ELECTROLYTIC DISINFECTANT PRODUCTION FOR SMALL WATER SUPPLIES

by

Dr. D.W. Wabner and W.D. Fleischmann

February 1986

International Reference Centre for
Community Water Supply and Sanitation
P.O. Box 93190, 2509 AD The Hague, The Netherlands

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FOREWORD

Disinfection with chlorine and chlorine products is an established process in the provision of safe drinking water, but in developing countries a regular supply of chemicals is a serious problem. Production is usually centered in large scale factories to benefit from greater efficiency and economy-of-scale, but this necessitates distribution by long and vulnerable transport lines, with inherent chance of environmental spillage and consequent health hazard. With the special attention to rural programmes in the International Drinking Water Supply and Sanitation Decade, on-site production of disinfectants could fill a need provided operation and maintenance could be simplified.

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 two state-of-the-art reports have been prepared. This publication has been prepared by Dr. D.W. Wabner and W.D. Fleischman of the Technical University of Munich. A second publication is: Hypochlorite Electro-generation for Drinking Water Disinfection by Dr. G.H. Kelsall, London.

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.

CONTENTS

FOREWORD

ANNEXES:

1. INTRODUCTION

Natural water may contain numerous germs, some of which are pathogenic. They may come from the soil or from polluted water; especially dangerous are the excreta of man and animal. Diseases like cholera, typhoid and paratyphoid, hepatitis and dysentery of amoeba or viral diseases like poliomyelitis can be conveyed by water.

A major part of mankind still drink unsafe water. As a consequence infectious diseases occur in many regions of the world time and again. These diseases can be avoided if suitable methods of water disinfection would be available.

An attractive option for disinfectant preparation are electrochemical processes, because of the possibility to produce strong disinfectants in a simple and effective manner. The chemical and technical possibilities of current processes are reviewed in this report and cell design and appropriate electrode materials discussed.

2. DISINFECTANTS PRODUCED BY ELECTROLYSIS

Strong oxidants have among the effective disinfectants a prominent position. Oxidants like chlorine, hypochlorites and ozone are today the most important chemicals for drinking-water disinfection. To produce these chemicals which have a high positive redox potential, electrochemical methods are preferred, as they can provide in a simple and elegant manner the strong oxidation conditions required. (Simple process controll, separate oxidation and reduction zones; no manufacture, storage and application of oxidising chemicals needed)

2.1. Chlorine

Chlorine, the most used disinfectant in water purification, is produced electrochemically in great quantities for more than 100 years. (1978 in USA 10 million tons). Numerous articles and patents exist for the well-known mercury-, diaphragm- and membraneprocesses /1-3/.
The products of the technical brine (approx. 310 g/l NaCl) electrolysis at 70 °C are chlorine, sodiumhydroxide and hydrogen according to the reaction scheme

$$2\ NaCl + 2\ H_2O \longrightarrow Cl_2 + 2\ NaOH + H_2$$

with an anodic reversible discharge potential of +1.247 V for the reaction

$$2\ Cl^- \longrightarrow Cl_2 + 2\ e^-$$

Possible anode side-reactions are:

$$2\ H_2O \longrightarrow O_2 + 4\ H^+ + 4\ e^-$$

$$6\ ClO^- + 3\ H_2O \longrightarrow 2\ ClO_3^- + 4\ Cl^- + 6\ H^+ + 1{,}5\ O_2 + 6\ e^-$$

The quantitatively more important reaction is the oxygen generation according to reaction 3. For drinking-water purification the chlorate formation should be watched because of its serious toxicity. Both reactions reduce the current efficiency with about 3-5%.

Other reactions reducing chlorine yield occur in solution:

$$2\ OH^- + 2\ Cl_2 \rightarrow ClO^- + Cl^- + H_2O$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

$$2\ HClO + NaClO \rightarrow NaClO_3 + 2\ HCl$$

The products are hypochlorite and chlorate; the latter can thus be formed anodically as well as in solution.

The cell voltage of mercury cells is 4.1-4.6 V with current densities of 10 kA.m^{-2} and for diaphragm cells 3.7-4.2 V and 2.5 kA.m^{-2}; this means an energy consumption of 3500 kWh.t^{-1} and 3300 kWh.t^{-1} chlorine respectively.

Bromine, sometimes used for water purification /4/, accompanies chlorine, if the electrolyzed brine contains bromides, for instance in seawater (70/mg.l^{-1} Br^-.) or "hard salt" solutions of the potash industry (100 - 300 mg.l^{-1}). It is generated more easily than chlorine because of its lower oxidation potential (E=1.09 V compared to 1.36 V for chlorine).

2.2. Hypochlorites

Hypochlorites belong to the most important disinfectants and are becoming important in disinfection /4/. They are produced electrochemically since 1801 as a by-product of chlorine production, so that this method is well investigated and documented /1-3/.

The generated hypochlorite can decompose on both electrodes:

anode: $6\ ClO^- + 3\ H_2O \rightarrow 2\ ClO_3^- + 4\ Cl^- + 6\ H^+ + 1.5\ O_2 + 6e^-$

cathode: $ClO^- + H_2O + 2\ e^- \rightarrow Cl^- + 2\ OH^-$

The rate of chlorate generation is proportional to the concentration of $HClO + ClO^-$ in the solution and can be minimized by short retention times of the electrolyte in the cell.

The cathodic reaction occurs mainly in undivided cells, if the anolyte can reach the cathode. This reaction can be suppressed by appropriate flow conditions in the cell or by addition of (poisonous) chromic acid or $CaCl_2$. The chemical chlorate generation from hypochlorite is negligible if the electrolyte is kept at temperatures under 30°C and pH values outside the range 4 to 6 /1,6/. The reaction $ClO^- \rightarrow Cl^- + 0.5\ O_2$ is slower than the chlorate reaction, but is catalyzed by impurities like Co, Ni and Cu. Hypochlorite solutions decompose according to these two reactions and cannot be stored. Therefore on-site generation is preferred. The optimal brine concentration is 10-30 $g.l^{-1}$ with current densities of 1500 $A.m^{-2}$.

The "anodic oxidation for water treatment according to Reis" /29/ is based on hypochlorite generation in the water to which sodiumchloride is added In this process the total flow passes through the undivided cell (no by-pass flow) The highly turbulent flow of the electrolyte and the use of bipolar electrodes have negative effects to the hypochlorite yield in undivided cells, so that this type of cell is less suitable as hypochlorite generator. Moreover, high haloform concentrations were found in these systems /30/, which is not acceptable for drinking-water treatment.

2.3. Ozone and Hydroxylradical

Ozone is one of the strongest oxidants (redoxpotential of 2.07 V). It is becoming more and more important for water-disinfection /4,7/, for which it was used for the first time in 1893 in the Netherlands for Rhine water /8/. Though ozone was discovered in the electrolysis of water in 1839 the most important method to produce ozone is still the silent electrical discharge in the Siemens-ozonisator. But in recent years the electrochemical generation was reinvestigated intensively when new anode materials became available /9-11/; yields were improved with concentrated phosphate buffers containing some fluoride at low temperatures using anodes with high oxygen overvoltage like PbO_2 electrodes. Ozone yields up to 18 vol% of the anodically generated gas can be obtained.

Experiments with PbO_2-electrodes used directly in waste-water treatment to generate the oxidant in-situ without the addition of other electrolytes are known as "electrolytic oxidation with lead-dioxide anodes" /12/. The oxidizing agent is mainly the ozone precursor hydroxylradical with an oxidation potential of 2.85 V. This method, could be very interesting for water purification, i.e. to electrolyse the total flow at small current densities. It could be used as a polishing step following the standard water treatment methods (especially to remove haloforms).

2.4. Percompounds

Inorganic peroxocompounds like peroxides, perborates, perphosphates, and percarbonates are strong oxidants and have been used for disinfection, for instance in oral hygiene, cosmetics and food industry /14/. Also in water purification they have some importance, for example H_2O_2, is used recently in USA and USSR /15/, with the advantage, that the final product is water. Solid peroxides are commercially available for swimmingpool-disinfection; they are combined with some metal salt activators for fast reaction. Peroxosulfuric acid was proposed for waste-water purification /16,17/. All these compounds can be electrochemically prepared /1,14/. The most important methods are those of H_2O_2 production, e.g. the industrial oxidation of sulfuric acid and hydrolyzing the so-formed peroxodisulfuric acid according to:

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$
$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

The last years have reactualized the reduction of oxygen according to:

$$O_2 + H_2O + 2\,e^- \longrightarrow HO_2^- + OH^-$$
$$HO_2^- + H_2O \longrightarrow H_2O_2 + OH^-$$

With the availability of the very effective gas cathodes of the fuel cell technology Kastening used activated graphite cathodes in KOH for air reduction with a current efficiency of 82% /18/. Side reactions of this method are the direct reduction of O_2 to OH^-:

$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$$

and the generation of hydrogen:

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$$

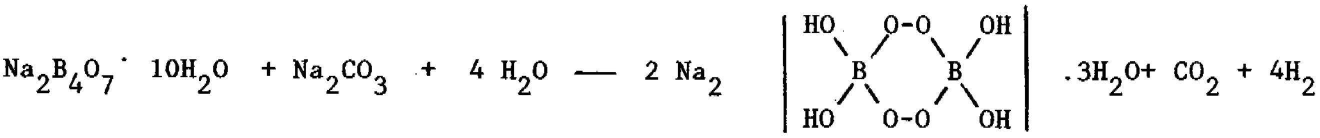
and the reduction of H_2O_2, if the cathode contains noble metals. The salts of the peroxoacids of sulfur and phosphor (M_2SO_5, $M_2S_2O_8$, M_3PO_5, $M_4P_2O_8$) are electrochemically available from the corresponding salts of sulfuric and phosphoric acid. Thus, $(NH_4)_2S_2O_8$ is synthesized in a divided cell with an

Al_2O_3-diaphragm, lead-cathode and platinum-anode from $(NH_4)_2SO_4$ at 45°C and current densities of $80\text{-}100 A.dm^{-2}$, the current efficiency is 92% /19/. For $K_4P_2O_8$, an undivided cell with Zr-cathode and Pt-anode is reported /20/.

Perborates are produced electrochemically from sodium borate since 1912. The current efficiency of this method is higher in the presence of sodium-carbonate. Probably the carbonate is first oxidized to percarbonate at the Pt anode according to:

$$2\ CO_3^{2-} \longrightarrow C_2O_6^{2-} + 2\ e^-$$

then hydrolyzed to H_2O_2, which oxidizes borate to perborate according to the brutto reaction:



The current efficiency is 60% at 10°C /21-23/.

2.5. Silver

The bactericidic effects of silver ions is used for some situations for long-time disinfection of drinking water. Solid silver salts are used for straight disinfection, also devices producing silver ions on-site by continuous anodic dissolving of silver-anodes are available. The simultaneous generation of copper ions by an anode of copper/silver alloy prevents the growth of algae /15,24-26, 28/.

2.6. Comparative evaluation

Certainly, chlorine is the most used agent for water-disinfection, either used directly as a gas or as hypochlorite (both having the same active component, i.e. HClO). Its bactericidic efficiency is excellent and it guarantees long-time disinfection. The production of chlorine is well-established, because chlorine-alkali-electrolysis is one of the best known technical processes. The hazard of storing large quantities of chlorine can be avoided by on-site production, however small production units have less efficiency.

A disadvantage of the chlorination of drinking water for which some concern is expressed and special precautions are required, is the formation of chloroforms and chlorinated aromates, when organic contaminants are present. Also, brines containing bromides are to be avoided, because bromoforms are formed more easily than its chlorine analogues. Process controll of the chlorine and hypochlorite generation is necessary in order to avoid the formation of the poisonous chlorate ion.

In many aspects ozone is better than chlorine. e.g. it is about 20 times more effective against bacteria and viruses /15/. It improves odour, taste and colour of the treated water, whereas chlorine produces the well-known unpleasant taste caused by the ClO^- ion, by chloramines, generated in the presence of NH_4^+-ions, and by chlorophenols. The ozonization does not introduce contaminants in the water, and its low stability causes the complete decomposition to O_2 in some hours. A disadvantage is the high costs of ozonization devices, which could be lowered with the further development of the electrochemical on-site generation. A distinct disadvantage is the fact, that ozone can only effect short-time disinfection because of its low stability, so that ozonized water must be used directly or disinfected in a second process by another chemical. If salt is present in the water, chlorine formed in the electrolytic process /12/ can provide a residual.

The only method of on-site disinfection of water by peroxocompounds could be the electrochemical reduction of air to H_2O_2, but in contrast to its good antiviral effect the bactericidic action is not so certain /27/. Percarbonates and perborates show a very low bactericidity /27/; These percompounds are by-products in the electrochemical oxidation process, if the electrolyte contains the corresponding salts, but in water disinfection they will not play a dominant role.

Silver is a very good disinfectant for small quantities of water. The silver-ion production is very simple, the ion is non-toxic and does not influence taste nor odour of the water. A disadvantage is the high price of the metal, the slow disinfection rate and the condition, that only clear and halogenide free waters can use this method.

3. DESIGN OF ELECTROLYSIS CELLS

Electrolysis cells are chemical reactors basically. One can distinguish between simple batch reactors for discontinuous operation, continuous flow cells eventually combined to cascades, and continuous tube cells with inhomogeneous concentration distribution. A characteristic of electrochemical reactors is the separation in electrolysis zones of the two partial reactions of a redox reaction namely located at the cathode and the anode, contrary to the homogeneous chemical redox reaction. Like in all heterogeneous catalytic systems, transport problems are very important, because the actual electrochemical reaction which occurs at the interface electrode/ electrolyte can be followed by some other reactions of homogeneous character in the electrolyte; an example is the hypochlorite generation.

3.1. Undivided Cells

Undivided cells, i.e. batch or tube cells with no separation of anode and cathode compartments, have a simple and cheap construction, and require little maintenance. Their electrical cell resistance is low, because they do not have diaphragms or membranes, thus lowering their cell voltage, i.e. their energy costs. 4)

A vertical position of the electrodes, has the advantage of easy mounting and maintenance; it allows the electrolyte to be pumped horizontally through the cell. This is possible only if the electrolysis products do not react at the counter electrode and if the electrodes have a small flow resistance like gauzes or grids combined to stacks (Fig.1). Another characteristic for this type of cell and its operation is the rather low conversion to avoid a too high concentration gradient between influent and effluent.

To minimize the voltage drop in the electrolyte, and minimize the energy costs it is important to make the distance between cathode and anode as small as possible. In undivided cells the electrode distance (a couple of mm to some cm) must not be too small however, because the electrolysis products can then reach the counter-electrode easily and because of the danger of short circuits. Back-reaction on the counterelectrode is the most important disadvantage of undivided cells, which can be avoided with certainty only in divided cells.

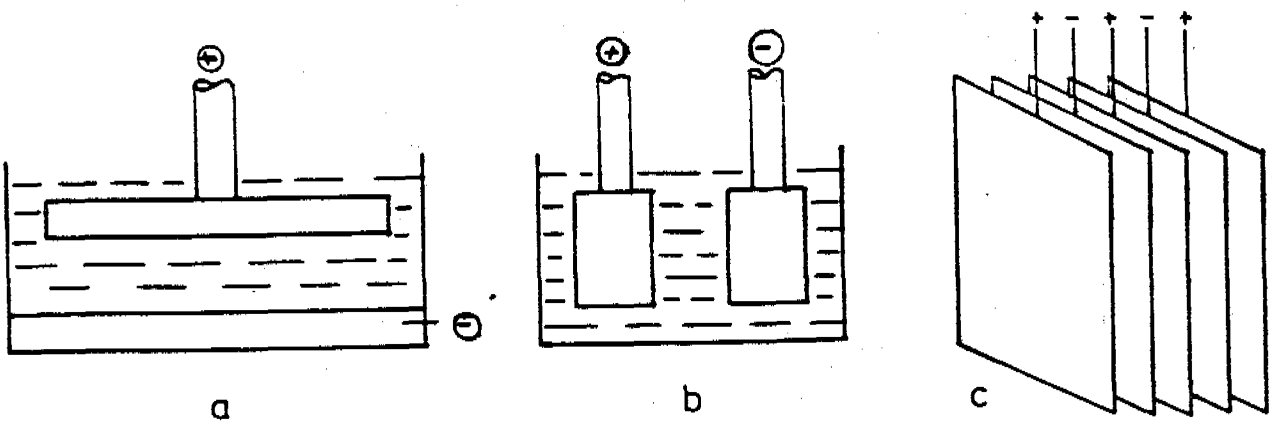


Fig.1: Electrode configuration, a) horizontal and b) vertical electrodes, c) Stack.

3.2. Divided Cells

3.2.1. Diaphragms

Porous separating walls, so called diaphragms are used to separate the cathodic and anodic zones efficiently, they prevent productmigration to the counterelectrode but do not hinder ion-migration in the cell. These contradicting conditions are to be optimized from case to case by the porosity, which influences the electrical resistance of the cell. Materials for diaphragms are non-conducting, chemically inert materials, like sintered Al_2O_3, porcelain, glass, asbestos, plastics or organic materials and gauzes from natural or synthetic fibers. Conductive materials cannot be used for diaphragms as these "middle conductors" can act as a counterelectrode if the voltage drop is high enough.

The separation efficiency of diaphragms decreases, if a high concentration-gradients is built up in the cell; this can be prevented by suitable flow and mixing conditions or by operation at low product concentrations.

3.2.2. Ion exchange membranes

If for the separation of electrode-compartments ion-exchange membranes /4/ are used, only counterions (e.g. Na^+ of the solidphase ion are allowed to pass. Cationic exchangers made of perfluorated polyethylene with sulfonic acid groups, like Nafion of Dupont, are resistant to chlorine or concentrated sulfuric acid at temperatures of 100°C . Their electrical conductivity is much better than that of diaphragms, and they can be used with very small electrode distances. Because of these advantages they are used more and more in technical electrolysis like chlorine-alkali electrolysis /1,2/. But especially for small systems the costs for the membranes are very high (600 $\$\ m^{-2}$). Also the water needs softening as Ca and Mg may precipitate as hydroxides and clog the membrane.

In some cases a mixing of catholyte and anolyte can be prevented without mechanical separation of the two compartments, for instance if the electrolyte is flowing laminarly through the cell parallel to the plate-electrodes which should have a smooth surface. Retention time and product concentration must not be too high to avoid convection. If catholyte and anolyte have different densities, mixing is prevented by using horizontal electrodes at laminar flow conditions.

3.3. Special Electrode Arrangements

Since the electrochemical reactions only occur at the interface electrode/electrolyte, large electrode surface is desirable. Therefore, electrodes are often constructed as parallel stacks to reach a high ratio of electrode-surface and cell volume (i.e. specific electrode surface). These stacks allow two kinds of electrical arrays:

3.3.1. Monopolar Array

By connecting all cathodes and anodes in parallel we have a so-called monopolar electrode array. It has a more complicated current feed line, but less problems with current distribution in the electrolyte and a simple cell construction (fig 2).

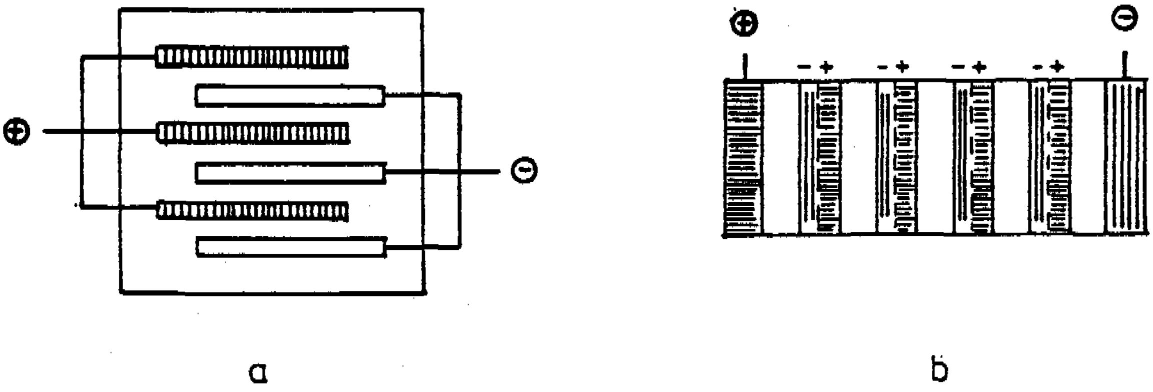


Fig.2: a) Monopolar and b) bipolar Electrodeconfiguration

3.3.2. Bipolar Array

In the Bipolar array the electrodes are connected in series, so that each electrode of a stack (except the two end-electrodes) works simultaneously as cathode and anode. In this way such a cell only needs two current connections to the two end-electrodes. The current passes from the anodic end-electrode to the next stack-electrode which acts as cathode, passes through this electrode, which functions as anode at its back side to the next electrode working as cathode at its front side and so on, until the current reaches the other end-electrode, the cathode.

Using this arrangement the different cellchambers must be separated completely by the electrodes so that the current cannot pass through the electrolyte or other electrical leakage between the chambers . Therefore, bipolar cells have a more complicated construction and need more servicing than monopolar cells. Another problem is, that one has to put the whole cell out of service for replacing one electrode. Their main advantage is the more favourable energy cost, as they work with high voltage and low current.

3.4. Technical Evaluation

The most used geometry of electrochemical cells is the rectangular tank, as a maximum electrode-surface per volume can be obtained. Several identical units of undivided cells or diaphragm / membranecells can be combined into stacks or large blocks like filter-presses. If a lower yield is tolerated, the cell may be a tube with its inner surface serving as working electrode. Corrosion resistant cell materials are ceramic substances or plastics or plastic coated steel.

For optimal operating conditions the electrolysis shall be carried out with constant and the same conditions of concentration, potential and current density over the whole electrode surface.

Another frequent problem is the deposit of isolating films by products of electrolysis or side-reactions, so that the electrode is partly or wholly passivated (see 3.4.2.).

3.4.1. Stirring

The transport mechanisms of the reactants to the electrode-surface under technical conditions are diffusion, migration in the electrical field (if the reactants are ions) and natural convection. The latter occurs, if gradients of temperature and/or concentration exist in the cell. To increase the transport velocity, a short and constant diffusion path, in a thin diffusion layer on the electrode, is desirable; this can be realized by stirring and turbulent flow conditions in the cell. Thus, by strong mechanical stirring of the electrolyte the whole concentration gradient of the cell is reduced to a small electrolyte layer at the electrode.

Rising bubbles of a gas generated at the electrode have the best stirring effect. In continuously working cells turbulent flow conditions prevent the formation of local concentration gradients, whereas laminar flows cause stationary gradients of flow and therefore of concentration. The most effective flow direction of the electrolyte is perpendicular to the electrode. But neither of these methods can totally prevent the electrode products from reaching the counterelectrode in undivided cells, (e.g. to minimize hypochlorite reduction).

3.4.2. Scale Deposits

Natural water as electrolyte has a permanent danger of electrode passivation; especially cathodes will be coated with isolating films: The cathodic hydrogen generation increase the pH near the electrode to strongly alkaline values according to $H_2O \quad 0.5\ H_2 + OH^-$.
As a result alkaline earth in hard waters precipitate as basic carbonates on the electrode. Analogously metal ions like Fe and Mn, will precipitate as basic oxides or carbonates and form an isolating layer. These reactions can be retarded by appropriate flow conditions in the cell like flows perpendicular to the electrode. Thus, the pH gradient occurs in a smaller zone and the coating is partly removed by the flow before aging to a hard film. But often it is necessary to clean the electrodes by reversing the poles of the electrodes from time to time, that means changing the direction of the pH gradient. Thus, the basic coating is partly dissolved and will partly crumble and accumulate on the cell bottom; filtering of the electrolyte may then be necessary.

3.4.3. Problems of Cleaning

If the water or the salt for the electrolyte contain disperse, solid impurities, which can clog the small passage between the electrodes or the inlet and outlet tubes of the cell, the electrolyte must be filtered before entering the cell. High concentrations of alkali earth and heavy metal salts must possibly be reduced by alkaline precipitation or ion-exchange. Also water, heavily contaminated by organic material, must be prepurified by some suitable degradation and precipitation reactions possibly followed by filtration, according to the well known methods of water purification. One should always look for a compromise between the cost of electrolyte prepurification and the cost of cell maintenance (changing the electrodes, cleaning the cell).

3.5. Economical Aspects

The selection of an economic cell design depends on investment costs and operation costs, the latter consisting of process control, maintenance and energy costs, which can be optimized.

Undivided cells have small investment costs, no service expense for diaphragms and membranes and lower electrical resistance because of the absence of a separating medium. But the latter is however offset by the greater electrode distance of undivided cells, necessary to minimize the possible reduction of anodic products at the cathode. This also requires precise flow conditions and often causes lower yields or low (product) concentration because of the necessarily short electrolyte retention times in the cell.

Bipolar cells have lower energy costs (monopolar cells have more connections current losses), but require higher investment and maintenance costs. Bipolar cells work at higher voltage and low current for which the required rectifiers are less expensive. The installation of pumps and stirrers for the electrolyte improve the production capacity, but increase the investment and maintenance costs.

4. ELECTRODE CONSTRUCTIONS

The electrode construction is determined by electrochemical conditions to the electrochemical reaction only occurs at the electrode surface. Maximal electrode surface in the smallest possible cell is desired. Also, its geometry and surface structure influence the flow conditions of the cell. Because the electrolyte resistance influences the actual current in the cell, constant electrode distances, i.e. constant electrode geometry, are important. The technically most important electrode forms are characterized on the following pages.

4.1. Plates

Parallel plates combined to stacks have a favourable specific surface (surface/cellvolume ratio) . With an appropriate thickness they are free of deformation and simple to mount and to service. Some separation of catholyte and anolyte in undivided cells is possible if the electrolyte flows parallel to the plates. Expensive electrode materials like noble metals are not used as plates because of their high material cost.

4.2. Rods

Rods are combined to packs to obtain large surfaces, this requires a more complicated cell construction, especially with respect to separation of catholyte and anolyte. A compromise is the fixation of parallel rods on an inert plate or as parallel grids. This construction, so called "spaghetti" electrodes, is often used in gas generating electrolysis, because gas bubbles can rise better and more quickly than for instance with stretched metal electrodes.

Fig. 3

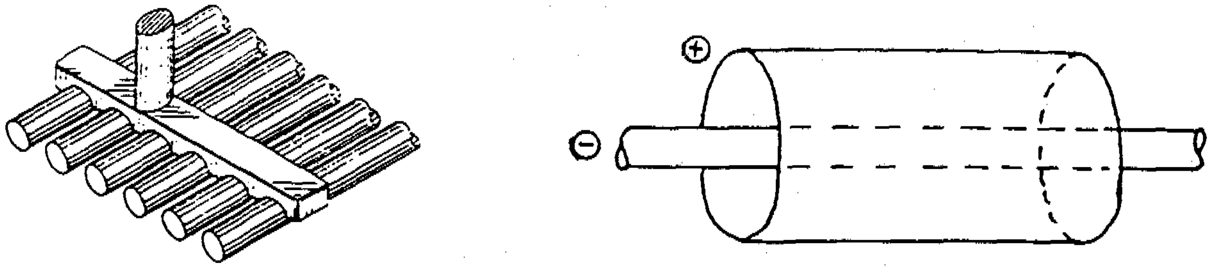


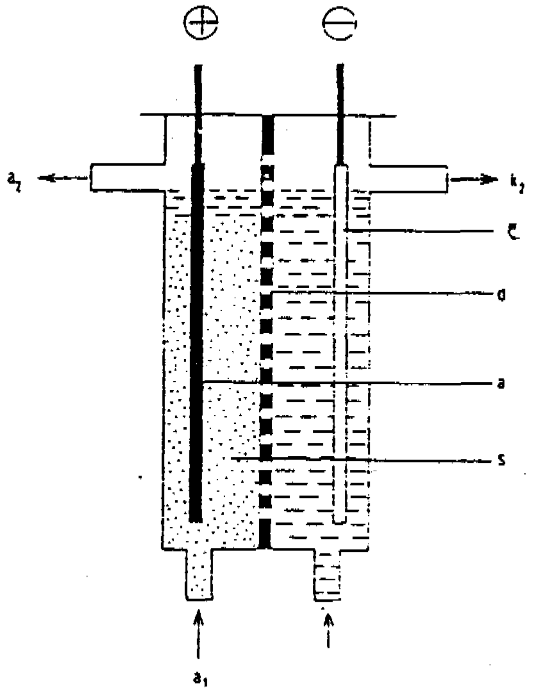
Fig. 3
a) Spaghetti-electrodes, loc.cit.3.2 b) Tubecell with rod and tube-electrode;

4.3. Cylinders

The inner side of cylinder and tube electrodes can function as an electrode. Such an electrode can simultaneously be the cell, if its outer side is isolated. The counter-electrode can be a rod in the center of the cylinder. Such constructions are preferred, if tube reactors are desired. They require corrosion free electrode materials to reach economical lifetimes of the cells. If the electrode reaction is strongly exothermic, so that the electrode must be cooled (due to Ohmic resistance and exothermic chemical reaction), tube-electrodes are used with the outer side working as electrode. The inner side of the tube contains the coolant. The counter-electrode for this case can be a concentric cylinder which surrounds the tube.

4.4. Packed Bed Electrodes

Plate electrodes have a relatively small specific surface area. Therefore, many attempts have been made to construct packed bed and fluidized bed electrodes from conductive particles. The current is conducted to the particles by a feeder-electrode while the electrolyte is flowing through the particle bed. Such three-dimensional electrodes have excellent space-time yield because of their very large surface area of the particles so that high currents with low effective current density and low electrolyte concentrations can be used. The electrolyte flowing from bottom to top, through the cylindrical electrode vessel keeps the particles in the electrolyte in a stationary floating condition, if a certain flow velocity is reached. With a lower rate the particles will sink and form a fixed bed.



a = Feeder-electrode
c= cathode
a_1, a_2 = In and outlet of Anolyte
k_1, k_2 = In and outlet of catholyten
s = Fluidised bed
d = Separator loc.cit. 3.2

Fig. 4 Fluidised bed-electrode

Packed bed electrodes have some disadvantages, especially abrasion of the particles, poor electrical contact between the particles and with the feeder electrode and an inhomogeneous potential distribution in the bed. Also the particles have some bipolar character, so that back reactions are possible, furthermore they will be corroded and passivated, if they don't have permanent electrical contact. These characteristics can only be overcome, if the operation parameters, especially the flow conditions, are held constant, which requires a sophisticated controll mechanism.

4.5. Porous Electrodes

Another possibility to obtain high effective electrode-surfaces is by using porous material, prepared e.g. by sintering metal powder mixtures and leaching, one of the metal components like aluminium chemically. How far electrolysis can take place in the pores depends on the charge transfer resistance of the reaction, on the electrolyte resistance and the geometry of the pores. Important for the reaction rate is also an effective rrplacement of the electrolyte in the pores, although high flow resistance can be expected. These electrodes which demand high maintenance and service standard, are used for gas generating reactions. Characteristics and technology of these electrodes were investigated thoroughly in fuel cell research.

4.6. Stretched Metal Electrodes

Stretched metals have a mesh strucure and is produced by punching and stretching a metal plate. They are favoured electrode material forms because of their low flow resistance, their low weight and therefore their low material costs, is suitable for electrode stacks (especially for small systems, with individual electrode if some dm^2 area which do not suffer mechanical deformation. Also stretched metals are easy to machine and generally available in nearly all metals.

4.7. Swiss Roll Electrodes and SPE-Systems

For a Swiss roll cell /1/, cathode and anode must be so flexible that they can be rolled up. This arrangement puts one electrode on top of the other, separated by a membrane or plastic net of the same size as spacers so that the electrolyte can pass through the cell. This triple pack is rolled up to arbitrary big rolls, which have a large specific electrode surface; they are favoured for electrolysis of dilute solutions and short retention times. Gas generating reactions e.g. Cl_2, H_2, O_2 can create difficulties, because the produced gases must be removed rapidly, before large bubbles can block the electrode surface.

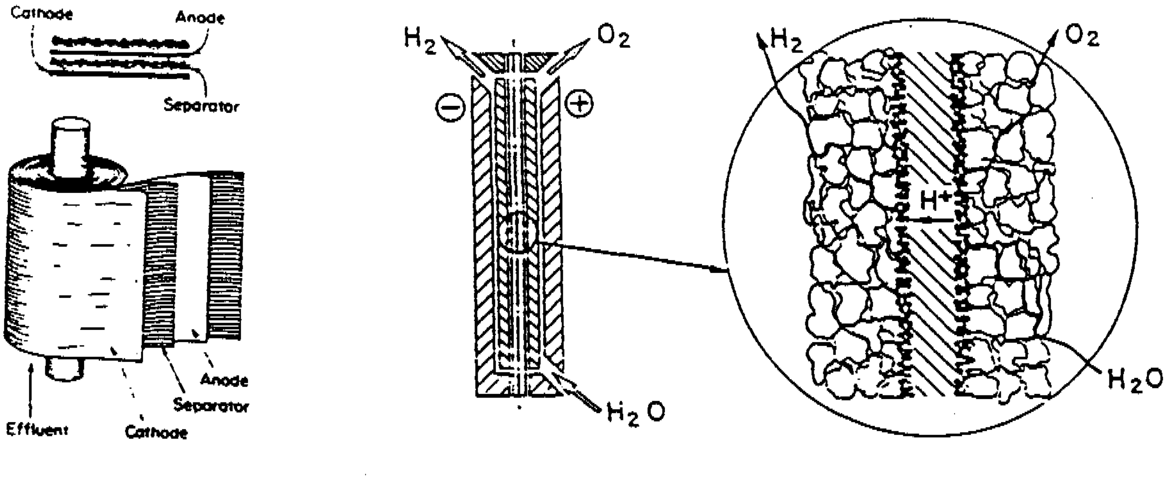


Fig. 5: a) Swiss roll, 4.1 b) SPE-Cell for water electrolysis loc.cit., 4.2

Another promising new development is the SPE-system (Solid Polymer Electrolyte) introduced by General Electric Corp. Their application in water electrolysis, electrochemical ozone generation and brine electrolysis are discussed /2/. In these systems the electrodes are directly fixed on an ion-exchange membrane, so that the membrane functions as a solid electrolyte. Electrodes and membrane form a unit, where the membrane also separates the cathodic and anodic region. The membranes must be chemically stable, like the teflon-based Nafion of Dupont. Because the thickness of these membranes is less than 0,5mm, extremely small electrode distances can be obtained. This permits the application of high current densities (up to 2 A cm^{-2}).

SPE electrodes must be so porous, that the reactants can reach the interface electrode/membrane with not too high lag times. The current feed can be realized by porous current collectors, which are fixed directly on the electrodes. This construction has the advantage, that the catalytic components of the electrodes are protected from corrosion and erosion. These membrane-electrode-units are supported by a plate, which can be the cell wall which has groves for the transport of reactants and products.

An example is a cell developed by General Electric for chlorine production /3/. The anode is a powdery mixture of oxides of ruthenium and titanium or iridium and teflon which is thermally fixed on the membrane, the cathode is made of a mixture of platinum black and teflon; the current collectors are the graphite cell walls or Metal nets are also used as spacers between cell walls and electrodes; anodic nets are made of nobium, cathodic nets of steel.

A similar system (for chlorine production) with comblike current collectors and platinized titanium nets is described by De Nora /4/.

4.8. Technical Assessment

For the selection of an electrode configuration the following factors are important:

1. The electrolyte flow characteristics in the cell, which are determined by the cell type (divided, undivided etc.) and the necessary retention time with the geometry and surface structure of the electrodes as major parameters.

2. The electrolyte resistance. The distance of the electrodes controlls the effective electrolyte resistance and so the energy costs.
3. The reaction yield, which because of the heterogeneous character of electrolysis reactions depends to a great deal on the specific electrode surface.

Special arrangements like packed fluidized bed electrodes or Swiss rolls show many mechanical, corrosion and abrasion problems, so that they can be used for special applications only.

4.9. Economical Considerations

To minimize investment costs electrode configurations should be as simple as possible. They should use material which is generally available like plates or stretched metals. The construction must permit a simple and rapid change of the electrodes to minimize operational costs. The energy costs are directly related to the electrode distance.

5. ELECTRODE MATERIALS

The electrode material is a determining cost factor for an electrochemical process. The materials should be cheap and simple to machine. Noble metals should be avoided because of their high costs, even though they can have excellent electrochemical characteristics. On the other hand, titanium has become an interesting electrode material, since industry has succeeded in machining this difficult material.

Another important point is a low overvoltage of the electrode reaction at the selected material, on the other hand, the overvoltage of possible side reactions should be as high as possible to obtain a high current efficiency, i.e. low energy costs. The corrosion characteristics of the material control the maintenance- and service-costs of an electrochemical cell. For drinking water disinfection it is important, that the products of electrode corrosion or of electrolysis side reactions do not contaminate the water with toxic substances.

Study of these numerous problems led to many new developments of electrode materials, especially for anodes in the last two decades, so that now a range of materials exists, which can solve at least some of these problems (see annex 1).

5.1. Anode Materials

5.1.1. Carbon, Graphite /1/

Carbon and graphite have been the most important anodic material in industrial electrochemistry until the late sixties. Graphite anodes have been extensively used in the most important electrolysis process, i.e. chlorine-alkali electrolysis. Therefore, the major part of investigations about the electrochemical characteristics of graphite were made relating to the conditions of brine electrolysis /2-6/.

The main advantages of graphite are its excellent electrical conductivity, its low price and the relatively high chemical and mechanical stability. Moreover, the overvoltage for chlorine generation is lower than for instance at platinum or magnetite /1/. But the severe conditions of the technical chlorine alkali electrolysis cause a serious corrosion, so that 2-3 kg graphite per ton chlorine are lost. The reasons of the corrosion are of physical and chemical nature: The porous structure of graphite and the strong gas evolution in the pores cause a mechanical wear of graphite particles (which settles at the bottom of the cell) resulting gradually in enlarges pores. A serious chemical corrosion is aused by traces of oxygen which is simultaneously generated at the electrode with chlorine; The oxygen oxidizes the carbon to CO_2. Also hypochlorite plays a role as it can decompose and produce oxygen /3/. Sulphate ions in brine promote CO_2 formation according to a linear correlation between CO_2- and SO_4-concentrations /2/. Other factors increasing the corrosion of graphite anodes are high temperature, alkaline pH values and low brine concentrations.

Another side reaction of these anodes in brine electrolysis is the formation of chlorinated hydrocarbones, but under the less severe conditions of on-site electrolysis for water purification this reaction would be negligible.

The mechanical wear is mainly a result of the graphite structure, which is determined by the production method. Thus, high porosity is bad, a high degree of graphitizing is favorable as a high graphite content of the electrode material improves the stability and electrical conductivity. The mechanical corrosion can be diminished by impregnating the electrode with organic resins and oils. The contact between the carbon- and graphite-praticles also becomes better. Krishtalik et al. /7,8/ have described such impregnation techniques in detail.

Though graphite anodes are replaced more and more by DSA electrodes (Dimensionally Stable Anodes) in chlorine-alkali electrolysis, they may be important for small systems which work under conditions of low temperatures and current data densities, and less corrosion. Thus in several newer patents of small chlorine-and hypochlorite generation cells for water purification graphite electrodes are proposed /9-13/. Skljrov et al. describe a graphite electrode which is impregnated with bitumen or pitch oil and doped with metals or their oxides to improve the catalytic properties /11/.

5.1.2. Platinum and Platinized Titanium /1,14/

Noble metals are excellent electrode materials because of their "inert" chemical character, their high electrical conductivity and good mechanical properties. But because of their extremely high price, especially of platinum, they do not have in pure, solid form any practical significance in technical electrochemistry. Some 50 years ago it was already attempted to deposit thin Pt-layers on cheap substrates like tungsten, tantalum or copper. These electrodes, however, were ineffective because it was very difficult to produce a dense Pt-layer free of pores, which protects the substrate effectively from oxidation. With the availability of titanium the first successful platinized electrodes with a titanium substrate were produced. At the beginning of the sixties, Titanium can be used with porous Pt-layers because of its excellent corrosion resistance, on the other hand the Pt-layer prevents the anodic deposit of a compact TiO_2-film. Pure titanium cannot be used as anodic material, as TiO_2 would passivate the anode.

The overvoltage of chlorine generation depends on the structure of the Pt-layer. Smooth layers, formed electrochemically from hexachloroplatinum acid or from platinum-"P"-salts solution, show overvoltages which are much higher than graphite anodes. Rough, porous Pt-layers with large effective surfaces have overvoltages up to 500mV lower and are therefore better than graphite. Such layers can be prepared effectively by thermal methods yielding surfaces 1000 times larger than smooth layers. The titanium surface is also roughened chemically or electrochemically before coating.

Though a noble metal, Pt is corroded in some electrolytes, especially in concentrated chloride solutions, where it is dissolved at rates up to 1 $ug.A^{-1}h^{-1}$. But depending on the electrolytic conditions, much lower rates are possible e.g. a seawater electrolysis cell is described which has an anodic loss of 0.05 $ug.A^{-1}.h^{-1}$, which is economically feasible /15/. These electrodes are also passivated with time which results in a higher cell voltage.

Experiments with other platinum-group metals have shown, that iridium coatings have much better characteristics as anode material, i.e. a lower overvoltage, slower passivation and corrosion rates. But iridium is much more expensive than platinum. Therefore, coatings of Pt/Ir alloys were developed with a Pt/Ir ratio of 70/30wt.%, which is the best mixture from an economic and electrochemical point of view. The coating process uses organometalic solutions containing appropriate compounds of both metals. These solutions are decomposed thermally on the Ti-substrate. Such electrodes are used to some extent in chlorine alkali electrolysis and hypochlorite production, but in large scale production the DSA electrodes are dominating.

For smaller systems of water purification platinized Ti-electrodes have some attraction, because of fewer problems of corrosion and passivation at lower brine concentrations and current densities. These anodes have been proposed in many recent patents /9,13,16-20/, however the Ir-containing anodes are less cited /21/, maybe because of their higher price.

5.1.3. <u>Leaddioxide and Lead /1/</u>

Leaddioxide has an excellent electrical conductivity, better than most metals, a good resistance against most oxidants and a low price. There have been many attempts to use it as anode material to substitute the expensive platinum in perchlorate and chlorate production. But until the sixties the difficulties to manufacture PbO_2-anodes hampered their commercial application. PbO_2 has been deposited on iron, copper or nickel, but these electrodes passivate quickly, by PbO_2 oxidation of the substrate metals. Also anodization of Pb-sheets was unpractical because the generated PbO_2-layers were scaly and had a poor adherence, as the oxidation process penetrated throughout the whole electrode gradually corroding it severely.

More successful were solid PbO_2-electrodes, which have had some technical application in Japan. They were produced by depositing PbO_2 electrochemically from a $Pb(NO_3)_2$ solution on the inner side of an iron cylinder anode. When the PbO_2-coating has a thickness of about 8mm, the iron cylinder was cut open and removed; the resulting PbO_2-cylinder could be cut to strips of appropriate dimensions /22,23/. The main disadvantage of these massive electrodes are their poor mechanical characteristics (they are very brittle and crack easily).

Technically more important was the deposition of PbO_2 on graphite /24,25/. Such electrodes, manufactured also in large dimensions by Pacific Eng.Co, Nevada and used in perchlorate production, show lifetimes of some 100h. They are also used in cells for hypochlorite production up to $30g.l^{-1}$ which can be used for on-site water treatment /1/. The main disadvantage of these graphite/PbO_2-electrodes is the rapid graphite degradation to CO_2, if oxygen is generated on the substrate. As the oxygen overvoltage on PbO_2 is higher than on graphite, a damaged PbO_2-coating can cause a rigorous oxygen generation on the substrate. PbO_2-coatings should therefore be free from pores and cracks. Another disadvantage is that a recoating of the graphite of used electrodes is not possible.

In the last years PbO_2-electrodes on titanium substrate were developed, especially by Wabner et al. /26-28/. This substrate is well suited for PbO_2-coating, because both TiO_2 and PbO_2 have the same rutile structure. First it was difficult to avoid the formation of a passivating TiO_2-layer during the electrolytic deposition of PbO_2 on the substrate, but it can be largely suppressed, if Ti (IV)-ions are adsorbed on the substrate surface.

These electrodes are very suitable for electrochemical ozone generation because of the high oxygen overvoltage of PbO_2 /29/ and they seem to be appropriate for small systems for drinking water disinfection by ozone or the oxidative waste-water purification /30/, especially if long-time disinfection is not necessary.

The Ti/PbO_2-electrodes can reach life-times of some 100h under favourable conditions, but their life-time is limited, because a passivating TiO_2-layer is built up slowly between substrate and PbO_2. However, the substrate can be recoated several times.

PbO_2 is a strong oxidant. Therefore, it reacts chemically, without current, with reducing substances of the electrolyte corrod the electrode. Also, it must be prevented, that the electrode is mounted as a cathode as the PbO_2-coating would dissolve. PbO_2 cannot be used for brine electrolysis, because it would dissolve appreciably in acid, concentrated chloride solutions, and deposited on the cathode as metallic lead. Inspite of these problems such electrodes were sometimes proposed for hypochlorite cells /31/.

Pure lead as anodic material can only be used in chloride free electrolyses because of severe corrosion problems. It could serve as oxygen generating electrode Under the oxygen generating conditions a scaly PbO_2-coating is built up, so that a poor PbO_2-electrode as mentioned above is obtained. The chloride sensitivity can be diminished by adding small amounts of silver to lead to favour the formation of a closed PbO_2-layer. Thus, Ag/Pb-electrodes can be viewed as PbO_2-electrodes.

5.1.4. Manganesedioxide, Magnetite and Spinels

Because of the good chemical and electrochemical characteristics of MnO_2 numerous investigations have been made to use this oxide as active coating. Thus, Stender et al. /32,33/ deposited MnO_2 electrochemically and thermally on titanium. They found, that these electrodes are well suited for technical HCI-electrolysis. A Japanese patent describes electrodes for water electrolysis, in which carbon rods are coated electrochemically with MnO_2 from a $MnSO_4$-solution /34/. In brine electrolysis they are not used, because they are inferior to the modern Ti/RuO_2 and Ti/Co_3O_4 electrodes due to a higher oxygen perdentage in the anode prododuct /35/.

Magnetite anodes /1,36/ are used technically for chlorate production. They show excellent corrosion- and wear-characteristics and operate many years at high temperatures without change of dimensions nor cell voltage. They also have been proposed for waste-water chlorination. The main disadvantages which limite their technical use, are the difficult preparation from melted hematite or by sintering processes, and the difficult machining because of the fragility of this material. Moreover, the conductivity is 20 times smaller than of graphite.

Magnetite (Fe_3O_4) belongs to the class of spinels. Some of them are very important anodic materials /36,37/. Their general formula is $A(B)_2O_4$ or $B(AB)O_4$, where A usually has the ionic charge +2 and B +3, A has a tetraedric, B an octeadric symmetry. The electrochemically most important spinel is Co_3O_4, which is coated thermally on titanium. Such anodes have excellent properties for chlorine-alkali electrolysis, which can be improved by additives like copper, magnesium or zinc and zirconium oxide according to the formula $M_xCo_{3-x}O_4yZrO_2$, in which M = Cu, Mg, Zn with 0 x, y 1. The spinel lattice can accomedate numerous 2- and 3-valence metal ions, therefore, many variations with different properties are possible. The Co_3O_4-anodes may indeed compete with the DSA-anodes, for instance they are in use in several chlorine plants of Dow Chem.Corp.

They are also proposed for seawater electrolysis and small chlorine cells. Thus, a Japanese patent /38/ describes an electrode coating consisting of 50-95mol% Pt, 5-50mol% SnO_2 and 20mol% Co_3O_4, which shows better potential- and current-efficiency values in seawater electrolysis at 20°C than DSA-electrodes. BASF developed a coating consisting of iron- and cobalt spinels coated on titanium by a plasma spraying method. This electrode is said to show long durability and low overvoltage in brine electrolysis /39/. Diamond Shamrock described an electrode made by a thermal coating process on titanium with a mixture of SnO_2, Sb_2O_3 and Co_3O_4 /40/.

5.1.5. DSA Electrodes

Investigations of platinized Ti-anodes and Pt/Ir-anodes have shown, that the noble metals exist as oxides in the active electrode layer. Therefore, oxides of the platinum group metals were systematically investigated as anodic coatings on titanium substrate.
In 1967 Beer found his Ti/RuO_2-electrode /36,41-43/, today called Dimensionally Stable Anode (DSA) which is the most important anode worldwide for chlorine-alkali electrolysis and other electrochemical processes. Its form stability and low weight, the high current densities possible (up to 15 $kA.m^{-2}$), the very low chlorine overvoltage and high current efficiency, the long life time of several years and the repeated use of the titanium substrate by recoating, make this anode superior to all other materials. The only disadvantage is the high price (US$ 200-600 m^{-2} for stretched metal DSA), cuased mainly by the ruthenium component. Beer gained his worldwide patent coverage with the assistance of O. de Nora, Milan in the years 1968-72. The TiO_2/RuO_2-coating is licensed globally by Diamond Shamrock.

The original Beer-electrode had a coating of 70 mol% TiO_2 and 30mol% RuO_2. To prepare it the titanium substrate was cleaned in hot oxalic acid, then the dry metal was sprayed with a solution containing butanol, HCl and $RuCl_3$, and heated to 300-500°C for 1-5 min. Since both TiO_2 and RuO_2 have the rutile lattice, the active layer is a mixed oxide with the formula $Ti_{1-n}Ru_nO_2$, n 1, depending on the preparation conditions. Another variant which is maybe the most used today in industry, contains 3 oxides, TiO_2 + RuO_2 + SnO_2 with typical mol ratios TiO_2/ (SnO_2 + RuO_2) of 1.5-2.5 with 35-50 mol% SnO_2. These electrodes have the adventage of a higher oxygen overvoltage and are cheaper because of their lower Ru-content. In another variant from Hoechst AG the substrate is first coated with a partly reduced titaniumoxide layer (TiO_x, x 2) followed by the Beer-coating. Ti-suboxide is an excellent conductor in contrast to TiO_2. This interlayer increase the lifetime of the electrode /44/.

The exact composition of the commercial DSA-electrodes is a trade secret. In the last years numerous attempts have been made to improve the electrochemical properties or to circumvent the existing patents. All these variants may be described by the formula Sub/VM + NM + NNM, where Sub = substrate, VM = valve metal, NM = noble metal and NNM = non-noble metal /43/. As substrates are used Ti, Zr, Hf, Nb, Ta, W, Al, Bi etc. individually or as alloys, the coating VM + NM + NNM was made of oxides, carbides, borides, nitrides, silicides etc. the noble metals Pt, Ir, Rh, Os, Pd and the non-noble metals Cu, Ag, Au, Fe, Co, Ni, Sn, Si, Pb, Sb, As, Cr, Mn etc. But none of these variants has reached the importance of the classical DSA-electrodes.

These electrodes have of course been proposed in many patents for seawater electrolysis, for on-site production of chlorine or hypochlorite for swimming-pool, drinking- and waste-water-purification. Diamond Shamrock describes cells for water purification with titanium anodes coated with a mixture of SnO_2, Sb_2O_3, TiO_2 and RuO_2 /45,46/. Several cells for seawater electrolysis from the companies O. de Nora, Milan, Krebskosmo, Berlin and Pennwood, Philadelphia have DSA-anodes /47-49/. The Japanese patents 16088-77 and 16089-77 describe a hypochlorite cell for drinking-water sterilization using DSA-anodes (50/. For this purpose De Nora and Heraeus, Hanau have also developed DSA cells /51,52/. The list could be enlarged, as the literature and patents of DSA electrodes are numerous.

5.2. Cathodes /1,36/

The chemical conditions in the cathode area are less aggressive than at the anode. Therefore, the criteria for cathode materials are less stringent, more materials can be used. But due to the lower pH some materials like iron may dissolve, if no current is flowing through the cell. Many hydrogen generating cathodes become brittle and breaks easily with time, losing their mechanical stability.

For hydrogen generation, for instance in brine electrolysis or electrochemical ozone generation, platinum is the best cathode material because of its low hydrogen overvoltage and its chemical inertness, but the high price prevents it technical use. The most used material in brine cells is steel or stainless steel which has lifetimes of some decades. Using technical current densities (1-2 $kA.m^{-2}$) steel has an hydrogen overvoltage of about 300mV.

Since the energy costs have risen dramatically, many attempts have been made to lower this overvoltage by applying catalytic coatings /53/. The most advanced methods use plasma-spraying procedures to coat a steel electrode with a mixture of Ni and Al or Zn, the Al or Zn are then dissolved, so that a porous, surface-active Ni-coating remains. These so-called Raney electrodes have lifetimes up to 2 years /54/.

Since titanium is available, it has been used widely as cathodic materials because of its excellent mechanical and chemical properties. But with hydrogen hydrides are formed which make the electrode brittle and easily cracking. Nevertheless, titanium is the most proposed cathode material besides steel for brine electrolysis in small cells. Graphite, nickel and lead have a minor role, the latter due to its weight and poor form stability.

An interesting alternative to hydrogen generation in brine electrolysis is the use of an oxygen reduction cathode developed in the fuel cell technology and based on the reaction

$$H_2O + \frac{1}{2}O_2 + 2\,e^- \longrightarrow 2OH^-$$

so that the cell must be supplied with oxygen or air. The advantages are an extremely low cell voltage and the absence of hydrogen, so that the formation of explosive hydrogen-oxygen mixtures is avoided. But the technical use in chlorine-alkali electrolysis has not yet been reported, because these electrodes require totally new cells which have critical operation conditions. Smaller systems give less problems. Thus Diamond

Shamrock has applied for a patent of a hypochlorite cell with such an electrode. It consists of ESE-fuel cell-electrode mass, containing as catalysts the oxides of Ag, Au, Pt, Co, Cu etc. The cell has a current density of 2.9 A.dm^{-2} and a brine concentration of 100g.l^{-1} /46/. Being free of hydrogen this system is proposed for on-site disinfection of small swimming pools.

A Japanese patent describes a cell for brine electrolysis with air and solar energy only, using a titanium semi-conductor anode and an oxyygen cathode /55/. But such systems certainly need more intensive investigations to get cells of convenient handling and of acceptable lifetimes.

5.3. Different Supporting Materials

Many attempts have been made to use materials like glass, ceramics or plastics as cheap substrates for electrodes in order to avoid the expensive titanium. It is possible to deposit noble metals on glass and ceramics by thermal decomposition of appropriate organic solutions /56,57/. PbO_2 can be deposited electrochemically on glass and ABS-polymers /58/. But these materials have no practical significance as electrodes, as the adhesive strength of the active coatings is problematic, especially if the electrodes are heated at high current densities. Another difficult problem is the electrical contact of these electrodes, as the coatings are damaged easily.

6. DISCUSSION OF THE VARIOUS POSSIBILITIES

We have seen that there are many possibilities to disinfect water electrochemically with various levels of complexity of the developed systems. The aim is a design which is as simple as possible with no maintenance and operation problems. The construction should be as cheap as possible and should not be too difficult technicaly. These demands can be more easily fulfilled in small on-site disinfection cells with capacities of some $kg.h^{-1}$ oxidant, than for large-scale chlorine-alkali electrolysis plants for which high current efficiency is important. To have a optimum of electrode distance, overvoltage and current efficiency may not be the first consideration for small plants.

6.1. Disinfection

As mentioned in chapter 2.6, the effective water disinfectants are chlorine, sodium-hypochlorite and eventually ozone. Their application in water disinfection is based on a broad experience.

Ozone however can be used only if the drinking water is consumed immediately, because ozone does not provide lasting disinfection. For the electrochemical ozone production only PbO_2-anodes are suited. But these electrodes require more development efforts to get sufficiently robust cells with long life-times.

The "electrolytic oxidation with PbO_2-anodes" producing the strongly oxydizing ozone-precursor hydroxyl-radical is not yet a practical method for drinking water disinfection. Like with ozone the most important disadvantage is the absence of lasting disinfection. Also, the total water flow must pass the cell. I.e. no bypass. Thus, this method is only suitable for special applications.

The Chlorine generation use costly divided cells. Chlorine and water mixing requires another technical installations. The caustic soda solution generated in the cathode area must be removed.

The direct generation of sodiumhypochlorite in undivided cells does not have these disadvantages.

6.2. Cells

Chloride containing water is very corrosive and attacks even welded steel joints. Therefore, it is favourable to construct the cells from plastics like PVC. The cell geometry is relatively simple, because hypochlorite can be produced in undivided cells. The geometry very much influences the flow conditions of the electrolyte. Cylindrical forms and tubes are to be preferred. Since hypochlorite in undivided cells is cathodically reduced easily to chloride, the anolyte must not reach the cathode. The flow should be as turbulance free as possible. This can be realized in round cells with short electrode paths and underdimensioned cathodes. For the same reason the retention time of the electrolyte in the cell must not be too long. Therefore, one is often satisfied with salt conversions of less than 50% and using dilute sodium chloride solutions (30 $g.l^{-1}$ or seawater) as a raw material. But then, one must accept some undecomposed NaCI in the drinking water.

The hydrogen generated at the cathode must be collected in the cathode compartment by a bubble-cup and removed in a manner, so that local hydrogen-oxygen mixtures cannot result. To guarantee a low hydrogen concentration, low current densities can be used, which also increases the life time of the electrodes.

<u>Conditions of electrolysis</u>: The favourable temperature range for sodium-hypochlorite sythesis is 15-30°C. At temperatures lower than 15°C the oxygen generation and at temperatures higher than 30°C chlorate formation is favoured. Because of this chlorate formation the electrolyte should have a pH over 7, simply obtained by choosing appropriate brine concentrations and current densities; usual values are 20-50 $g.l^{1}$ and 0.05-0.15 cm^{-2}.

Two very simple cells of a robust construction without sophisticated controll equipment which can be mounted quickly in any water tank, are described in /3/ and /4/.

6.3. Electrode Constructions

The electrodes should be realized as plates or of stretched metal to have the advantage of mechanical stability and simple manufacturing. They can be arranged as stacks which are simple to remove. Stacks minimize the danger of turbulent flows, if the electrolyte flows parallel to the electrodes. The electrode distance should not be too small because of the danger of hypochlorite reduction. A compromise is to be found between high energy costs and hypochlorite yield. Reduction at the cathode can also be decreased, if the cathode surface is smaller than that of the anode e.g. in a proportion of about 1 : 1,5 /1,2/.

The necessary cleaning of the cathodes from calcarous deposits (or heavy metal hydroxides etc.) can be done by reversing the poles from time to time. But some anodic materials do not tolerate this method. Reducible anodes like PbO_2 must be disconnected and replaced by an auxiliary electrode installed in the cell. Another possibility is immersing the cathodes in a separate acid bath if the electrodes can be removed rapidly and simply from the cell.

The electrodes are working monopolarly. Bipolar electrodes often show much more corrosion problems. They require a more complicated cell construction and more serving.

6.4. Electrode Materials

Possible anode materials for hypochlorite production are graphite, platinized titanium or DSA. Graphite will be oxidized with time and must be reset continuously so that the electrode distance will not be too wide. This requires an extra provision and permanent control. Moreover, chlorate can be generated on graphite. On DSA this ion is not found or in smaller amounts.

Platinized titanium is corroded in chloride solutions and also promotes chlorate generation. That is why DSA is the preferred anode material. Now special DSA coatings for dilute electrolytes are commercially available.

The preferred cathode materials are steel and titanium, of which the latter is much more expensive. Steel will be corroded more rapidly, if the current is disconnected. Another possible material is graphite. If both electrodes of the cell are made of graphite, there are no material problems when the poles are reversed.

6.5. Open Questions

Before a final recommendation can be made, some questions need to be answered. The life-times of the chosen electrode material must be tested under the conditions of drinking water disinfection, especially with varying water quality and climate in developing countries. The possible formation of haloforms must be studied quantitatively. Moreover, more information is required whether the concentrations of health-effecting chlorate ion eventually formed can be tolerated, especially for continuous use.

7. SUGGESTIONS AND CONCLUSION

The recommended disinfectant for drinking water treatment for developing countries is the electrochemically and on-site produced sodiumhypochlorite.

Simple undivided electrolysis cells with parallel (stretched) metal electrodes seem to meet the low maintenance requirements conditional for small drinking water supplies.

No doubt the most suitable anode material is DSA.
The hypochlorite is generated outside the drinking water stream from a brine with e.g. 30g $NaCl.l^{-1}$ to yield dilute hypochlorite solutions (e.g. about 5 $g.l^{-1}$ active chlorine). The bypass stream is then mixed with the main stream of the water.

The construction of the system must be compact. It is proposed to develop exchangeable units which require little maintenance.
Some commercial systems nearly meets above requirements; but their prices are still high.
Development and field testing of low-cost systems is recommended. If certain operational problems can be accepted, cells with cheap electrodes like graphite may also be considered.

The quality of the water used requires attention, as pre-treatment of the water (precleaning, filtration, ion-exchange, etc.) may be required.

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Table: Characteristics of some important electrode materials:

a) Anodes:

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5) Loc.cit 2.1, 70°C, 1,6mA cm^{-2}, 300 g l^{-1} NaCl
6) Loc.cit. 5.37, 70°C, 1mA cm^{-2}, 18% NaCl-solution
7) Deposited as layer on Titanium

b) Cathodes:

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a) Anodes

Material	Graphite	Platinum 7)	Iridium 7)	Magnetite	Co-Spinell 7)	DSA 7)
Relative. electr. conductivity	1 1)	100 1)	50 2)	0.05 3)	4)	20 1)
Overvoltage (Cl2) /mV/	29 5)	63-48 6a) 41,43 6b)	52-92 6a) 28,30 6b)	350 5)	6 5)	6 5)
Mechanical strength	average	good	good	breaks easily	very good	very good
Chemical resistance	oxidizes to CO_2	will be dissolved by Cl^-	good	good	very good	very good
Contamination	Cl-carbohydrate ClO_3-formation	ClO_3-formation possible	ClO_3-formation minimal	ClO_3-formation possible	ClO_3-formation minimal	ClO_3-formation minimal
Manufacture	electr. graphitation	therm. decomposition of Pt-compounds	therm. decomposition of Ir-compounds	Melt or sinterprocess	therm. decomposition of Co-compounds	therm. decomposition of Ru-compounds
Price	low	very high	higher than Pt	lower than DSA	lower than DSA	lower than Pt

b) Cathodes

Material	Platinum	Steel	Titanium	Graphite
Relative electr. conductivity	100 1)	5 2)	25 3)	1 1)
Overvoltage (H_2) /mV/	low	300 4)	550 5)	100 6)
Mechanical strength	good	good	good	average
Chemical resistance	good	can dissolve with power failure	becomes friable gradually	good
Contamination	-	-	-	-
Price	very high	low	high	low

9. List of Manufacturers*

1)	Chlorine Eng. Corp., Ltd., Tokio, Japan			C
2)	Conradty GmbH, 8500 Nürnberg, F.R. Germany			A
3)	Deutsche Katadyn GmbH, 8000 München, F.R. Germany			C
4)	Diamond Shamrock Corp., Cleveland, Ohio, USA	A		C
5)	Diversey GmbH, 6719 Kirschheimbolanden, F.R. Germany			C
6)	Electro Chlor AG, Basel, Switzerland			C
7)	Engelhard Industries USA			C
8)	General Elektric Co., Schenectady, N.Y., USA			C
9)	W.C. Heraeus GmbH, D-6450 Hanau, F.R. Germany	A	B	C
10)	Ionics Inc. USA			C
11)	Korthals AG, Rüschlikon, Switzerland			C
12)	Krebskosmo GmbH, 1000 Berlin, F.R. Germany		B	C
13)	Licento AG, Switzerland			C
14)	Lopex GmbH, 3550 Marburg, F.R. Germany			C
15)	Metallgesellschaft AG, 6000 Frankfurt, F.R. Germany			C
16)	O. de Nora Impianti ElettoChemici S.p.A., Milan, Italy	A		C
17)	OSPA-Schwimmbadtechnik, 7075 Mutlangen, F.R. Germany			C
18)	Pacific Eng. & Prod. Co. USA	A		C
19)	Pennwalt Corp., 19102 Philadelphia, Pa., USA			C
20)	Römer Technik GmbH, 2000 Hamburg, F.R. Germany			C
21)	Sigri GmbH, 8901 Meitingen, F.R. Germany			A
22)	Magneto-Chemie, 3100 AE Schiedam, Holland	A		C

A = Electrodes
B = Cells
C = Complete Systems

* for information only, not implying any recommendation by IRC whatsoever.

GLOSSARY

Anode

The electrode in an electrolytic process or galvanic cell (battery) at which negative ions (anions) are discharged; oxidation takes also place at the anode.

Bipolar electrode array

A configuration in an electrolysis cell in which more than two electrodes are connected in series.

Cathode

The electrode in an electrolytic process or galvanic cell (battery) from which negatively charged electrons pass into the electrolyte/solution; positive cations move to the cathode at which reduction takes place.

Current density

The electric current flowing per surface area of electrode ($A.m^{-2}$)

Current Efficiency

Percentage of current used effectively for the intended electrochemical reaction.

Diaphragm

A porous wall seperating anode and cathode zones, which however allows the electric current to pass.

DSA (Dimensionally Stable Anode)

A composite electrode developed by Beer with an electrochemically active TiO_2/RuO_2 layer deposited on a Ti-substrate.

Electrolysis

A chemical change caused by passing an electric current through an electrolytic solution (transfer from electrical to chemical energy).

Electrolyte

A chemical compound which dissociates in ions.

Galvanic Cell (Battery)

An electrochemical cell in which a spontaneous reaction takes place at the electrodes, which generates an electric current.

Divided Cell

An electrochemical cell in which cathode and anode zones are seperated by a diaphragm or ion-exchange membrane.

Heterogeneous reaction

Takes place between two phases, e.g. electrode reactions.

Homogeneous reaction

Takes place in one phase, e.g. ionic reactions.

Ion-Exchange Membrane

Polymer film with ion exchange capacity; application of an electric current allows the passing of cations (or anions) in a selective way (selective permeability)

Mercury process

Still a major process in NaCl-electrolysis; Na dissolves in the mercury cathode to a Na-amalgam, which is decomposed outside the cell to NaOH + H_2. The process is a source of Hg pollution.

Monopolar array

Parallel connection of the corresponding cathodes and anodes, if the electrolysis cell has more than two electrodes.

Packed/Fluidised Bed Electrode

This consists of a loose (packed) bed of conductive particles, which floats (becomes fluidised) at certain liquid (up) flow velocities. A feeder electrode is the contact electrode to a fluidised bed.

Passivation

Precipitation of an insoluble insulating layer on the electrode surface so that the electrolysis will come to a standstill.

Spacer

Netlike insulators inserted between cathodes and anodes.

Stack

Array of several plates or grids, in which the individual plates function as cathode and anode alternately e.g. to obtain a series of undivided cells.

Stretched metal

A netlike metal grid, fabricated by punching followed by stretching of a metal plate.

Undivided cell

There is no mechanical separation of cathode and anode zone.