming out of the cell. The cells are arranged in series up to and including twelve in number (total 5.4 kg/hr output), after which banks of cells are then arranged in parallel in order to keep the pressure drop through the system down to a minimum. The nominal design pressure of the cells is 2Kg/cm^2, but they can operate at any pressure up to 10 kg/cm^2.

The cells are supplied with low voltage D.C. from a transformer/rectifier control unit working off the normal A.C. electrical supply, and a flow switch assembly protects the cells from damage by shutting off the power if for any reason the water flow is reduced to less than about 4 m^3/hr. This device automatically switches the current on again when the water flow is restored to normal.

The liquor coming from the cells consists, therefore, of unconverted seawater containing up to 1000 mg/litre of hypochlorite, depending upon the size of unit employed. The concentration of hypochlorite is directly related to the amount of current passing, and the method of varying the output of the cells is to vary the current according to requirements, keeping the water flowrate constant at approximately 5 m^3/hr per module. The system has a turn-down ratio of 10 to 1, so it can be operated at any desired output between 10% and 100% of design output.

There are no moving components in the Chloropac system and the only part which requires replacement is the platinum on the anode surfaces which needs renewing every seven years or so. Depending on how the plant is operated, the life of the platinum could be extended to as much as 10 years.

All parts in contact with the seawater and hypochlorite solutions are either titanium or plastic, thus giving a virtually indefinite life to the basic components. Maintenance is, therefore, minimal.

Chloropac is readily adaptable for use in hazardous areas, and can be provided with intrinsically safe and water-tight enclosures.

When using seawater of approximately 35,000 micromhos conductivity, the power consumption of Chloropac is approximately 6.2 D.C. kilowatts per kilo per hour of hypochlorite produced (2.8 kW per pound). Including rectification and transformation (copper) losses, the total A.C. power consumed per kilo of hypochlorite is approximately 7.7 kVA per hour (3.5 kVA per pound per hour). Where the seawater temperature is high, and the salinity is also high enough to give a conductivity in excess of 35,000 micromhos, the power consumption is correspondingly reduced. For example, where the conductivity is 70,000 micromhos or more, as in Middle Eastern countries, representing a salinity of 4.0-4.5% sodium chloride at temperatures of 35 - 40°C, the total A.C. power consumption is reduced to about 4.2 to 4.5 kVA per kilo hypochlorite.

4. Controls and Safety Features

The following is a summary of the various controls and safety devices which are incorporated in the Chloropac generating cell assembly and power supply.

(i) Seawater Flow Switch

As mentioned already, this device protects the cells from damage by overheating and also prevents deposition of magnesium hydroxide from the seawater by cutting off the current when the water flow is interrupted and switches the current on again when the water flow is restored. With the design giving turbulent water flow in the cells, this means that no back flushing or acid washing of the cells is required.

(ii) Voltage and Current Limiting Devices

The complete system is protected by a voltage/current limiting circuit which gradually reduces the output to zero if there is a malfunction in the system. This is especially useful in cases where fresh water can get into the system, in which event the cell voltage could rise to a value which exceeds the break-down potential of the oxide film on the surface of the titanium, causing severe pitting corrosion.

(iii) Cell Balance Detector Circuits

Chloropac systems of 4.5 kg/hr output and more can be fitted with cell balance detector circuits. These devices monitor the voltage between neighbouring pairs of cells and compare this voltage to a standard. If the resultant out of balance voltage is more than 10% of the total design cell voltage, the device shuts the relevant module down and indicates a malfunction on the control panel.

(iv) Constant Hypochlorite Output

A sensing device in the system automatically compensates for changes in conductivity of the seawater passing through the cells, as long as the change is within the design limits, by increasing or decreasing the current delivered to the cells, thus keeping the hypochlorite output constant.

It can be seen, therefore, that Chloropac is designed to work on an automatic basis with little or no supervision. A manual control is also provided so that thiscan always override the automatic circuit if required.

5. Hydrogen Production and Removal

All electrochlorinators produce hydrogen as a by-product of the electrolysis of seawater, and the Chloropac system produces approximately 113 litres per hour (4 cu.ft. per hour) of hydrogen for each of the standard cells of output 0.45 kg/hr hypochlorite, i.e. 250 litres per hour of hydrogen for each kilo of hypochlorite. The gas is physically entrained with the water and is only released when the pressure is reduced to atmospheric. If the Chloropac system is used to treat water in an open circuit, then the hydrogen passes into the water being treated and disperses harmlessly in the air. If, however, it is being used in a closed circuit system where pockets of hydrogen can collect then it is necessary to remove the hydrogen by means of a hydrogen disengagement vessel placed between the outlet manifold of the Chloropac unit and the hypochlorite dispersal system.

This vessel, which can be either glass-reinforced plastic or rubber-lined steel, is normally of sufficient size to contain about five minutes production of the cells (e.g. approximately 4 m^3 for a 45 kg/hr Chloropac system) and as the water pressure is let down to atmospheric, the hydrogen is liberated and is vented to atmosphere using an air blower to dilute the hydrogen with air in the ratio of 100 to 1. An air pressure switch linked to the power supply of the Chloropac cells ensures that no current can be delivered to the cells until a positive pressure of air is present in the space above the liquid in the tank. Thus no hypochlorite can be produced, and hence no hydrogen can be in the system, until the required volume of air is admitted to the tank air space. This is, therefore, an intrinsically safe method of operation and has been safely used in a large number of installations. However, recent recommendations by the Health and Safety Executive indicate that an open-topped tank is to be preferred.

The hydrogen disengagement vessel serves a dual purpose in that it also provides a storage facility for the hypochlorite solution which can then be fed either by dosing pump or by gravity to the point of injection in the water to be treated.

6. Sodium Hypochlorite Dosing Levels

For effective control of mussel and other marine fouling of the mollusc variety, it has been found necessary to dose the cooling water continuously at a low level of hypochlorite concentration. Intermittent dosing at high concentrations has been successfully used for controlling slimes and algae, but molluscs require continuous treatment. Initial dosage rates of 1 or 2 ppm sodium hypochlorite are widely used, but in many shipboard applications, dosage rates of 0.5 ppm, or even lower,have been successfully employed.

Each 0.45 Kg/hr Chloropac cell produces approximately 100 ppm of sodium hypochlorite which, when diluted in the cooling water to be treated, is sufficient to treat 450 m^3/hour to an initial dosage level of 1 ppm.

7. Applications for 'Chloropac'

Because of its adaptability to either safe or hazardous area operation, Chloropac is being widely employed for chlorination in a variety of industrial applications in marine and coastal areas where seawater is readily available. The most important uses include water treatment in the following:-

1. Power stations
2. Desalination plants
3. Off-shore platforms
4. Shipboard circulating seawater systems
5. Sewage treatment plants
6. Oil refineries, L.N.G. plants, etc.
7. Chemical and fertiliser plants

The worldwide total number of Chloropac installations in all these applications is in excess of 600 and is growing rapidly.

Further details of the individual applications are as follows:-

7.1 Power Stations

In coastal power stations the quantity of seawater used for the condenser cooling systems is enormous, a typical station of 2000 MW output requiring some 227,000 m^3/hour. On the basis of an initial hypochlorite dosage rate of 1 ppm (1 mg/litre) this quantity of water would require 227 kg/hour (500 lb/hour) of chlorine. In general, the aim is to get a chlorine residual of about 0.1 - 0.2 ppm at the inlet to the condenser (or sometimes the outlet residual is specified), and depending upon the location of the power station this usually means an initial dosage rate of 1 to 2 ppm chlorine on a continuous treatment basis. Sometimes, shock treatment to a much higher dosage level is done instead of, or in addition to, the continuous treatment, especially in Middle East locations.

Chlorination of power station intake canals is usually carried out right at the front end, either in front of the bar screens which remove the majority of floating matter from the water before it goes to the rotary screens, or at the rotary screens themselves. Depending on site conditions, it may also be done at various other points along the intake canal and sometimes also at the condenser inlet. The electrochlorinator unit is usually, therefore, located in a convenient building and the hypochlorite is manifolded to the various injection points.

Several Chloropac units have been installed at power stations in the U.K. (see Figs. 2 & 3). Other power station installations include those at coastal sites in Hong Kong, the U.S.A., Mexico, South Africa, Japan, Indonesia, The Phillipines, Australia and Portugal.

7.2 Desalination Plants

Chlorination of the seawater feed to the evaporators is normally carried out to control fouling on much the same basis as in power stations, and sometimes the distillate is also treated.

In certain parts of the world, notably the Middle East, desalination plants are linked to power stations and there is a rapidly-growing demand for electrochlorination in these areas where transport of bulk liquid chlorine is difficult and very expensive.

Chloropac is already being used in desalination plants in the U.S.A. and in the Persian Gulf area.

7.3 Offshore Platforms

Seawater is used on off-shore platforms for cooling water and other utilities, for fire fighting systems and for waterflooding, and in all cases it is vital to ensure freedom from marine fouling. In the case of waterflooding, it is necessary to ensure that the seawater is biologically pure and this can only be done by chlorination. The supply and storage of bulk liquid chlorine on platforms is out of the question and apart from small-volume water circuits such as drinking water and sewage circuits, where hypochlorite in concentrated solid pill form is sometimes used, there is little alternative to the use of electrochlorination.

Chloropac is particularly suited to off-shore platform work because of its compact design and because of its adaptability for use in hazardous areas where the generating cell assembly may need to be housed in a water-tight enclosure, and the contact-making surfaces (flow switches, circuit breakers,etc.) have to be provided with explosion-proof/intrinsically safe enclosures.

As in the case of power stations, chlorination is usually carried out at the front end, i.e. at the mouth of the stilling tubes housing the main seawater lift pumps on the platform. In the case of fire pump systems, it is necessary to provide chlorination of the stilling tubes even when the pumps themselves are shut down, and this can conveniently be done by trickle feeding some of the already-chlorinated seawater through an orifice plate system which by-passes the main injection system. Full-flow hypochlorite treatment is done by a system of solenoid-operated valves on the Chloropac outlet manifold, and these are linked to the individual pump motor starters so that the hypochlorite liquor is fed to the appropriate pump as soon as its motor starts up.

7.3.1 Hydrogen Removal Vessel

The most convenient method of removing the hydrogen is by means of the normal knock-out tank, mentioned earlier, with its associated system of blowers and controls to ensure that the hydrogen/air mixture finally vented to atmosphere is less than 1% by volume of hydrogen and hence is non-explosive.

7.3.2 Hydrogen Venting in De-aeration Unit (Waterflood Schemes)

If no hydrogen disengagement vessel is used the hydrogen can be allowed to go through the water circuit, still under pressure in the water and hence unable to escape, until it reaches the de-aeration unit where it will be stripped out and can either be vented to atmosphere or can be sent to the flare boom and burned with other gaseous effluents.

In order to prevent an accumulation of hydrogen in the space above the water level in the main seawater lift pump stilling tube, it is desirable to have venting holes at the top of the tube above the platform level.

7.3.3 Hydrogen Removal in Seawater Return Line

In fire pump and other utility circuits where no waterflooding is involved, and hence there is no de-aeration unit, hydrogen removal can be effected (other than in a disengagement vessel) by allowing it to go through the system and to be returned to the sea still entrained in the water, at which point it will disperse harmlessly into the atmosphere.

More than 120 Chloropac units have been supplied for offshore platforms in the North Sea, Mediterranean, Persian Gulf and elsewhere. Examples of typical platform installations are given in Figs. 4,5 and 6.

7.4 Shipboard Applications

Ships' salt water circulating systems can be seriously affected by mussels and other marine growths, and if precautions are not taken to eliminate these, loss of vacuum on the condensers can occur, and this means the use of additional fuel to maintain the speed of the ship. In these days of slow-steaming and lay ups it is just as important to maintain clean cooling systems, so that the vessel is in good shape and can immediately be returned to full speed when conditions improve. During lay up, it is more important than ever to use Chloropac because fouling under these circumstances can be even more severe than when the ship is under way. Mussels can also cause an increase in erosion/corrosion of condenser tubes because of local increases of water velocity at the tube ends resulting from blockage by the marine growths.

Ships of all sizes from small tugs up to VLCCs and ULCCs have been successfully fitted with Chloropac units and the present shipboard installation list stands at over 300 units. Fig. 7 shows a unit installed in the engine room of a ship.

High pressure water up to about 7 or 8 bars gauge is taken from the discharge side of a salt water circulating pump, is passed through the cell unit and then injected directly into the sea inlet boxes, thus protecting the complete circulating system including condensers, pipework, valves, filters, etc.

In order to keep corrosion of normal condenser tube materials, such as aluminium brass, down to a minimum, the level of initial hypochlorite dosing should be limited to 0.5 ppm, and Chloropac units for shipboard applications are sized on this basis. This level of treatment is aimed at providing a chlorine residual of approximately 0.05 ppm in the overboard discharge and experience has shown that this is quite adequate to control mussel fouling on ships.

At the 0.5 ppm dosage level, each 0.45 kg/hr Chloropac unit can treat 900 m^3/hour of seawater (450 m^3/hour for the 0.225 kg/hr unit) and pro rata according to the size of the unit above 0.45 kg/hr.

So far as materials for construction of pipework, valves, etc. are concerned, normal ships' piping can be used for handling seawater up to theinlet of the Chloropac unit. Bare mild steel should be avoided in order to prevent rust solutions from entering the cells, and adequate filtration should aways be provided at the inlet to the unit. Depending upon the size of the unit concerned, the concentration of hypochlorite coming from the cells can vary within the range 50 - 1000 ppm approximately, and it is therefore necessary to use corrosion-resistant materials for the piping between the outlet side of the Chloropac unit and the point of injection in the sea chest. Plastics or other non-metallic materials are best for this purpose. Nylon-braided PVC piping has been successfully used and PTFE piping with a metal-braided outer cover is now also available. Where it is essential to use metallic piping at the outlet of the unit, the choice should preferably be 70/30 cupro-nickel, 90/10 cupro-nickel or aluminium brass in that descending order of corrosion resistance. Wall thicknesses should be as high as possible, consistent with cost, but should generally not be less than 2mm for reasonable life.

Experience with valves has shown that gunmetal bodies with nickel -copper alloy seats and trim have only a limited life in hypochlorite solutions, and wherever possible the shipside valve should be in titanium. Although the cost of a titanium valve is high it is regarded as a good investment because it will last the life of the ship and will require virtually no maintenance. Steel or SG iron valves lined with PTFE are also available at lower cost.

The dispersal pipe or nozzle which finally injects the hypochlorite into the sea chest should preferably be in titanium, particularly in large vessels, because this is the most vital part of the system and cannot be reached for maintenance between dry dockings.

Hydrogen removal from shipboard Chloropac units is not normally a problem, the hydrogen being carried through the system and dispersing in the overboard discharge. However, if there are pockets in the system where hydrogen can collect and cause an explosive hazard, then it is necessary to vent such systems to atmosphere in a safe place.

7.5 Sewage Treatment Plants

Because of the need to prevent the discharge of excessive chlorine residuals into rivers and water courses, the use of chlorination in Europe, and particularly the U.K., is not at present generally favoured for treatment of sewage. There are, however, exceptions to this, and in countries with long sea coastlines, such as Italy, discharge of treated sewage to the sea is possible and is such cases some form of chlorination is desirable, if not essential. In the U.S.A. and South Africa, for example, the restrictions on the use of chlorine for sewage treatment are not as severe as in some parts of Europe, and several large Chloropac units have already been supplied for this purpose in both countries where the treated sewage is being discharged to the sea.

In most cases, chlorination of the final effluent is done to a level of approximately 5 ppm, but Chloropac has also been used for treatment of the raw sewage to much higher dosage levels before discharge to the sea.

7.6 Oil Refineries and LNG Plants

Whenever these are located on sea coasts, there are likely to be problems with mussels in the cooling water systems and Chloropac units have been supplied to oil refineries in Australia, the Caribbean and Japan, and to LNG plants in Indonesia.

7.7 Chemical and Fertiliser Plants

Coastal installations will again require some form of marine fouling control, and there could be special problems in the case of fertiliser plants where the ammonia content of the water may increase the chlorine demand considerably. Chloropac units have been supplied to plants in the Caribbean, Southern Ireland and North Africa (see Fig. 8).

8 Future Development

Additional research and development work within the Engelhard organisation is aimed at further improvements in cell design, particularly with regard to simplification of cell configuration and reducing power consumption. This should further enhance the market for the once-through seawater cell which has proved to be so popular.

Another new design of Chloropac unit is in an advanced stage of development. This is based on a brine recycle system and will comprise a skid-mounted package system including a brine make-up unit, cells, transformer-rectifier unit, recycle tank, cooler, and product storage tank. The unit is intended for inland applications where seawater is not available for feeding to the cells, for example in swimming pools where a change over from gas chlorination to hypochlorite is expected to take place within the next few years.

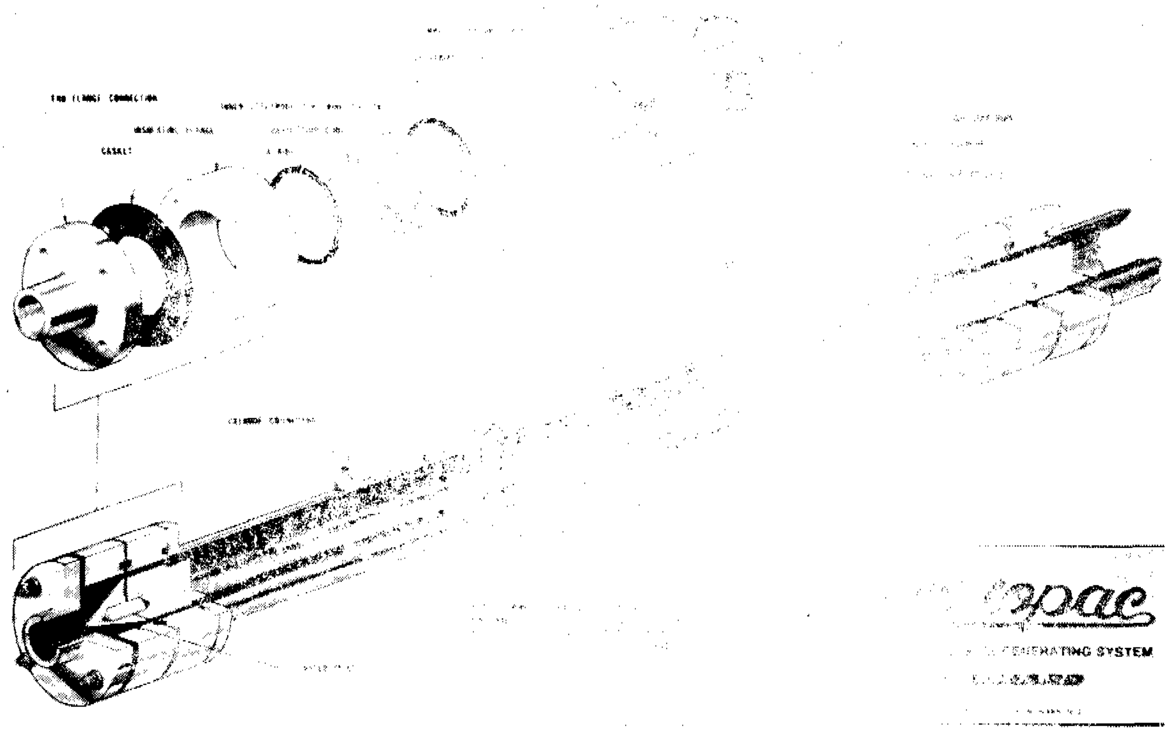


Fig. 1 — Exploded view of 'Chloropac' cell

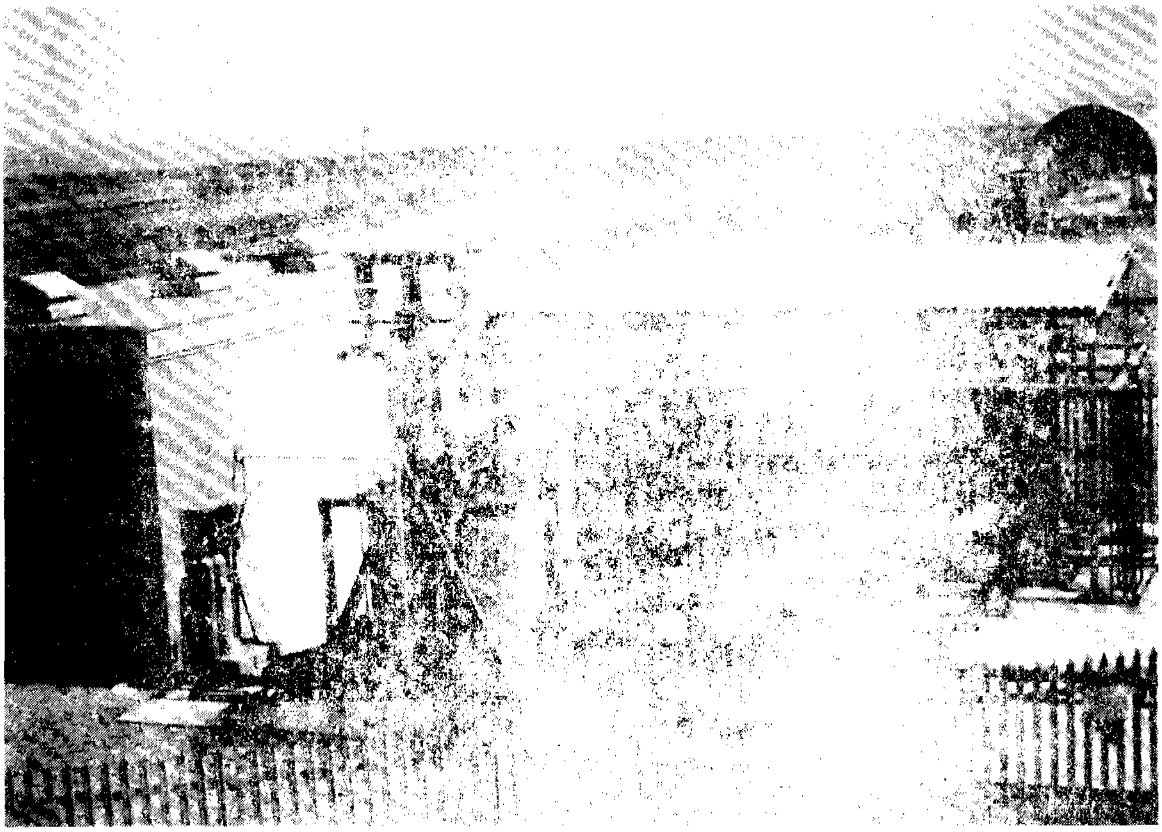


Fig. 2 — 'Chloropac' installation at coastal [illegible]

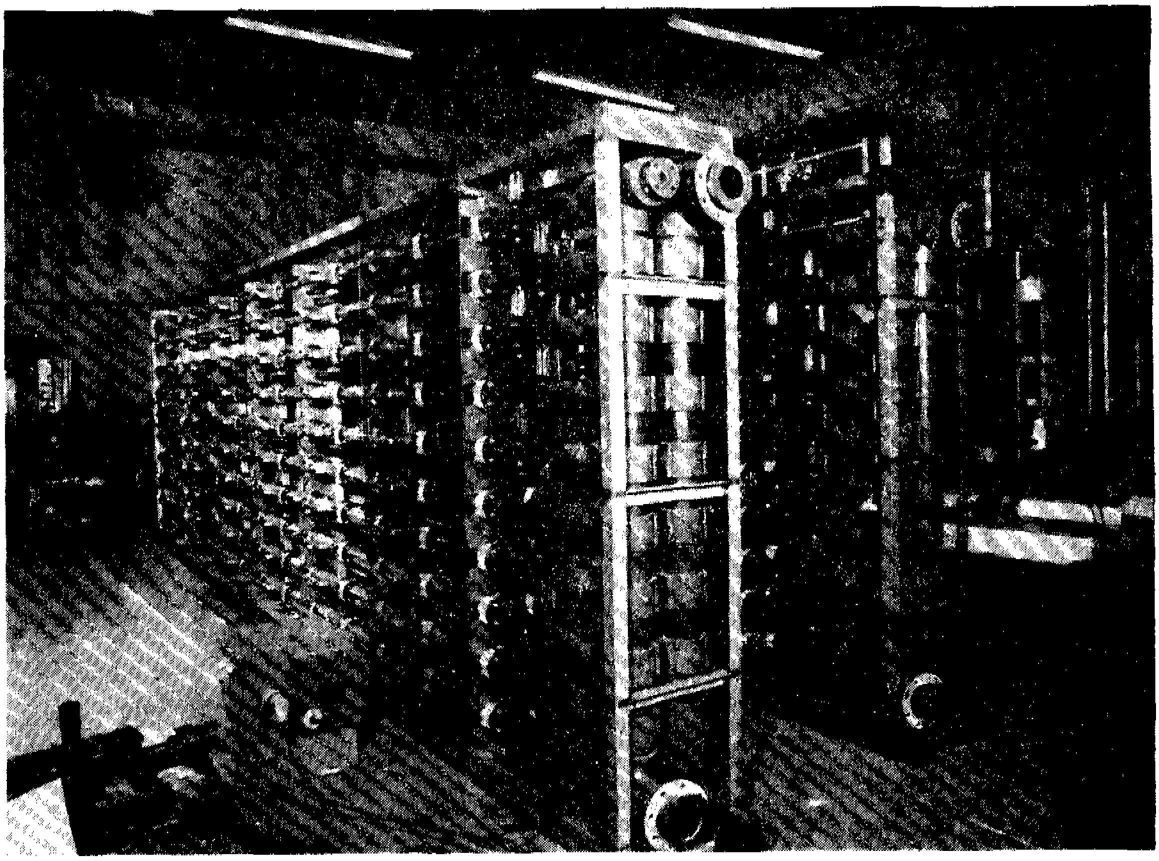


Fig. 3 — 'Chloropac' cell assemblies as installed at coastal power station

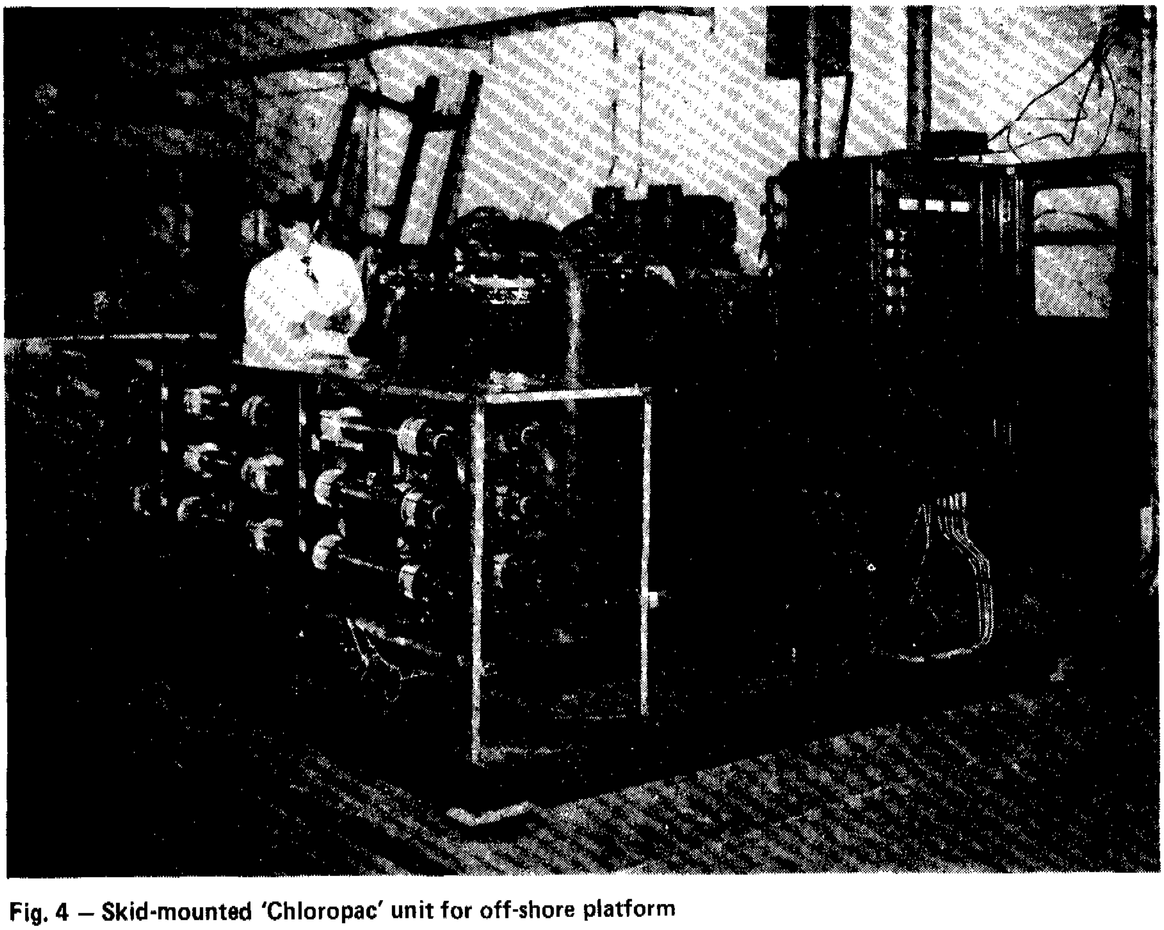


Fig. 4 — Skid-mounted 'Chloropac' unit for off-shore platform

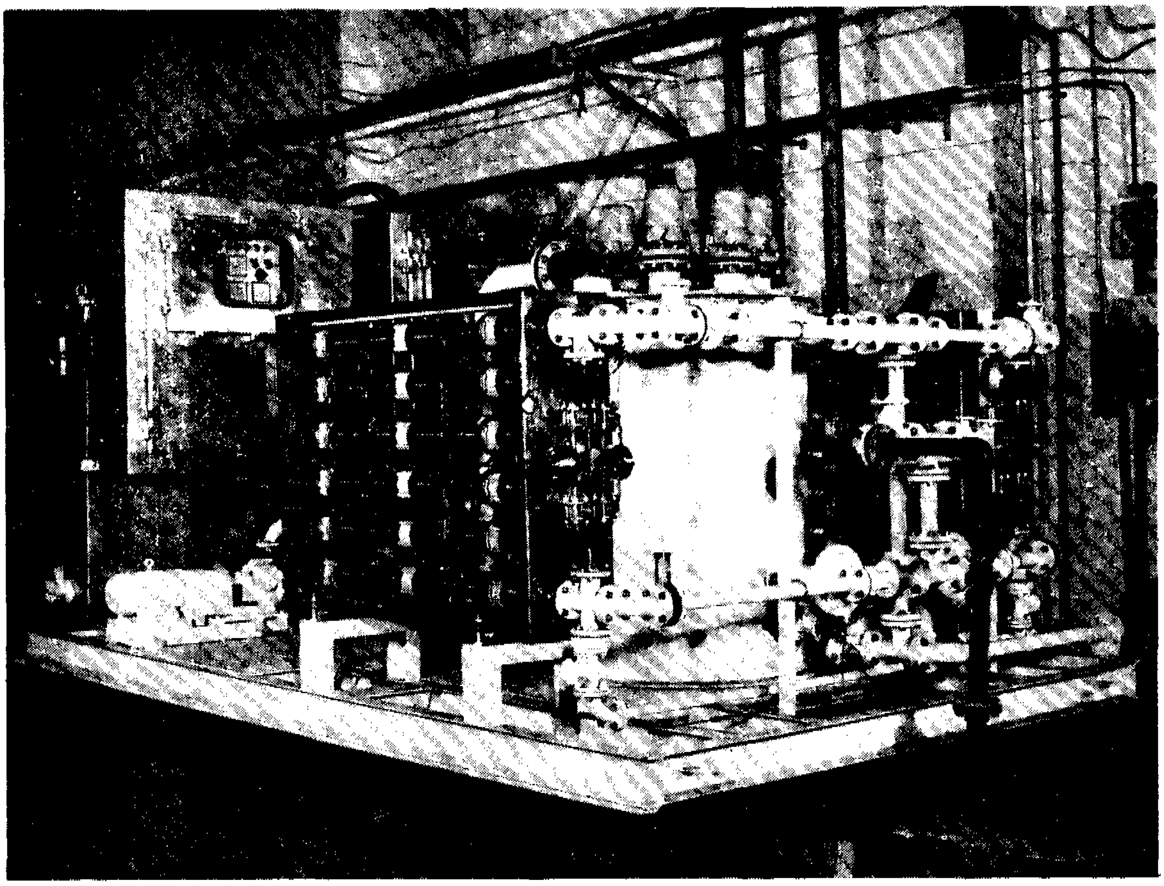


Fig. 5 — Skid-mounted 'Chloropac' unit for off-shore platform

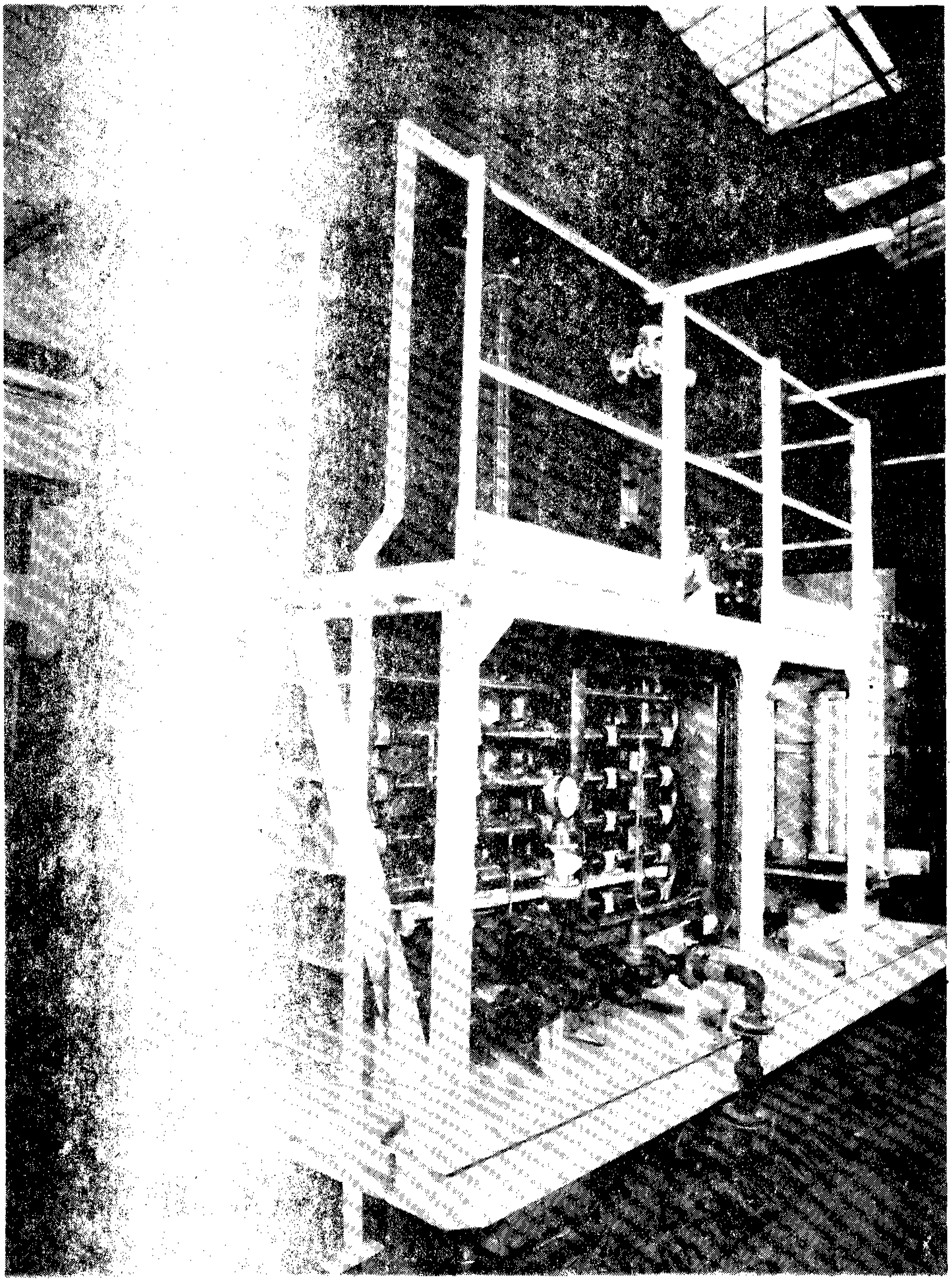


Fig. 6 – Sk [illegible] ed' unit for off-shore platform

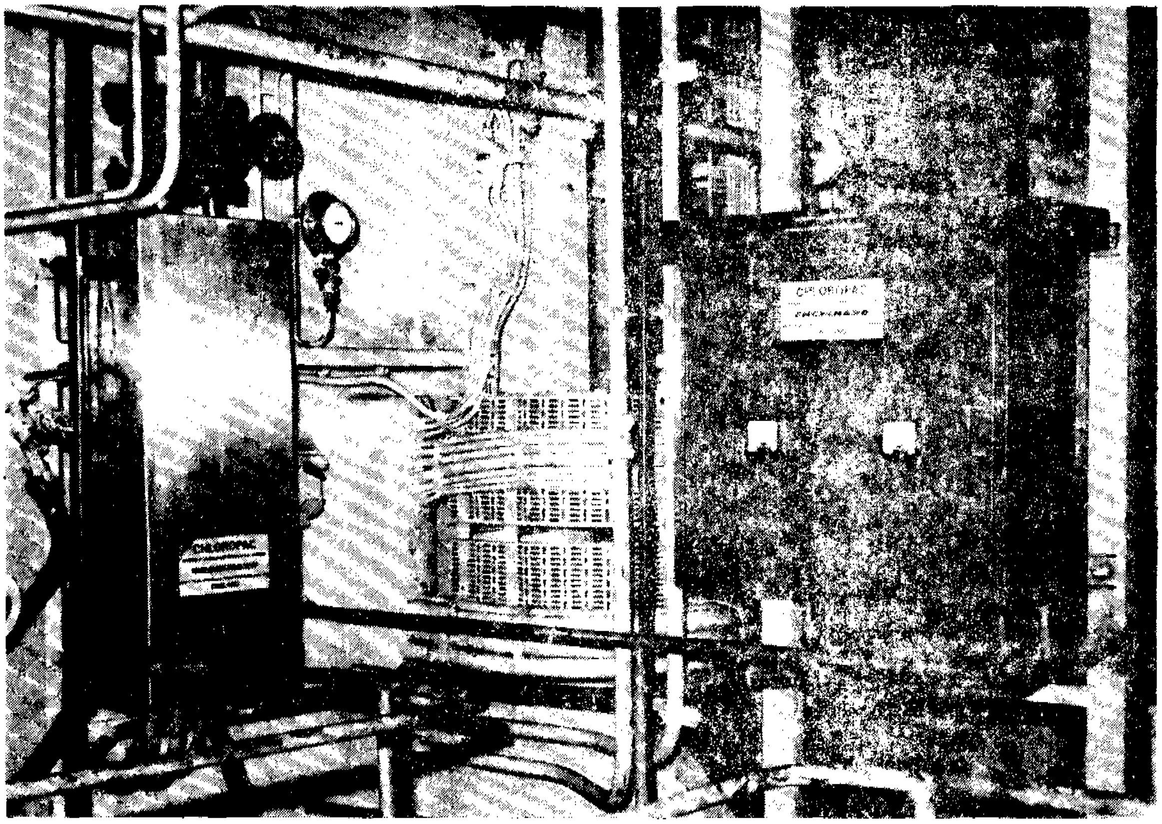


Fig. 7 – 'Chloropac' unit mounted in engine room of a ship

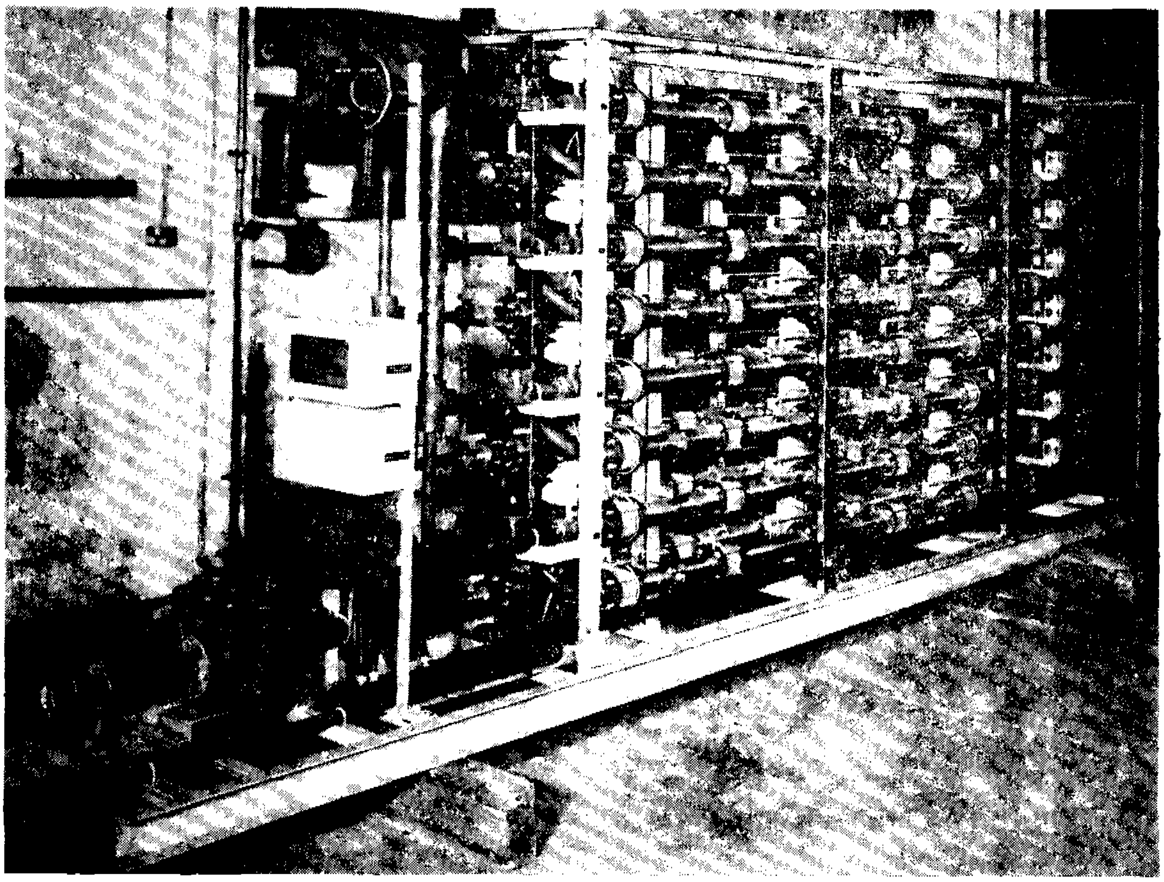


Fig. 8 – 'Chloropac' unit for land-based coastal fertiliser plant

SANILEC (R) ELECTROCHLORINATION EQUIPMENT:

SEAWATER AND BRINE SYSTEMS

K.P.HAINES

CJB DEVELOPMENTS LIMITED

CJB Developments has been involved with electrochlorination systems for many years. In the 1960's, plane parallel electrolysis cells were developed for the electrolysis of sea water primarily for the treatment of coastal discharges of sewage. A number of small 'Hypak' plants were installed and have operated successfully. There was, however, little pressure to treat sewage discharges at that time and marketing of this equipment was stopped in 1972. In the intervening years there have been significant advances in the chlor/alkali industry, the most notable of which is the development of DSA (R) anodes. These anodes have a titanium substrate with a coating of mixed metal oxides which catalyse the chlorine evolution reaction and therefore exhibit low overpotential characteristics. The world patent rights to the DSA technology are held by the Diamond Shamrock Corporation, a world leader in chlor/alkali technology. Diamond Shamrock have sought to extend the application for DSA electrodes and one of their developments is the SANILEC range ofsystems for the on site generation of sodium hypochlorite solutions. CJB Developments has chosen to market SANILEC systems in the UK in preference to redeveloping the now outdated Hypak systems.

The SANILEC range includes systems for the generation of "active chlorine" solutions from both seawater and synthetic brines. The economic and operational constraints imposed by these electrolytes has resulted in quite different cell and system designs.

SANILEC Brine Systems

The SANILEC brine systems are engineered around standard cell designs. These have nominal output capacities ranging from 9 kg to 900 kg of hypochlorite (expressed as chlorine equivalent) per 24 hour day. Within each cell box is located a number of electrolytic cells without diaphragms. These are in electric and hydraulic series. Partitioning between the cells provides a tortuous path through the cell box and prevents short circuiting of the electrolyte.

In the electrolysis of brine solutions without diaphragms an inefficiency arises through reduction of hypochlorite ion at the cathode. This inefficiency increases with increasing hypochlorite concentration. Recycling of electrolyte through a cell to build up the hypochlorite concentration results in a relatively low overall efficiency. With the SANILEC brine cell a single pass of electrolyte through the series cells is used so that the hypochlorite concentration is increased progressively. By this means the inefficiency due to hypochlorite reduction is kept to a minimum in each cell and the overall efficiency is maximised. In addition to optimising the current efficiency, the effects of brine strength and current density on salt and electricity costs were extensively studied and an optimum operating condition computed. An account of the development and optimisation of the SANILEC brine cell and sytem is given in a paper by J. E. Bennett of Diamond Shamrock (ref. 1.)

The SANILEC brine system uses potable grade water and good quality salt, typically water softener grade. The water is treated by a base exchange water softener to remove calcium, magnesium and impurity metal ions which would form basic deposits at the cathode. Some softened water passes to a brine make- up tank which also functions as a salt store. The brine level in the tank is controlled by a float valve.

Saturated brine is drawn from the make-up tank by means of an eductor. The brine is diluted to 3%^{w}/w concentration by more softened water. Rotameters provide visual indication of the water and saturated brine flows which are set by manual valves. The diluted brine passes to the electrolysis cell.The flow of water and brine solution through the system to the electrolysis cell is effected using mains water pressure only and does not involve rotating equipment unless it is necessary to boost the available water pressure.

The complete SANILEC brine system also includes automatic, time controlled regeneration of the water softener bed, a transformer/rectifier unit to provide d.c. current, appropriate alarm switches for temperature, cell electrolyte level and power malfunction alarm switches and electrical interlocks to protect the system.

The smaller SANILEC brine systems, up to 45 kg chlorine equivalent per day output are completely factory assembled on pallets and merely require to be sited on a level floor and connected up with the appropriate pipework and electrical supply. The larger systems are supplied as discrete sub-assemblies which require interconnection on site.

The systems evolve hydrogen which has to be disposed of safely. With the larger systems an air blower is included which forces air into the top of the electrolysis cell diluting the hydrogen to a safe concentration before it is vented from the cell. With the smaller systems the quantity of hydrogen evolved is quite small. For example the 45 kg per day system evolves about 17 litres of hydrogen per minute. It is normally considered adequate to pipe this hydrogen to the outside of a building where it may be vented at a safe height. Forced air dilution can be provided for the smaller systems if required.

All the SANILEC brine systems are designed to operate under constant conditions of flow, brine concentration and operating current: less than maximum output is arranged by intermittent operation. The systems are automatic in operation and the intermittent operation can be initiated by level switches in a receiving tank, by a time clock, or by a residual chlorine analyser.

With all the brine systems the sodium hypochlorite is generated at 0.8 ± 0.1% and the consumption of raw materials should not exceed 125 litres water, 3.5 kg salt and 5.5 kWh electricity per kg of chlorine equivalent generated. At June 1980 costs for these materials this represents a cost of about 35 pence per kg of chlorine or £350 per tonne.

SANILEC Seawater Systems

The SANILEC seawater electrolysis cell has a number of alternate anodes and cathodes connected in parallel within a polypropylene cell frame with an acrylic cover plate. The anodes are of the DSA type, in an expanded metal grid form, while the patented cathodes are plane sheets of Hastelloy 'C' alloy.The standard DSA anodes used in the SANILEC cells have an operating temperature range from 15°C to 35°C, however, a specially formulated anode coating is available which is suitable for operation down to 5°C.All the materials of construction including the fastenings are of corrosion resistant materials. The interelectrode gap is very small i.e. at about 0.8mm.

There are three standard sizes of SANILEC seawater cell with nominal output capacities of 34, 68 and 136 kg/day chlorine equivalent. The largest cell is also now available with a slightly increased capacity of 150 kg/day. The cells are all of the same height and width and use the same size electrodes. The seawater flowrates required by these cells are 6, 10 and 20 m^3/h and the nominal cell currents are 1375, 2750 and 5500 amps or 6000 amps for the uprated version.

The SANILEC seawater systems are supplied as factory assembled modules. The cells are mounted on a steel frame and base plate together with the necessary seawater flow controls, cell interconnections and low flow and high temperature alarm contacts. Up to eight cells may be connected together in hydraulic and electric series giving a range of module capacities from 34 kg/day up to 1.2tonne/day of equivalent chlorine. The concentration of hypochlorite generated depends upon the number of cells in series and ranges from about 330 mg/l up to 2.35 g/l.

Evolved hydrogen increases the effective resistance of the seawater electrolyte and with a number of cells in series would tend to increase the power requirement. For modules of four or more cells intermediate hydrogen gas disengagement cyclones are included after every 3 cells.

The low overpotential characteristics of the electrodes, the small interelectrode gap and the use of intermediate hydrogen gas disengagement all contribute to the good power consumption characteristics exhibited by the seawater systems. Power consumption is also a function of seawater salinity and temperature which is shown in Figure 1. It can be seen from Figure 1 that a SANILEC system on full load with 100% seawater (defined as 18,900 mg/l chloride ion) at 15 to 25°C uses about 3.9 to 4.0 kWh of electricity per kg of chlorine equivalent generated. These figures include rectification losses. The power consumption is lower at less than full load operation. Reduced output where required can be arranged either by intermittent operation or preferably by reducing the power to the electrolysis module.

A particular problem with the electrolysis of seawater is the formation of basic deposits of magnesium and calcium at the cathode (ref. 2). These deposits if allowed to build up will bridge the gap between the electrodes causing hot spots and damage to the electrodes. The SANILEC seawater system overcomes this problem in three ways. Firstly, the seawater cell has been designed and the operating conditions chosen to minimise the build up of these deposits; secondly the tranparent acrylic cover of the cell allows the interior of the cell to be inspected and thirdly pipework is included on the electrolysis module to facilitate acid cleaning of the cells. Acid cleaning is easily carried out in situ with 10% hydrochloric acid and takes about 3 to 6 hours. Cleaning may be required two or three times per year, however, some users elect to clean more frequently as part of planned maintenance programmes.

The scope of supply for a SANILEC seawater system typically includes a seawater strainer to prevent suspended matter from fouling the electrodes, the SANILEC electrolysis module, a transformer/rectifier unit and standard control package, and equipment for hydrogen gas disengagement. The last may be a cyclone with small installations or a tank with forced air dilution of the hydrogen for larger installations. In addition seawater pumps, hypochlorite transfer pumps, non standard transformer rectifier units, and residual chlorine controllers can be supplied and the systems can be designed for installation in hazardous zones.

The SANILEC seawater systems are normally supplied for the direct dosing of a seawater supply as hypochlorite generated from seawater has a poor stability, however, the produced hypochlorite may be stored for several hours where both continuous dosing and intermittent shock dosing are practised.

Installations

Both the SANILEC brine systems and the seawater systems have been widely installed throughout the world for a variety of applications.

The first brine system was installed in 1973 and up to June 1980 over 90 separate plants have been installed or ordered, with a total capacity in excess of 25 tonnes chlorine equivalent per day. The largest single installation has a capacity of 8 tonnes chlorine equivalent per day. The major applications for the SANILEC brine systems have been for the treatment of potable water, for the treatment of waste water and sewage and for the treatment of cooling water. Systems have also been installed for laundry bleaching, odour control, cyanide destruction and for swimming pool water disinfection. Recently a SANILEC brine system was chosen for the Clinch River fast breeder nuclear power station in the United States. SANILEC is understood to have been chosen because it does not involve gaseous chlorine at any stage.

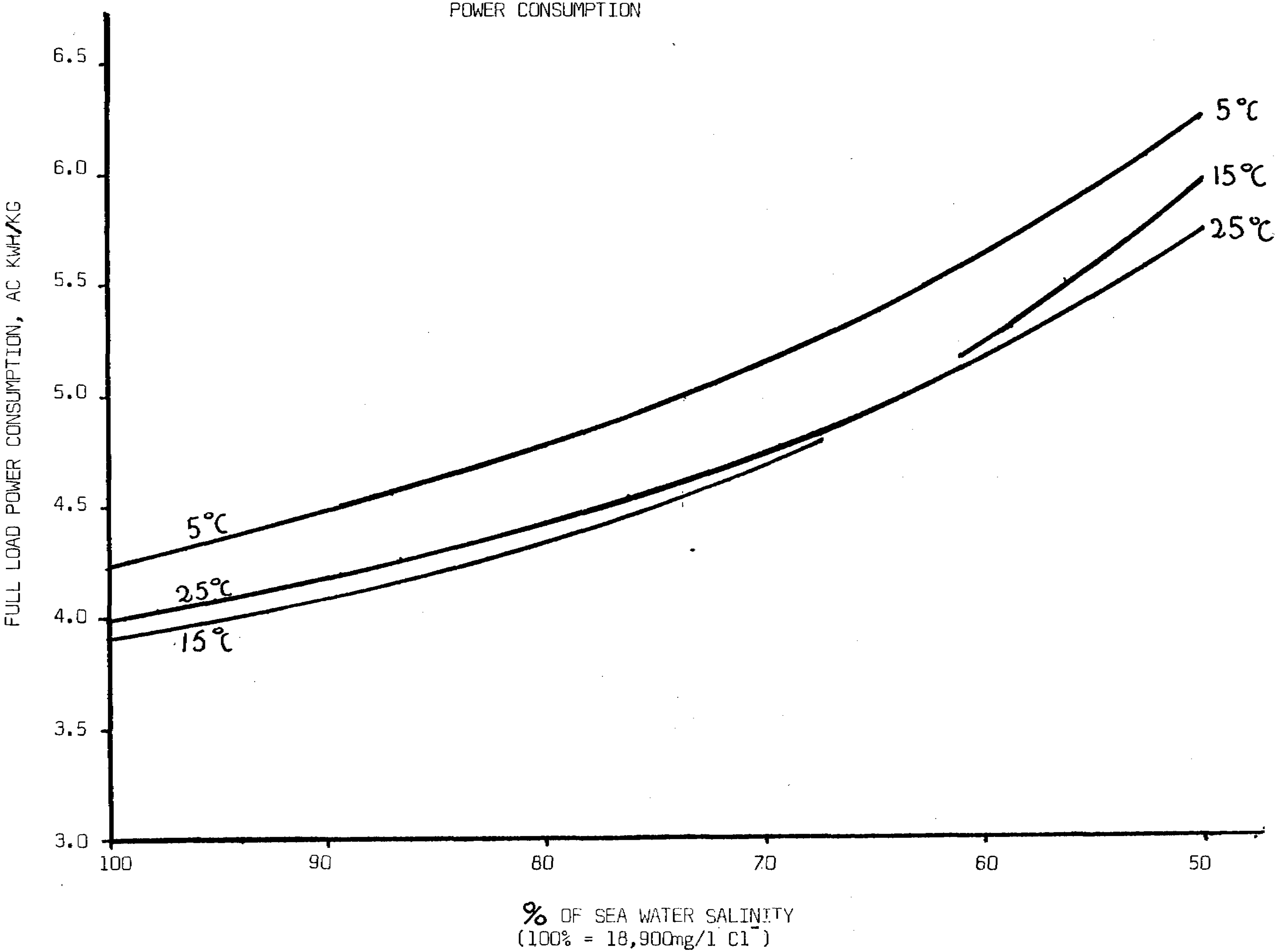
The first seawater system was installed in 1974 and up to June 1980 about 36 separate plants have been installed or ordered with a total output capacity in excess of 55 tonnes chlorine equivalent per day. The largest individual installation has a capacity of about 16 tonnes per day. The major applications for the SANILEC seawater systems have been for the treatment of cooling water and waste water and for the sterilisation of oil field injection water.

All the SANILEC systems are available from CJB Developments who provide a complete engineering service to meet individual requirements.

References

1. J.E.Bennett, Non diaphragm electrolytic hypochlorite generators. Chem.Eng.Prog. Vol 70, No. 12, 60-63.
2. J.E.Bennett, On site generation of hypochlorite solution by electrolysis of sea water. AICLE Symposium Series No. 178, Vol. 74, 1978, p.265.

FIGURE 1. SANILEC SEA WATER CELL POWER CONSUMPTION



CHLORINE AND HYPOCHLORITE IN THE PULP AND PAPER INDUSTRY

BY

T.W. MALONEY
CHEMETICS INTERNATIONAL LTD.
VANCOUVER, B.C., CANADA

I. Introduction & Historical Background

Wood and cotton have much in common. Both contain fibers essentially comprising of cellulose and substances chemically related to cellulose. Both can be converted into paper; in fact, cotton rags and worn-out clothing were used for papermaking long before wood was considered for this role. Originally these rags were bleached by exposure to air and sunlight - the first oxygen bleaching process. Berthollet in 1785 observed that chlorine destroys the colouring of vegetable matter on contact. The dangerous nature of chlorine led James Watt to the discovery that chlorine could be absorbed in soda solution and to the resultant establishment of the first commercial bleachery. Later, it was found that a dry bleaching powder could be made by passing chlorine gas through lime; the first commercial product was made in Rumford Falls, Maine, in 1893.

In a physical sense, however, wood and cotton differ significantly. Cotton fibers occur as seed hairs clustered around the cotton seed. The fibers can be cut from the seed and used with little further purification. Wood fibers are solidly embedded in a rigid mass which constitutes trunk and branches of the tree. This mass of fibers is held together by means of a polyphenolic cement, known as lignin.

Lignin is present in appreciable quantity, comprising 25-30% of the total weight of coniferous woods and somewhat less of deciduous woods. It predominates in the spaces between the fibers and a minor proportion permeates the fiber as far as the hollow tubular center - the lumen. Lignin is chemically distinct from the cellulosic components. Progressive depolymerization of cellulose leads ultimately to glucose, whereas the flavouring agent vanillin is a product of a similar breakdown of lignin.

Modern papermaking from wood centers around separation of the cellulosic fibers from the solid matrix into discreet entities. This can be accomplished either by mechanical or by chemical means. Mechanical pulps are used extensively in the less sophisticated paper grades, for example, in newsprint manufacture. However, production of high quality white papers requires selective, chemical dissolution of the lignin cement. The overall process is known as delignification and can be sub-divided into pulping and bleaching. This discussion will be restricted to production of bleached chemical pulps, with emphasis on the use of chlorine-based chemicals. A section is included which describes the supply, formulation and handling of these reagents.

II. Chemical Pulping

The lignin cement holding the fibers together is solubilized and progressively removed by chemical degradation, until the mass of cellulose fibers is disintegrated by the mild mechanical action produced from "blowing" the cook. The two common methods of chemical pulping are the kraft and sulphite processes. In kraft pulping, a mixed solution of sodium hydroxide and sodium sulphide is the active ingredient of the cooking liquor. Calcium, magnesium, sodium or ammonium bisulphite, usually with excess sulphur dioxide, is the active component of sulphite pulping liquor.

Although virgin lignin is not highly coloured, it is susceptible to development of colour during pulping. In the kraft process, the lignin turns dark brown, this colour being imparted both to the liquor and the pulp. Cellulosic material is naturally white and is not severely attacked by the pulping reagents. The fibers, therefore, would be white if lignin removal were complete; subsequent bleaching would then be unnecessary. However, delignification is not complete. Lignin residue remains on the surface and within the fiber. Although the residual lignin comprises only 4 or 5% of the pulp, it is highly coloured, chemically modified and tenaciously held by the cellulosic fibers. For production of white pulp of suitable strength characteristics, the lignin residue must be removed without damage to the cellulosic fibers. This is the primary objective of modern bleaching technology.

III. The Multi-Stage Bleaching Sequence

Cellulosic materials are more resistant to chemical attack than is lignin; this characteristic has been exploited for many years in the bleaching of chemical pulps. Sulphite pulp is more amenable to bleaching than is kraft. Bleaching techniques were first devised for sulphite; the pulp was mixed with calcium hypochlorite at low consistency and allowed to react for a stipulated period. Kraft pulp did not respond well to these methods and it was not until multi-stage bleaching emerged, based on the use of chlorine, that serious attempts were made to upgrade the quality of this pulp.

The availability of chlorine in the early part of this century contributed to the development of multi-stage bleaching. The first sequence, chlorination, caustic extraction, hypochlorite (CEH), was applied initially to sulphite pulp and readily resulted in high brightness products. Applied to kraft, this sequence produced semi-bleached brightness, but the pulp could be upgraded using additional stages, as in the five-stage process CEHEH. New bleaching chemicals developed after World War II were incorporated into multi-stage bleaching technology. These included alkaline hydrogen peroxide and chlorine dioxide. The latter reagent possesses unique advantages which led to widespread adoption of two sequences, namely C_DEDED and C_DEHDED. These remain the preferred sequences for production of fully bleached kraft pulp; the ensuing discussion will concentrate on these processes. Tables 1 to 3 describe typical consumptions of chlorine-based chemicals in these bleaching sequences.

A bleaching sequence comprises a series of chemical treatments designed to solubilize lignin, while inflicting the minimum of damage to the cellulosic component of the pulp. Each stage in a sequence is subject to four principal variables. Probably of equal importance and very much interdependent, these are, quality of the incoming pulp, level of chemical application, retention time and temperature. Control parameters such as pH, residual chemical analysis and a variety of pulp quality values are extensively monitored throughout the sequences.

a) Chlorination Stage (C)

The first two stages of the bleaching sequence, chlorination and extraction, are intended to remove over 80% of the residual lignin. To a large extent, therefore, a fine control of these stages is very important to the quality of the final product.

The level of chlorine and subsequent chemical applications applied to the pulp are directly related to lignin content. This is measured by indirect methods, the most common determinations being permanganate number and kappa number. The chlorine demand of a pulp will also be a function of the efficiency to which the pulp has been washed. Carryover of alkaline black liquor from the wood cooking stage will consume substantial quantities of chlorine. As a general rule, high washing efficiency is essential to the economy of a bleach plant operation. In a typical mill situation, the chlorine requirement for a softwood stock is about 120-140 lb/ton of pulp; hardwoods require about 70-90 lb/ton. Modern bleaching technology uses chlorine dioxide in the chlorination stage, which replaces equivalent oxidation levels of chlorine. A replacement of 15% of the chlorine demand is typical and is described in Tables 1 to 3. This trend will be discussed in further detail in a subsequent section.

b) Extraction Stage (E)

Chlorinated lignin is yellow in colour and very reactive to sodium hydroxide when it is broken down to soluble derivatives. This is the principle behind the caustic extraction stages of a typical bleach plant.

The charge of caustic soda is primarily influenced by the preceding chlorine charge and the degree of acidic effluent carryover from the chlorination stage washer. A bleach plant is considered to have high efficiency washing when its vacuum filters displace 80% or more of the spent bleach effluent. Under these conditions, the caustic requirement in a typical extraction corresponds to about 55% of the chlorine applied in the first stage. For example, a properly operated chlorination having been charged with 120 lb chlorine per ton of pulp, will require about 65 lb. sodium hydroxide in the first extraction stage.

c) Hypochlorite Stage (H)

Hypochlorite is an effective bleaching agent, its main disadvantage being its tendency to degrade the fiber along with the lignin residue. This tendency is more pronounced when the fibers are relatively lignin-free, as in the final stage of bleaching. When applied in the third stage, the degradative effect is not severe provided suitable conditions are maintained. These include a temperature not exceeding 45°C and sufficient alkaline buffer (lime or caustic soda) to result in an exit pH of at least 9.0. pH control is very important; if it is allowed to fall below a value of 8.0, severe fiber degradation will occur due to release of hypochlorous acid.

In practice, chemical concentrations (available chlorine) are adjusted to reach a pulp brightness in the vicinity of 70 G.E. This will generally require 20-25 lb/ton for softwood and about 10-15 lb/ton for hardwood.

d) Chlorine Dioxide (D)

When applied to hardwood, the fourth stage treatment is usually all which is required to provide a market quality product of high and stable brightness (Table 3). Chemical requirements will be in the approximate range 12-16 lb/ton of pulp.

In softwood pulp bleaching, the hypochlorite stage is often omitted and the pulp treated directly with chlorine dioxide (C_DEHDED vs. C_DEDED) (Tables 1 and 2). The route chosen will have an important effect on the chemical requirements to achieve a particular final brightness. In the event the first dioxide treatment follows hypochlorite, the chemical applied is usually in the range 10-14 lb/ton of pulp. In a C_DEDED system, the first dioxide application is approximately 20-24 lb/ton of pulp. Total chemical requirements, with associated operating costs for the various bleach sequences, are summarized in Tables 6 and 7.

Chlorine dioxide is a unique bleaching agent in that it has the capacity to eliminate resistant lignin residue completely, while causing no damage to the cellulosic fiber. In a softwood operation, the first three or four stages, C_DED or C_DEHD, are designed to essentially remove all of the lignin residue. The subsequent ED repetition is intended to remove the last traces of colour and to provide a stable brightness. The final ED stages are the most standardized in the system. Caustic soda to a level of 10 lb/ton is added; the final chlorine dioxide stage is conducted using 4-8 lb chemical per ton of pulp.

Pulp shrinkage observed across a softwood bleach plant will normally be in the range 7-8%; the loss in yield associated with hardwood bleaching is typically about 5%. These differences, of course, reflect the differences in lignin content of the unbleached materials.

e) Product Quality Control

In the final bleaching stages, pulp brightness and viscosity become the dominant quality control parameters. To a large extent, these properties will determine the product's acceptance by the papermakers and as a result exert a strong influence on its market price. A top quality bleached market pulp will have a brightness of at least 88. In the case of softwood pulp, the viscosity will typically be in excess of 18 cps., while for hardwood it should not be less than 12 cps.

IV. Supply, Formulation and Handling of Chlorine-based Chemicals

More than 90% of the chloralkali consumed by the North American pulp and paper industry is supplied from merchant scale plants. Even those very few mills which operate on-site chloralkali facilities generally export a varying proportion of their output as merchant product. This enchances the feasibility of the relatively small on-site plant, which is competing against the considerable economic benefits of large scale production. A bleached softwood kraft pulp mill, capacity 1,000 TPD, will have a consumption of chlorine in the range 60-70 tons per day. Without very extreme legislation being passed which forbids the shipment of chlorine, this situation of supply is unlikely to change drastically for the foreseeable future.

It should be realized, however, that by efficient utilization of waste wood, a pulp mill can produce energy in excess of its requirements; many modern mills are presently self-sufficient in energy by this technique. It could be foreseen that given the extreme legislation as described above, the pulp and paper industry could go a long way in producing the energy required for economical on-site electrochemical generation.

From rail car storage, chlorine is injected as a gas into the aqueous pulp slurry. The use of static mixers and a large pressure drop across the point of injection results in a vigorous turbulence in the process stream. This provides the efficient initial mixing essential to an effective pulp chlorination. Chlorine addition is controlled automatically by in-line instrumental methods, such as measurement of oxidation-reduction potential.

Hypochlorite is invariably formulated on-site, adjacent to the point of use. Sodium hydroxide, delivered at 50% concentration, is diluted to a strength of about 5% and chlorine gas is injected into this solution in an in-line mixer. The rate of chlorine addition is controlled automatically by in-line measurement of oxidation-reduction potential and/or pH. Periodic checks are also made by chemical analysis of available chlorine concentration. The hypochlorite solution is pumped to a storage tank, before being metered to the pulp system.

Because of its hazardous characteristics, chlorine dioxide is always generated at the pulp mill site by reduction of sodium chlorate which is usually supplied from a merchant facility as crystal, or in solution of concentration 400-600 gpl. Dilution is conducted in accordance with the specification of the particular type of chlorine dioxide system in operation. Most systems today employ sodium chloride as the reducing agent which is present as a desired impurity in the chlorate. In these systems, sulphuric acid provides the required level of pH; the basic oxidation reduction reaction is represented by the following equation:

$$ClO_3^{\ominus} + Cl^{\ominus} + 2H^{\oplus} \longrightarrow ClO_2 + \frac{1}{2} Cl_2 + H_2O$$

Some units in operation also use sulphur dioxide or methanol as the reducing agent. The by-product chlorine can be utilized as pulp dilution water in the chlorination stage, or the chlorine alternatively can be absorbed in caustic soda to form hypochlorite.

Another type of chlorine dioxide system uses hydrochloric acid as both the reducing agent and source of acidity. The brine effluent from the generator is usually integrated with an on-site chlorate plant to result effectively in a closed system. The by-product chlorine can be used as previously described, or alternatively, it can be returned to combine with hydrogen from the electrolytic plant to re-form hydrochloric acid. Although absent in North America, the integrated concept is in active operation in certain European and developing countries not accessible to a merchant chlorate supply. It is also used in at least one other location where in addition to its remote location, the mill employs a sulphur-free pulping system. The generation and handling of chlorine dioxide is conducted in the absence of UV light, as irradiation can initiate explosive decomposition of this compound to its elements.

In the North American industry, the effluent from a sulphuric acid based generator is of practical importance as it contains sodium sulphate, which is required as make-up in the kraft chemical recovery system. The average kraft pulp mill is much tighter in the recovery and containment of sulphur than sodium. This is due to stringent pollution abatement regulations applied to emissions of reduced sulphur gases from recovery boiler stacks and other vents. As a consequence, sodium sulphate (in addition to generator effluent) formerly the primary source of chemical make-up is being replaced by sodium hydroxide. In certain cases, this will have the effect of placing the mill's consumption of chloralkali more in balance with the stoichiometric output of the electrolytic plant. However, the situation in this regard is very much site specific and will depend on local pollution abatement legislation and the type of bleaching in operation. In support of this, one major chloralkali producer quoted two extremes of consumption among his clients. Whereas a certain mill consumes 0.73 tons of sodium hydroxide per ton of chlorine, another in the same market territory consumes 1.60 tons of sodium hydroxide per ton of chlorine. With astute technical planning, however, there is no good reason why a mill should not consume a chloralkali balance close to that of the electrochemical plant. Economically, this is the most desirable situation, as often a premium payment is required for any demands in excess of this balance.

V. Trends

Approximately 14% of the U.S. chlorine requirement is consumed by the pulp and paper industry. As previously mentioned, a trend in the industry is favouring an increasing replacement of chlorine with equivalents of chlorine dioxide in the first stage of bleaching. Some reputable sources claim that the greater this substitution up to a level of 70%, the more beneficial the effects on pulp quality and bleached pulp yield. This has not been demonstrated conclusively, but massive levels of substitution as described will have a very positive effect on pollution abatement. This is mainly due to the marked reduction in the levels of mutagenic compounds in the form of chlorinated organics, found in the chlorination and extraction stage effluents. This tendency will, of course, be of concern to the major chlorine producers, but it could assist some pulp mills further towards consumption of a chloralkali balance equivalent to that of the electrolytic plant. Such steps need to be considered alongside the pulp mill's chemical make-up requirements as discussed earlier. It should also be remembered that even in terms of oxidizing equivalents, chlorine dioxide is 60-90% more expensive than chlorine.

A second trend beginning to gain momentum is the adoption of oxygen/alkali treatment of pulp prior to chlorination. Existing installations delignify the unbleached pulp by approximately 50%, which results in a corresponding reduction in chlorine and caustic demand in the subsequent bleaching stages. Tables 4 and 5 describe the effects of an oxygen stage on the consumptions of chlorine-based chemicals; the resultant effects on bleaching costs are summarized in Tables 6 and 7, when bleach chemical savings of more than $3/ton of pulp can be realised.

The effluent from an oxygen delignification stage is perfectly compatible with the pulp mill's chemical recovery system. By recycle of the oxygen stage filtrate back to the recovery area, a reduction of about 50% in the pollution load of the bleach plant effluent is achieved, relative to a conventional system. The reduction in pollution approximately corresponds to the degree of delignification conducted in the oxygen stage.

In summary, for reasons of pollution abatement if no other, the use of chlorine dioxide and oxygen delignification as replacements for chlorine is expected to exert a gradually increasing influence on the market for chlorine suppliers to the pulp and paper industry. It may be projected that at least a portion of this lost market will be absorbed by the unusually large growth trends anticipated for VCM/PVC and MDI.

TWM/cjb

TABLE 1

C_DEDED BLEACH SEQUENCE - TYPICAL CHEMICAL REQUIREMENTS

[lb/unbleached B.D. Ton]

	C_D	E	D	E	D	Totals
Chlorine	120					120
Sodium Hydroxide		77		10		87
Chlorine Dioxide	8		22		6	36

ASSUMPTIONS:

Unbleached softwood pulp, permanganate number: 20

Final brightness: 88

TABLE 2

C_DEHDED BLEACH SEQUENCE - TYPICAL CHEMICAL REQUIREMENTS

[lb/unbleached B.D. ton]

	C_D	E	H	D	E	D	Totals
Chlorine	120		25				145
Sodium Hydroxide		77	33		10		120
Chlorine Dioxide	8			12		4	24

ASSUMPTIONS:

Unbleached softwood pulp, permanganate number: 20

Final brightness: 88

TABLE 3

C_DEHD BLEACH SEQUENCE - TYPICAL CHEMICAL REQUIREMENTS

[lb/unbleached B.D. ton]

	C_D	E	H	D	Totals
Chlorine	66		12		78
Sodium Hydroxide		44	16		60
Chlorine Dioxide	5			14	19

ASSUMPTIONS:

Unbleached hardwood pulp, permanganate number: 12

Final brightness: 88

TABLE 4

OC$_D$EHD BLEACH SEQUENCE - TYPICAL CHEMICAL REQUIREMENTS

[lb/unbleached B.D. ton]

	O	C$_D$	E	H	D	Totals
Oxygen	50					50
Chlorine		55		16		71
Sodium Hydroxide	50		36	21		107
Chlorine Dioxide		4			12	16
Magnesium	1					1

ASSUMPTIONS:

Unbleached softwood pulp, permanganate number: 20

Permanganate number after oxygen treatment: 9

Final brightness: 88

TABLE 5

OC$_D$EHD BLEACH SEQUENCE - TYPICAL CHEMICAL REQUIREMENTS

	O	C$_D$	E	H	D	Totals
Oxygen	30					30
Chlorine		30		8		38
Sodium Hydroxide	30		19	11		60
Chlorine Dioxide		2			10	12
Magnesium	1					1

ASSUMPTIONS:

Unbleached hardwood pulp, permanganate number: 12

Permanganate number after oxygen treatment: 5

Final brightness: 88

TABLE 6

COMPARISON OF BLEACH CHEMICAL COSTS - SOFTWOOD

	C_DEDED		C_DEHDED		OC_DEHD	
	Requirement [lb/ton]	Cost [$/ton]	Requirement [lb/ton]	Cost [$/ton]	Requirement [lb/ton]	Cost [$/ton]
xygen					50	2.00
hlorine	120	7.20	145	8.70	71	4.26
Sodium Hydroxide	87	5.22	120	7.20	107	6.42
Chlorine Dioxide	36	9.00	24	6.00	16	4.00
Magnesium					1	1.50
TOTALS		21.42		21.90		18.18

UNIT COST ASSUMPTIONS [$/lb]

Chlorine : 0.06
Sodium Hydroxide : 0.06
Chlorine Dioxide : 0.25
Oxygen : 0.04
Magnesium as Mg^{++} : 1.50

TABLE 7

COMPARISON OF BLEACH CHEMICAL COSTS - HARDWOOD

	C_DEHD		OC_DEHD	
	Requirement [lb/ton]	Cost [$/ton]	Requirement [lb/ton]	Cost [$/ton]
Oxygen			30	1.20
Chlorine	78	4.68	38	2.28
Sodium Hydroxide	60	3.60	60	3.60
Chlorine Dioxide	19	4.75	12	3.00
Magnesium			1	1.50
TOTALS		13.08		11.58

UNIT COST ASSUMPTIONS [$/lb]

Chlorine : 0.06
Sodium Hydroxide : 0.06
Chlorine Dioxide : 0.25
Oxygen : 0.04
Magnesium as Mg^{++} : 1.50

ALLIED CHEMICAL CORPORATION
CHEMICALS COMPANY
SYRACUSE RESEARCH LABORATORY

APPROPRIATE TECHNOLOGY FOR ON-SITE CHLOR-ALKALI GENERATION

BY

R. H. Fitch
B. E. Kurtz
E. H. Larson
C. J. Kaminski

INTRODUCTION

The purpose of this study is to determine the optimum technology for on-site chlor-alkali production in bipolar permselective membrane cells using Nafion® 300 series membranes and chemically treated brine. To obtain the needed information three flow configurations in commercial scale electrolyzers were examined; parallel catholyte flow (PCF), series catholyte flow (SCF) and parallel-series catholyte flow (P-SCF) over the range of 12 to 20 weight percent caustic soda product. Data gathered included voltage and current efficiency responses to various operating variables including brine depletion, current density, and caustic soda concentration.

DESCRIPTION OF EQUIPMENT

The electrolyzers are of conventional bipolar filter press design with injection molded reinforced polypropylene frames which include the cell divider. Anodes are ruthenium oxide coated expanded titanium metal mesh and cathodes are perforated mild steel plate. DuPont Nafion® membranes were used in this study. The total cell cross section is nominally 1.3 m^2.

Sodium chloride brine was fed in parallel fashion to each cell from a common header. Depleted brine and chlorine gas were collected in a common header with means for sampling the liquid and gas phases from individual cells (except in the parallel flow electrolyzer). In the parallel catholyte flow electrolyzer (PCF) water was fed in the same manner as the brine, and the caustic soda product and hydrogen gas were similarly collected. Provision was made for collection of individual cell samples of product. Nafion® 390 was used in the parallel flow electrolyzer (Allied Chemical's 5 metric ton chlorine per day commercial prototype).

In the series catholyte flow (SCF) configuration (Figure 1) water is fed to the first cell. The first cell caustic product is then fed to the second cell after hydrogen separation. The third, fourth and fifth cells were also fed sequentially in the same manner. In the parallel-series flow (P-SCF) the first two cells were fed water. The product from these cells was used to feed the third cell, the third cell product to feed the fourth cell and so on. Allied Chemical's five cell commercial scale experimental electrolyzer using Nafion® 324 was employed to gather SCF and P-SCF data.

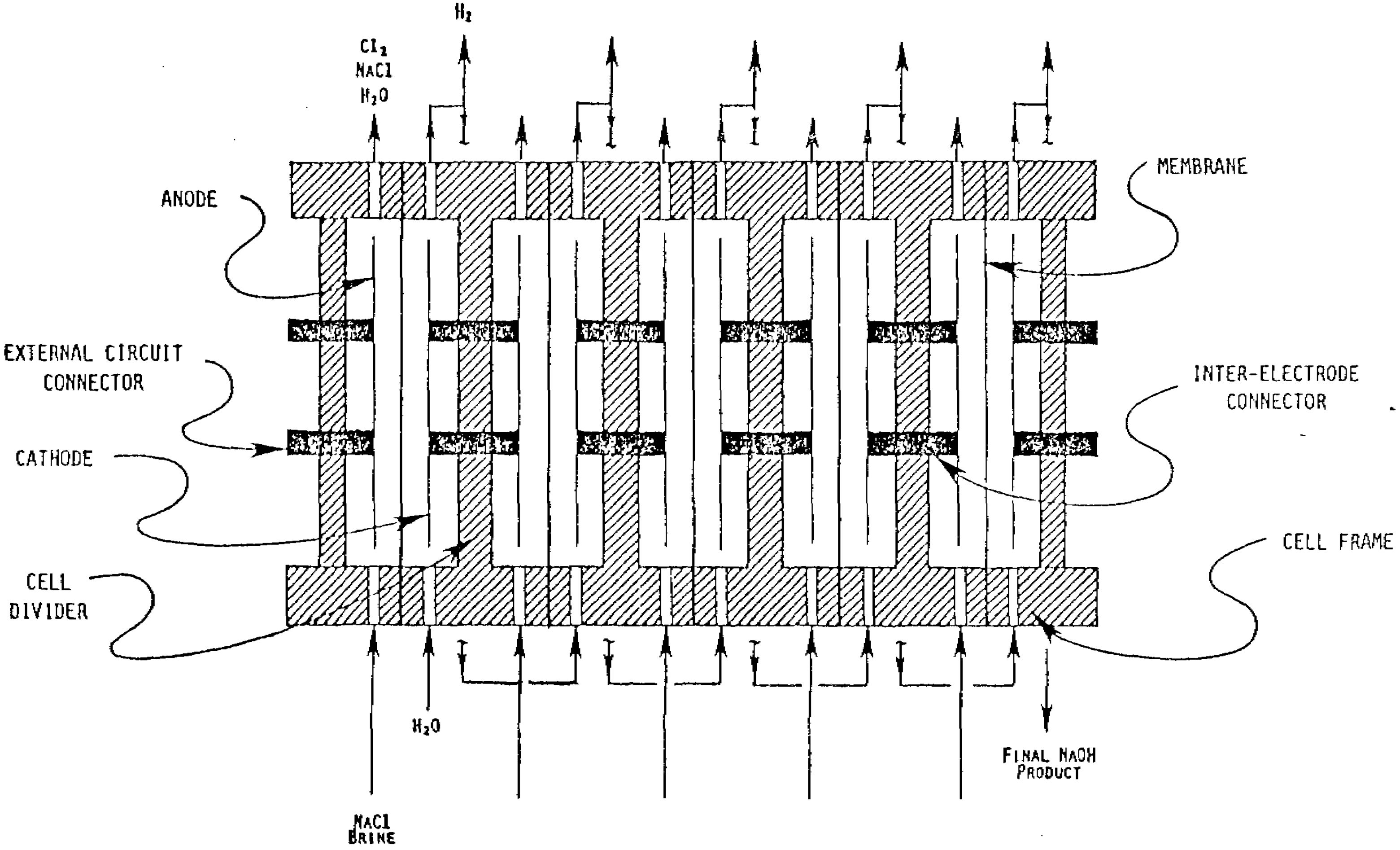


FIGURE 1

BIPOLAR PERMSELECTIVE MEMBRANE CELL ELECTROLYZER

EMPLOYING SERIES CATHOLYTE FLOW

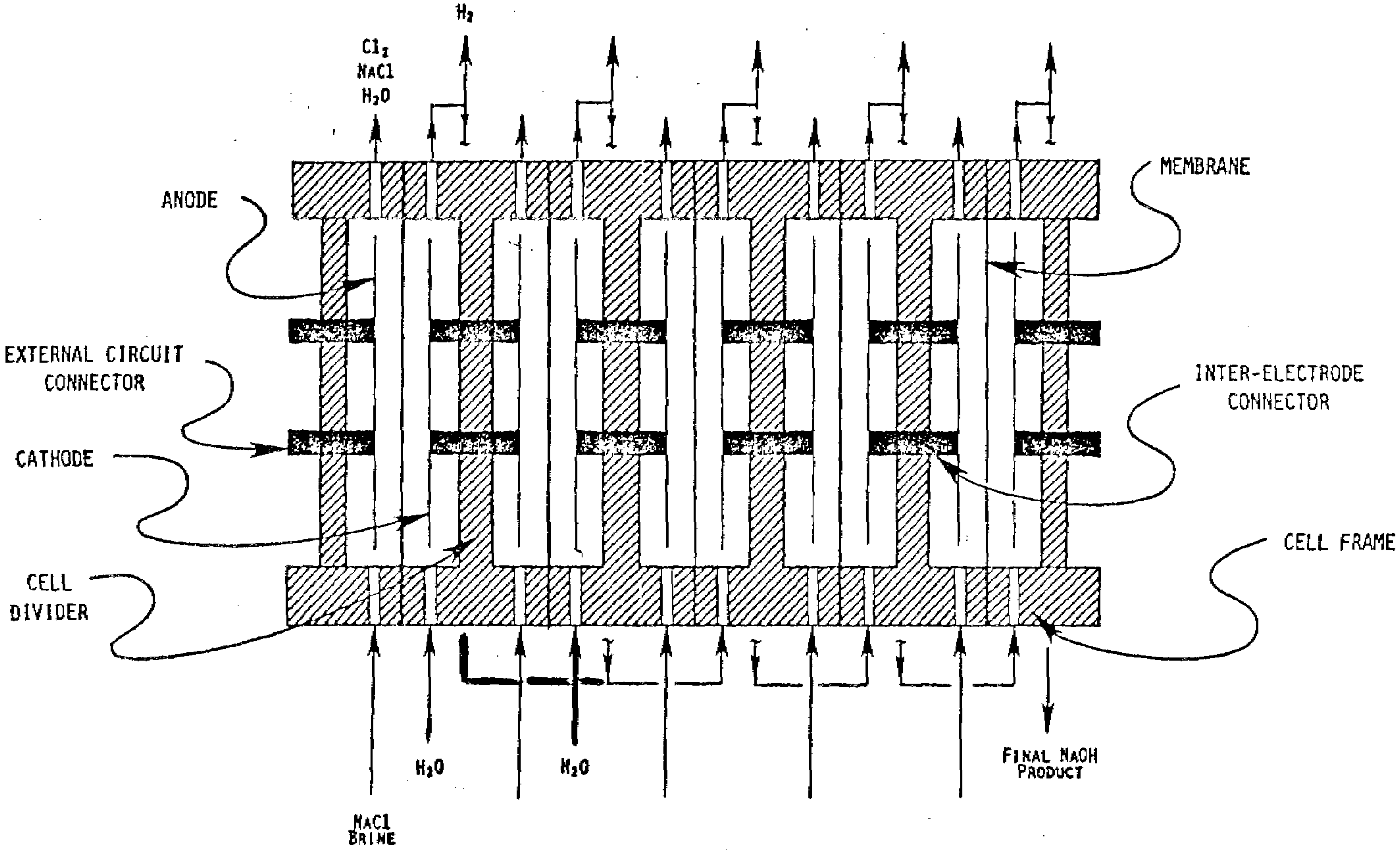


FIGURE 2

BIPOLAR PERMSELECTIVE MEMBRANE CELL ELECTROLYZER

EMPLOYING PARALLEL SERIES CATHOLYTE FLOW

AQUISITION OF DATA

An experimental run plan for the SCF and P-SCF configurations was devised using a full factorial statistically designed set of run conditions. Independent variables were amperage, brine depletion, caustic soda strength and acid equivalents ratio.(1) Several dependent variables were measured including cell temperatures, cell voltages, chlorine gas concentrations and caustic soda production rates. From these measured variables power and current efficiencies were calculated.(2)

Experimental data on the parallel catholyte flow configuration were gathered in the course of operation at normal run conditions.

RESULTS

The dependent variables chosen as measures of performance are caustic soda and chlorine power efficiencies. Cell voltages and current efficiencies from which the power efficiencies were derived are included as a matter of interest.

Mean values and ranges for the important independent and dependent variables for the SCF and P-SCF experiments are presented in Table 1. In all cases except cell temperature, the values are for the overall electrolyzer. Cell temperature was taken at the fifth cell and represents the caustic soda product temperature.

---

(1) - Acid equivalents ratio is defined as the ratio in mole equivalents of HCl added to feed brine to the mole equivalents of hydroxyl ion produced at 100% current efficiency.

(2) - In the calculation of chlorine gas test current efficiency, it was assumed that the predominant inefficiency occurred due to the discharge of hydroxyl ions at the anode. Thus the chlorine current efficiency = $\frac{\%\ Cl_2}{\%\ Cl_2 + 2(\%\ O_2)} \times 100\%$

Table 2 presents mean values and ranges for important independent and dependent variables for the PCF flow configuration. In all cases the data are for the overall electrolyzer.

These results were evaluated using a multiple regression analysis. In each case, the F-distribution was used in the analysis of variance to select a regression equation. In all cases the null hypothesis(1) was rejected with greater than 95% confidence. In all cases, a linear regression model was used. In the following graphical presentations of the regression results the average values of the independent variables in the regression equation were used to reduce the regression equation to a function of one variable.

In determining the effects of operating conditions on cell voltages four independent variables were found to exert significant effect. These are brine depletion, sodium hydroxide concentration, cell temperature and current density. Figure 3 presents the variation of average cell voltage with caustic soda concentration. Note that over the range of 12-15 weight percent, the PCF configuration shows a clear advantage over series flow configurations. Also indicated by the difference between individual SCF and P-SCF voltages and PCF voltages is the advantage of lower resistance shown by Nafion® 390 membranes.

Chlorine gas test current efficency was found to depend solely on acid equivalents ratio for the SCF and P-SCF. Normally, sodium hydroxide concentration would be expected to affect chlorine gas test results. However, it appears that because most of the series flow cells operate at reduced caustic concentration, this is not an important variable over the range of caustic soda concentration examined. Figure 4 shows the variation of chlorine gas test current efficiency with acid equivalents ratio. Note that the PCF data was obtained at 13 weight percent caustic soda.

---

(1) - The null hypothesis is a test of the significance of the regression coefficients. The hypothesis is that the null regression equation (all coefficients zero) better explains the data than the proposed equation.

TABLE 1

MEAN VALUES AND RANGES OF IMPORTANT VARIABLES FOR SCF AND P-SCF EXPERIMENTS

Independent Variables	SCF Average	P-SCF Average	SCF Range	P-SCF Range
Weight % NaOH Product	17.4	17.6	15.3-20	15.1-20.4
Current Density (A/m^2)	2538	2535	2320-2694	2321-2695
Acid Equivalent Ratio	0.038	0.044	0.011-0.077	0.011-0.107
% Brine Depletion	26.77	25.9	19.1-40.5	18.1-39.5
Feed Brine Weight %	25.4	25.6	25.0-25.9	25.1-25.8
Dependent Variables				
Cell Voltage (Average)	3.74	3.71	3.60-3.99	3.62-3.91
Cell Temperature (5th Cell)°C	65.4	68.1	53-78	56-79
Cl_2 Gas Test C.. % (overall)	92.6	91.9	87.9-97.2	88.5-96.7
NaOH C.E. %	83.9	81.9	78.8-87.3	76.8-84.8
Cl_2 Power Efficiency (%)	55.3	55.3	51.7-59.6	50.4-58.6
NaOH Power Efficiency (%)	50.1	49.3	45.3-53.8	46.60-52.8

TABLE 2

MEAN VALUES AND RANGES OF IMPORTANT VARIABLES FOR COMMERCIAL PROTOTYPE PARALLEL CATHOLYTE FLOW ELECTROLYZER

Independent Variables	Average Value	Range
Weight % NaOH Product	13	12-14
Current Density (A/m^2)	2450	2320-2500
Acid Equivalent Ratio	0.01	0.0-0.2
Feed Brine wt. %	25.5	25.0-26.0
Dependent Variables		
Cell Voltage	3.65	3.55-3.75
Cell Temperature (°C)	70	63.5-75
Cl_2 Gas Test C.E.	94.7	93.8-96.0
NaOH C.E. (%)	90.1	88.0-92.0
Cl_2 Power Efficiency (%)	58.2	57.4-58.6
NaOH Power Efficiency	54.5	53.5-54.9

Chlorine power efficiency was found to depend primarily on current density and acid equivalents ratio for the SCF and P-SCF configurations. In the PCF mode, caustic soda concentration was found to affect power efficiency as well. Figure 5 shows the variation in chlorine power efficiency with current density. Note that the PCF data was obtained with Nafion® 390 membranes and 13% caustic soda. Figure 6 shows the variation of chloride power efficiency with acid equivalents ratio and Figure 7 with caustic soda concentration.

Caustic soda current efficiency was found to be primarily a function of caustic soda concentration. Figure 8 shows the effect of caustic soda concentration on current efficiency.

Caustic soda power efficiency was found to be affected by current density, caustic soda concentration, brine depletion and cell temperature. Figure 9 shows the variation of caustic soda power efficiency with caustic soda concentration. Note the extrapolation of PCF power efficiency to 15 weight percent caustic soda.

CONCLUSIONS

(1.) The parallel-series flow configuration enjoys a small performance advantage over the series flow configuration. This is most noticeable in cell voltage and caustic soda power efficiency measurements. In other measures of performance the difference was not found to be statistically significant.

(2.) Nafion® 390 membranes show a voltage savings over Nafion® 324 membranes.

(3.) Series and parallel-series flow configurations have a performance advantage over parallel flow operation at caustic soda concentrations in excess of 15 weight percent.

(4.) Based on the experimental work of this paper commercial installations manufacturing greater than 15 weight percent caustic soda should consist of series or parallel-series flow electrolyzers.

(5.) The P-SCF flow configuration used was not the optimum flow configuration for maximum power efficiency in the range of caustic soda strengths studied. Other configurations such as parallel feeds to the first three cells may yield better results, particularly for caustic soda concentrations near 15 weight percent.

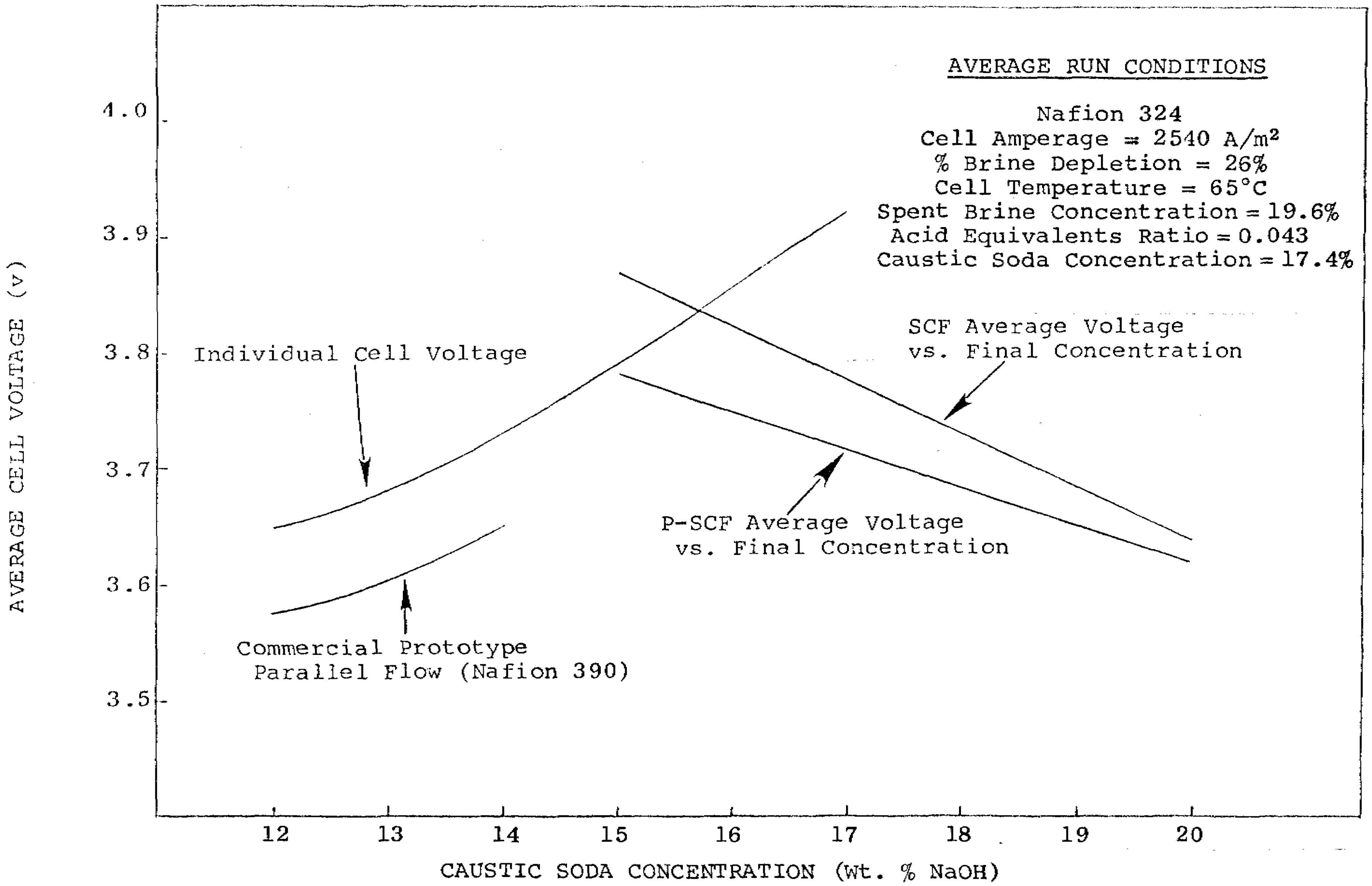


FIGURE 3

CELL VOLTAGE VS. CAUSTIC SODA CONCENTRATION

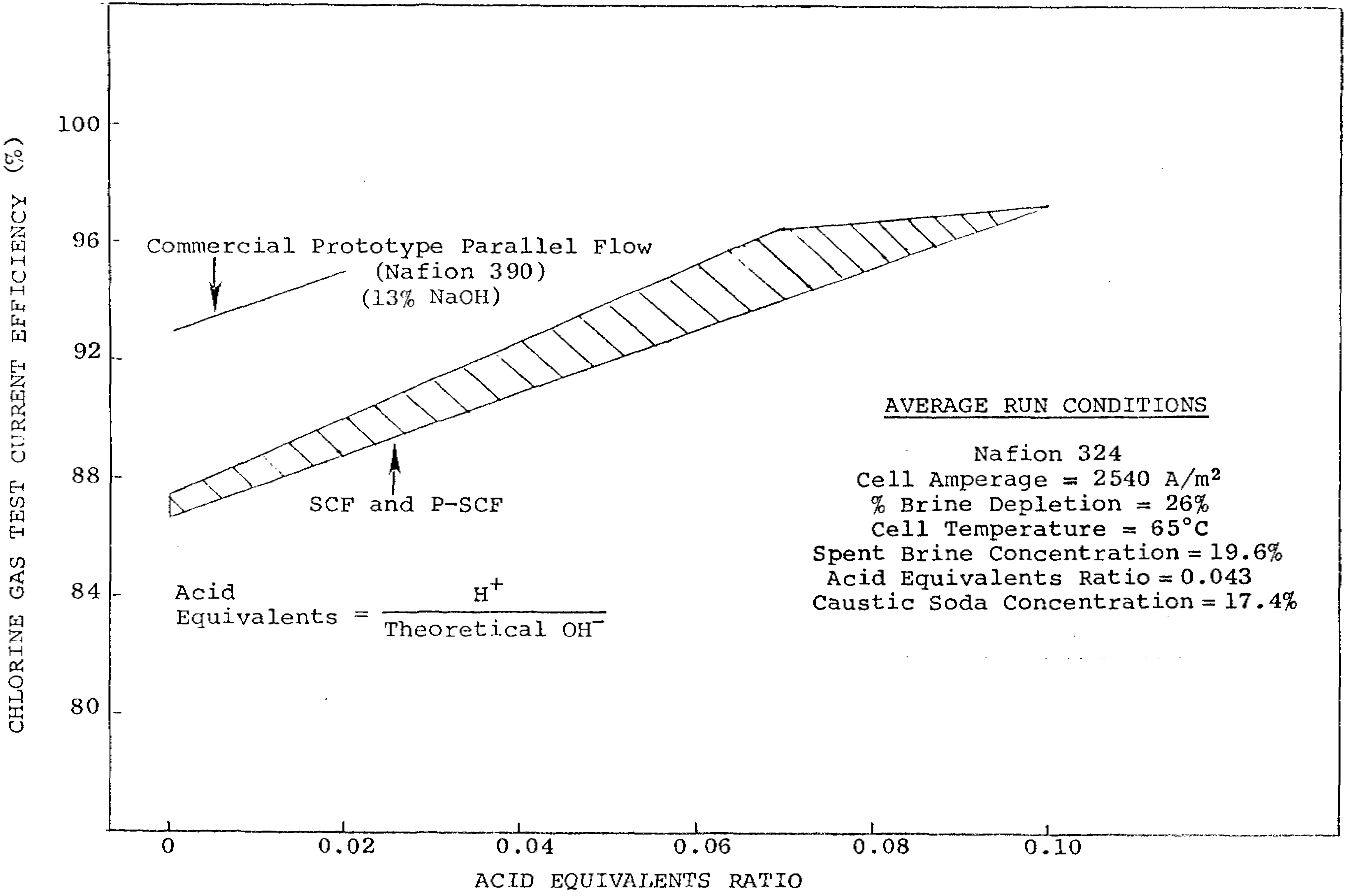


FIGURE 4

CHLORINE GAS TEST CURRENT EFFICIENCY
VS. ACID EQUIVALENTS RATIO

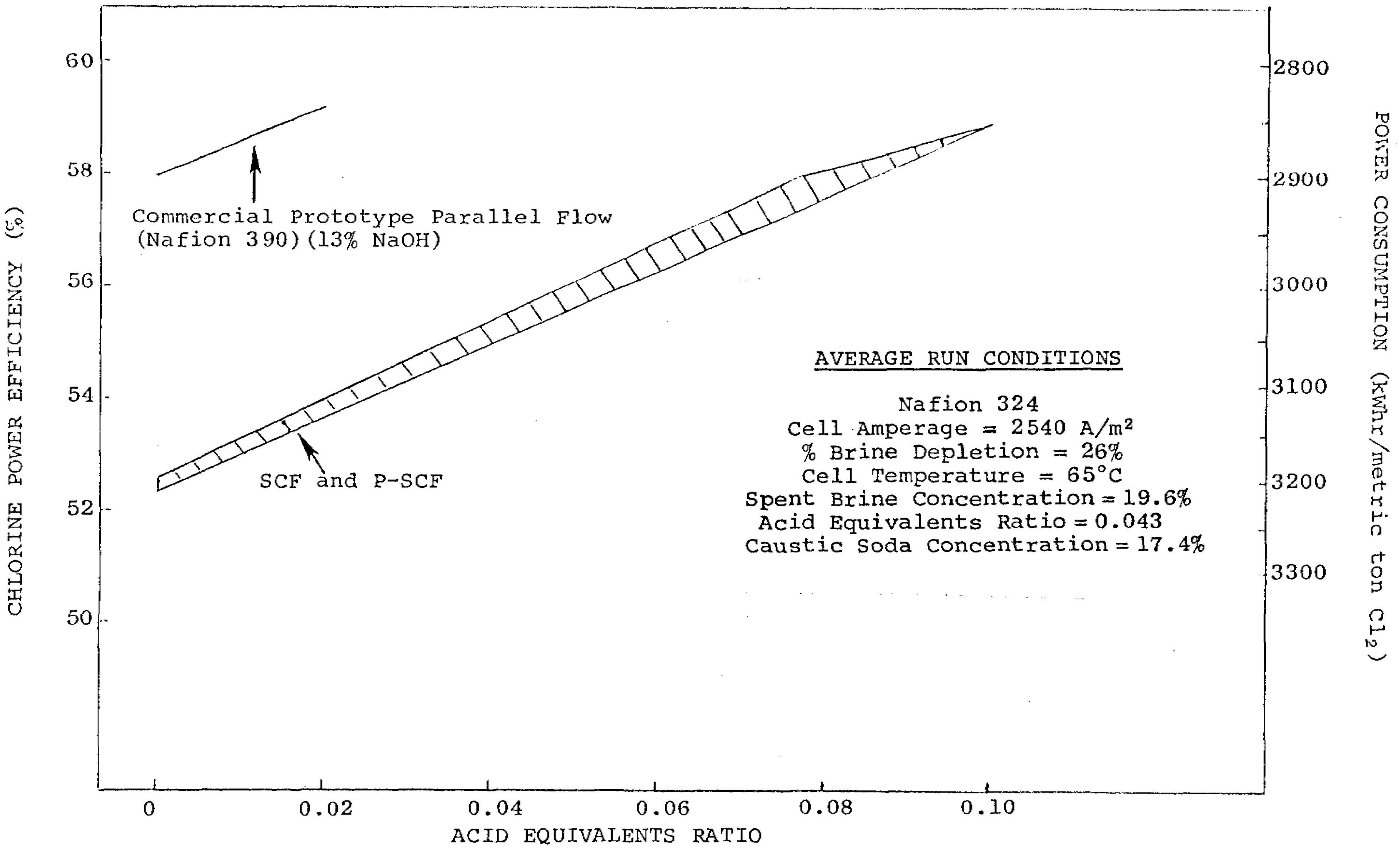
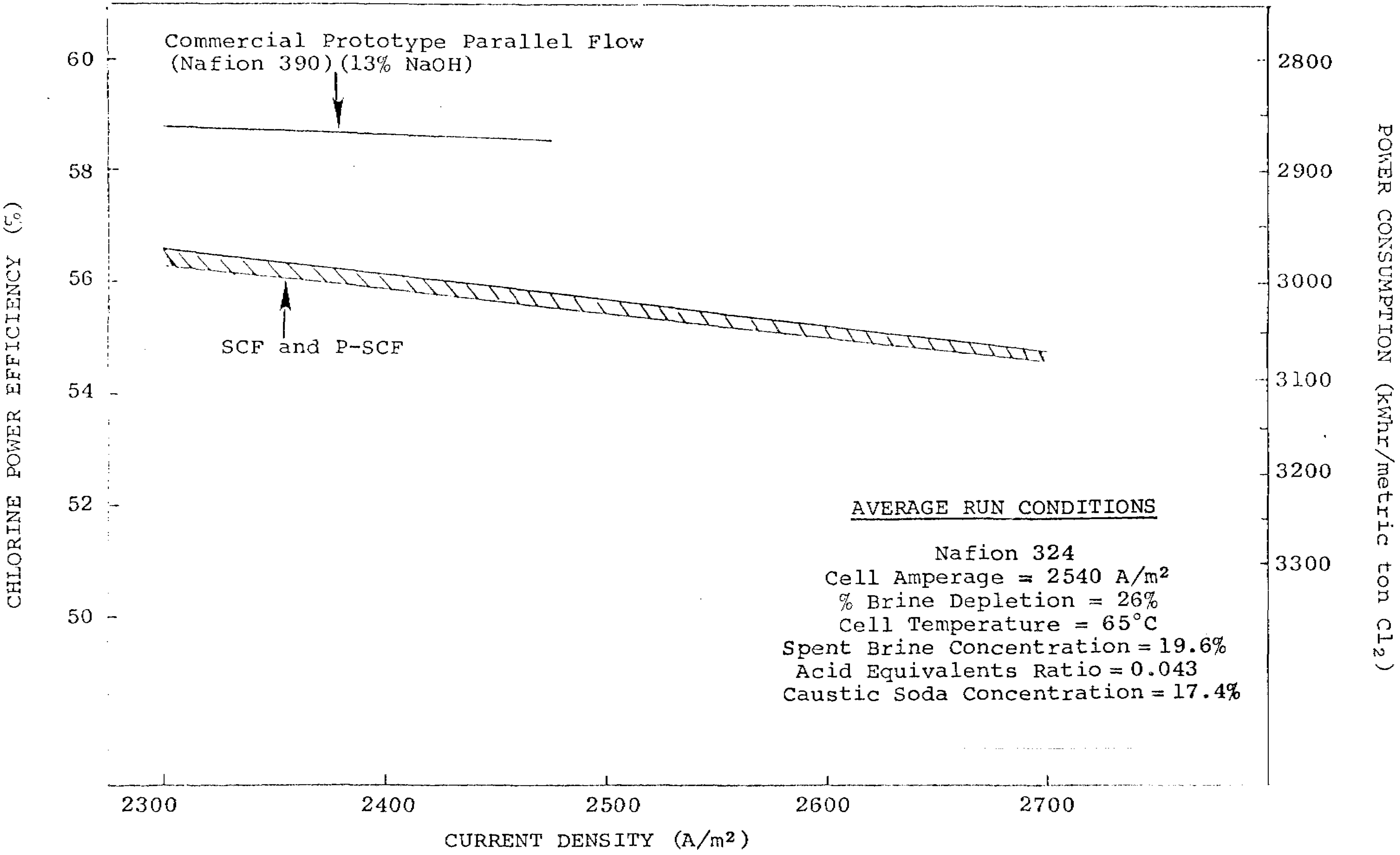


FIGURE 5

CHLORINE POWER EFFICIENCY AND POWER CONSUMPTION VS. ACID EQUIVALENTS RATIO



AVERAGE RUN CONDITIONS

Nafion 324
Cell Amperage = 2540 A/m²
% Brine Depletion = 26%
Cell Temperature = 65°C
Spent Brine Concentration = 19.6%
Acid Equivalents Ratio = 0.043
Caustic Soda Concentration = 17.4%

FIGURE 6

CHLORINE POWER EFFICIENCY AND POWER CONSUMPTION
VS. CURRENT DENSITY

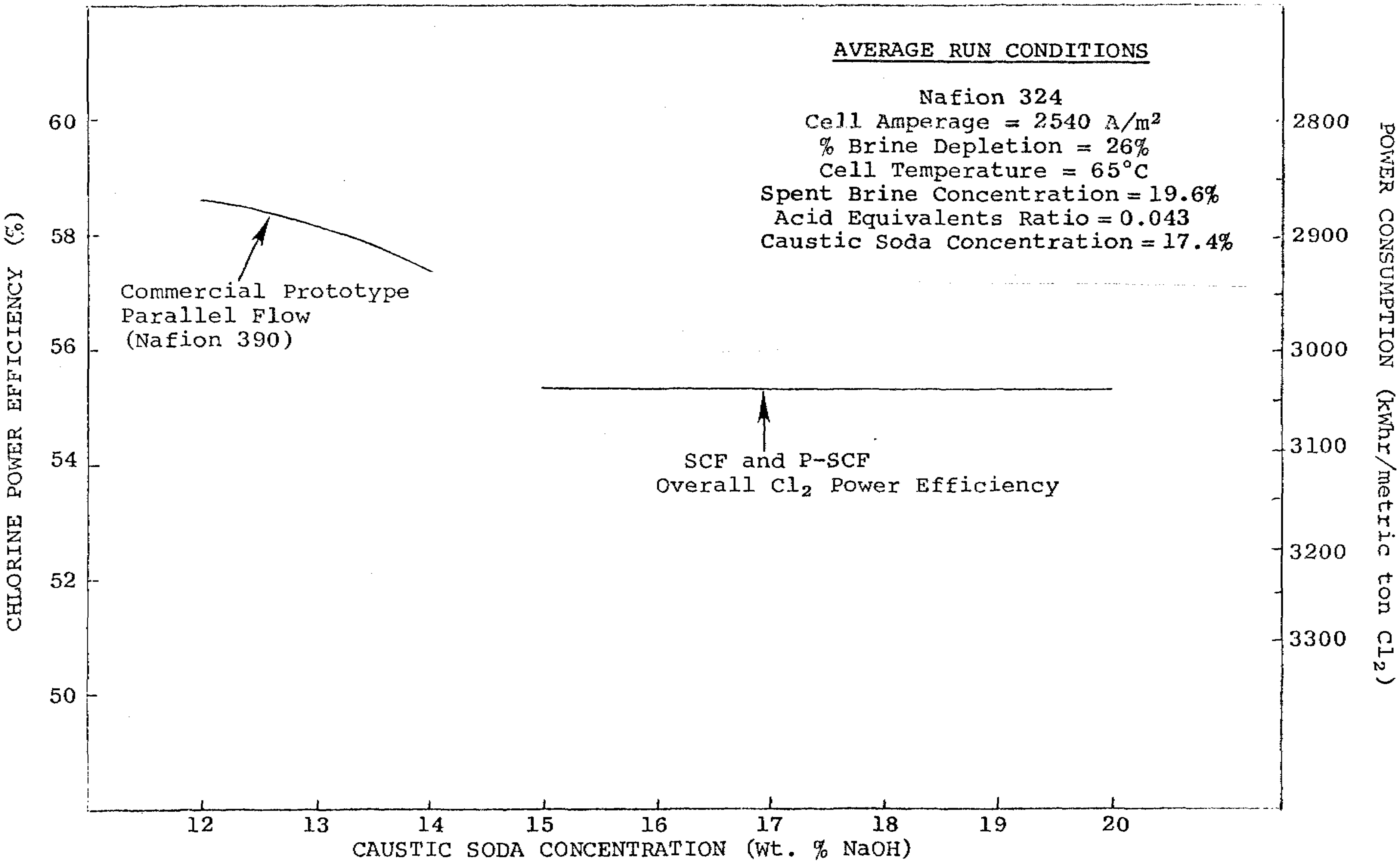


FIGURE 7

CHLORINE POWER EFFICIENCY AND POWER CONSUMPTION
VS. CAUSTIC SODA CONCENTRATION

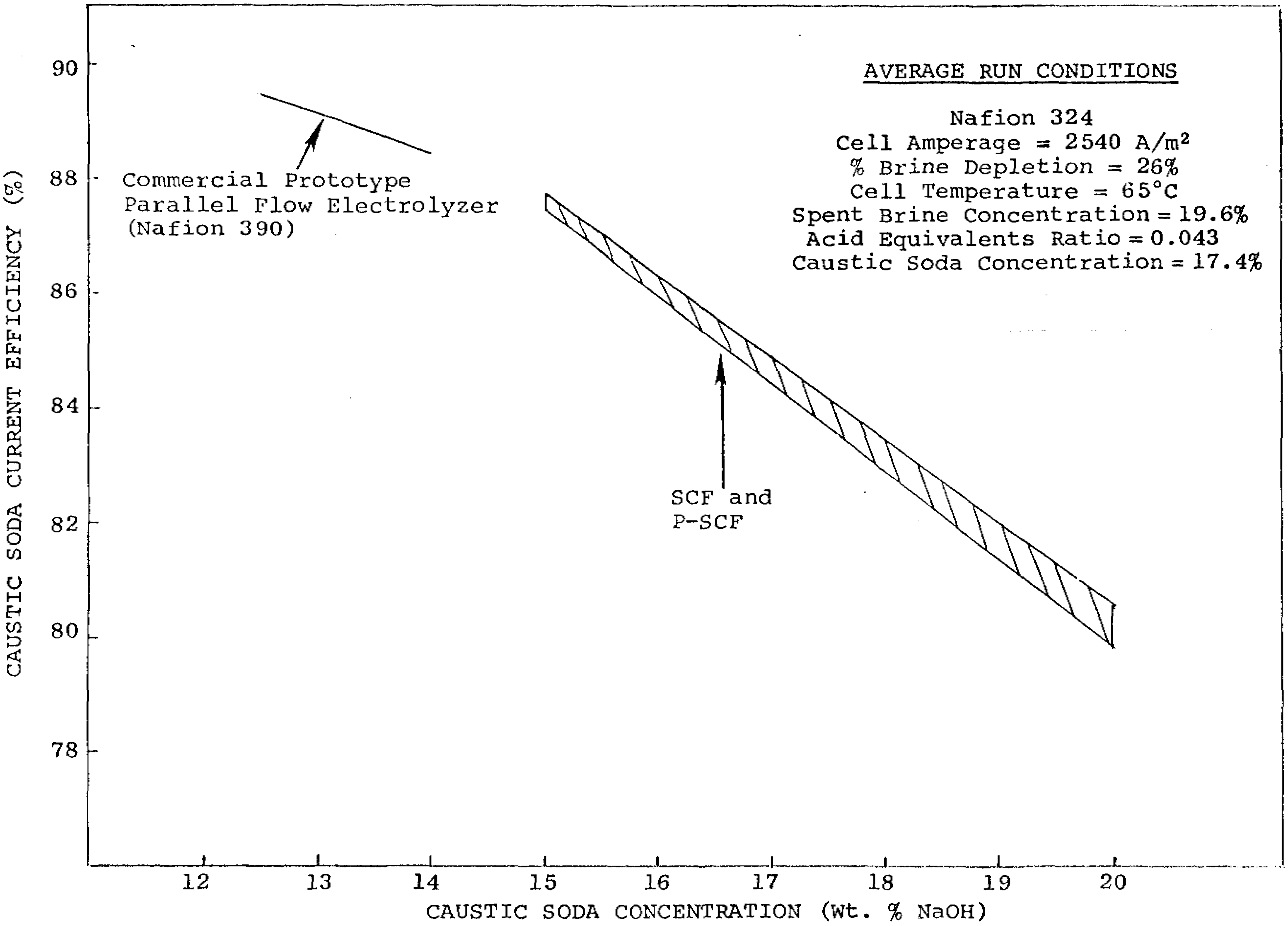


FIGURE 8

CAUSTIC SODA CURRENT EFFICIENCY
VS. CAUSTIC SODA CONCENTRATION

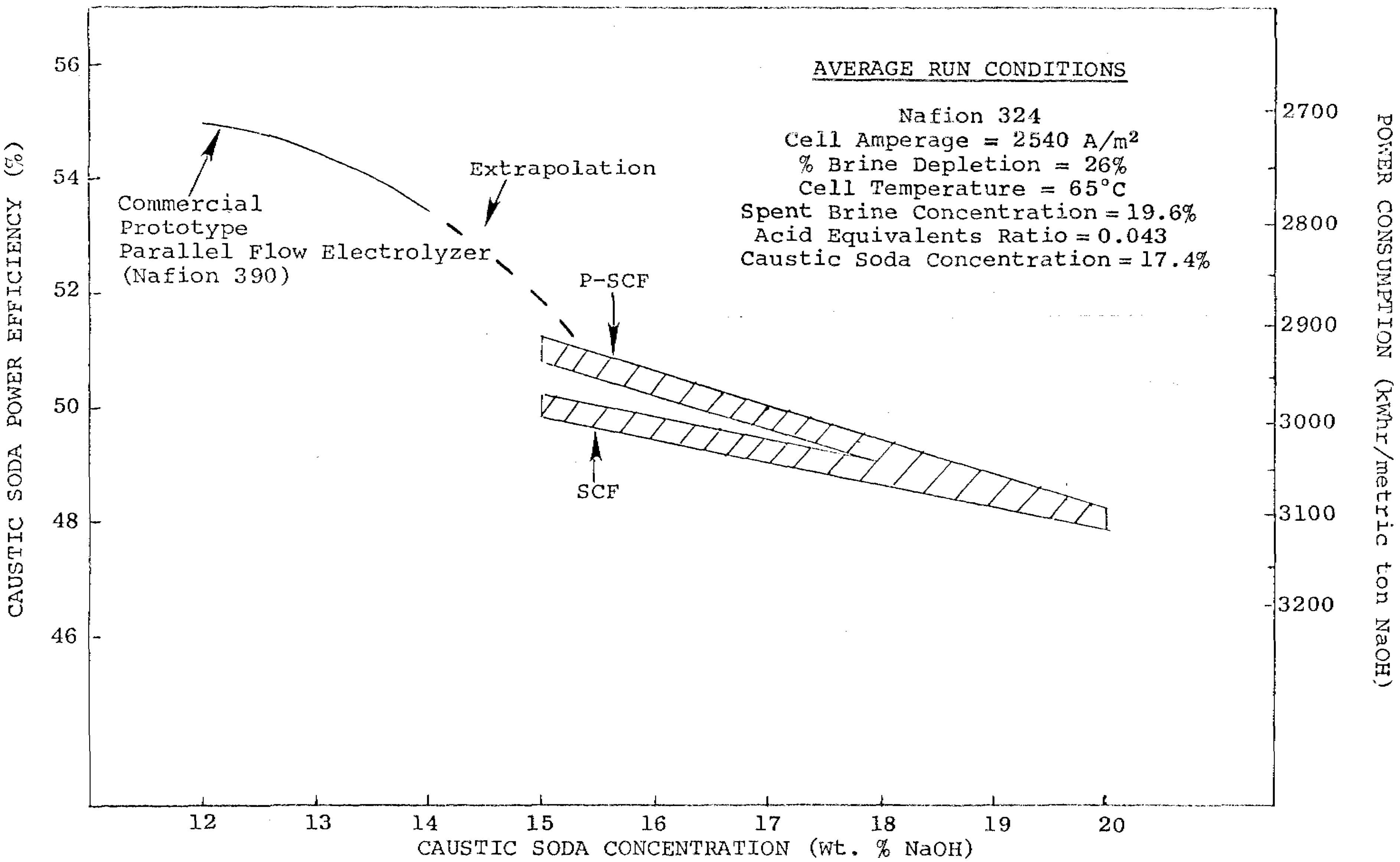


FIGURE 9

CAUSTIC SODA POWER EFFICIENCY
AND POWER CONSUMPTION

MODULARIZED CHLOR/ALKALI PRODUCTION FACILITIES

by

R. J. Scola and P. J. Vitale - Diamond Shamrock Corporation

The merits of membrane cell technology as compared to those of diaphragm and mercury cells, and membrane cells' associated performance, have been well documented in technical papers and demonstrated in commercial operating plants. Membrane cells have come of age, and should be considered for all new chlor/alkali projects. There are approximately six such plants in operation by cell licensors, while approximately 12 plants are run by licensees. Papers presented at conferences indicate that although there is still much to learn about membranes and the membrane cell process, the technology is commercially viable.

The advantages of shop modularization versus field construction have also been documented. Reports demonstrating that shop assembly can produce savings in manpower and improvements in product quality and overall project timing have been published. Clearly, as more sophisticated processes are sold to companies not accustomed to producing chemical products, shop construction has more application.

The purpose of this paper is to demonstrate the manner in which Diamond Shamrock Corporation has modularized its membrane cell technology for small scale chlor/alkali facilities.

Diamond Shamrock, as you may be aware, is, among other things, an international marketer of chlor/alkali products. Activities in this area include the production of approximately 4000 tons per day of chlorine in its own plants by the diaphragm, mercury and membrane cell processes. Also, since 1972, Diamond Shamrock's diaphragm cell and related chlor/alkali technologies has been licensed to some 62 projects throughout the world. Membrane cell technology, licensed since 1976, has become a significant portion of its licensing effort, and presently there are 7 plants under license. Just recently, Diamond Shamrock announced a 600 ton-per-day chlorine capacity increase for its Battleground plant in Texas using its membrane cell technology.

Diamond Shamrock determined approximately two years ago that it would further expand its licensing endeavors by developing a modularized plant design for chlor/alkali production employing as its base the membrane cellroom. We felt then, and still do today, that there is a separate and significant market for this type of plant. Our reasons were: (1) increasing problems concerning hazardous material shipment; (2) a rise in inquiries to us for smaller plants; and (3) the maturing of the membrane cell technology.

Market studies confirmed a need for on-site production of chlor/alkali products. These studies also indicated that the capital investment required may be very high. For small plants, the engineering costs become a larger portion of the overall project investment, due to their fixed cost nature. For example, a 100 ton-per-day plant may cost $2,000,000 for basic and detailed engineering. For a smaller plant, there is nothing different about the process which would require any less engineering. Equipment costs, obviously, will vary with capacity but engineering will be roughly the same. A prospective customer considering the construction of one small plant may therefore be hard-pressed to economically justify such a plant.

Recognizing this problem, Diamond Shamrock determined that in order to meet the economic needs of the small-scale plant market, it would be necessary to spread the cost of such engineering over many projects, and allow the customer to gain the benefit of the entire engineering package for a fraction of the engineering cost.

Further in our consideration of the small plant market, we examined carefully the type of customer which generally inquired about such plants. A profile of a "typical" customer is as follows:

a) non-chlor/alkali producer

b) strong manufacturing firm without an engineering staff to run a project.

c) located in a country with a limited infra-structure in the sense of being unable to procure equipment within the country and with difficult export/import logistics.

Based on the above factors, Diamond Shamrock decided to supply a modularized process equipment package. However, we continue to have a significant commitment to the offering of cellroom equipment only and definitive engineering for the entire plant. This approach is preferred by a large percentage of our total prospective clients. But most such applications to this type of supply are for larger plants, or for small ones which require a custom-design approach.

It is our feeling that modularized plants make a good deal of sense for several producer markets - most importantly bleach manufacturers and pulp and paper mills.

There are at least three reasons why household bleach producers are candidates for on-site production of chlor/alkali chemicals. First, the market for their product is usually localized. (Their product is 94% water.) Secondly, because they supply a local market, they need to be concerned about liquid chlorine transportation and storage in populated areas. And finally, it is difficult to justify in an economic sense paying someone (the large scale chlorine producer) to liquefy the chlorine, and to evaporate the caustic to 50% concentration when the bleach producer must then return the chlorine to a gaseous state and dilute the caustic soda.

Pulp mills are in a similar position. They too find themselves paying someone else for product processing - processing which they "un-do" when they use the products. Another reason for consideration of on-site production by pulp mills is that such facilities are usually located near forests, away from chlor/alkali facilities, and therefore must pay relatively high transportation costs. Obviously, these costs are eliminated if product is produced on-site. In addition, if the location is remote, on-site production prevents problems of transportation interruption or inaccessibility.

Although not revealed in preliminary market studies, but disclosed after further consideration, was the fact that several producer markets which appeared initially to be primary use areas for on-site plants now seem not to have as great a need for such plants.

Existing waste-water chlorination facilities may not be viable candidates for on-site production of chlorine. In most countries of the world, liquid chlorine is used for water disinfection purposes. As a country becomes more economically self-sufficient, it usually seeks to limit imports and produce previously-imported goods within the country.

However, the step from importing chlorine in cylinders to producing <u>liquid</u> chlorine is quite significant. Although an on-site chlorine plant with a liquefaction process is a possibility, alternative chlorination technologies should be studied, such as Diamond Shamrock's SANILEC® chlorinator system. This produces a dilute solution of hypochlorite generally suitable for such an application.

A second market which originally looked attractive, but which may not be as well-suited for a modularized plant is in the replacement of existing diaphragm or mercury cell facilities. Membrane cells make a good deal of sense in this application but a standardized, modularized plant may not. This is generally true because much of the existing equipment can usually be employed in the updated facility. Also, there is a good deal of in-house expertise which the licensee will wish to employ, and this will result in maintaining some existing process equipment. The licensee will also have good ideas regarding design of the new plant which will necessitate a custom design. Such use of membrane cell technology and adaptability is just the sort of approach Diamond Shamrock offers through its custom design equipment and engineering package.

Keep in mind that the foregoing comments on markets are generalizations. Each case needs to be evaluated on its own merits. Specific site conditions could well make a bleach producer a poor candidate, and a water disinfection plant a good one, for a modularized plant.

A review of the capital requirements for a chlor/alkali facility will demonstrate that modularization of small scale-plants will not produce the capital cost per ton of chlorine numbers which are enjoyed by large plants. The next slide illustrates this. It demonstrates generally a curve for chlor/alkali plant costs. What is plotted is fixed capital investment dollars (U.S.) versus plant capacity. For a larger plant - let us say, 1000 tons per day of chlorine - the fixed capital investment is about $150,000,000. This figure decreases to about $55,000,000 for a 200 ton-per-day plant, and $19,000,000 for a 30 ton-per-day plant. The plot shows that there are certain fixed capital investment costs associated with a process (much the same as the engineering costs mentioned previously) which do not scale down as quickly as the plant size decreases. Small plants must distribute these reduced, but still relatively high, fixed capital costs over smaller amounts of product, thus generating higher costs per ton of chlorine. Fig 1

Although accurate, this trend is somewhat offset by two process areas which do not apply, generally, to small chlor/alkali plants; i.e., chlorine processing for liquefaction and caustic evaporation. Modularized plants fall below the dotted portion of the curve, due to these two factors plus standardized engineering, but not well enough below to achieve large scale plant economics. This is demonstrated on the next curve which shows fixed capital investment per ton per day of chlorine. Today, large scale plants enjoy a $150-275,000 per ton day figure. Smaller plants only approach this. Fig 2

The philosophy of equipment design has received much consideration in the engineering of Diamond Shamrock's modularized on-site chlor/alkali plants. In designing the equipment, certain base conditions were assumed. One major area where assumptions had to be made was in the basic site conditions. But since we were developing a "universal" package, we had to be careful to provide for flexibility. If we had been designing something basic, like a heat exchanger, we could achieve universality, but for a process package, this is difficult. Varying salt sources, atmospheric pressures, electrical supplies, etc., all complicate the "universal" approach. Throughout the design of a "universal" plant, we found ourselves caught between two conflicting philosophies.

One is that we supply as much of the equipment as possible, thus minimizing the amount of work required of our customer. (The intent is not to increase our scope of supply for the sake of increasing our income, but rather, it is to leave the usually uninitiated customer with as little to do as possible.)

The other approach is to let the customer supply as much as possible. When a non-U.S. customer, this allows him to purchase goods within his own country. In the extreme, this would amount to supplying the customer with an engineering package, and letting him procure equipment on his own.

We felt the Diamond Shamrock modularized system needed to fall somewhere between these two limits.

The results of our study regarding where between these limits our modularized system is positioned is depicted on the next slide. This shows our typical scope of supply. The next slide explains the process areas included. Fig 3

In very brief terms, as you can see from this simplified flow sheet, salt is fed to the brine saturators where treated water and depleted brine from the electrolyzers are concentrated to produce a saturated brine solution. After saturation, the brine is fed to the brine purification area where caustic soda, and soda ash are added to precipitate harmful impurities. After removal of these precipitates, the brine is fed to ion exchange columns which purify the brine to levels necessary for efficient membrane cell operation. Fig 4

The purified brine is then fed to the electrolysis modules where it is converted to chlorine, caustic soda, and hydrogen. Unreacted salt is recycled back to the saturator.

To gain a better understanding of our system, more detailed discussion of the major process areas of the Diamond Shamrock On-Site design is appropriate.

Brine Saturation

For even a small modularized plant, there are many factors which need to be considered in the design of brine saturators. Composition of the raw salt, frequency of salt delivery, and available storage space are important considerations, but obviously are deterrents to a universal design.

To be prepared for the variety of such factors, we developed basic designs which we then modify. For example, with relatively pure salt as feed, and rather short delivery times, a standard FRP, pneumatically-fed saturator may be appropriate.

For impure salts and long delivery times, large pit saturators or elevated up-flow saturators can be used. For this case, we supply the detailed design for the saturators, and also supply the piping internals, instrumentation and controls.

Brine Treatment

As with brine saturation, primary brine treatment can also most economically be designed taking into account the raw salt's particular characteristics and the site conditions.

Relatively pure salts can be treated with soda ash and caustic soda and filtered in a polishing filter. Impure salts demand larger doses of treatment chemicals, and may require several sand filters and a polishing filter to remove impurities. In some cases, large clarifiers may be more practical.

In any event, the most economic system for primary brine treatment will be designed into the plant. A basic design has been developed, and this is modified to meet the customer's needs.

The final step in the purification process is by means of ion exchange columns.

Cellroom

In designing a chlor/alkali plant, regardless of capacity, significant effort should be devoted to cellroom engineering. Extra design time in this area is justified since the cellroom forms the nucleus of the facility, and its operation has the greatest impact upon overall plant performance.

Some of the more important considerations in the design of a cellroom are capital investment, operating cost, process control, maintenance, and personnel safety. The inter-relationships among these factors are rather complex, and there is no single correlation that can be used to arrive at the best design. This is especially true when one considers that each new plant has different economic constraints and that membrane cell technology has become a commercial reality only in the last five years.

Considering these factors, two basic cell designs have evolved. One is a
bipolar cell (Diamond Shamrock's DB-10) and the other, a monopolar Fig 5
(Diamond Shamrock's DM-14). Several slides here show the basic cell con- Fig 6
figuration in each case. Each design has its own merits and finds accep- Fig 7
tance in different applications. Operation and performance of the two Fig 8
types of cells are basically the same. The main difference lies in the

electrical flow characteristics. At this point, perhaps a word or two of definition would be helpful. For purposes of this discussion, a cell is defined as a single anode and a single cathode separated by a membrane.

It is the smallest component that theoretically can make chlorine and causstic soda. An electrolyzer is a group of cells with common electrical and process connections. The cells in a bipolar electrolyzer are connected in series resulting in a low amperage-high voltage circuit. The cells in a monopolar electrolyzer are connected in parallel resulting in a high amperage-low voltage circuit. These next slides illustrate these concepts Fig 9 Fig 10

A study was made to determine which cell and circuit design would best satisfy the needs of the small, modularized plant. Our conclusion is that the two-cell monopolar electrolyzer offers the most advantages to the small capacity chlor/alkali plant.

Each two-cell monopolar electrolyzer has a capacitry of 0.25 metric tons of chlorine per day at the rated current density of 3.1 KA/M^2. For a modularized plant, five of these electrolyzers are connected in series to form an electrolysis module. A single electrolyzer module is shown in the following slide, and has a capacity of 1.25 tons of chlorine per day. The typical 5 ton-per-day plant would employ 4 electrolysis modules connected by a center aisle piping module (slide). All the piping and necessary operating controls are included. The circuit arrangement is also illustrated (slide). Fig 11 Fig 12 Fig 13

There is not sufficient time to review all the details involved in the cellroom design analyses for small plants. However, a few of the major points are worth presenting to illustrate their relative importance.

1. Circuit Design versus Capital Cost

For any chosen capacity, the capital investment for the rectifier and associated electrical buswork is directly related to the circuit amperage. To minimize the rectifier cost, the circuit should be designed to operate at low amperage and high voltage. The electrolyzer cost is inversely proportional to amperage which means that the unit cost per cell decreases as the number of cells per electrolyzer is increased. The reasons for this are reduced piping and cell material cost. These two effects are illustrated in the next slide for a 5 ton-per-day chlorine plant. Here the relative investment for rectification and cells are plotted versus circuit design. Fig 14

2. Circuit Design versus Operation Cost

Depreciation of the equipment and rectifier efficiency affect operating costs. The higher the rectifier output voltage the higher the efficiency of converting AC to DC power. Depreciation varies directly with the capital investment. In our analysis case, depreciation was the sum of the capital cost of the rectifier and the cells depreciated over a 10 year life. On the same bases as shown in the previous slide, the operating expense for these two variables are plotted versus circuit design for a 5 ton-per-day plant (slide). Fig 15

It can be seen that the higher circuit voltage results in a lower gross operating expense.

From the previous two slides, one can calculate the most economic cellroom for various plant capacities. These graphs show that a low amperage - high voltage cellroom is relatively the most economical.

With just this analysis, we concluded that monopolar electrolyzers with 2 or 6 cells per electrolyzer and larger bipolar electrolyzers would have similar economics. However, the totality of operation, maintenance and design considerations led us to select for our on-site, modularized plants the two-cell monopolar electrolyzer rather than a larger monopolar or bipolar electrolyzer. (The six cell monopolar electrolyzer is employed for larger on-site cellrooms). Our reasoning was based on the following points:

1. The monopolar cell readily lent itself to the two-cell electrolyzer configuration. The double anode compartment was an existing design with proven fabrication techniques. The double cathode compartment only had to be divided in two in order to form the end half cathodes.

2. All copper connections are made externally for the monopolar cell instead of internally for the bipolar cell. The external cell connections make electrolyzer modularization much simpler.

3. Removal of one two-cell electrolyzer from the circuit only lowers production by 1/20 in a 5 ton-per-day plant.

4. The lifting equipment is much less for a two-cell electrolyzer - about 10% of that required for a 20-cell bipolar electrolyzer.

5. Periodic membrane changeout and anode recoating can be accomplished through short scheduled outages.

6. Removal of one electrolyzer does not disturb the membranes and gaskets in other cells. This is very important in small plants. Possible damage can occur to membranes once they are removed.

7. Spare parts are kept at a minimum since the frequency of removing cells is low.

Keep in mind that although we selected the monopolar cell design, we could have easily selected the bipolar cell. Both cell types use the same membrane and are operated based on similar techniques. High performance characteristics are achieved in both types of cells.

Brine Recirculation

When we considered the design of our modularized plant, we determined to incorporate depleted brine recirculation. Other approaches would have been to combine the depeleted brine with the hypochlorite product, or simply send it to a sewer.

We have found that membrane cells operate most efficiently, on a long term basis, at depleted brine strengths of 180 - 220 gpl NaCl. Sewering a brine of this strength, at raw salt costs of $20 to $40 per ton, is expensive. Roughly speaking, for the non-recycle case the salt cost would be 70-80% greater than it would be for the recycle case. Another economic factor is the cost of the chlorine product which is dissolved in the dumped depleted brine. For these same reasons, we chose not to combine it with the hypochlorite product.

There were other factors to be considered in designing the process area. Because the anolyte is saturated with chlorine gas, recycle directly back to the saturators, although technically possible, could result in unnecessary equipment corrosion, environmental and worker safety problems.

Because of our recycle approach, a simple and reliable dechlorination scheme had to be designed. Several methods are used in large scale plants, including vacuum or steam dechlorination. We chose air dechlorination with relatively high acid addition mainly due to its simplicity and the fact that a typical, on-site, plant will not have steam available.

After dechlorination, the brine is then adjusted to basic pH. A purge stream is taken at this point, mainly to control the sulfates in the raw salt.

Chlorine Emissions Module

Another module I will discuss is referred to as the chlorine emissions module. This unit eliminates the major sources of chlorine discharges to the environment, namely the chlorine pressure seal and the brine dechlorination tower.

To protect the cells from extreme excursions in pressure, a simple water seal is provided. Because the plant might be in a residential community, we have chosen to pipe this seal to the chlorine emissions module. Only inert gases would be vented.

Similarly, the air from the dechlorination tower is also sent to this module. The resultant air leaving the system will not be an environmental or safety nuisance.

Other Modularized Equipment

There is other significant process area equipment included in the typical supply of a Diamond Shamrock modularized plant. This equipment includes, among other things, anolyte receivers and caustic cooling and recirculation. This next slide shows once again the usual process area supply for a Diamond Shamrock on-site plant. Fig 16

Products

The basic Diamond Shamrock modularized chlor/alkali system will produce wet, hot chlorine gas; wet, hot hydrogen gas; and a 33% caustic soda solution. A major advantage of the system is that through additional investment several other chlor/alkali processes can be added. Thus a 20 ton-per-day system could have attached to it a 5 ton-per-day hydrochloric acid unit, a 10 ton-per-day bleach unit, and a 10 ton-per-day caustic evaporation unit. As markets change, the product mix can be changed. In many of our inquiries, further processing is required. Below are the most often requested additional processes and comments on the suitability of each to our modularized system.

Hydrochloric Acid Production

The modularized system readily lends itself to hydrochloric acid production since chlorine gas and hydrogen are produced, with hydrogen in slight excess. These co-products are readily combined in a burner. Many prospects have a large hydrochloric acid market, or internal requirements, or both. Much of the hydrochloric acid produced in the world is a by-product of organic reactions. If a customer needs a dependable supply of hydrochloric acid, the usual source may not always be available because of the acid's by-product status. Also, since the majority of hydrochloric acid is available as 20° Baume, (32% by weight), it is expensive to ship the companion amount of water over long distances.

Sodium Hypochlorite

This product by far has generated the most interest. The inquirers can be categorized as hypochlorite producers that presently manufacture bleach from purchased chlorine and caustic soda and "entrepreneurs" that recognize unique market opportunities. Most of the inquiries from customers that manufacture bleach from purchased materials are either seeking reliability of supply, or relief from handling liquid chlorine.

The bleach module is easily integrated into the modularized system. The wet, hot chlorine gas, and caustic soda can be combined as they are produced. With this process on site, the customer can avoid paying for liquefied chlorine, concentrated caustic soda, and transportation.

Finally, because high strength caustic soda is produced in the system, concentrated hypochlorite can be the result. In order to produce 15.6 wt.% hypochlorite, at least 19 wt.% caustic soda is required, and the caustic concentration out of the cell is 33 wt.%.

Liquid Chlorine

This is a frequently requested product option. Using the commercially accepted process of cooling and chilling in titanium heat exchangers, and then using sulfuric acid drying towers, acid-ring compressors, and Freon liquefiers, the costs quickly become prohibitive in the normal economic sense. Engineering studies even for a 10 ton-per-day plant indicate the fixed capital for this equipment is in the range of $1,500,000 to $2,000,000.

Caustic Evaporation

Most potential customers are satisfied with 33% caustic soda concentration out of the Diamond Shamrock cell and feel it can be used internally or marketed as is.

However, a handful of inquirers have expressed a desire for higher strength solutions. In these cases, we have contacted evaporator suppliers and described the need to them. In turn, they have provided us with estimates for unmodularized equipment, to which we have added modularization costs and passed it along to our prospective customers.

Occasionally a prospect will desire anhydrous caustic. In this case, we ask the anhydrous caustic technology supplier to contact the prospect directly.

We have determined that there are certain commonly-asked questions about the Diamond Shamrock On-Site System. To help put the technology and system in proper perspective, let us review responses to typical questions.

1. How sensitive is the membrane cell technology and the system to operating upsets?

   This question is of primary importance. Some of the considerations in answering it relate to the entire plant technology, but yet the biggest fact is the membrane cell.

Refinements of this question will bring the problem further into focus.

- What would happen if impure brine were fed to the cells?

Of course, the answer to this question can be hedged by saying it depends on how <u>much</u> impurity is fed to the cells. But for purposes of illustration, let us assume the brine treatment system will supply brine to the cells which contains 50 ppb hardness as calcium. Let us say further that there is an upset, and 5 ppm (5,000 ppb) hardness is fed to the cells. Within a day, the cell voltages would noticeably escalate and current efficiency would disintegrate, clearly indicating a problem. Although certain procedures instituted quickly could partially return the voltage to a proper value, there would be a long-term voltage increase in the cells, and the current efficiency would remain lower. To regain prior performance, membranes would have to be replaced and this would be costly.

A similar operating upset might occur if other heavy metals were sent to the cell, since these might attack the anode coatings. Complete replacement of the anode coatings, assuming there is no damage to the titanium structures, would cost about twice the membrane replacement cost. If the titanium structures also needed to be replaced it would cost about as much as the coatings.

Obviously there is a strong incentive to feed pure brine to the cells.

- How would an unplanned power interruption affect cell performance?

Short outages, on the order of one-to-two hours, can be tolerated. That is, the cells can remain full of anolyte and catholyte, with no detrimental effect to the membranes. This is the mode of operation for cell renewal. If power is not restored within this time period, however, cells should be drained, and provisions for this are provided for in the designed tankage.

Changing power loads, without complete loss of power, can also be tolerated. Because of this relative insensitivity to power upsets, the On-Site System is particularly suited to take advantage of off-peak power. Control schemes for operating the cells at lower loads during the day, and higher loads at night have been formulated, and significant power cost savings are realized.

3. <u>How many and what type of operators are required for the On-Site System?</u>

On a U.S. Gulf Coast basis, the basic process areas, for up to 10 tons per day of chlorine capacity, can be properly run with one operator per shift. Other processes, such as hydrochloric acid, hypochlorite, or caustic soda evaporation would require one additional operator per shift. Chemical operators much as one might find in any power generation, or water treatment, plant are required.

4. Is the modularized approach cheaper than a custom-designed approach?

Each project must be viewed based upon its particular requirements. Even a small plant may more cheaply be supplied by a custom-engineered approach. However, in the typical case, a modularized plant will likely be less expensive. This savings in expense may result from a lower total price or it may be the indirect result of a savings in time between initiation of the project and plant start-up. The details of how savings can result are described below.

Keep in mind that with a custom-designed plant, a company must do basic engineering, detailed engineering, and then procure equipment, and construct the plant.

For a modularized system, virtually all of these activities are essentially assumed by the plant supplier.

Looking at the typical Diamond Shamrock On-Site case, within a month of contract execution, Diamond Shamrock representatives will visit the plant site. Here a standard engineering package is presented. Included is a recommended layout for the modules, including loadings (for foundations), as well as the recommended interconnecting piping details for this layout. After this visit, the customer can begin any necessary site development work.

At about nine months into the project, the customer will send his engineers or head operators to an operating Diamond Shamrock plant for training. The training program covers all details of the operation, including safety, maintenance, troubleshooting, and laboratory procedures.

Within approximately 14 months of contract signing the modularized equipment arrives at the plant site, typically in sea containers. Close examination of these modules shows the scope is quite extensive. An example of completeness is demonstrated in the following slide showing the caustic recirculation module. The utility connections are shown, as well as the process connections. Note that within the module supply is complete. No additional labor or materials need be supplied (with the possible exception of the removal of certain bracing or supports added for shipment). Note further that the module base has eyelets for attachment to a "cherry picker" crane (required for installation only). This module is simply located on the foundations/ anchor bolts that were installed according to the original engineering package. Fig 17

Next, the interconnecting piping must be completed. If the labor and materials are available and the labor is sufficiently skilled, this piping can be installed using the initial engineering package.

Similarly, the electrical wiring must be completed. Although it is not clear from the model, all wiring to the motors and motor starters is supplied. All that needs to be done is to run the conduit from the electrical supply to the various boxes located on each module. Again the recommended detailed wiring scheme is supplied with the initial engineering package.

Once these activities are completed, the system is ready for chemical charges, and pre-commissioning activities. Checklists have been developed and are also included in the Diamond Shamrock engineering package.

As you can see, a minimum amount of involvement is required by the customer prior to starting up the plant. It is also important to note that the timing for commissioning of this type of plant is probably less than the usual case. An On-Site System modularized plant will typically require 14-18 months between contract signing and start-up. This period for custom-designed plants may be in excess of two years.

Conclusion

We at Diamond Shamrock can provide a reliable, efficient, and long-lasting modularized chlor/alkali plant for on-site use. In addition, the system has been designed for flexibility in operation and in product employment and can thus meet the needs of most on-site producers. We should stress, however, that a custom-designed membrane cell plant may be more suitable for the on-site user, depending upon his circumstances, and such designs, of course, are available from us. Our SANILEC® System of low strength hypochlorite production may also be a better fit for a specific need for this type of product. The point to remember is that our company, as an experienced producer of chlorine and caustic, and as a long-standing supplier of chlor/alkali technology, is capable of providing whatever is needed to fulfill the requirements of virtually any prospective producer - large or small - of chlor/alkali chemicals.

PJV/RJS/rm

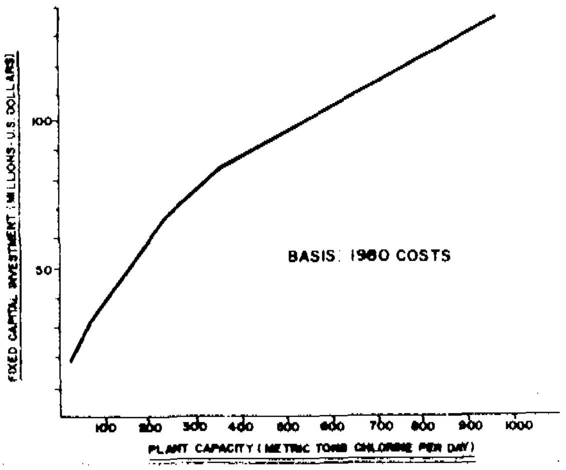


Fig. 1 Fixed capital investment versus plant capacity

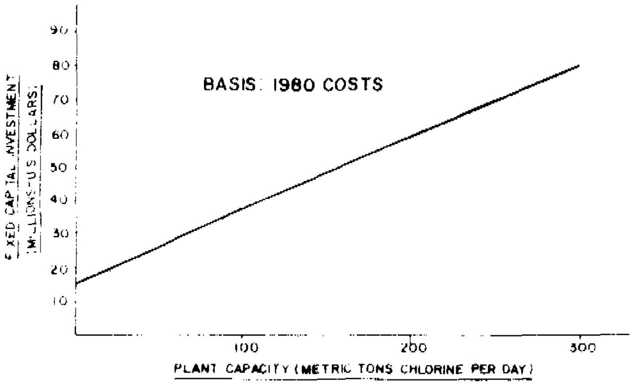


Fig.1A Fixed capital investment versus plant capacity

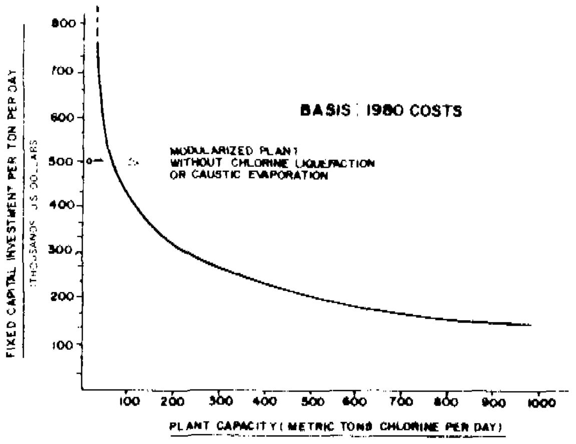


Fig. 2 Fixed capital investment per ton per day versus plant capacity

MODULARIZED PLANT - SCOPE OF SUPPLY

DIAMOND SHAMROCK
- MODULARIZED PROCESS EQUIPMENT
- ENGINEERING PACKAGE, INCLUDING
  - PROCESS FLOWSHEETS
  - MECHANICAL FLOWSHEETS
  - PROCESS DESCRIPTIONS
  - PIPING SPECIFICATIONS
  - ELECTRICAL DIAGRAMS
  - PLANT LAYOUTS
  - INSTALLATION, OPERATION & MAINTENANCE MANUALS
- TECHNICAL SERVICES
  - PRE-INSTALLATION CONSULTATION
  - PERSONNEL TRAINING
  - START UP SUPERVISION
  - TECHNICAL SERVICE FOLLOW-UP

CUSTOMER
- STORAGE TANKS
- SITE PREPARATION
- FOUNDATIONS
- BUILDINGS
- UTILITY GENERATION
- INTER-MODULE CONNECTIONS
- INSTALLATION MATERIALS & LABOR

Fig. 3 Modularized plant - scope of supply

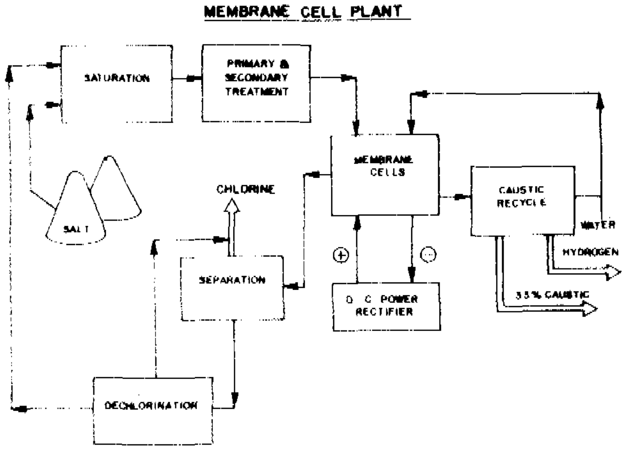


Fig. 4 Membrane cell plant-process flow sheet

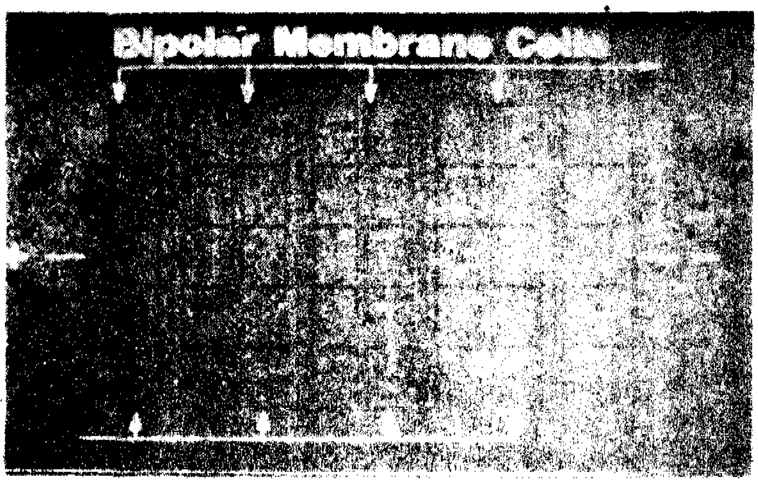


Fig. 5 Bipolar membrane cell - schematic

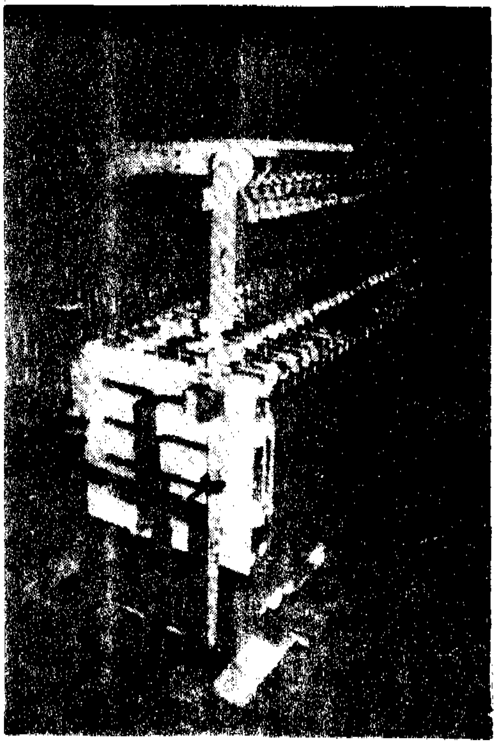


Fig. 6 Bipolar membrane cell

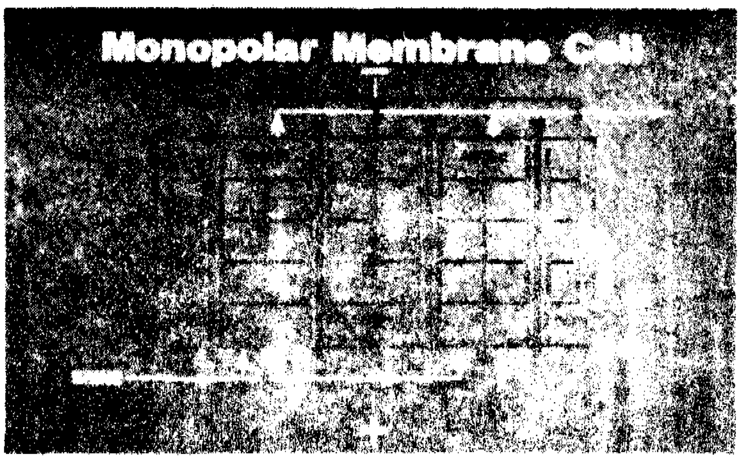


Fig. 7 Monopolar membrane cell - schematic

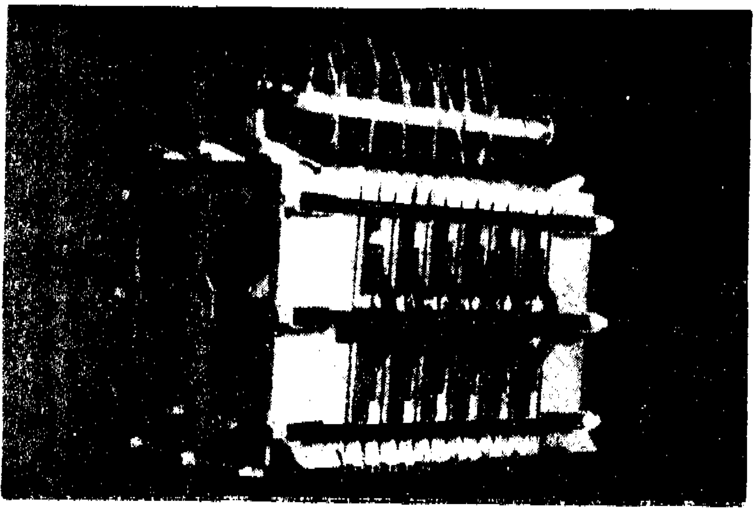


Fig. 8 Monopolar membrane cell

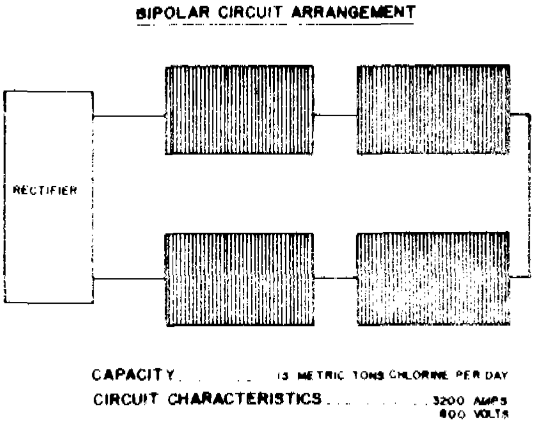


Fig. 9 Bipolar circuit arrangement

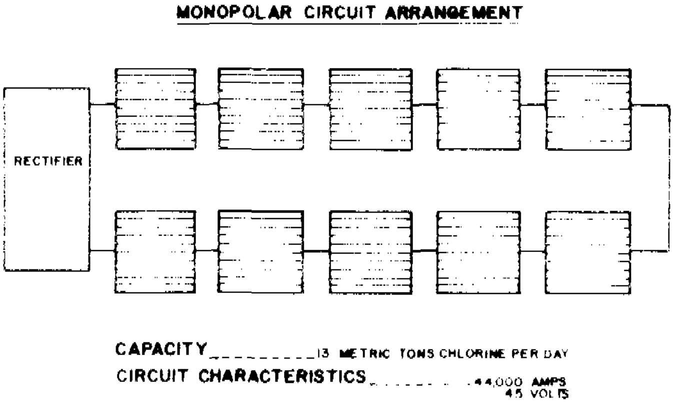


Fig.10 Monopolar circuit arrangement

Fig. 11 Electrolyzer module

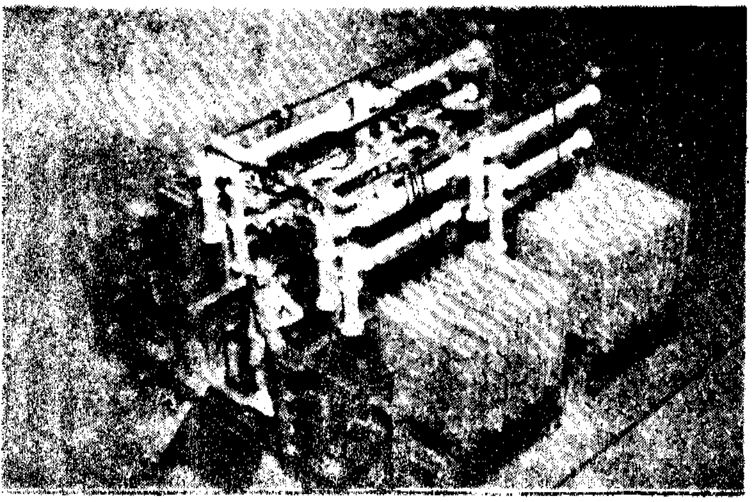


Fig.12 5 T/D electrolysis area

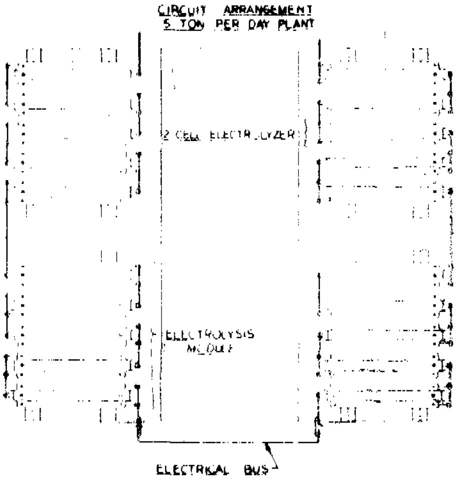


Fig.13 Circuit arrangement - 5 T/D plant

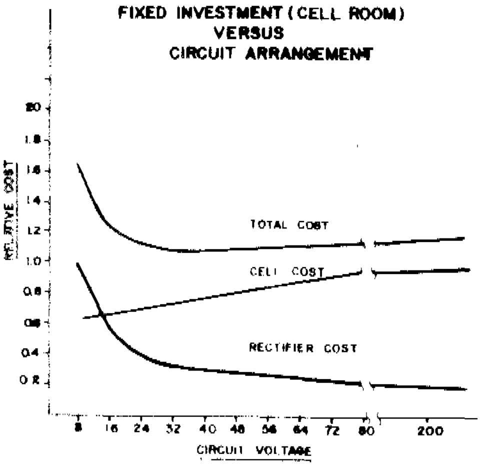


Fig.14 Fixed investment (cell room) versus circuit arrangement

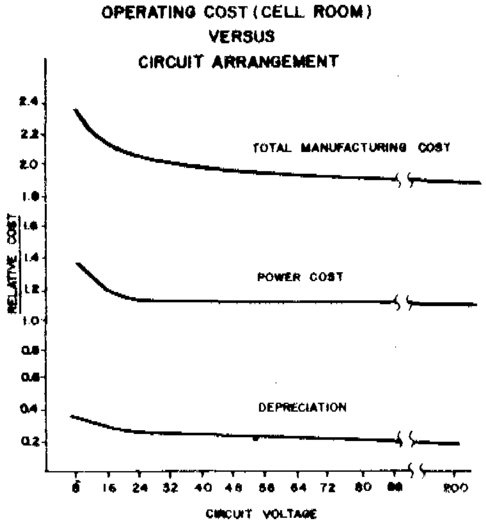


Fig.15 Operating cost (cell room) versus circuit arrangement

DIAMOND SHAMROCK ON SITE PLANT
PROCESS AREA SUPPLY

BRINE SATURATION

PRIMARY BRINE TREATMENT

SECONDARY BRINE TREATMENT

MEMBRANE ELECTROLYSIS CELLS

DEPLETED BRINE RECIRCULATION

DEPLETED BRINE DECHLORINATION

CHLORINE EMISSIONS CONTROL

CAUSTIC CIRCULATION

Fig.16 Diamond shamrock on-site plant-process area supply

[illegible]