THE LE SUEUR PROCESS FOR THE ELECTROLYTIC PRODUCTION OF SODIUM HYDROXIDE AND CHLORINE.[1]

BY CHARLES LATHROP PARSONS.

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HISTORY.

ERNEST A. LE SUEUR enjoys the distinction of having invented the first electrolytic process for the commercial decomposition of sodium chloride, which became a regular contributor to the markets of the world. Since February, 1893, caustic soda and bleaching powder have been manufactured at Rumford Falls, Maine, on a commercial scale. Le Sueur is now general manager of the plant, and deserves the highest credit for his efforts in this important branch of chemical science and industry.

He first began his experiments in the winter of 1887-88, and after associating with him Charles N. Waite, who afforded him valuable assistance and some facilities at his chemical works at Newton, Mass., they together ran an experimental cell from October, 1890, to May, 1891, in a paper mill at Bellows Falls, Vermont. In the meantime, Le Sueur had applied for his patents, and having obtained a cell giving an efficiency of rising seventy per cent., he went to England in May, 1891, for the purpose of presenting his process at the seat of the alkali industry. There he met with much encouragement from scientific men, but with discouragement so far as the adoption of his method on a commercial scale was concerned. The article of Cross and Bevan[2] gives a good description of the method at the time, but as theirs is the only authoritative article ever published regarding the process, it is not at all strange that Lunge[3] has some doubts of a method which must renew its diaphragms every forty-eight hours, and which converts its caustic solution into bicarbonate. As a matter of fact, carbonate of soda, as sodium carbonate or acid carbonate, has never been a product and the diaphragms are renewed so seldom that their cost is a mere incident of the process.

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[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

[2] *J. Soc. Chem. Ind.*, December, *1892*.

[3] Alkali Industry, Vol. III.

In 1892, an association was formed, which in August of that year began the erection of a plant at Rumford Falls, and in February, 1893, began the manufacture of caustic soda and bleaching powder, using, to generate the required electricity, one 200 kilowatt dynamo of the Thompson–Houston pattern. The success of the venture was such that three more dynamos of the same capacity were installed in the fall of 1894, and the Electro-Chemical Company was organized. As a member of that company since its inception, I am fortunate in having the cooperation of Mr. Le Sueur and in being authorized to present to you a description of the process as it is running to-day, with such comments on past experience as I may deem of interest to you.

THE PROCESS.

The first practical working cell devised and used is well illustrated in the accompanying figure (Fig. 1), and is much the same as that described by Cross and Bevan in their aforementioned article. It consisted essentially of a bell of earthenware containing the gas carbon anode, and having its mouth covered by the diaphragm which was in contact with the anode, and was held in place by iron wire gauze forming the cathode of the cell. The whole was placed in an iron tank containing saturated brine and the bell was filled with brine to a level above that of the cathode compartment. The electrodes were close together,

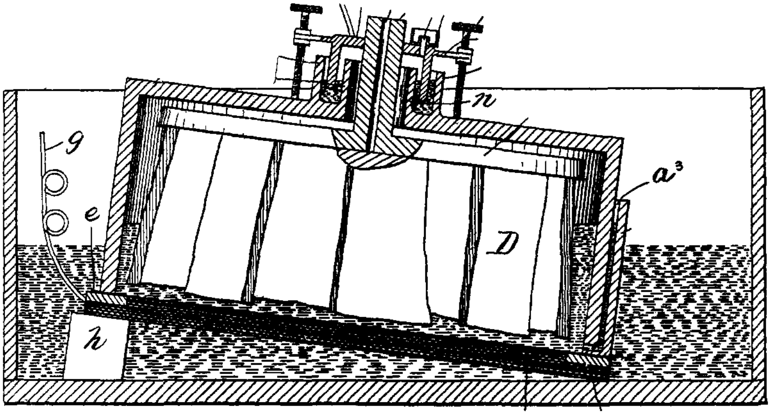

FIG. 1.

and the internal resistance of the cell was small. The carbon anode was produced from large pieces of gas carbon imbedded in lead at one end above the liquid, and usually packed with smaller pieces of carbon, so as to give a large anode surface in contact with the diaphragm (see Figs. 2, 3, and 4). The iron wire gauze forming the cathode was never in contact with the chlorine gas, and was so little acted upon by the caustic soda solution that it was one of the most permanent parts of the cell. This is also true of the iron tanks containing the cells and caustic solution. The diaphragm consisted of asbestos and had to be renewed every few weeks. This diaphragm was by no means expected to entirely prevent all diffusion of sodium hydroxide into the anode compartment nor of some hypochlorite in the reverse direction, but it did largely prevent the two solutions from mixing. Such a cell gave a working efficiency of about seventy per cent. and could be worked with an electromotive force of about four volts. It was soon found that the earthenware bell was not a practical form of apparatus, as they were easily broken, and even cracked by change of temperature. Consequently a new form of covering was devised, made from slate, with a spruce frame, which came in contact with the

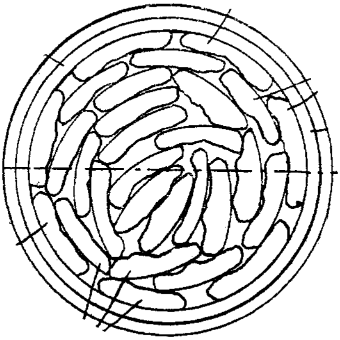
FIG. 2.

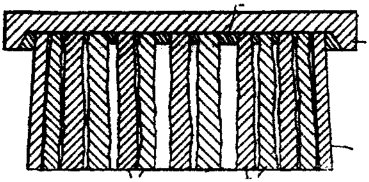
FIG. 3.

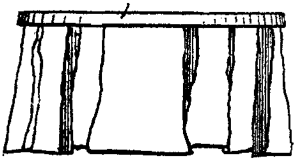
FIG. 4.

caustic solution only, and was little effected thereby. The essential features of the process remain the same.

On passing the current reactions took place much as described by Oettel,[1] the main one being the electrolysis of sodium chloride, forming sodium and chlorine, the sodium immediately attacking the water in the cathode compartment, giving off hydrogen and leaving sodium hydroxide in solution. The chief difficulty of the process has always been to keep the sodium hydroxide in its proper compartment, for with the very best of diaphragms a limited amount of diffusion into the anode compartment will take place. Secondary reactions at once set in between any diffused sodium hydroxide and the chlorine present, forming sodium hypochlorite, which in turn will partially diffuse into the outer space and, contrary to Oettel's experience, is not reduced at the cathode, but is oxidized to sodium chlorate either before diffusion or during the evaporation of the cathode solution, and is eventually recovered as a by-product in the form of potassium chlorate. Besides the formation of hypochlorite, the diffusing sodium hydroxide is itself partially electrolyzed and the oxygen produced will immediately attack the carbon of the anode, very much complicating matters by forming carbon dioxide. The electrolysis of sodium hypochlorite will also give rise to nascent oxygen and increase the amount of carbon dioxide produced. This formation of carbon dioxide is a very serious matter in the production of bleaching powder, for unless removed from the chlorine gas it renders impossible the manufacture of a standard grade. The carbon anodes may be graphitized, rendering them much more resistant, but this difficulty is entirely eradicated when platinum is used. All of the reactions taking place in the anode compartment have been, without reference to the diaphragm, largely reduced by two patents of Le Sueur, which have broadly protected features that are, in my opinion, essential to the successful production of sodium hydroxide and chlorine by any method electrolyzing salt solution and using a diaphragm. The first of these is to have the liquid of the anode compartment at a higher level than that of the cathode, thus diminishing the entrance of sodium hydroxide by diffusion; and the second is to add hydrochloric acid to

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[1] *Chem. Ztg.*, *1894*, pp. 18 and 69.

the anode compartment so as to keep the solution slightly acid. This hydrochloric acid so added at once decomposes any hypochlorite, and is itself oxidized so that all of its chlorine is regained in the form of that gas. No chlorine is lost by this operation, for the chlorine obtained as bleaching powder is just so much greater than the equivalent of the sodium hydroxide as the amount of chlorine in the hydrochloric acid added. To the Electro Chemical Company this use of hydrochloric acid is a matter of some expense, for an equivalent of chlorine at Rumford Falls costs a little more in the form of hydrochloric acid than it is worth in bleaching powder. It will readily be seen, however, that in other localities and, especially near Le Blanc soda factories, the use of hydrochloric acid would be a positive advantage from a standpoint of economy.

The Le Sueur cell at present in operation at Rumford Falls embodies all the essential features which I have outlined, but it is larger, simpler of construction, and the carbon anode has at last been discarded in favor of a special form of platinum anode recently invented by Le Sueur. The cell as now used (Fig. 5) is contained in a tank five by nine feet and one and one-half feet deep, and made of one-quarter inch boiler steel. Excepting the asbestos, which composes the diaphragm, the wire netting of the cathode, and the materials of the positive electrode, it is built entirely of spruce, red brick, Portland cement, sand, and slate. These substances are so disposed in the cell as to be practically permanent, the wood being exposed to no action except that of the caustic solution, which has little effect upon it. The anodes are introduced from the top of the cell and may be removed singly without interrupting the process. Troublesome

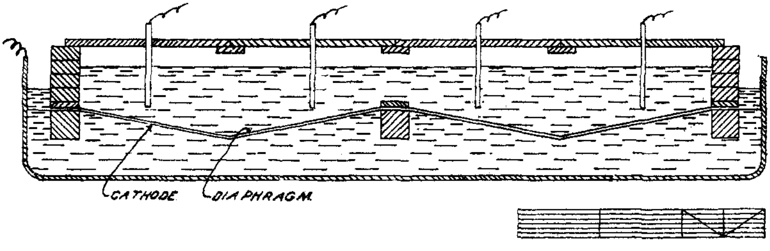

FIG. 5.

joints are closed with a specially prepared plastic cement. The diaphragm is tipped somewhat from the horizontal for the purpose of permitting the easy egress of the hydrogen bubbles. The foundation of the cell within the tank consists of an oblong frame of spruce, eight feet four inches by four feet ten inches, outside measurement, and eight inches less on both dimensions inside. This frame is eleven inches deep, only the side pieces, however, resting upon the floor of the tank. The end pieces consist of four four-inch timbers whose upper surfaces are ten inches above the floor of the tank and one inch below the top surface of the longer side. The frame is divided transversely by a timber, similar to each of the end timbers, which crosses the middle of the frame at the same level as the end pieces. This center beam forms a bridge over which the flat iron ribs supporting the cathode are hung. The cell is thus divided into two equal spaces merely for mechanical convenience. The ribs referred to consist of four parallel pieces of flat iron, three of them being one and one-half by three-eighths inch, and the fourth, twice as wide. This wider piece is fastened at both ends to the containing tank, so as to receive from the latter the electric current which enters through the material of the tank and communicates the current to the cathode which rests upon these iron ribs. The diaphragm rests directly upon the cathode. The depth of the trough formed by the slanting ribs is four inches. There is an adequate arrangement at the ends of the bridge pieces by means of which the hydrogen, finding its way to this higher level, is delivered to exit pipes communicating with the atmosphere or with any system of piping to which it is desired to deliver it. The inch of space between the tops of the cross timbers and the side pieces is utilized to take a piece of slate four feet long by four inches wide by one inch thick. This presses down upon the diaphragm and the cathode netting and keeps all solid. On top of the sides and ends of the frame there are four courses of common brick laid in clear cement. There is a coating of cement applied to the inside walls of the portion of the cell forming the anode compartment, and this includes not only the brick walls, but the small portion of the wooden sides above the cathode which would otherwise come in contact with the anode liquid. The ceiling of the cell consists simply of pieces of slate two feet by one foot, and suitably supported by transverse strips of slate one inch thick by four inches wide. Through the ceiling plates pass the glass tubes to which the anodes are attached.

The anodes which are now used are made from an alloy of iridium and platinum, and are so constructed that a very large anode surface is presented at an almost incredibly small cost when it is considered that it is not at all of the nature of a plated surface, but is an anode of solid metal. Sixty anodes on an average are used to each cell, and each anode costs seventy-three cents at the present market price of platinum. They are acted upon chemically but slightly if at all. If the glass holders break there is no loss of platinum and a new anode can immediately be put in place. The total cost for the anodes of a plant producing, per month, 200 tons of bleaching powder, is approximately $5,000, or $40 for a cell producing fifty-five pounds of sodium hydroxide and fifty pounds of chlorine per day; and this allows for a very low cell efficiency. The total cost for the renewal of the platinum, including labor, is less than half the cost of the bare carbon alone as it was formerly used. Besides, it must be remembered that carbon anodes are certain to give more or less carbon dioxide if hypochlorite be present, while with these iridio-platinum anodes no carbon dioxide can possibly be produced.

At Rumford Falls, the Electro-Chemical Company obtains power at a very low cost, so that it pays to obtain a maximum of work from each cell by using a higher current density in proportion to the anode surface than might be tenable under other conditions. As the cells are now constructed, a current of 1,000 amperes is passed through each cell under a pressure of six and one-half volts. I am aware that this voltage is high, and from a statement in Lunge,[1] he would probably, at first thought, condemn the process on this ground alone. But it will readily be understood how this increased voltage can be economically employed when it is considered that at $8.00 per electrical horse power per year, which is the cost of power to the company at Rumford Falls, the extra cost per pound of product, on an average efficiency of eighty per cent., is but $0.00015 for each extra volt used. This high voltage is, by no means, an essential of the

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[1] Alkali Industry, Vol. III.

process, and each cell can be run on a lower amperage when, of course, less pressure would be required. It is simply a fact that, at Rumford Falls, it is economical to run the cells on this voltage, forcing through them all the current they can take without undue heating. Under these conditions, the renewal of the cell is usually made necessary only on account of the deterioration of the diaphragm. The diaphragms have an average life of seven weeks, and have been used twenty-four consecutive weeks without renewal. The cathodes are but little acted upon, and the steel tanks are practically indestructible.

The cells are arranged so that twenty-two are in series, and three series are run in parallel on two dynamos. The hydrogen is used only for working platinum, the larger part being allowed to escape into the atmosphere. The chlorine is conducted by earthenware pipes to lead chambers and absorbed by lime in the usual manner, although, at present, a part is used for the manufacture of potassium chlorate. The caustic solution is concentrated by evaporation *in vacuo* and is separated from the major part of the undecomposed salt by centrifugals. Any chlorate is now readily removed, and the solution is then boiled down in cast-iron kettles to a first quality caustic soda analyzing about seventy-four per cent. sodium oxide. The recovered salt is converted into brine and is used in the cathode compartment of the cells,—nothing but fresh brine and some hydrochloric acid being ever added to the anode side. Whole bays of twenty-two cells have shown daily averages of over ninety per cent. chlorine efficiency, and weekly averages of eighty-seven per cent. If the anode compartment could be kept constantly acid, as can be done with single cells, a chlorine efficiency approaching very closely to the theoretical may be reached. The efficiency reckoned upon the sodium hydroxide produced is not quite so high.

One great field for electrolytic processes is the production of bleaching liquors and caustic solutions for bleacheries, paper mills, and the like. Large economies might be introduced by companies of this kind by making their own solutions electrolytically instead of by the usual method of first transporting the chlorine in the form of bleaching powder and the alkali in the solid state. This is almost self evident when one considers that juice at 17.5° C. Such methods of estimating solids are, of course, only applicable in the case of fresh juices, before the beginning of the alcoholic fermentation. The following table gives the percentage of solids, as estimated and actually determined in a number of different juices.

No.	Kind of juice.	Specific gravity 17.5° C.	Degrees Brix.	Solids by formula 245 (S—1). Per cent.	Actual solids at 70° C. *in vacuo*. Per cent.
1	Apple juice (second pressing)	1.0376	9.39	9.21	9.14
2	" "	1.0474	11.73	11.61	11.36
3	" "	1.0481	11.90	11.78	11.81
4	" "	1.0484	11.97	11.86	11.87
5	" "	1.0488	12.07	11.96	11.71
6	" "	1.0517	12.75	12.67	12.78
7	" "	1.0525	12.94	12.86	12.77
8	" "	1.0539	13.26	13.21	13.29
9	" "	1.0559	13.73	13.70	13.94
10	" "	1.0560	13.76	13.72	12.83
11	" "	1.0568	13.94	13.92	13.84
12	" "	1.0613	14.99	15.01	14.90
13	" "	1.0722	17.50	17.69	16.82
14	Strawberry juice	1.0420	10.44	10.29	9.64
15	Red raspberry juice	1.0463	11.47	11.34	11.01
16	Black raspberry juice	1.0567	13.92	13.89	13.65
17	Red cherry juice	1.0461	11.42	11.29	11.22
18	Black cherry juice	1.1034	24.42	25.33	24.30
	Average	......	13.42	13.41	13.16

The formula, as a rule, gives results slightly closer to the actual percentage of solids, except in case of juices of very high gravity, as No. 18 of the preceding table. The difference between actual and calculated results rarely exceeds 0.2 or 0.3 of a per cent.; there is occasionally, however, a notable discrepancy as in the case of apple juices Nos. 10 and 13. Calculating the solids from the gravity of a juice is sufficiently accurate for many purposes; such an estimation is preferable, in any case, to the old method of determining solids by drying at 100° C.

Ash.—This was determined according to the official method, about 20 grams of material being taken for analysis. In incinerating large quantities of material, to obtain ash for the ash analysis, it is necessary to exhaust the charred mass first with water. The insoluble residue is collected on a filter, burned, and this ash added to the residue left on evaporating the aqueous extract. The whole is then heated to a low redness till the ash is white.

Reducing Sugar.—This was calculated, in the various analyses given, simply as invert sugar. Strictly speaking this is not correct, for the dextrose and levulose of fruit juices are present in, by no means, equal proportions, as in apple juices where the percentage of levulose is nearly double that of dextrose. Nevertheless, when these sugars are not separately determined, it has seemed to the writer more accurate to consider the reducing sugar as invert rather than dextrose or levulose alone. The invert sugar is calculated from the weight of reduced copper according to the tables of Meissl and Wein ; such small amounts of sucrose, as are present in fruit juices, do not affect the accuracy of the determination.

In the determination of reducing sugar in fruit juices, 20 cc. of the filtered juice are measured out into a 500 cc. flask, about 300 cc. of water are added, and, after neutralizing carefully with sodium hydroxide using phenolphthalein, the volume is completed to the mark. Twenty-five cc. of this solution (1 cc. of original liquid) are taken for the copper reduction. The reduced cuprous oxide is filtered in asbestos tubes and, after drying, reduced in a current of hydrogen, and the weight of copper determined. In case of partly fermented juices larger amounts of liquid can be used for dilution. With completely fermented ciders and vinegars, which contain but very little sugar, the liquid after neutralizing needs little if any dilution. In calculating the percentage of reducing sugar, it is, of course, necessary to take into account the specific gravity of the liquid analyzed.

In determining reducing sugar in apples and other whole fruits the following method was adopted : 100 grams of the grated pulp are washed on a muslin filter in a large funnel, with repeated quantities of cold water, the filter being squeezed after each addition of water to hasten the removal of the sugar. The filtrate is caught in a 2-liter flask, and the washing continued until the liquid is nearly up to the mark. After completing the volume, the flask is shaken, and 200 cc. (10 grams of fruit) of the filtered solution are transferred to a 250 cc. flask ; this solution is neutralized with soda as before and the volume made up to 250 cc. from which 25 cc. (1 gram of fruit) are taken for the copper reduction.

The same method is used with evaporated fruit products, as with whole fruit, except that a smaller amount of material is taken for analysis. Twenty-five grams of the finely cut material

DAILY OUTPUT.

20,000 pounds bleaching powder, at 1½ cents	$300.00	
7,000 pounds caustic soda, at 1½ cents	105.00	
	405.00	
Less freight to market and commission	55.00	
Total daily income		$360.00

Local conditions effecting cost of raw material, freight, and power, and changes in market price of product, would greatly influence the value of this estimate. With these figures, however, any one may readily calculate the probable cost in any locality when the conditions affecting it are known.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE.]

COMPOSITION OF OHIO WINES.

BY ALBERT W. SMITH AND NORMAN PARKS.

Received September 2, 1898.

NORTHERN Ohio is one of the most important grape-growing regions in the United States, and produces no inconsiderable quantity of wine from the yearly growth, but, so far as we are aware, no systematic study of the chemical composition of these wines has ever been undertaken. In order to determine whether a sample of wine is pure or not, it is often necessary to know what is the average chemical composition of samples of guaranteed purity, made from the same kind of fruit and grown in the same region. An examination of a large number of Ohio wines, bought in this market, showed a considerable variation in composition from the average of French, German, and California wines. It was thought desirable to ascertain if this was due to a very universal sophistication of Ohio-made wines in this market, or whether it was due to an actual difference in the nature of the fruit grown here, or possibly in the method of manufacture and fermentation.

In the fall of 1894, and of 1895, samples of most of the prominent varieties of Ohio grapes were collected, the juice expressed