# Laboratory Section

## ELECTROLYTIC PRODUCTION OF SODIUM HYPOCHLORITE.*

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So much has been said and written about the use of hypochlorite, and so many cities and towns have adopted it for disinfecting their water supplies, that we seem to be living now in the age of hypochlorite.

From the very beginning of this movement many chemists and engineers have felt that the public would object to the application of bleaching powder to their water supply, and also knowing some of the disagreeable features incident to its use, felt that the very unique and attractive method of passing an electric current through salt water would not only overcome all aesthetic objections to the disinfection of public water supplies, but would offer a clean, cheap and attractive method of purification.

Calcium hypochlorite, the active constituent of bleaching powder, has, however, been almost universally adopted in preference to the sodium-hypochlorite produced electrolytically, for the reason that no electrolyzer has been put on the market that has proven itself successful from an economical standpoint, for water purification at least, and any new process, no matter how ingenious or unique, must be able to produce a better product, or the same product at a less cost, before it can hope to supplant older and tried out methods.

Charles Watt was the first chemist to discover (1851) that hypochlorite solutions could be produced by electrolysis. The electrolytic production of hypochlorite then remained dormant until 1884. Since that time a number of cells have been developed, but the original reactions and principles are the same as patented by Watt and the electrolyzers that have been developed since differ only in points of construction.

There are two general types of electrolyzers for dissociating sodium chloride. In one the cathodic and anodic products are allowed to recombine in the main body of the electrolyte and in the other, known as the diaphragm process, the products are removed separately from the cell as produced.

For the production of sodium hypochlorite the non-diaphragm process has been considered best because it dispenses with the destructible diaphragms and the loss of energy that all such diaphragms occasion.

As previously stated the hypochlorite cells differ only in matters of construction and may be described as follows:

The bath is divided into compartments by numerous electrodes with small spaces between them, through which the salt solution is made to circulate. Each set of two electrodes becomes a cell, and the vat a battery of cells. By adopting this chamber arrangement or multipolar electrode arrangement, hypochlorite electrolyzers can be built to utilize almost any current conditions that are available. For instance, if a dynamo of 220 volts and 25 amperes is at one's disposal 50 electrode plates can be employed, forming 49 cells. In each cell there will be a tension of 4.5 volts and a current of 25 amperes will pass; thus the action of a current of 4.5 volts and 1225 amperes will be attained.

When a direct current of electricity is passed through a solution of sodium chloride, sodium is liberated at one pole and chlorine at the other. The liberated sodium reacts on the water breaking it up into hydrogen and hydroxyl ions to form sodium hydrate. The sodium hydrate in turn combines with the chlorine to form sodium-hypochlorite. (Na O Cl.)

There are however, many side reactions taking place and what actually happens in the electrolytic production of sodium hypochlorite solutions is about as follows:

First, electrolysis of sodium chloride with formation of sodium-hydrate, hydrogen and chlorine. Second, formation of sodium hypochlorite, by action of chlorine on sodium hydrate. Third, formation of sodium chlorate by oxidation of sodium hypochlorite. Fourth, electrolysis of sodium hypochlorite and chlorate as soon as they begin to be present in appreciable amounts. Fifth, the reduction of the sodium hypochlorite by the action of hydrogen produced at the cathode. Here we have the electrical energy impressed on the electrolyte first consumed in oxidizing chloride to hypochlorite and subsequently reducing it again to chloride, the net result being the conversion of electrical energy into heat, heat favoring the formation of chlorates.

The side reactions make it difficult to build high current efficiency cells.

Two methods have been suggested for preventing the oxidation of the hypochlorite to chlorate.

First, by keeping the electrolyte at a very low temperature.

Second, Lunge* has suggested that enough sodium, calcium or magnesium hydrate be added to absorb and utilize the excess chlorine usually found in electrolyzed salt solutions, since the presence of free chlorine is favorable to the conversion of hypochlorite to chlorate.

A method for checking the reducing action of hydrogen on the hypochlorite is described in an English patent. The electrolyte is made by adding to every 14 liters of 10% salt solution, 40 grams of calcium chloride, 30 grams of lime and 50 cc. of a strong solution of resin in caustic soda. In this way, a film, probably calcium resinate, is formed on the cathode and hinders the hydrogen from acting on the hypochlorite.

In the electrolytic dissociation of sodium chloride there is a definite minimum voltage required for carrying out the reaction, and this voltage figured according to the thermochemical equation is computed to be 2.3 volts, but Lunge† has shown that in the production of sodium hypochlorite where the chlorine formed at the anode combines with the sodium hydrate formed at the cathode, the calculation is different and the minimum theoretical voltage required to carry out the reaction is 3.54 volts.

Taking this minimum theoretical voltage required to bring about the desired reactions, one kilowatt gives 282 amperes. One ampere hour is theoretically capable of producing 1.32 grams of chlorine, so that 1¼ kilowatt hours are necessary to produce one pound of available chlorine. This represents a process of 100% efficiency on both current and energy basis. One pound of available chlorine represents the dissociation of 1.6 pounds of salt. (Na Cl.)

Placing a value of two cents per kilowatt hour on the current, and assuming the cost of salt to be three pounds for one cent, the cost of one pound of available chlorine would be a little more than three cents. One pound of available chlorine as bleaching powder costs in the market from 3.5 to 4 cents.

The electrolyzers that have already received industrial trial have shown very low efficiencies.

Roscoe and Lunt‡ discuss in detail the results obtained by electrolyzers that had received industrial trials up to 1895.

According to their figures:

The Corbin  cell showed an energy efficiency of 21%
The Hermite   "      "     "     "      "       23%
The Kellner   "      "     "     "      "       25%
The Woolf     "      "     "     "      "       31.5%
The Vogelsang    "      "     "      "       35.5%

* Journal Soc. of Chemical Industry. 1885, page 722.
† Sulphuric Acid and Alkali. Lunge. Vol. 3, page 637.
‡ Journal Soc. of Chemical Industry. 1895. page 24.

Taking the best of these we find that with the current costing 2 cents per kilowatt hour one pound of available chlorine would cost 5.5 cents for elcetrical energy alone.

Among the more recent cells that have attracted some attention are the Dayton Cell and the Hass-Oettel. The first is described by Rickards* and his most favorable results show that one pound of available chlorine can be made with 2.62 kilowatt hours of current and 6.9 pounds of salt. These figures were obtained by keeping the electrolyte at a very low temperature by means of ice. Without the cooling process 3.62 kilowatt hours and 7.2 pounds of salt were necessary.

With the second cell Duckworth† was able to make one pound of available chlorine using 2.84 kilowatt hours and 11 pounds of salt.

In our own experiments and in the practical operation of the cells that have been subjected to practical tests, it has been necessary to use an electromotive force of 4 to 4.5 volts to carry the current through the salt solution. On account of the side reactions involved current efficiencies have been low, and owing to the fall in efficiency which accompanies the proportion of hypochlorite present in the electrolyte, the resultant liquid always contains large quantities of sodium chloride in its original form and rarely more than 18% or 20% of the chlorine present in the form of chloride is converted into hypochlorite. Even though a cheap current is available, further salt savings than have yet been secured are necessary, before electrolyzers, in which the recombination of the anode and cathode products take place in the main body of the electrolyte, can compete with calcium hypochlorite.

* Quarterly Bulletin Ohio State Board of Health, Oct.-Dec., 1909.
† Soc. of Chem. Industry. Nov., 1905.