Using Salt for Production of Electrolytic Solutions to Sterilize Polluted Wastes

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ABSTRACT

The "in situ" production of chlorine by electrolysis of a brine of sodium chloride and the injection of this brine into an effluent which to be sterilized are achieved in a simple and economical way by the STERELEC process. The brine used is either sea-water, if the works are by the sea-shore, or brine obtained by dissolving sodium chloride in the case of inland plants.

This process opens the perspective for a new utilization of salt and this use is very large within the scope of pollution prevention, (industrial sewage water, demineralization, treatment of domestic effluent, etc . . .).

INTRODUCTION

The production of chlorine by electrolysis of a solution of sodium chloride may be done in plants established at the actual places where this treatment is needed. The chlorinated solution produced is injected directly into the water or the raw effluent in order to carry out the sterilization or the oxidation process. This process advantageously replaces the use of chemical products such as liquefied chlorine or sodium hypochlorite in solution. It is thus possible to avoid the danger inherent in the transportation and storage of these products and to avoid the expense involved in their handling, especially the handling of liquid chlorine. For industries which happen to be on the sea-shore, the solution of sodium chloride used is natural sea water. In some cases it may be worthwhile to use a more concentrated brine, for example brine coming from a salt-works, if such a plant exists in the vicinity, or brine obtained by dissolving sodium chloride in the water.

For industries inland, an artificial solution of sodium chloride is obviously used. In this case, the concentration of sodium chloride in the solution may be higher than that of the sea-water in order to obtain a better energy efficiency of electrolysis while rendering the conversion rate of the sodium chloride into chlorine more efficient.

PRINCIPLE OF THE ELECTROLYTIC CELLS

The plants comprise three distinct constitutive parts—the electrolytic cell, the electrodes and the power supply (Fig. 1). In the cell, constituted either by a tank or by a vertical stacking of frames, electrodes are disposed vertically and spaced at intervals of a few millimeters. The brine is fed through the bottom of the cell and circulates in the apparatus, spreading among the electrodes. The electrolyzed brine is reclaimed at the top point of the cell and then is directed towards a degasser for the elimination of the hydrogen before use. Only the end electrodes are fed with electric current, the intermediate electrodes acting as cathode on one of their faces and as anode on the other. Each pair of electrodes there constitutes a unit cell which is in series with the neighbouring unit cells. The power supply is provided by a D.C. generator comprising current-regulating auxiliaries.

Lastly, and there is the difficulty of operating this process at low cost. When seawater or a solution of ordinary sodium chloride is in the course of being electrolyzed, deposits of magnesium hydroxide and calcium carbonate rapidly form on the cathodes. The result is a gradual drop in the faradic efficiency incompatible with smooth operation. To solve this problem, the electric plant uses the device of periodical and programmed reversal of electrode polarity; thus the cleaning of the electrodes is done automatically. The frequency of the polarity reversals is variable and adjustable according to the nature of the electrolyzed solution.

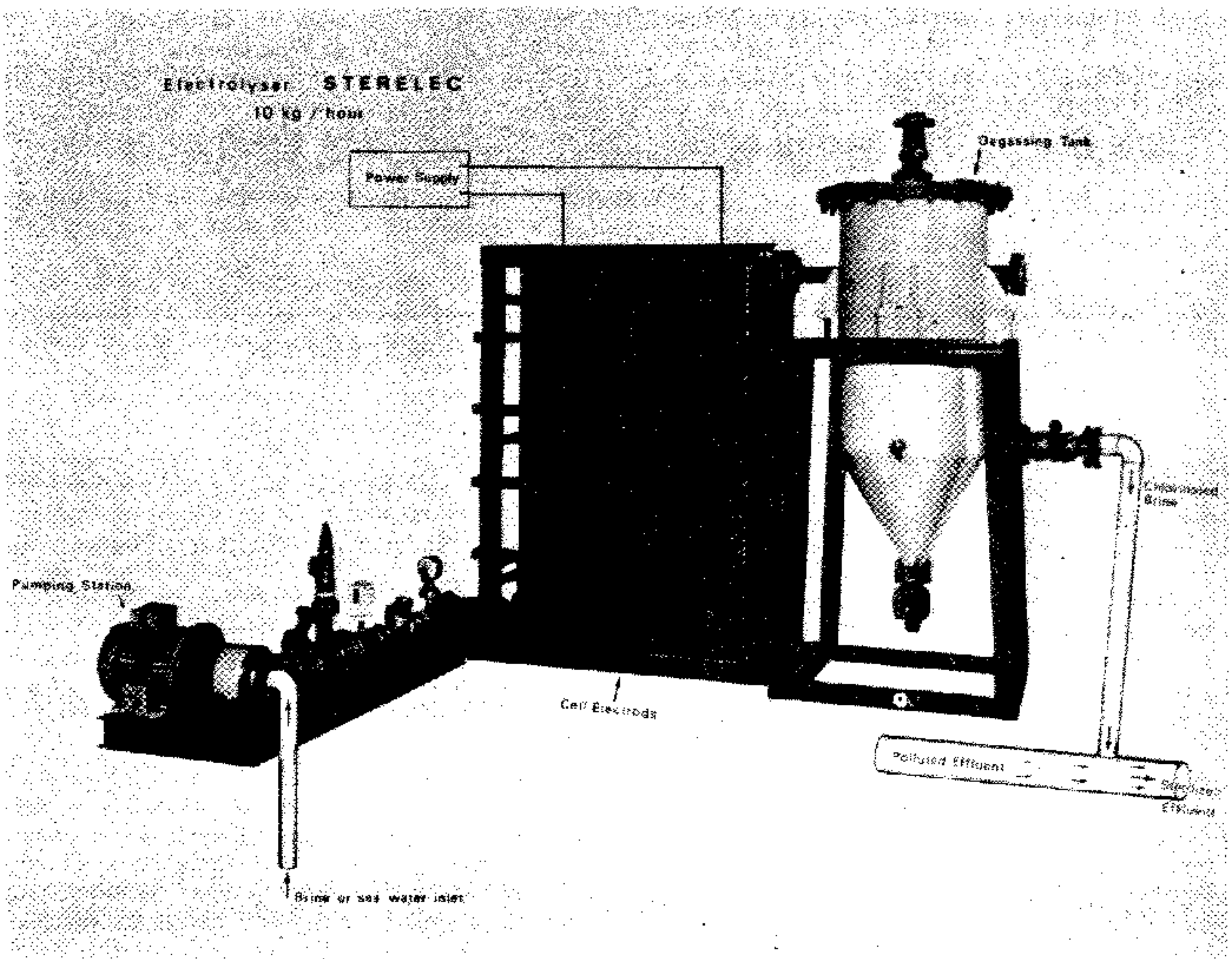

Figure 1.

CONSTRUCTION OF THE ELECTROLYTIC CELLS

The production in situ of chlorine by electrolysis of a sodium chloride solution has not been possible using a reliable technique at low cost until very recently. However, the use of new technologies and materials have in fact made possible the construction of light, electrically well-insulated and corrosion-proof units.

The cells

Plastics, polyvinyl chloride, polyethylene and polypropylene materials were used in construction of the cells. This polypropylene is particularly useful when the plants are set up in the open air (offshore platform equipment) and are exposed to high ambient temperatures. Accessories such as piping, valves, pumps, regulation and control equipment, are also made in these materials.

The electrodes

Several choices of materials were possible in this well known field of the electrolytic chlorine industry. Titanium covered with precious metals like platinum or rythenium is inert to anodic oxidation and has interesting characteristics from the view-point of duration of life and dimensional constancy. However, these electrodes are very costly as compared to electrolytic graphite, the manufacturing qualities of which are now quite satisfactory. Thus the use of graphite appeared to be the very best solution in terms of both technology and overall cost.

Power supply

Particular care is given to the construction of the D.C. generator. The use of thyristors has made it possible to solve the problem of continuous regulating of the current intensity supplied to the electrolyzer and therefore regulation of the quantity of chlorine produced, this production being directly proportional to the current strength. In other respects, recent studies have shown the advantage of using D.C. with a low rate of current fluctuation and the necessity of eliminating the function of polarization of the electrolyser at the time of the cyclic reversals of the polarity of the electrodes.

OPERATION OF THE PLANT

The operation and adjustment of the electrolyzers essentially consists of controlling and regulating the production of chlorine in the brine by regulating the strength of the power supply. This action is obviously combined with the regulating of the output of the brines traversing the cell. Although the need for, and therefore the production of, chlorine can be considered relatively constant for the application of this system to the sterilization of the seawater used for the refrigerating of industrial waste water systems, this is not therefore the application of the process to the bactericidal treatment of urban effluents. In the latter case, the discharge and the contaminating capacity of the effluent may vary to a great extent. The regulation of the chlorine production of the electrolyzer should be automatically adjusted to these variable needs. To solve this problem, the current intensity supplied to the electrolyzer is automatically regulated in accordance with the chlorine demand of the effluent. One or several chlorine analysers continuously check the residual chlorine contained in the treated effluent and automatically control the electric plant.

APPLICATIONS

Sterilizing seawater

Seawater is generally used as refrigeration fluid by the industries established on the sea shore. The growth of micro-organisms such as spores, sea-weed, mussels and other shellfish is enhanced by the temperature conditions reigning in the plants and considerably disturbs their operation. The fouling of the seawater systems sometimes reaches considerable proportions and also has the result of accelerating corrosion phenomena. A means currently used for evading these difficulties consists in injecting chlorine in the pumped water, but that involves the always dangerous handling of liquefied chlorine (sometimes in very great quantities). The purpose of the electrolysis plant is to produce the chlorine required for this sterilizing treatment directly from the seawater. Taking into account the requirement of about 1 ppm of chlorine sufficient to sterilize the seawater, an only small part of the discharge of raw seawater is fed into the electrolysis cell. The chlorine content of the treated brine in the electrolyzer is several hundreds of times higher than needed for sterilization.

As an example, for the treatment of cooling water at 1 ppm, a cell producing 10 kg of chlorine/hr. will take care of a discharge of 10,000 m^3/hour of seawater treated continuously, while only 10 m^3/hr. of seawater will be conveyed through the cell and electrolyzed. On the other hand, it is possible to carry out either a continuous treatment by injection and direct mixing of the electrolyzed brine with the raw seawater or a discontinuous treatment by intermittently injecting electrolyzed brine at a more or less high rate of concentration. This last-mentioned process is used to fight against the incrustation of certain types of shellfish which tend to become accustomed to the presence of a constant quantity of chlorine in water. Of course the operating of these industrial plants is automated and requires no particular supervision.

Disinfection of sewage and/or foul water

The ill-considered discharge of effluents containing a great number of micro-organisms (pathogens, bacteria, virus) into rivers, groundwater or the sea, constitutes a threat for the environment and public health. In particular, the bacteriological contamination of the sea exceeds, in numerous points, the threshold considered as allowable. This has occurred to such an extent, as has already happened in France, that the health authorities are obliged to prohibit bathing on certain beaches. For the same reasons, shellfish may attain a degree of bacteriological and viral pollution that it becomes necessary for these shellfish to undergo a special treatment before they can be used commercially.

The sterilizing treatment of these effluents can be done with electro-chlorination plants, and we recently have carried out very conclusive tests on the efficiency of the process (Fig. 2). Recalling schematically that the action of chlorine on contaminated effluents is due to its bactericidal power and its oxidizing power with regard to the impurities of organic or mineral origin contained in these effluents, it is clear that the efficiency of these actions depends very much on the physicochemical characteristics of the raw liquids.

Efficiency of the treatment

Bactericidal action of chlorine. The total destruction of bacteria contaminating seawater in a concentration of 10^7 bacteria per cm^3 has been obtained by injecting this water with chlorinated brine so that the content in residual chlorine of the treated water remains in the neighbourhood of 1 ppm after a contact period of 30 minutes. For urban effluents the chlorine requirement measured by the breakpoint method may vary from 20 to 40 ppm, and the sterilization of these effluents has also been obtained by maintaining in the treated effluents a residual chlorine content of 1 ppm after a contact of 30 minutes.

Oxidizing action of chlorine. For these same urban

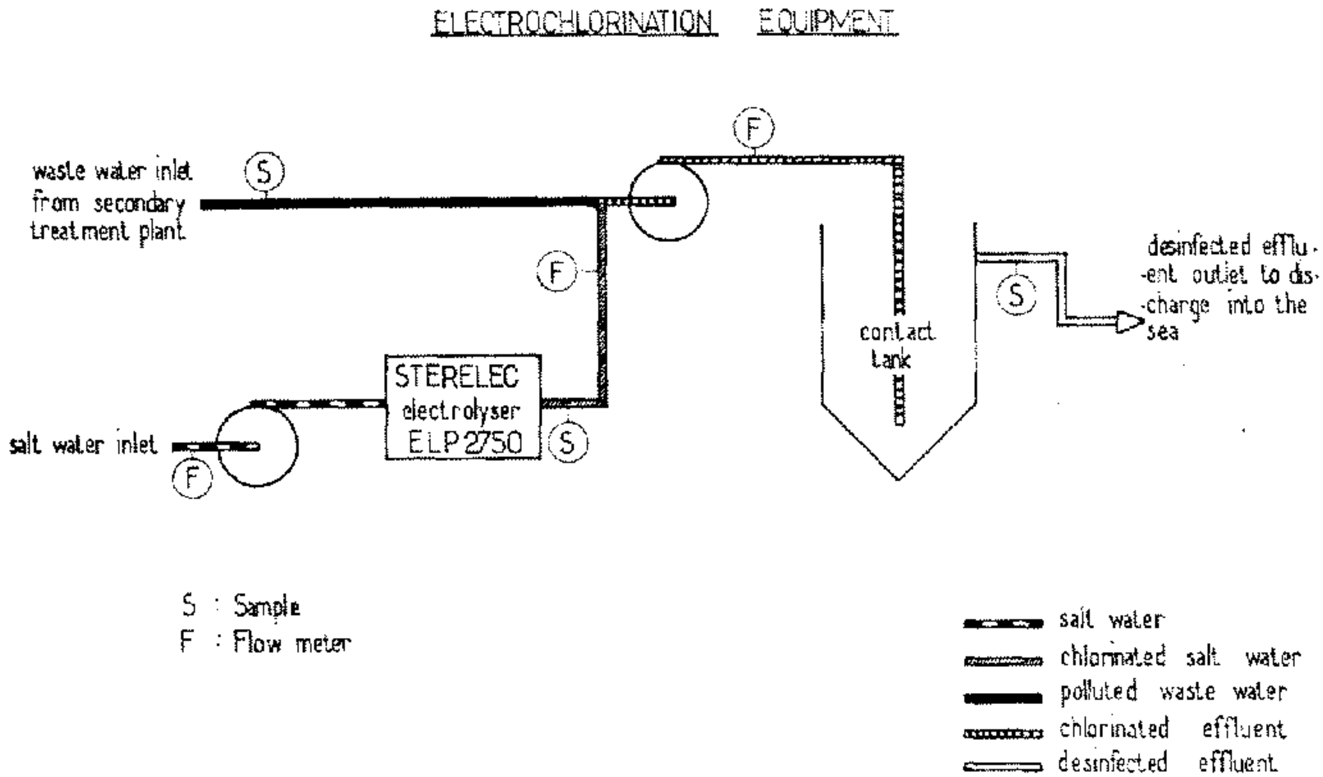

Figure 2.

effluents for which the chlorine requirement was from 20 to 40 ppm, the reduction of the initial Biochemical Oxygen Demand 5 of about 70% and the Chemical Oxygen Demand of about 30 to 50% was obtained by injection with chlorinated water at a concentration between 20 and 40 ppm and for a contact time of 30 minutes. Other treatment tests on urban effluents have given the following results (Table I)

TABLE I

Quantity of chlorine injected : 9 ppm
Quantity of residual chlorine : 1 ppm

	Condition of the Water	
	Before Chlorination	After Chlorination
Aerobic germs at 20° per 1 ml	11,000,000	380,000
Coliform bacteria per 100 ml	110,000,000	46,000
Escherichia Coli per 100 ml	11,000,000	0
Streptococci Group D per 100 ml	4,600,000	0

These results show that the pathogenic germs (fecal Streptococci and Escherichia coli) have been entirely destroyed.

Other applications

Very varied applications are possible within the scope of the basic processes just described. For example, a sample list might include

1. the shipbuilding industry: condensers, distillation of potable water, treatment of the waste water before flushing it away.
2. Municipal plant for treating domestic effluents: chlorination, disinfection, deodorization.
3. Pumping stations, fresh water or seawater: protection of pipes, pumps, valves, reservoirs, etc ...
4. Sterilization of the washing water for food products.
5. Sterilization and rendering demineralized water drinkable.
6. Disinfection of pleasure ports and ponds.
7. Treatment of seawater swimming-pools.
8. Protection of softening or demineralizing resins against blockage by micro-organisms.

USE OF THE ELECTROLYZERS WITH ARTIFICIAL BRINES

Electrochlorination was first done using seawater as the electrolyte. This arrangement is the most economical, but limits its field of application to users situated on the sea shore. For the treatment involving the sterilization of industrial or domestic effluents located inland, electrochlorination from artificial brines nevertheless remains a worthwhile process, because it has the advantage of being simple and reliable as compared to the conventional chlorination units where the use of gaseous chlorine is always tricky if not dangerous. In order that the electrolyzers may operate with great efficiency, both from the practical viewpoint of saving cost, we have perfected their operation in order to obtain improved conversion rate of sodium chloride into chlorine, because this means a reduction in the volume of brine to be prepared and injected into the raw liquid.

There are two methods of obtaining this result 1) Use a brine with concentration in sodium chloride about that of seawater and recycle this brine several times in the electrolyzer. This method allows the consumption of sodium chloride to be limited to 5 kg. for a production of 1 kg. of chlorine, the electric power consumed is then about 12 kWh per kilogram of chlorine. 2) Use a brine with concentration in sodium chloride double that of seawater. In this case the consumption of sodium chloride is about 8 kg for a production of 1 kg of chlorine, and the electric power consumption is 10 kWh per kg of chlorine.

Chlorine production versus electrical energy consumption

One important aspect of the search for the maximum conversion rate resides in the reduction of the sodium chloride content in the sterilized effluents which are finally discharged outside in the open (Fig. 3). The acceptable substitution of this electrochlorination process for the conventional method of chlorination should not result in

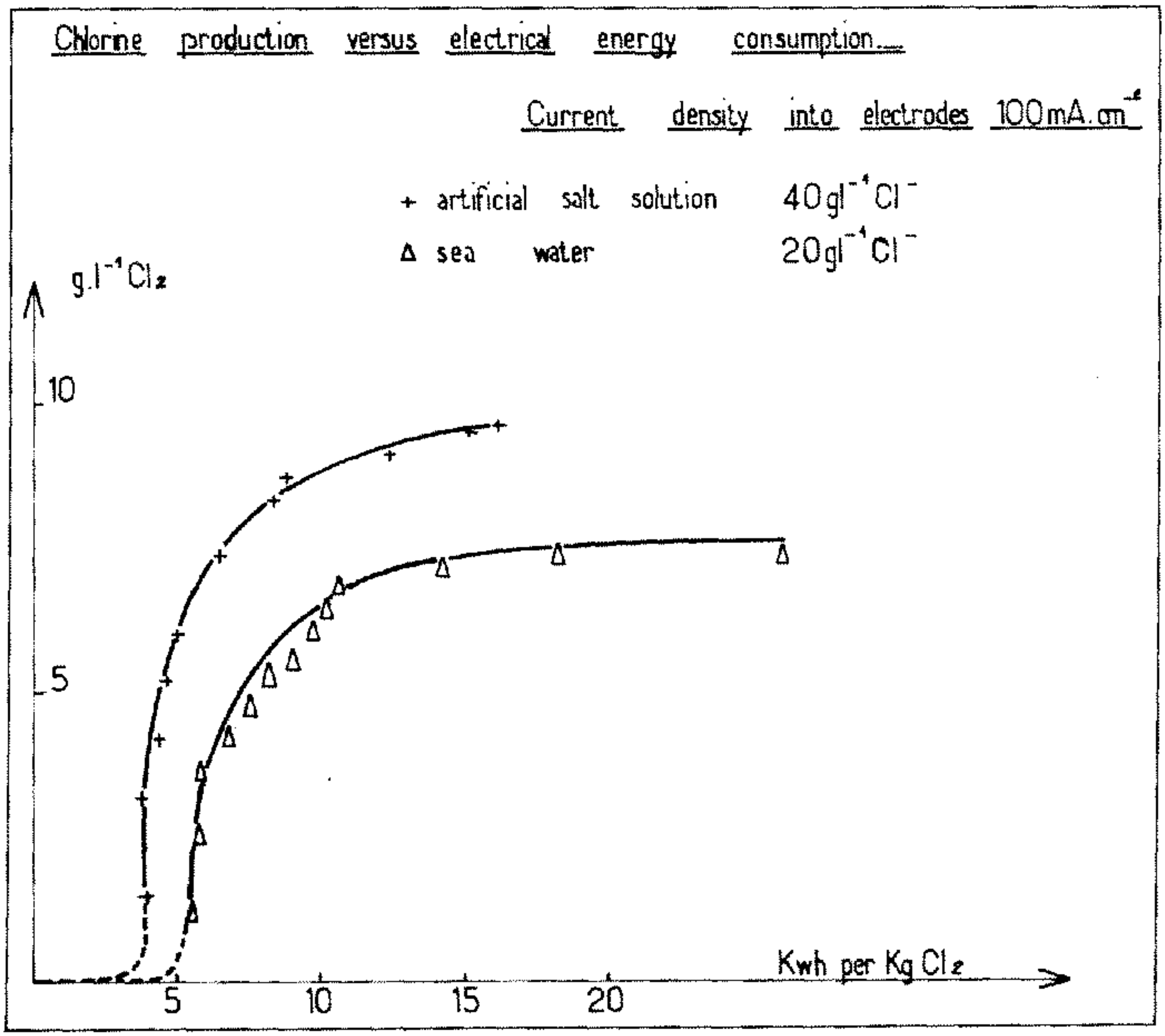

Figure 3.

any pollution, since for an effluent treatment at 4 ppm of chlorine, the sodium chloride content of the effluent, sterilized and discharged in the open, would be only 30 ppm. This is quite acceptable, in fact is negligible. The applications of electrochlorination for sterilizing effluents of all kinds and in all places are therefore possible.

CONCLUSION

Within the scope of man's action worldwide to reduce and suppress the pollution of nature, in particular the sea, rivers and ground water, we believe that the simple and reliable characteristics of electrochlorination may be a safe and economical solution on sterilization problems. Inasmuch as the supplies necessary for the operation of these plants are restricted to sodium chloride or seawater and to electric power, the reliability and operating problems are singularly limited as compared to those which involve the handling of the chemical products currently being used.