HYPOCHLORITE ELECTROGENERATION FOR DRINKING WATER DISINFECTION

by

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APPENDICES

PREFACE

Disinfection with chlorine and chlorine products has proven to be an established process in the provision of safe drinking water, however, in developing countries a regular supply of chemicals is very much a problem. Production is usually centered in large scale factories to benefit from greater efficiency and economy-of-scale, but necessitating distribution by long vulnerable transport lines, with inherent possibilities of environmental spillage and consequent health hazard.
With the special attention to rural programmes in the Drinking Water Supply and Sanitation Decade, on-site production of disinfectants could fill a need if operation and maintenance could be done in a simple way.
Electrolytic production of chlorine is a well-known process in the chemical industry, though small cells have still to prove their reliability and low maintenance requirements.
IRC's study on Local Manufacture of Disinfectants aims at the promotion of the technology of on-site hypochlorite electro-generation. In this context, state-of-the-art reports have been prepared.

1. Hypochlorite Electro-generation for drinking water disinfection by Dr. G.H. Kelsall, London.

2. Electrode and Electrode Materials for On-site generation of disinfectants by Dr. D.W. Wabner and W.D. Fleischmann of the Technical University of Münich.

They hopefully would assist to promote testing and experimentation to support the worthwhile cause to provide more safe water to the most deprived areas.

T.K. Tjiook, IRC

1. INTRODUCTION

This report is intended to provide background information about the 'state-of-the-art' of hypochlorite electrogeneration, and follows a more extensive survey published in 1977 (Appendix 2). It is not comprehensive in itself, although a relevant recent literature review is included and the previous review (Appendix 2) appended, as is the computer search of recent patents (Appendix 3). However, it should provide sufficient detail for policy decisions to be made about the choice of suitable commercially-available hypochlorite electrogenerators for drinking water disinfection in third world locations. Also, it identifies some of the outstanding research and development requirements for hypochlorite generation in general, and in the context of the drinking water application in particular.

2. CHEMISTRY OF HYPOCHLORITE ELECTROGENERATION

The major reactions which occur when dilute aqueous sodium chloride solutions are electrolysed can be described as follows:

Anode: $2\ Cl^- \rightarrow Cl_2 + 2\ e$ (1)

Cathode: $2\ H_2O + 2e \rightarrow 2\ OH^- + H_2$ (2)

Solution: $Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+$ (3)

$HClO \rightleftharpoons H^+ + ClO^-$ (4)

Loss Reactions

Anode: $6\ ClO^- + 3\ H_2O \rightarrow 2\ ClO_3^- + 4\ Cl^- + 6\ H^+ + 1.5\ O_2 + 6e$ (5)

$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4e$ (6)

Cathode: $ClO^- + H_2O + 2e \rightarrow Cl^- + 2\ OH^-$ (7)

Solution: $2\ HClO + ClO^- \rightarrow ClO_3^- + 2\ Cl^- + 2\ H^+$ (8)

$2\ ClO^- \rightarrow O_2 + 2\ Cl^-$ (9)

$ClO^- + H_2 \rightarrow H_2O + Cl^-$ (10)

In an undivided hypochlorite cell (Fig.1.), chlorine is produced by reaction (1) from a neutral/alkaline electrolyte, and is hydrolysed by reactions (3 & 4) to hypochlorite ($HClO + ClO^-$) within a reaction layer at the anode. Hydrogen evolution by reaction (2) produces hydroxyl ions which neutralise the protons from reaction (3) and make the bulk electrolyte slightly alkaline. Hypochlorous acid ($HClO$) is a weak electrolyte with a pK_a of 7.49, such that ClO^- ions predominate over the free acid at $pH > pK_a$.

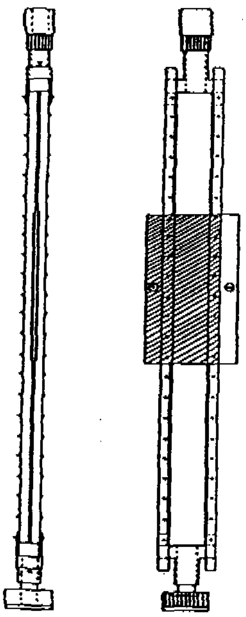


Fig. 1. Simple parallel plate monopolar hypochlorite cell

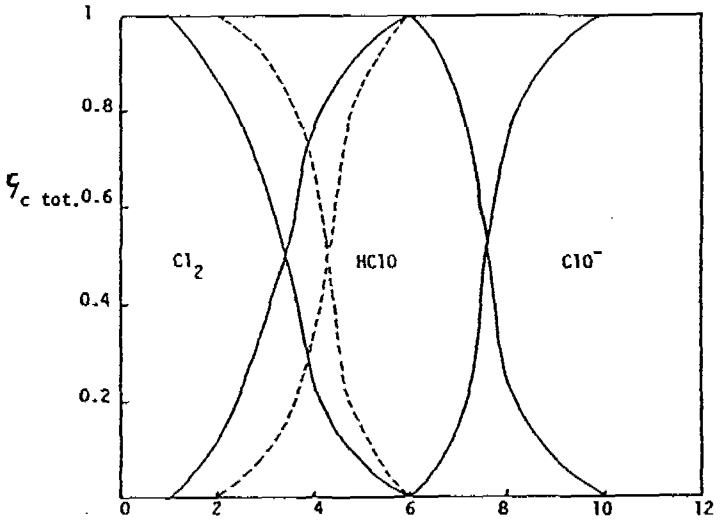


Fig. 2. Influence of pH on the ratio of concentration c of Cl_2, HClO and OCl^- to total concentration ($C_{tot}= C_{Cl2} + C_{HClO} + C_{ClO^-}$). Solid lines-calculated from equilibrium equations for reactions (3) and (4) at 280K in H_2O ($[Cl^-]=[HClO] + [ClO^-]$). Dashed line- in 4M Nacl ($[Cl^-] \gg [HClO] + [ClO^-]$). (Ref. 27 in Appendix 2).

Once formed, (3) hypochlorite may be decomposed by:

(i) further oxidation at the anode by reaction (5),

ii) reduction at the cathode by reaction (7), which is mass transport controlled at most cathode materials, as the inherent electrochemical kinetics are comparatively fast. Thus, for given hydrodynamic conditions, the rate of hypochlorite reduction is at a maximum.

iii) disproportionation to chlorate and chloride by reaction (8), the rate of which is pH and pCl dependent, but which may be neglected at electrolyte temperatures less than say 30° C and in alkaline solutions. (This also implies that in warm climates hypochlorite would have to be utilised shortly after production and not stored).

In the absence of conducting catalysts such as metals/metal oxides and/or light, loss reactions (9) and (10) may be neglected. However, the hydrogen produced by reaction (2) should be disengaged from the hypochlorite efflux stream using a cyclone, particularly if the cell is used in recycle or cascade mode, so that the effective resistivity of the electrolyte, and hence the cell voltage are reduced. For single cell operation, again the hydrogen should be disengaged and properly vented, to avoid any possibility of explosive reaction with oxygen, although for pressures of 5 - 5000 mm Hg, and H_2/O_2 ratio of 2 the explosive boundary of the reaction lies at $>$ 400°C. (The H_2/O_2 molar ratio depends on the rates of the loss reactions, which again depend on the bulk hypochlorite concentration).

In a properly operated hypochlorite cell, no free chlorine gas should be produced, since the concentration of that species is negligible at pH$>$ 6 (Fig. 2); hence, there should be no possibility of a thermally- or photolytically-assisted chain reaction between hydrogen and chlorine. Thus, the make-up water for the NaCl electrolyte should not be acidic.

3. ELECTRODE MATERIALS

3.1 Anodes

Hypochlorite anode materials are required both to be corrosion resistant and to have a high chlorine current efficiency, which may be 90% for Ti/RuO_2 or Ti/Pt-Ir oxide, so that the anodic loss reaction (6) is minimised. The former material has the benefit of lower anode overpotential (η_a) operation; hence cell voltages should be lower and energy yields greater. These and, probably to a lesser extent, Ti electroplated Pt anodes also have the advantage that the rate of the anodic loss reaction (5) is controlled by slow heterogeneous kinetics, rather than being mass transport controlled as on graphite. Hence, the rate of hypochlorite oxidation occurs at less than its maximum (i.e. mass transport controlled) rate on such materials.

The corrosion rates of these anodes increase rapidly with increasing anode overpotential (η_a), produced by increasing current density, and/or decreasing chloride concentration or temperature (say $< 10°$ C)). Typical operating conditions are 1 - 1.5 kA m^{-2} at 20-30 g/l NaCl and 15° - 25°C.

3.2 Cathodes

Hypochlorite cell cathode requirements are:

(i) a low hydrogen overpotential to minimise the cell voltage and hence the specific energy requirement, kWh $(\text{mol ClO}^-)^{-1}$,

(ii) corrosion resistance in the absence of an applied current/voltage,

(iii) freedom from sites for the nucleation and growth of calcium and magnesium hydroxide precipitates caused by the high local pH.

These criteria have led some manufacturers to use smooth Hastelloy (17% Mo, 16.5% Cr, 6% Fe, 4% W, 1% Mn, 1% Si, 0.15% C, balance Ni - Cabot Corp) cathodes.

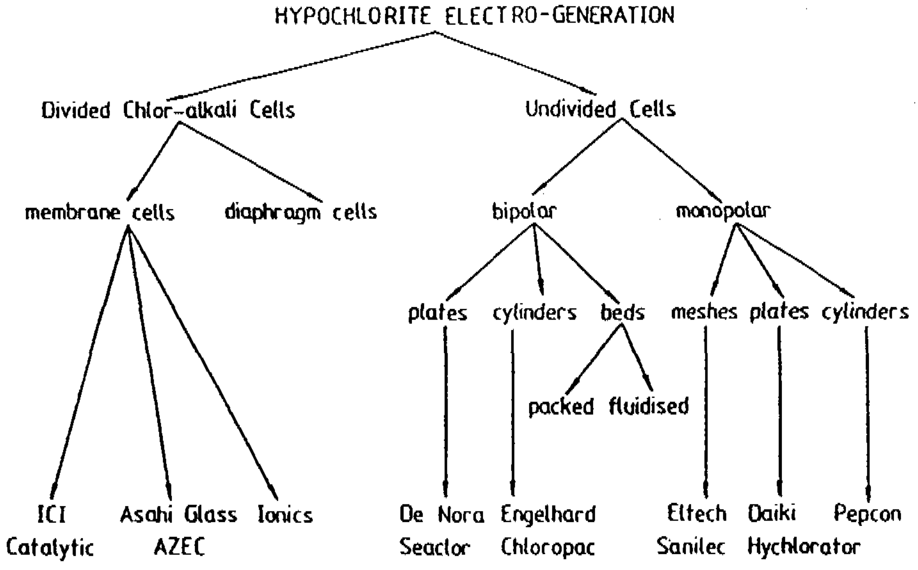


Fig. 3. Hypochlorite Cell Design Options

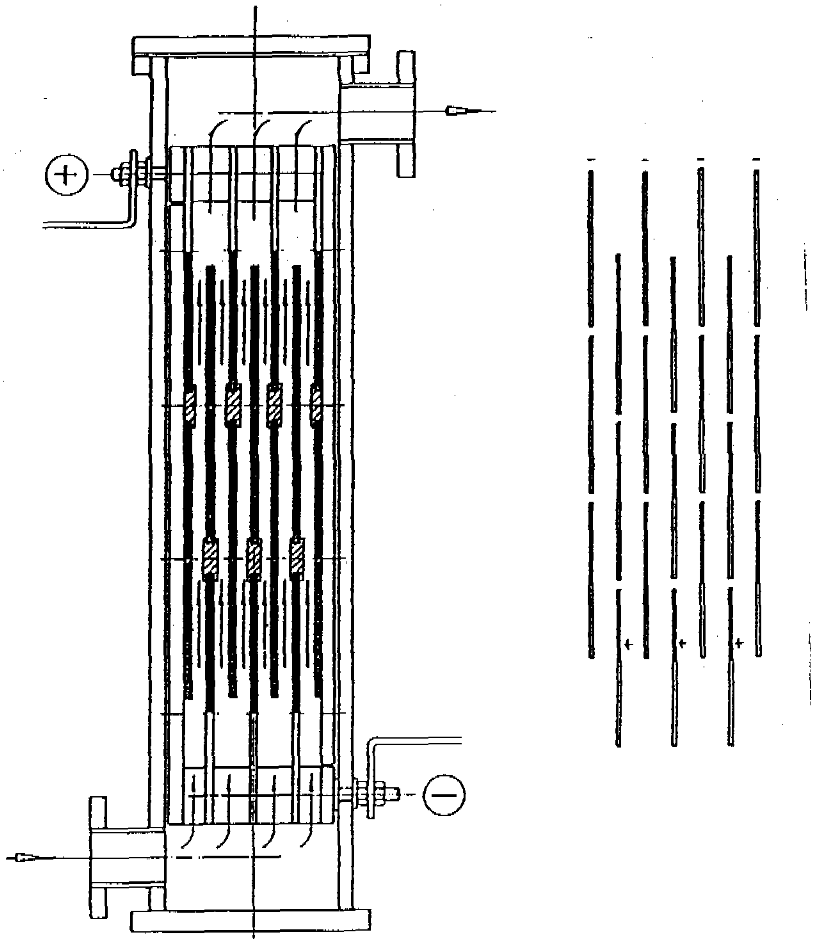


Fig. 4. De Nora Seaclor Hypochlorite Cell and schematic bipolar electrode arrangement.

4. CELL DESIGN

Some of the cell design options are given in Fig.3, with schematic diagrams of two of the cells (bipolar planar electrode - De Nora Seaclor, and bipolar cylindrical electrode - Engelhard Chloropac) shown in Figs. 4 and 5. In both of these designs, the current flows longitudinally in the electrodes and perpendicular to the electrode surface in the electrolyte. Fig. 6 shows a more conventional monopolar tubular cell (PEPCON); as it employs graphite/PbO_2 anodes, it may not be acceptable for drinking water disinfection, although the rate of loss of lead, as particulate PbO_2, is very low.

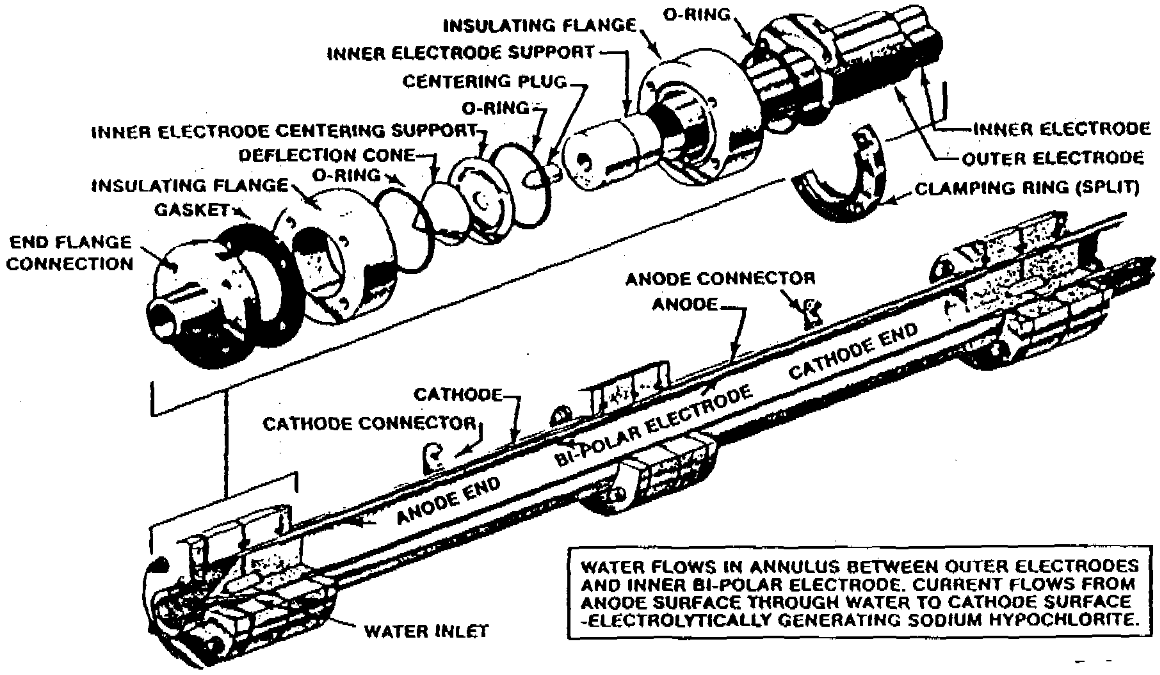
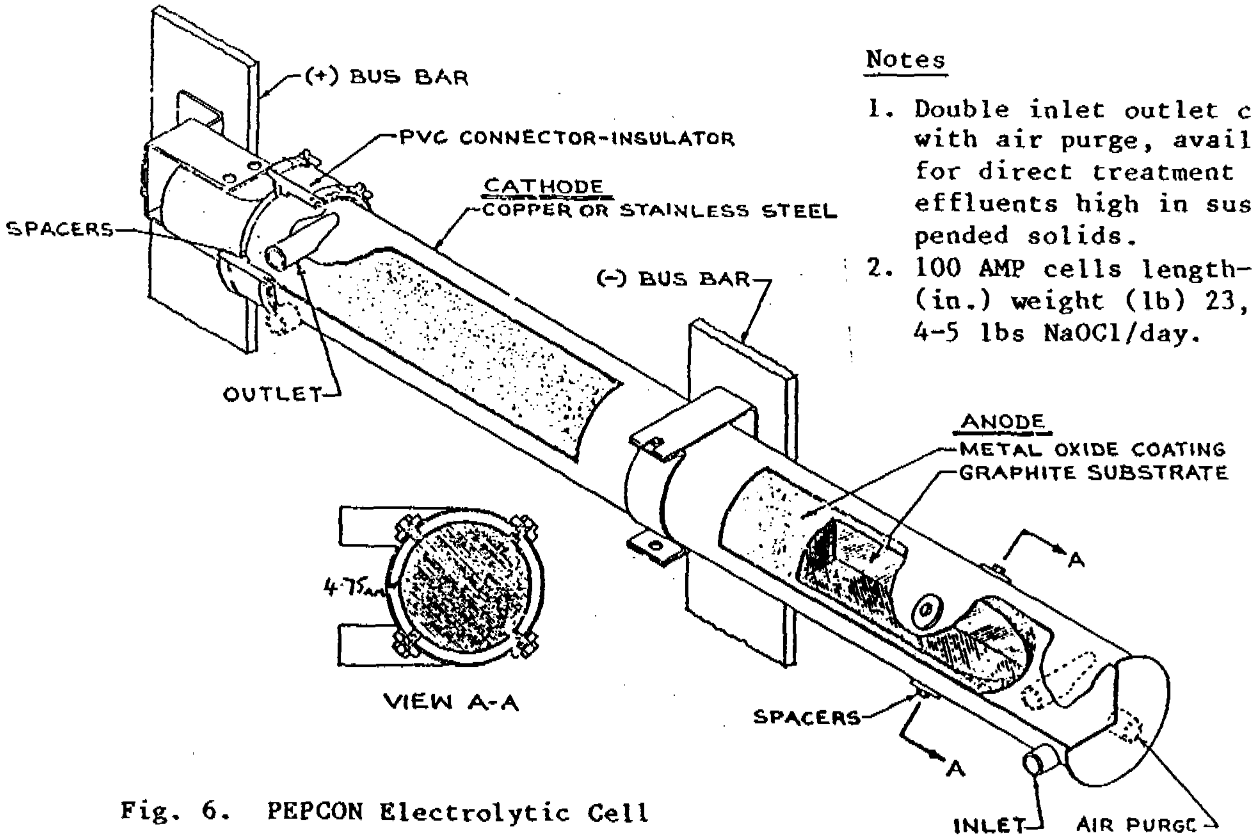


Fig. 5. Engelhard Chloropac Hypochlorite Cell



Notes

1. Double inlet outlet cell, with air purge, available, for direct treatment of effluents high in suspended solids.
2. 100 AMP cells length- 16 (in.) weight (lb) 23, cap. 4-5 lbs NaOCl/day.

Fig. 6. PEPCON Electrolytic Cell

4.1 Undivided/ Divided cells

The first choice is between the relative simplicity of design of an undivided hypochlorite cell, and the complexity of a miniature chlor-alkali cell, state-of-the-art examples of which incorporate cation exchange membranes, such as Nafion (Du Pont, U.S.A.) or Flemion (Asahi, Japan). The former type of cells have higher running costs and lower capital costs than the latter, so the decision depends, inter alia, on the scale of hypochlorite production required. However, some UK power stations with chlorine requirements of even 5 - 10 tons per day, consider the operation and maintenance of chlor-alkali cells more demanding than (sea water) electrochlorination in undivided cells and the relative complexity of the total plant unattractive, despite their technical/economic benefits and their provision of by-product hydrogen and sodium hydroxide. The main problem with using these cation exchange membranes is their intolerance of Ca and Mg ions, which can precipitate as hydroxides within the membrane. These ions are therefore removed with ion-exchange resins to give a residual concentration of a few ppb.

4.2 Monopolar/bipolar cells

The second option is between monopolar and bipolar cells. Monopolar connection of multiple electrodes involves parallel current flow at low voltage (V), such that if an individual anode/cathode pair operate at I amps, then n electrode pairs will require nI amps at V volts (Fig.7).

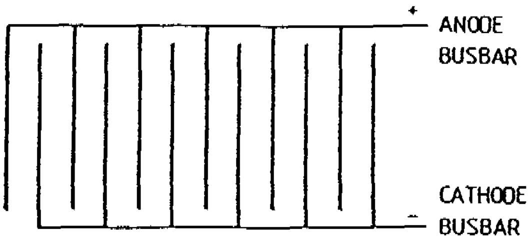


Fig. 7 Monopolar Multiple-Electrode Arrangement

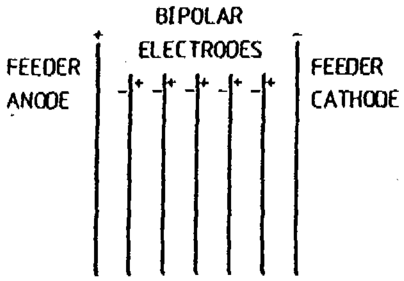


Fig. 8 Bipolar Multiple-Electrode Arrangement

Bipolar electrodes are connected in series via the electrolyte such that the same current I would pass through (n-1) bipolar electrodes driven by a voltage nV applied between two (monopolar) feeder electrodes, where V is the voltage required by an individual anode/cathode pair (Fig.7). This high voltage/low current operation is attractive as the cost of a transformer/ rectifier set would be lower than that required by a low voltage/high current monopolar cell for the same hypochlorite production rate.

However, bipolar cells may suffer to some degree from:

(i) the so-called by-pass current which passes directly between the two feeder electrodes, usually via the electrolyte in the manifolds to the bipolar elements. This efect may be minimised by judicious cell design, by making the inter-bipole resistance low and the by-pass current path as resistive as possible.

(ii) depending on the cell design, the bipolar elements may be materially more complex, to avoid hydrogen transport through the bipole from the cathode to the anode surface, and to minimise corrosion of any areas in the corrosion potential range. This constraint precludes the use of an all titanium bipolar element, since the molar volume change associated with the formation of TiH_x has been found to cause bending of such bipolar electrodes, producing possible short-circuiting and cracking of the anode electrocatalyst. A variety of low hydrogen overpotential, hydrogen-impermeable cathodes such as steel, nickel, Monel (Cu-Ni) and Hastelloy have been used to avoid this problem. Alternatively, hydrogen-impermeable conductors have been sandwiched between the Ti-based anode and cathode, as discussed in Appendix 2.

4.3 Bipolar bed electrodes

The advantages of the bipolar design and that of a three-dimensional electrode (high specific surface area) have been combined in a fluidised bipolar bed electrode (FBBE), using carbon/graphite particles and a pair of suitable feeder electrodes (Fig. 9), short-circuiting between which is prevented by expansion of the bed. As the particles rotate freely within the bed, acting alternately as anode and cathode surfaces, there should be no problem with hydroxide precipitates, which would also be prevented at the cathode feeder electrode by the scouring action of the bed. The design also offers the possibility of ease of electrode replacement with cheap graphite particles of a suitable size, and operation at a high salt conversion in a single pass through the cell.

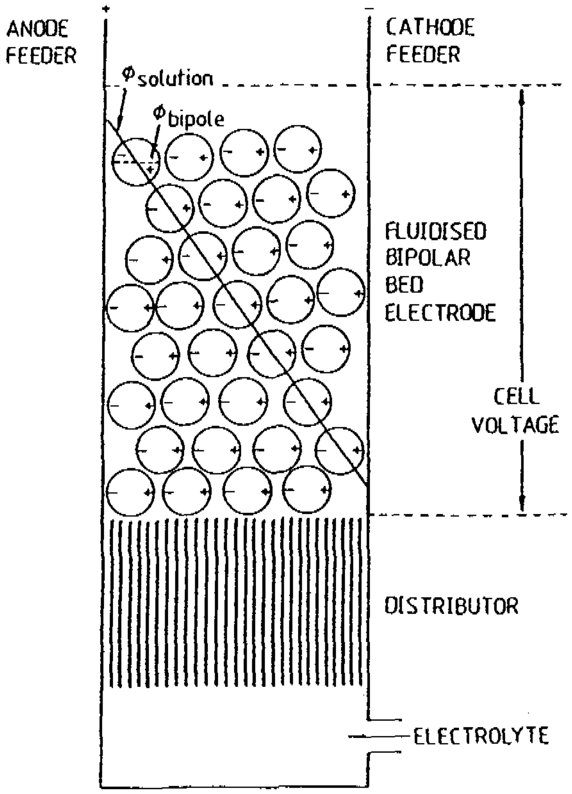


Fig. 9 Schematic Diagram of Fluidised Bipolar Bed Electrode

However, results to date indicate that energy yields are very low (about 0.6-0.7 mol ClO^- kWh^{-1}, compared with 2-3.5 mol ClO^- kWh^{-1} for conventional designs). This is due to the high electric field requirement in the electrolyte, such that the voltage drop across each particle a few -mm across is sufficient to drive both anode and cathode reactions; coupled with the large bed voidage, this produces a high-pass current. An analogous packed bipolar bed electrode, with a lower bed voidage, has been found to be susceptible to hydroxide precipitate problems.

For locations with access to cheap hydro-electricity, and with small hypochlorite requirements, the simplicity and low capital cost of the FBBE may override its high running costs. However, further R & D effort is needed before a suitable design could be given to a manufacturer.

5. CELL SELECTION CRITERIA - include:

(i) Capital costs - cells, pumps, reservoirs, transformer-rectifiers etc.
(ii) Running costs - electrolytic and pumping electrical energy,
 - salt for brine electrolytes,
 - acid for back-washing hydroxide deposits, etc.
 - recoating of Ti anodes with electrocatalysts
(iii) Current Efficiency (C.E.) - is the proportion of the total current used for the generation of hypochlorite.

$$\text{C.E. } (\%) = \frac{100\ c\ (\text{mol m}^{-3}) \times 2 \times 96500\ (\text{A s mol}^{-1}) \times u\ (\text{m}^3\ \text{s}^{-1})}{I(\text{A})}$$

where c is the efflux hypochlorite concentration, and u is the electrolyte flow rate

(iv) Energy Yield (E.Y.) - defined by:

$$\text{E.Y. } (\text{mol kWh}^{-1}) = \frac{3.6 \times 10^6 \times c(\text{mol m}^{-3}) \times u\ (\text{m}^3\ \text{s}^{-1})}{V\ (\text{V}) \times I\ (\text{A})}$$
$$= 0.165\ \text{C.E.}/V$$

Defining E.Y. in molar terms avoids ambiguities in comparing cell performances, which may be specified either in terms of 'active chlorine' or sodium hypochlorite; on acidification of the latter material, the reverse of reaction (3) occurs, such that 1 mol ClO^- = 1 mol Cl_2, and 74.5 g NaClO = 71 g Cl_2, the latter figures being the respective relative molar masses.

In the technical literature, the (erroneously named) terms energy efficiency (E.E.) or power efficiency are used, which are related to E.Y. by:

E.E. (kWh (kg Cl_2)$^{-1}$) = 1/14.085 E.Y.

Higher current densities/specific hypochlorite production rates lead to higher cell voltages and hence lower energy yields (mol ClO^- kWh^{-1}) but lower capital costs for a given production rate. The inverse relationship of E.Y. and cell voltage (V), indicates that cell designs should minimise V, though the increasing concentration of bubbles in the electrolyte from cell inlet to outlet and the non-linear effect on its conductivity, may lead to current density distribution problems with very narrow inter-electrode gaps, as discussed in Appendix 2.

The spatial distribution of potential in a hypochlorite cell is shown in Fig.10, which indicates the importance of minimising the anode and cathode overpotentials, as discussed in section 2.

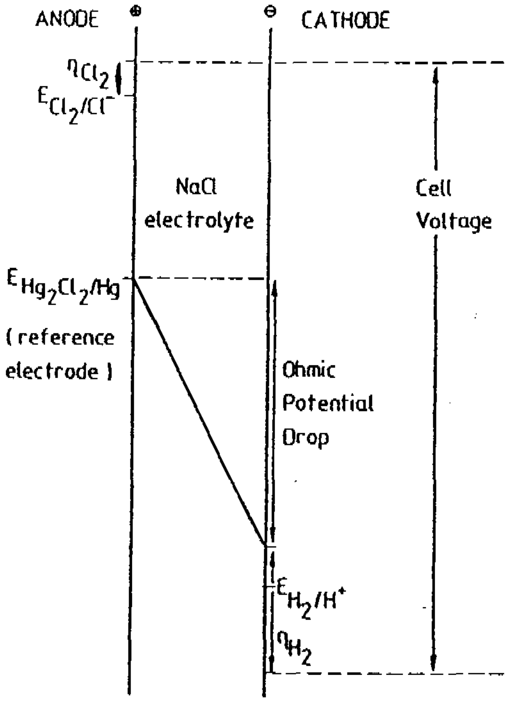


Fig. 10. Schematic Potential Distribution in Hypochlorite Cell

(v) Anode Life - titanium-based RuO_2-containing mixed oxide or Pt-Ir oxide electrocatalysts are available with guaranteed service lives of 5-7 years under specified operating conditions, which normally require current densities of 1.6 kA m^{-2}.

(vi) Susceptibility to cathode precipitates/blockage

The Mg^{2+} and Ca^{2+} ions in sea water or in naturally 'hard' water used in brine electrolytes, precipitate at cathode surfaces due to the high local pH produced by reaction (2). Though this decreases the rate of hypochlorite reduction by reaction (7), it increases the cell voltage and hence decreases the energy yield, as well as increasing the pressure drop and hence pumping costs. Eventually the cell may block, possibly with catastrophic failure of the anode, due to excessively high local current densities. Some manufacturers such as Daiki (Hychlorator) claim that this is not a problem with their cells.

The conventional solutions are acid back-washing to dissolve the hydroxide precipitates or operation at high flow rates, which dilutes the (single pass) hypochlorite concentration and increases pumping costs. Ion-exchange treatment of brine electrolyte make-up water is an expensive alternative, which is unavoidable for chlor-alkali cells, the membranes of which would otherwise be subject to deterioration by internal hydroxide precipitation.

The technique of periodic current reversal has been used to overcome problems with cathode deposits, but this requires anodes which will not suffer from being operated cathodically, and cathodes which can operate anodically without dissolving. In principle, a cell with platinised titanium electrodes would fulfil these requirements, but enhanced corrosion and peeling of the platinum electrocatalyst has been found to occur under such conditions, due to the solubility of hydrogen in the platinum and the formation of titanium hydride. However, it is understood that more recently, thick (50 g m^{-2}) RuO_2 coatings on titanium have been operated successfully with current reversal. Ti_4O_7 has also been used in this mode, as will be discussed in section 6 below.

(vii) Salt utilisation/conversion efficiency

The mode of operation (single pass, recycle, cascade cells in series) and the rate of loss reactions (5) and (7) constrain the maximum attainable hypochlorite concentration, the time evolution of which has been modelled (see Appendix 2). In a miniature chlor-alkali cell, the gaseous chlorine produced by reaction (1) could be hydrolysed (reactions 3 & 4) in an external reactor by hydroxyl ions from reaction (2). The stoichiometry of reaction (3) would result in a $(ClO^-):(Cl^-)$ molar ratio of unity. However, in an undivided cylindrical cell with an anode/cathode area ratio of about 100 (such that loss reaction (7) was minimised) and operating at low chloride concentrations (3-6 g NaCl/1), molar ratios as high as it have been reported recently (1), with chloride conversions as high as 70%. That these solution conditions are likely to lead to high anode potentials and hence high Ti/RuO_2 anode corrosion rates, was not mentioned.

(viii) Susceptibility to anodic MnO_2 deposition

Some sea water electrolytes have been found to contain Mn(II) concentrations well above the usual level 30 ppb, which has led to anodic deposition of MnO_2. For some anodes this has been reported to have a deleterious effect on the current efficiency for chlorine evolution, since some forms of MnO_2 catalyse the evolution of oxygen by reaction (6); some manufacturers claim that this presents no problem for their anodes.

(ix) Low maintainance requirements

In addition to items (v), (vi) and (viii) above, possible operational problems include pump failure due to electrolyte shortage, which may cause consequent power supply and cell failure. This potential difficulty may be obviated by the use of a suitable transducer for electrolyte level sensing (giving a voltage or current output proportional to the magnitude of parameter monitored), and electrical protection on the power supply.

(x) High anode: cathode area ratio

A high anode:cathode area ratio enables a higher hypochlorite concentration, and hence cumulative energy yield, to be achieved in recycle operation. This, and the effect of electrode texture has been discussed in the recent literature for the general case of transport controlled reactions in undivided cells [2], as well as for hypochlorite production [3] in particular. (See also section 5. (vii) above).

6. RECENT LITERATURE

The open academic literature on the subject since 1977 is limited to:
(i) the study of chloride conversion [1] by maximising the anode:cathode area ratio, as discussed in section 5. (vii) above. This is potentially of great significance for the economy of disinfection of drinking water (and swimming pools).
(ii) two studies showing the effect of $Mg(OH)_2$ and $Ca(OH)_2$ deposits in decreasing the rate of ClO^- reduction (reaction (7)) by physically blocking access to cathode surfaces, so enabling a higher hypochlorite concentration to be achieved in recycle electrolysis [3,4]. However, there was no mention of the ohmic voltage penalty due to the presence of such materials, or of the catastrophic blockage of cells operated for long periods, particularly with sea water electrolytes.
(iii a parametric study [5] of a parallel plate cell using a Ti/PbO_2 anode and Ti cathode, for which the cell voltage, current efficiency and energy yields were reported as functions of current density, inter-electrode gap, chloride concentration, electrolyte flow rate and temperature. A more limited Japanese study [6] also showed the reduction in cell voltage by closing the inter-electrode gap.

In addition, the information from the thirteen papers on electrolytic bubbles, in J. Appl. Electrochem. (15(4) (1985)may be of relevance to hypochlorite cell design.

To obtain long term reliability data on hypochlorite cells, the electricity supply industry of the UK conducted their own trials on a number of commercially available units, including the Seaclor (De Nora), Sanilec (Eltech/CJB), Chloropac (Engelhard), OSEC (Wallace and Tiernan) etc. Unfortunately this information is confidential at present, though it is known that all units suffered to some degree from problems of anode corrosion/wear and blocking by hydroxide precipitates.

Only one report [7] of commissioning and initial operating results of commercial hypochlorite cells (De Nora Seaclor - installed at Le Havre for Electricité de France) appears to have been published. Whilst the conclusions were favourable overall, the conditions used (sea water electrolyte and low temperature) were not those typical of envisaged third world locations; however, the conditions at Le Havre are likely to have been more demanding in terms of anode wear and cell blockage by cathode precipitates.

7. RECENT PATENTS

Nearly 100 patents (Appendix 3) on hypochlorite electrogeneration and related fields subjects have been filed in the 7 years since the last survey. However, other than general details of construction, the patents usually include little information which would enable a choice of the most promising units to be made. Usually, even the manufacturers sales literature does not provide adequate detail to enable even the energy yields of different designs to be compared, since the current density, hypochlorite concentration, temperature and salinity are frequently not all specified.

In recent years small manufacturers have entered the market.
However,
(i) they are critically dependent on the suppliers of anode materials and possibly membranes,
(ii) they are unlikely to have the technical support required to transfer the technology to the third world on the scale required, and in particular, to recoat anodes.
Such types of cells could easily be assembled in the third world using imported anodes such as manufactured by Eltech in the USA, IMI in the UK etc.

8. NEW DEVELOPMENTS

IMI (Birmingham, UK) have developed a Ti oxide material with the trade name "Ebonex", which the company has tested for hypochlorite production with periodic current reversal to prevent cathode deposit formation, although at very low current densities (about 50 A m^{-2}). More recently they have thermally deposited RuO_2 electrocatalysts, and again have run the electrodes for many months with half-hourly current reversal, but at the more industrially realistic current density of 500 A m^{-2}. The material is a ceramic with a composition approximating to Ti_4O_7 and unlike elemental titanium has a low solubility for hydrogen transport, so enabling hydrogen to be evolved without adverse effects during current reversal. However, it is unlikely to be produced in plates of sizes greater than 0.1 m^2, which has implications for cell designs.

The Swiss company Korthals AG, Rueschlikon, is reported 1 to have taken a provisional patent on the high anode:cathode area hypochlorite cell, and to be producing 50 g Cl_2 hr^{-1} units which can achieve 70% salt conversion. Anode corrosion may be a problem for the conditions reported 1 , but the commercially available cells and the design concept should be investigated further.

Although manufacturing costs have decreased considerably, solar energy converters such as photovoltaic arrays are not as yet an economic source of electrical power for hypochlorite generation and are generally more suited to lower power applications. However, there may be remote locations where their use may be justified for small scale hypochlorite production.

9. RECOMMENDATIONS

(i) It is suggested that a similar test programme to that of the UK electricity supply industry be established at sites which are typical of the third world locations requiring hypochlorite technology, and where the cell performance can be well monitored. The most direct way would be to convince experienced manufacturers that because of the size of the potential market, they should provide cells for field trials.

(ii) Such manufacturers should be encouraged also to develop smaller capacity, comparatively unsophisticated units appropriate for developing countries.

(iii) With a supply of imported titanium-based anodes, locally produced steel cathodes and power supplies, small simple PVC-bodied cells could be produced to meet hypochlorite requirements of say 500 g per day, which would need anodes of 200 - 300 cm^2 and a power supply of 15 - 20 A at 4 - 8 V. A development study is needed to arrive at a suitable cell design.

(iv) Some independent research be funded to examine:
(a) the more novel materials such as Ebonex and appropriate cell designs.

(b) other cell concepts such as the fluidised bipolar bed electrode (FBBE) and high anode/cathode area ratio cells capable of producing the high ClO^-/Cl^- molar ratios ideally required for drinking water disinfection, should also be examined in more depth.

(c) the direct conversion of chloride to hypochlorite with solar energy and suitable semiconductor electrodes.

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J.Chem.Tech.Biotechnol., 30 (8) (1980) 423.
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5) G.H.Kelsall, J.Appl.Electrochem., 14 (1984) 177.
6) K. Yanagase, T. Yoshinaga, Denki Kagaku 49 (1981) 274.
7) H.Guyader, Revue Generale de l'Electricite, 86 (7/8) (1977) 611.
8) UK Patent Application GB 2 113 718A, 26 January 1982.

APPENDIX 1

LIST OF MANUFACTURERS*

UNDIVIDED CELLS

Italy

1. Oronzio de Nora (SEACLOR)
Impianti Elettrochimici S.p.A.
Milan

Japan

1. Daiki Engineering Co. Ltd. (HYCHLORATOR)
Tokyo

Netherlands

1. Magnetochemie (CHLORANSITU)
P.O. Box 217
3100 Schiedam
Netherlands

Switzerland

1. Korthals A.G.
Rueschlikon

United Kingdom

1. C.J.B. Developments Ltd. (SANILEC)
Portsmouth, Hampshire PO3 5PG

2. Cumberland Engineering Co. Ltd. (ROTACHLOR)
Bootle, Mersey Side L20 1BR

3. Engelhard Industries Ltd. (CHLOROPAC)
Portskewett, Newport, Gwent NP6 4YN

4. HypoCell Ltd.
Lenham, Kent ME17 2EA

5. Cogen Environmental Ltd.
Sunrise Parkway
Linford Wood, Milton Keynes
MK14 6LQ

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* Inclusion of names does not imply any endorsement by IRC whatsoever.

7. Plenty Metrol (SEA CELL)
Berkshire RG14 5TR

8. Steetley Engineering Ltd.
Lenches Bridge, Kingswinford
West Midlands, DY6 8XA

9. Wallace and Tiernan Ltd. (OSEC)
Priory Works
Tonbridge, Kent TN11 OOL

United States of America

1. Eltech Systems Corporation (SANILEC)
Chardon, Ohio 44024

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A REVIEW OF HYPOCHLORITE ELECTROGENERATION

by

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SUMMARY

After a brief review of the commercial situations in which 'active chlorine'/hypochlorite ($HOCl + OCl^-$) is used, the basic chemistry of the chloride electrolysis system is described. Suitable electrode materials are discussed, followed by a short resumé on possible cell designs and their implications. The few reports available in the literature on hypochlorite cells per sé are then reviewed, followed by a description of available hardware taken largely from the patent literature.

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1. INTRODUCTION

Although it had become unfashionable because of the more economically attractive route via gaseous chlorine and sodium hydroxide, the in-situ electrogeneration of sodium hypochlorite has received increasing attention over the last two decades, due to the potential dangers of transporting and storing large volumes of chlorine. As a strong chemical oxidant, sodium hypochlorite has been used commercially:-

a) As a biocide/bactericide/disinfectant in sewage treatment processes as devised by PEPCON (1, 2) and CJB Ltd. (3, 4). The chemistry involved in electrolytic sewage treatment (EST) has been reviewed by Millington (5).

b) for reducing marine growths, mussels, slime, algae and other organic fouling in sea waters used on board ship and for cooling in coastal power stations. A concentration of 1-10 ppm active chlorine (as hypochlorite) is said to be adequate for such applications (2). The results of French and Italian trials at power stations have been reported by Marchesi (6).

c) to sterilise water for injection into oil and gas bearing strata to boost falling pressure. If not sterile, the small fissures in the rock become blocked and yields suffer. Englehard (6) have sold several large units for use in the North Sea Oil Fields (2, 8).

d) for oxidising chemicals, such as in cyanide destruction (9) and for desulphurising waste gases. Namikawa (10) claims a reduction of SO_2 concentration in waste gas from 700 ppm to 1 ppm, by adsorption in NaOCl.

Other applications such as deodourising in tobacco plants, sterilising in the food and brewing industries, and treating swimming pools (11) are reviewed by Kuhn (2, 8).

The theory and practice of hypochlorination of water is reviewed by Dessart (12), a historical survey is given by Brown (13), and Corpel and Creissels (14) cover the use of electrochlorination in fighting water pollution. Comparative disinfection methods as alternatives to chlorination have been discussed by Hoehn (15), and the technical and economic considerations of biocide system options for cooling waters have been reviewed by Siegrist et al (16).

2. THE CHEMISTRY INVOLVED

The electrochemistry of chlorine has been reviewed by Mussini and Fiati (17). In general, the chemistry of the halogen oxy-acids is very complicated (18), as can be seen from the thermodynamic description of the chlorine-water system, described by Pourbaix (19) in terms of potential-pH diagrams. However, the basic reactions involved in the electrogeneration of sodium hypochlorite, were formulated by Foerster and Muller (20) at the turn of the century:

Anode: $2Cl^- \rightarrow Cl_2 + 2e$ (1)
Cathode: $2e + 2H_2O \rightarrow 2OH + H_2$ (2)
Solution: $Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$ (3)
$HOCl \rightleftharpoons H + OCl^-$ (4)

Loss Reactions

Anode: $6OCl^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3/2O_2 + 6e$ (5)
$2H_2O \rightarrow O_2 + 4H^+ + 4e$ (6)
Cathode: $2e + OCl^- + H_2O \rightarrow Cl^- + 2OH^-$ (7)
Solution: $2HOCl + OCl^- \rightarrow ClO_3^- + 2Cl^- + 2H^+$ (8)
$2ClO^- \rightarrow O_2 + 2Cl^-$ (9)
$H_2 + OCl^- \rightarrow H_2O + Cl^-$ (10)

Equilibrium constants for reactions (3) and (4) have been determined by various authors (21-24). Approximate values at 273K are:

$$K_3 = \frac{(HClO)\ \ (Cl^-)\ (H^+)}{(Cl_2)} \sim 2 \times 10^{-4}\ mol^2\ \ l^{-2} \qquad (A)$$

$$K_4 = \frac{(H^+) \quad (ClO^-)}{(HClO)} \quad 2 \times 10^{-8} \text{ mol } l^{-1} \qquad (B)$$

Relatively little information which could be used for design purposes, is available in the open literature on hypochlorite electrogeneration per se, although considerable interest has been shown in the anodic loss reaction (5) of chlorate formation (in an attempt to minimise its effect on current efficiency loss in the chemical production of chlorate from hypochlorite (reaction 8). The chemistry and physics of the process are quite complex, the electrochemistry being coupled to a chemical reaction in the anodic reaction layer, in which chlorine is hydrolysed to form hypochlorite. Theories on anodic chlorate formation have been proposed by De Valera (25), Ibl and Landolt (26 - 28), Beck (29), Hammar and Wranglen (30), and Jaksic et al (31 - 33). The net conclusions of these studies can be summarised as follows:-

a) The primary electrode reactions are the kinetically controlled discharge of chlorine (reaction 1) and hydrogen (reaction 2).

b) The chlorine evolved is hydrolysed by a chemical reaction in a reaction layer at the anode. A study of the absorption kinetics of chlorine into aqueous media has been carried out by Spalding (34).
It was shown to react with both water molecules and hydroxyl ions, and that either or both of these reactions could be rate-determining, depending on the solution pH. From pH 3 to 10.5, the forward reaction (3) predominated and an apparent first order rate constant of 20.9 s^{-1} at 298 K was determined for reaction of chlorine with water molecules. From pH 10.5 to 12.5, the chlorine reacted with both hydroxyl ions and water molecules, and above pH 12.5, the second order reaction between chlorine and hydroxyl ions became rate controlling. It is assumed, therefore, that at the pH values encountered in hypochlorite electrogenerators and chlorate cells, the concentration of dissolved molecular chlorine may be neglected.

c) Both the anodic (5) and cathodic (7) loss reactions are mass transport controlled on graphite electrodes. (Choa (35) has determined the diffusion coefficients of the hypochlorite ion, hypochlorous acid and chlorine in aqueous media). The influence of the electric field on the transport of hypochlorite ions to the anode (attraction) and to the cathode (repulsion) will depend, inter alia, on the ratio of OCl^-/Cl^-. The reduction of hypochlorite has been investigated by Harrison and Khan (36) and by Schwarzer and Landsberg (37), and found to be a 2 electron irreversible process on platinum or carbon electrodes. The cathodic reduction of anions in general (and the anodic oxidation of cations) has been treated theoretically by Wagner (38), who mentions the use of 'chemical diaphragms' of magnesium and calcium hydroxides, chromates (8, 39-41), molybdates and vanadates (42), to diminish the loss in current efficiency by OCl^- reduction. At high current densities, the adverse potential gradient in the porous films produced is sufficiently high to diminish ion transport and reduction of OCl^-. The idea of a diaphragam has been extended to the use of ion exchange membrane coatings on cathode surfaces (8, 43, 44), which also avoids problems due to $Mg(OH)_2$ and $Ca(OH)_2$ precipitation resulting from a high local pH at cathode surfaces.

d) Ibl and Landolt (26,27) proposed that part of the OCl^- formed was used to buffer the anodic reaction layer, as the $HClO/OCl^-$ equilibrium is both pH and Cl^- concentration dependent, such that chlorine hydrolysis could occur at a sufficient rate. At low Cl^-(0.1 M), the anodic loss current was much higher than that anticipated from a purely mass transport controlled process, (this was interpreted as indicating that the hydrolysis reaction was taking place at a mean distance from the anode less than the diffusion layer thickness,), while at high Cl^- (1 M), the converse was found. Jaksic et al (32, 33) explained these results as an effect of the Cl^- molarity on the activity coefficient of the hypochlorite electroactive species, and its associated chemistry. By using an experimentally determined value for the individual activity of the hypochlorite ion, it was shown that the gradient in chemical potential rather than concentration, has to be used as the driving force for diffusion in the theoretical description of the system.

Consequently, reasonable agreement was achieved between the experimental chlorate yield and the theoretical yield based on the combined hydrolytic and diffusional fluxes of active chlorine ($HClO + OCl^-$).

e) Ibl and Landolt (26-28) were first to investigate the chloride electrolysis system under well characterised hydrodynamic conditions, and to allow for the effect of gas evolution on the mass transport situation, by using a correlation established by Ibl and Venczel (45). They were followed by Hammar and Wranglen (30) and Beck (29), who ratified the mass transport controlled loss reaction of ClO^- reduction at the graphite or steel cathode and further oxidation at the graphite anode. A mass transport study of two phase flow in an electrochemical reactor has been made by Jennings et al (46), who concluded that the mass transport rate enhancement was due mainly to the reduction by gas bubbles, of the effective cross-sectional area of the cell, leading to an increase in the mean linear velocity of the liquid phase.

Hammar and Wranglen (30) found the following dependencies for the cathodic reduction (7) and anodic oxidation ((5) rates:

(i) proportional to ClO + HOCl
(ii) inversely proportional to current density
(iii) increased with temperature by about 3% and 2% per K, respectively
(iv) independent of pH between 6.5 and 10.5, at constant $HClO + OCl^-$
(v) decreased with increasing NaCl and $NaClO_3$ at higher $HClO + OCl^-$, because of increasing electrolyte viscosity.

Following Ibl and Landolt's work (26, 27) on graphite as an anode material, their use of Ti-Pt anodes (28) led to a lower loss of OCl^- to ClO_3^- by anodic oxidation in 4M NaCl. They attributed this to the slow heterogeneous kinetics, preventing OCl^- from being oxidised at a mass transport limited rate. Unfortunately, all Ibl's published work was done using too low a current density to be typical of a hypochlorite electrogenerator, such that the mass transport situation was always dominated by electrolyte flow rate rather than gas evolution rate.

However, Hammar and Wrangler (30) extended the range covered to 2 kAm ^{2}.

f) Subsidiary Reactions (6, 8-10)

The kinetically controlled loss reaction (6) of water decomposition with oxygen evolution leads to the major loss of current efficiency at low HOCl + OCl concentrations in hypochlorite electrogenerators. Its effect may be minimised by judicious selection of an anode material with a high oxygen overpotential and low chlorine overpotential. In closed cycle electrolytes (such as in perchlorate production), the current efficiency loss may be further reduced by the addition of inhibitors (for oxygen evolution) such as NaF (47-49).

Chemical chlorate formation by reaction (8) proceeds slowly at ambient temperature, its rate being greatest in the neutral pH region, where both HOCl and OCl$^-$ are present, and declining sharply with increasing pH (32). According to Pourbaix (19) the reaction can be neglected at 298 K but attains an appreciable rate at 323 K. The hypochlorite decomposition reaction (9) involves the oxidation of water by hypochlorite, which itself is reduced to chloride with the evolution of oxygen. Except in the presence of catalysts such as MnO_2, NiO_2 and CoO_2, or under the action of light, the reaction is slow especially in alkaline solutions. This confers a large degree of stability on neutral and alkaline solutions of HOCl and OCl$^-$, despite their great oxidising power (19). On acidification, hypochlorous acid decomposes to give chlorine and water, the reaction rate being more rapid the higher the Cl$^-$ concentration. The direct oxidation of hydrogen at the anode (50) may be neglected, since its solubility is so low (0.00076 M in water at 298 K).

The reduction of hypochlorite by hydrogen (reaction 10) appears to be a thermodynamically possible reaction which has escaped mention in the literature on the subject, probably because of its minimal effect in practice. However, particularly in the case of concentrated hypochlorite solutions, the hydrogen produced in an undivided cell should be disengaged from the hypochlorite efflux stream.

The oxidation of chlorate to perchlorate (47-49) can largely be neglected in a hypochlorite cell, unless the chlorate concentration has built up during recycle electrolysis. Industrially, the reaction is carried out with a high chlorate concentration, low electrolyte temperature and a high current density. Both chlorates and perchlorates are stable and have no oxidising properties, except in very acid solutions (19), i.e. they are not normally reduced to any appreciable extent at a cathode.

3. ELECTRODE MATERIALS

a) Graphite: it is the traditional anode material in the chlor-alkali industry, but suffers from high wear rates which are current density, pH and electrolyte temperature dependent (51, 52) and consequently lacks dimentional stability. Its electrochemical performance is adequate, though it is not an outstanding electrocatalyst for chloride oxidation.

b) Noble metal/noble metal oxide coated valve metal electrodes: Platinised titanium has been reported to give problems at high current densities, especially with low electrolyte temperatures (say 285 K) when a high anode potential causes rapid Pt loss and possible mechanical stripping of the coating. Reports on the matter have been published by the C.E.G.B. (53,54), Marshall and Millington (55, 56), Khodkevich et al (57)and Veselovskaya et al (58). The use of Pt/Ir coated Ti anodes (59, 60) reduces these problems by their having lower corrosion rates and better electrocatalytic performance.
Atanososki et el (59) described the polarisation behaviour, in 5 M Na Cl + 3 g l^{-1} Na ClO_3 at pH 6 and 313°K, of PbO_2, graphite, Pt (Pt + Ir) on Ti, Ir on Ti and RuO_x + TiO_x on Ti, of which the last three had far superior electrocatalytic performance.
Probably the best anode available for chloride electrolysis is the so called dimensionally stable anode (61,62) (DSA), based on a mixed oxide coating of RuO_2 + TiO_2 + another metal oxide onto a titanium substrate. The DSA manufactured by De Nora (63,64) is claimed to have virtually zero wear rate and a replacement life of 2 - 3 years at the rated current density of 1.6 kA m^{-2}. For operation with electrolyte temperatures in the range 277 - 285°K, as may be encountered in sea water electrolysis, a special coating is

available. I.C.I. Ltd. also hold several patents (65) on Ti-RuO_2 type anodes, and a considerable number of papers have appeared in the literature on the subject (66).

A failure mechanism for metal oxide coated valve metal anodes in general, has been postulated by Bystrov (67). Operating conditions such as high current density/low electrolyte temperature are said to cause depletion of n-type charge carriers in the TiO_x/MO_y semi-conducting layer, leading to an apparent rise in electrode potential due to ion movement/film growth under the influence of the electric field, with consequent electrode failure.

c) Alternative cheaper electrocatalytic coatings for valve metal substrates, include MnO^2 (68-71), which has about the same performance as graphite and a high wear rate (61). PbO_2 appears to be a better compromise between cost and performance, again being a camparable electrocatalyst to graphite, but with a low wear rate. Its production by anodic desposition on a suitable substrate such as Ti or graphite, has been reviewed by the author (72), and its uses surveyed by Narasimhn and Udupa (73), and by Kuhn and Wright (74).

d) The two main requirements of the cathode in a hypochlorite cell:

(i) good electrocatalysis (low overpotential) for the hydrogen evalution reaction (HER).

(ii) little or no corrosion in service or at rest potential,

may be contradictory in that the corrosion rate of many materials, such as Fe/steel, is determined inter alia, by their facility to evolve hydrogen. A compromise is required also between these criteria and capital cost, as the best cathodes would be the noble metals such as Pt or Pd.

Information about the HER on different materials is given by Reutschi (75) and Pourbaix (19). This shows that Ti has fairly good overpotential performance, and it is known to have exceptional resistance to sea water environments, even under high velocity conditions (76), a consequence of its tenacious passive oxide. Its one shortcoming is its cost compared say to stainless steel, which has been used in many hypochlorite cells. The corrosion/electrochemical behaviour of steel, Ti and Pt cathodes in chloride-chlorate media has been investigated by Ginzberg and Tetereva (40).

e) With bipolar electrodes, anode coating failure can occur also by hydrogen diffusing interstitially from the cathode area, through the Ti substrate, possibly with the formation of the brittle TiH_2 phase (77) (in addition to that formed at the cathode surface). The usual solution to the problem is to sandwich a material impermeable to hydrogen, between the anode and cathode surfaces. This material may be a metal such as Cu, Pb, Ni, Sn, Cr (78, 79) Ge (80), a metal silicide or silicon (81), boron (82) or an electronically conducting cement (83).

4. CELL DESIGN

4.1 As mixing of the primary anodic (chlorine) and cathodic (hydroxide) reaction products will increase the rate of the hydrolysis reaction (3) by which hypochlorite is formed, an undivided electrochemical flow cell may be used with its attendant advantages of cheapness and simplicity. The cell may be of either monopolar (c.f. parallel resistors/impedances, for multi electrode cells) or bipolar design (c.f. series resistors/impedances), the latter type having the potential for scale-up in terms of both current and voltage, with the advantage of reduced power supply costs by scaling up in terms of voltage rather than the current alone.

4.2 Monopolar cells usually consist of plate or mesh electrodes alternately connected together via external bus bars. The use of a monopolar fluidised bed electrode (FBE) of Pt coated ballotini in a divided cell (84) failed to achieve the expected increase in active electrode area due to the formation of insulating oxychloride films on the particles.

4.3 The choice of design is wider in the bipolar cell as external connections are made only to two feeder electrodes across which a sufficient voltage is applied such that the potential gradient in the solution produces cathodic and anodic areas on each intermediate electrode, i.e. electrical connection between the bipolar elements is made through the electrolyte. This allows small interelectrode gaps to be used, but demands judicious design to avoid the current by-passing the intermediate electrodes, especially at higher cell voltages. A stack of parallel plate electrodes could be used, or layers of electrode particles or Raschig rings etc., electronically insulated between layers by plastic mesh (packed bipolar bed electrode (PBBE)), or electrode particles fluidised between the feeder electrodes so that the particles became 'stochastically isolated'. Such a fluidised bipolar bed electrode (FBBE) creates an electrode materials problem as the particles, being free to rotate in the applied electric field, need to act both as inert anode and cathode. Graphite is the only material which is both inexpensive and readily available in a suitable form.

4.4 The two main practical problems with hypochlorite electrogenerators have been:-

(i) Blockage, during sea water electrolysis, by $Mg(OH)_2$ and $Ca(OH)_2$ deposits, nucleated at cathode surfaces where hydrogen evolution leads to a high local pH. To overcome this, high electrolyte flow rates have been used (with Reynolds Numbers up to 25,000), but clearly this leads to high pumping costs, lower hypochlorite concentrations at cell output, and lower Cl^- conversion (for single pass operation).

If the efflux is recycled to increase HOCl + OCl^-, the high rates of mass transport will lead to a reduction in current efficiency by loss reactions (5) and (7).

The fluidised bipolar bed electrode (FBBE) would be particularly attractive in combating precipitation problems, and is potentially least expensive of possible cell designs. Such a cell has been described by Goodridge et al (85) and by Wright (86), although energy efficiencies are relatively poor compared to conventional designs. A packed bipolar bed electrode (87-91), though having better power efficiency that the FBBE, would suffer from recipitation problems.

Following the first model, relating reaction areas of a bipolar bed electrode to the applied electric field and power efficiency, due to Fleischmann et al (81), and the work of Osifade (91), Wright studied both packed and fluidised bipolar particulate electrodes. The Fleischmann model (88) was extended to cover the fluidised bipolar bed electrode for both spherical and rod-shaped particles, and an electrical analogue model was used to describe the current distribution in bipolar particulate electrodes in general. Parametric studies were carried out on both packed and fluidised electrodes for the oxidation of NaBr to NaOBr (cf NaCl to NaOCl) and its use as an electrogenerated reagent for the oxidation of styrene to styrene oxide. The influence of applied electric field, particle size, Br concentration and electrolyte voidage on the power and current efficiencies, and the space-time yield, showed the packed bed electrode to be superior to its fluidised counterpart.

(ii) There will be some limit (dependent on anode material) to the anodic current density, above which the rate of loss of anode material becomes unacceptable. The economic 'trade-off' between anode current density, anode replacement costs and cell size/capital costs may also be influenced by factors such as, say the lead ion concentration, due to PbO_2 anode corrosion, in the cell efflux. As mentioned in section 3(b), with Ti-Pt anodes operating at low electrolyte temperatures and high current densities, the resulting high anode potential is accompanied by loss of platinium. In general, such corrosion may be reduced on lowering the anode potential by preheating the electrolyte or by using lower current densities.

4.5 The current density on a plate electrode in channel flow will vary with position. If the reaction is kinetically controlled, then the distribution is usually symmetrical with the current density (determined by the distribution of potential) at the leading and leading and trailing edges of the electrode being greater than that in the middle (depending on the interelecrode gap to length ratio) since the current can flow in the electrolyte beyond the edges of the electrodes. If the reaction is mass transport controlled, then the current density distribution will be determined by the distribution of mass transport rates, and, if there is appreciable depletion of the electro-active species between cell inlet and outlet, by the mixing/dispersion of reactant. Thus, the current density will generally decay in some manner from the leading to the trailing edge of the electrode. Intermediate cases where the current density is an appreciable fraction of its limiting value, will involve a superposition of these distributions. These situations have been treated theoretically by Parrish and Newman (92, 93) and by Caban and Chapman (94).

However, in a simple, vertical, parallel plate, undivided hypochlorite cell it is the distribution of electrolyte voidage, due to gas (H_2), which controls the current density distribution with electrode height, via its effect on the local effective electrolyte ohmic resistance (95). Depletion of Cl^- within the cell may also affect the distribution, depending on the cell current/electrolyte flow rate ratio). Assuming a uniform gas bubble rise velocity, accumulation of gas with electrode height will occur, such that the current density and electrode potentials will tend to decay from the lower edge of the anode/cathode, and the electrolyte mean linear velocity to increase with height from that position. The current distribution can be controlled by the cell current/electrolyte flow rate ratio, which determines the maximum electrolyte voidage (E max) at the top of the electrode. A simple mathematical model by Tobias (95), assuming linear polarisation over the range of current density considered, showed that a minimum cell voltage should occur at a mean electrolyte voidage (E) of 0.4 but that relatively little was to be gained above = 0.2. The effects of gas void fraction on current density distributions, have also been studied by Hine et al (96), Funk and Thorpe (97) and by Nagy (98).

4.6 Divided Cells

With the development of new ion exchange membrane materials, based on perfluorosulphonic (99) or perfluorocarboxylic acid (100) reinforced with PTFE mesh capable of withstanding the highly oxidising conditions of the chlor-alkali industry, the concept of a divided cell to produce hypochlorite should be considered, despite membrane typical cost of \$320 m^{-2}. Such a cell could produce chlorine gas for direct injection into the water to be treated, thereby avoiding NaCl contamination (except by reaction (3), or could be used to produce NaOCl solution for short term storage prior to use. These devices are equivalent to miniature chlor-alkali plants, and seem certain to gain increasing acceptance in the hypochlorite market.

4.7 Mode of Cell System Operation

As it is impossible to optimise the operation of a hypochlorite cell without reference to its 'end use' situation, Englehard (7,8) have described the five most important modes of operation. If sea water is available, the main emphasis will be on the efficient use of electrical power, whereas is salt has to be paid for, then its efficient use, measured as the conversion ratio of NcCl to NaOCl, is of prime importance.

(i) Single pass system - where the salt is free, capital costs need to be low, and a low efflux NaOCl concentration and low chloride conversion can be tolerated e.g. sea water electrolysis at coastal power stations or on board ship.

(ii) Single pass (solid salt) system - where salt is cheap and where capital costs need to be low. e.g. inland industrial plants and drainage utilities.

(iii)Sea Water Recycle System - which allows NaOCl concentration to be increased until its formation rate equals its rate of decomposition by loss reactions (5, 7, 8, 9) (with an attendant decline in power efficiency). Such a situation allows high electrolyte velocities to be used to overcome precipitation problems (with increased pumping costs), without concern for the low conversion of chloride per pass through the cell. The system can be bled to a storage tank or point of use.

(iv) Sea Water Recycle with Cooler - lower electrolyte temperature enable higher conversions to be achieved and lower NaCl and power losses, as the rates of loss reactions (5, 7, 8, 9) are reduced.

(v) Brine Recycle with Cooler - this facilitates the most efficient use of NaCl and electrical power.

5. LITERATURE ON HYPOCHLORITE ELECTROGENERATORS

The most comprehensive study to date of a hypochlorite electrogenerator, has been carried out by Lartey (101). Using Ti/Pt electrodes, recycle electrolyses were carried out, and the effects of current density, Cl^- concentration, electrolyte temperature, flow rate and $CaCl_2$ additions, on three dependent variables, hypochlorite concentration, current and energy efficiencies, determined as a function of time.

High electrolyte flow rates or high rates of gas evolution (high cathode current density) were found to increase the rates of the mass transport controlled loss reactions (5 and 7), as did a reduction in NaCl concentration, by increasing the amount of oxygen evolved at the anode. The current efficiency increased with current density, however, as reduction losses were decreased. An increase in the inter-electrode gap increased the maximum hypochlorite concentration achieved, but decreased the energy efficiency (Kg hypochlorite kWh^{-1}), by increasing the cell voltage. A maximum energy efficiency was obtained with an electrolyte temperature of 283 K. The addition of 0.08% $CaCl_2$ made very little difference but at 0.8%, a substantial increase in the maximum hypochlorite concentration and current efficiency were achieved, although an increased cathode potential and cell voltage led to a lower energy efficiency. Alternative additives, such as Turkey Red oil, colophony soaps and chromates have been used by other authors (102-104). The hypochlorite concentration/time curve was described by a mathematical model, which was developed on the assumption that the loss reactions (5 and 7, page 2) were largely mass transport controlled (in spite of the results of Ibl and Landolt (28)). The effective diffusion layer thicknesses at the anode and cathode were assumed to be the results of two processes acting in parallel, the thinning of the diffusion layer due to forced convective flow (δ_f) and that due to gas evolution (δ_{bubble}), such that:

$$1/\delta_{eff} = 1/\delta_f + 1/\delta_{bubble}$$

δ_f was calculated from correlations due to Levich (105, 106) for laminar flow across a flat plate (electrode), and δ_{bubble} from correlations due to Janssen and Hoogland (107) and Fouad and Sedahmed (108), such that δ_{eff} could be determined. As a check on the accuracy of the values obtained, data for the mass transport controlled reduction of Ce^{4+} with simultaneous hydrogen evolution, at various current densities, was used to obtain δ eff values from the Nernst limiting current equation. Corrections to the hypochlorite/time curve were applied for current efficiency loss due to Cl^- depeletion, from the current efficiency/Cl^- concentration data obtained previously. Using computer generated plots, reasonable agreement was obtained between the mathematical model and the experimental results.

Adamson et al (109) described laboratory scale experimental work on hypochlorite production using a variety of anode materials, mainly containing Pt as electrocatalyst, which were characterised by polarisation curves. Cell voltage/current density data showed the expected decrease in cell voltage with decreasing inter-electrode gaps (down to 0.5 mm), especially at high current densities. The energy efficiency was found to be a linear function of current density over the range 0.5 - 4.5 kA m^{-2}, being typically 5.68 kWh Kg^{-1} Cl_2 at 2.15 kA m^{-2}, and 7.78 kWh Kg^{-1} Cl_2 at 4.84 kA m^{-2}. Lower cell voltages (by 400 - 500 mV) were found by using Ti/Pt as a cathode rather than Ti (as used to obtain the above data), due to its greater electrocatalytic activity for hydrogen evolution.

Using the data from the small scale work, a bipolar stack of 11 parallel plate elementary cells was built to produce 0.45 kg Cl_2 hr^{-1}, using insulating extenders fitted to the electrodes, to reduce the bypass current problem. A full scale plant to produce 45 kg Cl_2 hr^{-1} was described, to be installed at Blyth 'B' C.E.G.B. power station. A method of biasing the positive terminal of the cell, to provide cathodic protection to adjacent metal work in contact with the cell outlet or inlet streams, was devised and patented (110), as the cells were designed to operate at up to 240 V.

A series of C.E.G.B. reports described the operating performance and problems of these cells. Following a decline in their chlorine output, Ormerod (111) investigated the effect of temperature on the efficiency of the process, as the decline in performance was directly related to a fall in sea water temperature, but could not be accounted for, in terms of the dependence of sea water conductivity on temperature. Using a Ti/Pt anode, 3% NaCl and a cell voltage of 8.15 V, the current efficiency for hypochlorite production was found to maximise at 281 - 283 K (75%), being 65% at 304 K, and falling by 4% K from 281 - 278 K to 55%. At 283 K and 8.15 V, the dependency of current efficiency on NaCl concentration was non-linear rising from 42% at 1% NaCl, 60% at 2% NaCl, to 70% at 3% NaCl. At lower sea water temperatures, the current efficiency was improved by using current densities of 1.5 kA m^{-2}. Omerod and Umpleby (53) investigated the effects of sea water temperature on anodic platinum losses, and a logarithmic relationship was established between electrode life and electrolyte temperature (273 - 288 k). A minimum cell inlet temperature of 286 K was recommended for a current density of 4.5 kA m^{-2}.

The problems associated with $Mg(OH)_2$and $Ca(OH)_2$ precipitates blocking the cell and causing increased pumping costs have been studied by Cook and Ormerod (112). The deposits were nucleated at the points of contact of plastic cell materials and cathode surfaces, where the pH was locally high due to the hydrogen evolution reaction, and at 291 K, pH values of 9.2 and 12.6 respectively were calculated to be sufficient to cause $Mg(OH)_2$and $Ca(OH)_2$ to precipitate. Bypass currents in the cell resulted in a greater accumulation of deposit towards the cathode feeder electrode end of the cell. Increasing the flow rate was found to help control the problem but accumulation was still evident at 3.65 $m\ s^{-1}$, whereas the original design specification was for 0.09 $m\ s^{-1}$. Injection of high velocity water into the bottom corners of the electrodes, particularly the terminal cathodes, was found to further reduce deposits. Polypropylene and perspex were recommended as cell stack materials as some charring occurred with the original PVC cell, at cell voltages 200 V.

Other C.E.G.B. reports relate to improving efficiency by reducing bypass currents with judicious cell geometry design (113, 114), platinum coating damage (54), the cell reactions and electrode processes (115), and the control of marine organisms with hypochlorite (116).

An improved version of the hypochlorite cells used at Blyth Power Station, employing Ti-Ti/Pt-Ir bipolar electrodes is marketed by Paterson Candy International Ltd. (101) as their 'Chlorocell', with a claimed power consumption of 5 - 5.5 kWk kg ^{1} Cl_2. Similar bipolar cells have been patented by D.J. Evans (Research) Ltd. (118).

Pacific Engineering and Production Company of Nevada (1) (PEPCON) originally developed their PbO_2 coated graphite anode (119) for the production of (Figure 2) perchlorates. However, the same cell design (120), of a tubular cathode (Cu or stainless steel) down which the cylindrical PbO_2 coated graphite anode is located, has found application in the hypochlorite market and in electrolytic sewage treatment. Several pamphlets (121-124) are available from PEPCON on various aspects of the commercial units. The cell is designed to operate at 1.55 kA m ^{2} anodic current density with a typical 'charge concentration' at 5.504 Ah litre^{-1}, to give an energy consumption of 5.56 kWh Kg^{-1} Cl_2. The cost of producing hypochlorite is said to vary little over the electrolyte temperature range 288 - 308 K. Some of PEPCON's own economic data (105) are included in the review articles by Kuhn (2, 8), and additional costings of a sea water feedstock PEPCON unit are given by Haemer (125). Kuhn (2) also reviews a brine feedstock electrolytic sewage treatment installation at Clark County, Nevada, which required 4.2 - 8.4 kWh kg^{-1} Cl_2 and 2.9 - 3.3 kg NaCl kg^{-1} Cl_2, depending on operating conditions. At 100 ppm Ca^{2+}, $CaCO_3$, $Ca_3(PO_4)_2$ and $Ca(OH)_2$ are precipitated at pH's of 7.4, 8.8 and 13.1 respectively (126). To overcome these precipitation problems at the cathode, due to hard water, intermittent air injection into the PEPCON cell was used (126).

A British electrolytic sewage treatment plant manufactured by CJB Ltd. (3) is described by Eales (127). It incorporated the CJB Hypack hypochlorite cell, using Ti/Pt anodes, steel cathodes and a sea water feedstock, and had an energy consumption of 7.2 kWh kg^{-1} Cl_2. The $Mg(OH)_2$ produced as a precipitate at the cathode was used as a flocculant for suspended solids.

Bennett (128) described development work that led, via a mathematical model, to the Diamond Shamrock Sanilec Cell, which used DSA (61-64) anodes, Ti cathodes, and, according to Kuhn (8), employs a water from which the Ca, Ba and Mg have been removed by conventional water softening techniques. Despite the resultant higher electrolyte costs, this removed the constraint on electrolyte velocity to avoid precipitation, so reducing pumping costs, hypochlorite loss reactions (5, 7, 8, 9) and obviated the need for acid backwashing and cell stripping. Beaker scale parametric experiments were carried out to determine the dependency of current efficiency on concentration of 'available chlorine' ($HOCl + OCl + Cl_2$). At a current density of 1.55 kA m^{-2} and an electrolyte temperature of 298 K, current efficiency losses to oxgen were 15% (almost independent of available Cl_2 concentration), 15% to ClO_3, and 30% by reduction back to Cl^-, at 10 g l^{-1} available Cl_2. At a current density of 0.775 kA m^{-2}, the reduction loss was doubled to 60%. Using a mathematical model based on such data, lowest operating costs were found to be achieved at 9 - 10 g l^{-1} available Cl_2, as at lower concentrations salt utilisation was poor, and at higher concentrations loss of current efficiency became critical. A multi-stage cell was built to produce 23 kg day^{-1} available Cl_2 at 9 - 9.5 g l^{-1} and an overall current efficiency of 65%, using a 3% NaCl feedstock, and requiring 5.07 kWh (AC) and 3 kg NaCl kg^{-1} available Cl_2. Minimum power consumption was achieved at 288 K and maximum salt utilisation at 283 K, with the multi-stage cell operating at some 25% greater current efficiency than an equivalent single compartment cell.

Diamond Shamrock Corporation (129) hold a number of patents for both horizontal (130) and vertical bipolar plate electrode stacks (131, 132), designed to reduce precipitation problems. Turbulent flow and occasional acid backwashing (without electrolysis) are advocated in a patent (133) on one of their simpler parallel plate cells, with graphite/Pt anodes and steel, Ni or Ti cathodes. In a later design (134), expanded Ti anodes coated with a TiO_2-RuO_2 solid solution are used with Ni cathodes at a current density of 0.775 kA m^{-2}, to electrolyse sea water flowing at 0.73 m s^{-1}. Yields of 0.43 and 3.48 g l^{-1} available Cl_2 were produced at 86% and 21.6% current efficiency respectively. By reducing the flow rate of 0.23 m s^{-1}, 3.32 g l^{-1} available Cl_2 was produced at 60.1% current efficiency, but cathode precipitates were then formed.

Connolly (135) and Kuhn (2, 8) describe the Engelhard (7) Chloropac Cell (136) (see Figure 3), which uses a cylindrical bipolar Ti electrode located down two tubular electrically isolated Ti feeder electrodes, and creating an annular flow channel. Anode surfaces are usually coated with platinum (5 m thick) and are guaranteed for 5 years. Sea water ofrbrine electrolyte is pumped down the 4 mm annular gas at 3 m s^{-1} (Reynolds Number 25,000) so that precipitation problems are claimed to be avoided completely. Power consumption per kg active chlorine varies non-linearly with electrolyte resistivity/inversely with temperature, though not linearly, being typically 5.7 kWh kg^{-1} at 283 K and 5.4 kWh kg^{-1} at 293 K using sea water electrolyte. However, output concentrations are low, so rates of hypochlorite losses reactions are negligible; a 1.8 kg hr^{-1} unit has an efflux concentration of 440 ppm available chlorine. Using series/parallel combinations of an appropriate number of the basic cell modules, a range of production capacity of 0.23 to 13,500 kg hr^{-1} available Cl_2 can be achieved.

Lamb (137) has described a more conventional Engelhard cell using plate type coated Ti anodes to produce NaOCl at a rate of 0.45 kg hr ^{1} from sea water. At a concentration of 2-3 ppm this was found to be as efficient an antifoulant as liquid Cl_2.

The Cyclor cell manufactured by Morgan Berkeley Ltd (138), 139), again using a sea water electrolyte, is designed to be located actually inside the condenser boxes on board ship, with the cathode electrically linked to provide them with cathodic protection.

Unfortunately, the remaining recent literature on the subject (from Chemical Abstracts) is largely a catalogue of patents, of which only the more interesting will be mentioned.

(i) Perhaps the most enterprising design is by Cumberland Engineering Co. Ltd. (140,141). This cell consists of a stack of Ti bipolar electrodes rotating between two feeder electrodes, and providing a pumping action which also prevents fouling at cathodes. Insulating extenders are used to reduce the bypass current problem and anode sufaces are coated with platinum. In concept the design is similar to the rotating version of the capillary gap cell (142) and the colloid mill/pump cell (143).

(ii) Raetzsch and Cunningham (144) describe a cell incorporating bipolar steel-Ti-Electrocatalyst electrodes arranged such that the anode/cathode surface of one element is interleaved between two cathodes/anodes of adjacent bipolar elements.

(iii) This design resembles the De Nora Seaclor (63, 145) cell, which has vertical overlapping DSA (e.g. steel-Cu-Ti-RuO_2) bipolar electrodes, in the form of rod, strip, plate, mesh or expanded metal. The example cited in the patents (145), had a 3.5 mm interelectrode gap was was operated at 1.6 kA m^{-2} with an electrolyte of 20 gl^{-1} NaCl at 297 K, flowing at 0.11 m s^{-1} to give an efflux of 2 g l^{-1} equivalent Cl_2 at 95% current efficiency. For chlorate production, a current density of 2.25 kA m^{-2} was used with an electrolyte of 110 g l^{-1} NaCl at 368 K flowing at 0.4 m s^{-1}, to give a current efficiency of 98%. The standard range of cells could produce 24 - 800 Kg day^{-1} (equivalent chlorine) operating at 150 - 5000 A and 25 - 32 V, to give a maximum equivalent chlorine concentration of 3 g l^{-1} with sea water electrolyte, and 8 g l^{-1} with brine. Using sea water, 4 - 5 kWh kg^{-1} equivalent (Cl_2) was required, and 4 - 5.5 kWh kg^{-1} using 25 - 45 g l^{-1} NaCl Kg^{-1} equivalent Cl_2.

(iv) Yoshida et al (146) have devised a filter press type cell using Ti based anode/Fe cathode bipolar electrodes to produce hypochlorite at 4.96 kWh kg^{-1} available Cl_2 and 95% current efficiency.

(v) The Johnson Sea Cell (147) consists of a number of Ti based bipolar wedge electrodes separated by plastic spacers to give a zig-zag flow channel. However, the design suffers from having a low specific electrode area and a large volume of expensive Ti(2).

(vi) The Daiki Engineering Cell (148,2) uses Al covered with platinised Ti as anodes, and mild steel cathodes, which may be Cr plated to produce a $Cr(OH)_3$ chemical diaphragm. Under rapid laminar flow of sea water, $Mg(OH)_2$ is said to be carried out of the cell, so preventing OH^-reaction with Cl_2 until it reaches a chamber above the electrodes. In this way, it is claimed that OCl^- reduction is avoided, and $Mg(OH)_2$ accummulation is diminished. Performance figures are summarised by Kuhn (2).

(vii) Persson (149) describes a concentric cylindrical cell for use with swimming pools, and which embodies a non-conducting anode brush assembly which can be rotated to sweep the cathode surface free of deposits.

Divided Cells:

(viii) An American ion-exchange membrane manufacturer (150) has patented a membrane cell (see Section 4.6), which is claimed (2) to produce 5-10% NaOCl operating at 3.7 V and 2.4 kA m^{-2}, with an energy efficiency of 3.53 kWh kg^{-1} of hypochlorite, and using 0.954 kg of salt at 80% efficiency (based on salt).

(ix) Cooper (151) describes a cell consisting of a tubular Ti-Pd anode and outer tubular cathode 'partially' separated by Na^+ permeable ion exchange membrane. 25% NaCl solution is used an anolyte, and water is introduced into the cathode compartment to dilute NaOH formed. A cylindrical plastic reaction zone, where the Cl_2 and NaOH react, is sited above the cell. With this design, only 2.3 parts of NaCl are needed to form 1 part of NaOCl, compared with 5 - 10 parts NaCl as required for most other hypochlorite cells.

(x) Eng and Clarke (152) have patented a cell with 3 compartments, separated by ion exchange membranes. Cl_2 is produced from NaCl in the anolyte, and NaOH from water in the catholyte, with NaCl and NaOCl formed in the intermediate buffer compartment. The chlorine gas produced may be used to make NaOCl or $NaClO_3$ externally or may be sold as gas.

(xi) Scoville (153) has used Cl^- permeable membranes and graphite electrodes, such that the cell can be used for producing Cl_2, H_2 and hydroxide separately, or the Cl_2 and hydroxide can be mixed to product hypochlorite.

Descriptions of the more traditional hypochlorite cell designs are given by Regner (39) and Milazzo (154), and a general review of the sodium hypochlorite cell is given by Adhia (155).

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Appendix 3

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  Moore, S.H.; Smith, M.R., - Olin Corp.

- U.S. Pat.No. 8302288 (830707); CA 99(12)095845
  Electrocatalytic Electrode
  Hinden, J.M., C.S. - Diamond Shamrock Corp.

- Germ. Pat. No. 3138438; (830414); CA 98(24)20662
  Electrolysis Cells
  Fabian, P., C.S. - Heraeus, W.C., G.m.b.H.

- Fr. Pat. No. 2504942 (821105); CA 98(18)151834
  Electrolytic Apparatus with Bipolar Electrodes for Electrolysis of Brines
  Holca, R., - Degremont S.A.

- Jpn. Pat. No. 82192276 (821126); CA 98(18)151816
  Filter Press-type Electrolytic Cell for Sodium Hypochlorite Production
  Japan Carlit Co., Ltd.

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  Apparatus for the Production of Aqueous Alkali Metal Hypochlorite
  Langley, R.C.

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  Process and Apparatus for Electrolytic Production of Alkali Chlorate
  Akazawa, T., C.S. - Hodogaya Chemical Co., Ltd.

- USSR Pat. No. 968102 (821023); CA 98(08)062161
  Bipolar Filter Press Electrolyzer for Producing Alkali Metal Hypochlorite
  Zhuk, A.P., C.S.

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  Method and Apparatus for Producing Sodium Hypochlorite
  Teixeira de Almeida, N.

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  Electrode Assembly for Manufacture of Chlorate and Hypochlorite
  Chemetics International Ltd., - Can. CA

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  Electrode and Electrolytic Cell using such Electrode
  Steel, H.; Peter, C. - IMI Kynoch Ltd., - United Kingdom GB

US Pat. No. 4329215 (820511); CA 97(04)030334
Sodium Hypochlorite Production and Storage
Scoville, F.

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On-site Generation of Chlorine and Hypochlorite for Water Treatment
Osaka Soda Co., Ltd.

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Electrode Assembly for Diaphragmless Production of Chlorate and Hypochlorite
Chemetics International Ltd., - Can. CA

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Treatment of Brine
Mucenieks, P.R., - FMC Corp.

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Diaphragmless Brine Electrolysis Cell
Tsurumi Soda Co., Ltd.

- Jpn. Pat. No. 8216182 (820127); CA 96(20)171154
Diaphragm-type Brine Electrolytic Cell
Osaka Gas Co., Ltd.

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Hypochlorites via Brine Electrolysis
Daiki Engineering Co., Ltd.

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Electrode Provided with Spacers for Electrolysis
Hodogaya Chemical Co., Ltd.

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Apparatus for the Small-Scale Manufacture of Chlorine and Sodium Hydroxide or Sodium Hypochlorite
Lynn, S., - Hydro-Chlor International, Inc.

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Diaphragm Type Brine Electrolysis Cell
Osaka Gas Co., Ltd.

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Purification of an Aqueous Potassium Chloride Solution Containing an Antiagglutination Reagent
Itoi, E., C.S. - Asahi Glass Co., Ltd.

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Apparatus with Bipolar Electrodes for the Electrolysis of Saline Solutions to Produce Hypochlorite
Holca, R., - Degremont S.A.

- Jpn. Pat. No. 81105487 (210881); CA 95(24)212015
Diaphragmless Brine Electrolysis
Tokuyama Soda Co., Ltd.

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Brine Electrolysis Cell
Kobayashi Denchi Kenkyujo Y.K.

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  TDK Electronics Co., Ltd.

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  Saito, K.; Shibata, H., - Asahi Glass Co., Ltd., - Japan JP

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  Kunaev, A.M., C.S. - Institute of Metallurgy and Ore Beneficiation, Academy of Sciences,

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  TDK Electronics Co., Ltd.

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  Brine Feeder for Small Scale Electrolytic Cell
  Japan Carli Co., Ltd.

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  Roemer, H.G.; Strohbach, H.J., - Roemer Technik G.m.b.H.

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  Chlorine Engineers K.K.

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  Apparatus for electrolyzing synthetic and natural brines to produce sodium hypochlorite
  Conkling, W.C., - Pennwalt Corp.

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  Apparatus for electrolyzing an aqueous solution
  Teruo, I.; Yoshitugu, S., - Chlorine Engineers K.K., - Japan

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  Hausmann, E.; Will, H.; Klein, K.
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  Pellegri, A.; De Nora, O., - Impianti Elettrochimici S.p.A., - Italy

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  Isomura Hosui Kiko K.K.

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  Electrode for Electrolysis of Dilute Brines
  Goe, K.; Kawashima, Y., - TDK Electronics Co., Ltd.

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  Electrochemical Production of Sodium Hypochlorite
  Kobayashi Denchi Kenkyujo Y.K.

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  Electrode for Electrochemical Manufacture of Hypochlorite
  Kanai, H.; Itai, R.; Yamazaki, T., - Japan Carlit Co. Ltd.

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  Chlorine Gas-Producing Apparatus
  Scoville, F.J. - USA

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  Stack Pack Electrolytic Cell
  Loeffler, J.; Edward, Jr., - Diamond Shamrock Corp.

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  Lynch, R.W.; Dotson, R.L., - Olin Corp. USA

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  Electrochemical Cell for Producing Chlorine, Alkali, Hypochlorites and Chlorates
  Kuusinen, O.J.; Rintanen, V.O., - Finnish Chemicals Oy, Finland

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  Electrochemical Production of Organic Hypohalite Compounds in an Undivided Cell
  Dotson, R.L.; Lynch, R.W., - Olin Corp. USA

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  Nakamura, K., - Ebara-Infilco Co., Ltd.

- Belg. Pat. No. 875975 (030979); CA 92(04)031038
  Electrode Comprising a Valve Metal Substrate, an Intermediate Semi-conductor Coating and a Surface Coating of Manganese Dioxide
  Diamond Shamrock Corp., - USA

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  Method and Apparatusfor Brine Electrolysis to Manufacture Hypochlorite
  Nakamura, K., - Ebara-Infilco Co., Ltd.

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  Electrolysis of Seawater
  Nakagawa, T., C.S., - Kobe Steel, Ltd.

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  Improvements in or Relating to Electrolytic Cells
  Jansen, H.J.; De Beer, F.M., - Magneto-Chemie B.V., Netherlands

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  Apparatus for Release of an Entrained Gas in a Liquid Medium
  Wiseman, R.M., - Diamond Shamrock Corp.

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  Ion-exchange Membrane Electrolysis of Sodium Chloride
  Ogawa, S., C.S., - Asahi Chemical Industry Co., Ltd.

- Jpn. Pat. No. 7906898 (190179); CA 91(10)080948
  Sodium Hypochlorite from Brine
  Hashimoto, S., C.S., - Ishikawajima-Harima Heavy Industries Co., Ltd.

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  Electrolytic Cells
  Wheatley, S.M., C.S., - Johnson, A., and Co., (London) Ltd.

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  Plating Lead Dioxide
  Oehr, K.H., - British Colombia Research Coucil

- Belg. Pat. No. 869313 (161178); CA 90(12)112132
  Cell for Electrolyzing Sea Water
  Nakamatsu, S., C.S., - Chlorine Engineers K.K.

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  Electrode Assembly for an Electrolytic Cell
  Kircher, M.S., - Olin Corp. USA

- Jpn. Pat. No. 781156873 (091078); CA 90(08)063624
  Cathode for Brine Electrolysis Cell
  Sat, S.; C.S., - Tsurusaki Kyodo Doryoku K.K.

- U.S. Pat. No. 4126526 (211178); CA 90(06)046036
  Cyclic Process for Production of Alkylene Oxide Using Electrolysis of Brine
  Kwon, J.T.; Gelbein, A.P., - Lummus Co., USA

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  Cathode and Bipolar Electrode Incorporating it
  Pellegri, A., - Diamond Shamrock Technologies S.A.

- U.S. Pat. No. 4118307 (031078); CA 90(02)014084
  Batch Sodium Hypochlorite Generator
  LaBarre, R.L., - Diamond Shamrock Corp.

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  Electrode Assembly for an Electrolytic Cell
  Goldsmith, F.W., - Portals Water Treatment Ltd.

- Jpn. Pat. No. 78100998 (020978); CA 89(24)206555
  Alkali Metal Hypochlorite and Electrolytic Cell for Manufacturing it
  Goto, N.; Naito, M., - Chlorine Engineers K.K.

- Germ. Pat. No. 2806441 (240878); CA 89(24)206549
  Sodium Hypochlorite
  Goto, N., - Chlorine Engineers K.K.

- Jpn. Pat. No. 7816390 (150278); CA 89(20)168539
  Hypochlorite Production by Brine Electrolysis
  Shoda, T.; Nakamura, S.; Nakata, M., - Daiki Engineering Co., Ltd.

- U.S. Pat. No. 4097358 (270678); CA 89(18)154744
  Apparatus for Release of an Entrained Gas in a Liquid Medium
  Wiseman, R.M., - Diamond Shamrock Corp.

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  Apparatus for Sodium Hypochlorite Production
  Itakura, T.; Nakamura, S., - Daiki Engineering Co., Ltd.

- Brit. Pat. No. 1496660 (301277); CA 89(19)082137
  Improvements in and Relating to Electrochemical Cells
  Fleischmann, M.; C.S., - National Research Development Corp.

- Jpn. Pat. No. 7839996 (120478); CA 89(08)067582
  Sodium Hypochlorite by Electrolysis of Sodium Chloride Solution
  Matsuki, K., - Osaka Oxygen Industries Ltd.

- U.S. Pat. No. 4085028 (180478); CA 89(06)050606
  Electrolytic Chlorination Device
  McCallum, J., - Electro-Chlor Corp.

- Germ. Pat. No. 2746332 (200478); CA 88(26)200007
  Bipolar Electrolytic Cells
  Wheatley, S.M., C.S., - Johnson, A., and Co. (London) Ltd.

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  Brine Electrolytic Apparatus
  Yamagishi, R., C.S., - Hitachi Cable, Ltd.

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  Electrolytic Cell for Hypochlorite Generation
  Shoda, T,; Nakamura, S., - Daiki Rubber Industry Co., Ltd.

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  Multitube Bipolar Cell
  Fukuzuka, T., C.S., - Kobe Steel Ltd.

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  Multipurpose Electrolysis Cell
  Fukuzuka, T., C.S., - Kobe Steel Ltd.

- Jpn. Pat. No. 77129684 (311077); CA 88(18)128299
  Bipolar Cell for the Manufacture of the Oxy-Acids of Halogens
  Sato, S., C.S., - Tsurusaki Kyodo Doryoku K.K.

- Germ. Pat. No. 2730757 (190178); CA 88(16)112565
  Cell for Electrolysis of an Aqueous Alkali Metal Chloride Solution
  Bourgeois, L.; Nicolas, E., - Solvay et Cie.

- Brit. Pat. No. 1480807 (270777); CA 88(06)043162
  Improvements in or Relating to Electrodes for use in Electrolytic Processes or Cathodic Protection
  Beer, H.B., - Diamond Shamrock Technologies S.A.

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  Apparatus for Manufacturing Sodium Hypochlorite
  Kobayashi, K., - Kobayashi Storage Battery Kenkyusho Co., Ltd.

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  Electrolytic Hypochlorite Generator
  Ban, S.C., - USA

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  Electrolysis Cell for Sodium Hypochlorite
  Mita, M.; Yamagishi, R.; Maeno, T., - Hitachi Cable, Ltd.

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Iodine from Brine
Takahashi, T., C.S., - Ise Chemical Industries Co., Ltd.

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  Halate Cell Top
  Nawrot, C.R., - Hooker Chemicals and Plastics Corp.

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  Brine Electrolysis Cell
  Yamagishi, R., C.S., - Hitachi Cable Ltd.

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  Anode Containing Lead Dioxide Deposit
  Rhees, R.C.; Halker, B.B., - USA

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  Purification of Aqueous Sodium Chloride for Membrane Electrolysis
  Nibe, T., - Sumitomo Chemical Co., Ltd.

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  Expandable Anode Assembly for Electrolytic Cell
  Pohto, G.R.; Olson, R.O. - Diamond Shamrock Corp. USA

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  Anode Unit for an Electrolysis Cell
  Ritti, S.; Policardi, S. - Solvay et Cie.