THE HERMITE ELECTROLYTIC PROCESS AT POPLAR.

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DR. F. MOLLWO PERKIN, TREASURER, *in the Chair.*)

This Paper is a contribution to the data at present available on the subject of the electrolytic production of hypochlorites. It is unnecessary here to recapitulate the history of the various processes for effecting the electrolysis of chlorides so as to produce hypochlorites, or to allude to the purposes for which hypochlorite solutions are adapted; for purposes of reference these subjects are briefly treated of in Appendices A and C. The utility of the substance being well proved by practical experiment and by scientific investigation, it only remains to show how it may best be produced on a commercial scale. A variety of processes are in existence, and of those which have been reduced to a practical form the best known are the "Hermite," "Electrozone," and the "Oxychloride." Which of these processes is the most advantageous at present, *i.e.*, which produces the largest quantity of stable fluid for the least expense in electricity, labour, and salt, is a question which only careful observation of the apparatus under working conditions can properly decide. Unfortunately, hitherto, the accessible examples of plants actually working on more than an experimental scale (involving the constant and costly alterations natural to experiments) have been extremely few; the author only knows of one in this country, namely, the Hermite plant at Poplar. The following data have therefore been collected from runs undertaken at this installation in the ordinary course of working for supplying disinfectant to the borough. They go to show the eminently practical nature of this installation, as well as its efficiency, and the small amount of supervision and labour which is necessary.

The system adopted at Poplar is to mix a certain quantity of fluid in an elevated tank, and then to allow this fluid to flow through four double troughs or cells, placed one above the other so that the liquid descends continuously by gravity. Each trough is divided laterally by a partition, and in each of the two divisions five distinct "elements" (consisting of one positive and two negative plates) are suspended (Fig. 1). The positive plates are of thin platinum wire wound upon slate slabs and the negative plates are of zinc. There are thus four troughs each containing ten "elements," or forty cells in all. The liquid enters through the funnel visible towards the top left-hand side of the illustration, passes along the front division of the top trough, back through the division behind, over a weir and into a sub-division, from which it is drawn off by the bent glass tube discharging into the second funnel; it passes along the front division, back through the division behind, over the weir into the pocket of the second trough, and so on to the final bent tube, which discharges it into a carboy. A bottle arranged at the right-hand side of the tier of cells supplies the sodium hydroxide used as a preservative, which flows drop by drop into the carboy as it is filling and

FIG. 1.—General View of the Poplar Plant.

serves to neutralise free hypochlorous acid. As the liquid passes through the troughs it is subjected to the action of a current of 15 amp. at 230 volts, being 5.6 volts per cell. During the run the liquid in the carboy is thoroughly stirred by means of an ebonite rod provided with rubber flaps, and as each carboy fills it is subjected to a further stirring by means of the same appliance hung from a set of gear-wheels. This is an improvement introduced by Dr. Alexander, and obviates shaking the carboys. As each carboy contains 15 gallons, and will therefore weigh when full, with its case, something like 200 lbs., the impracticability of the latter process is obvious.

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of the tank, at the end of which is a ball-valve, into a small flushing cistern at the side, in order to obtain an even flow, otherwise as the tank emptied the flow would be slower; thence through another pipe into the funnel leading to the first row of cells. The second pipe mentioned has a cock for regulating the flow. The rate of flow adopted is $3\frac{1}{2}$ pints (1.9 litres) per minute. This works out at 25 gallons (113.5 litres) per hour, or about 185 gallons (840 litres) in the eight hours. The chemical action taking place in the cells is described by Dr. Hodgkinson as quoted in Appendix C. It appears that the NaCl acts as a vehicle for the current; the Mg and Cl ions being given up at the — and + poles, and combining with H_2O to form $Mg(OH)_2$ and $2HCl$, with $2HClO$, H_2 being given off. A final re-combination takes place, leaving $MgCl_2$ and $Mg(OC1)_2$ with a little $Mg(OH)_2$ as waste. The results of four runs with different currents are shown below:—

Time.	Grammes per Litre.	Grammes per B.T.U.	Amps.	Volts.	Temperature.			Remarks.
					Tank.	1st Row.	Final.	
10.0	—	—	12	214	—	—	—	Room Temp. 62° Flow 1.9 litres per min. ($3\frac{1}{2}$ pints) 113.5 litres per hour.
10.40	3.312	146	—	—	—	—	—	
11.5	3.180	141	12	212	—	—	—	
11.20	—	—	12	212	—	—	—	
11.30	3.117	139	12	212	60	—	80	
11.30	—	—	19	244	60.5	70	80	Room Temp. 64°
12.0	—	—	20	246	—	—	94.5	
12.15	—	—	20	245	—	—	95	
12.20	5.3	123	20	244	60.5	70	98	
12.30	5.3	124	20	242	—	—	98	
12.45	5.48	128	20	242	60.5	72	98	
12.55	—	—	17	232	60.5	—	—	Temp. falling owing to reduced current.
1.45	4.818	138	17	232	—	72.5	95.5	
2.0	4.968	142	17	232	—	—	94	
2.15	—	—	18	234	—	—	—	
2.30	4.818	139	17	230	—	—	—	
2.30	—	—	16	224	61	—	—	
3.0	—	—	16	224	—	—	93	
3.10	4.676	17	16	230	—	71	93	
3.30	—	—	16	230	—	70	93	
3.45	4.818	149	16	228	60	70	94	

The currents employed were those which the rheostat admitted. The plant is designed to work at 15 amp. and a flow of 1.9 litres per minute.

The curves which have been plotted from readings taken on these runs are appended (Figs. 2 and 3). The abscissæ on Fig. 2 are merely arbitrary

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divisions indicating that the liquid has passed through one set (of ten electrolyzers), two sets, three sets, or four sets (final liquid). The ordinates show the strength obtained in grammes per litre. It will be noticed that the

increase of 1 gramme per litre in each ten cells is fairly maintained, but has a tendency to fall off after thirty cells.

Fig. 4 gives the rise in temperature for each amperage from the tank to

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the final liquid. The high amperage naturally gives the greatest difference 21°C. (38°F.), the low amperage the least, 11°C. (20°F.).

Figs. 5 and 6 show rise in temperature of the liquid during $1\frac{1}{2}$ -hour runs. It appears that, after attaining a certain temperature (27°C. (80°F.) and 37°C. (98°F.) respectively) the tendency is to increase slowly.

Fig. 3 shows the efficiency curves, *i.e.*, the grammes of chlorine per B.T.U. It will be noticed that the highest efficiency is obtained at 16 amp.; also that the last row of cells does not show so good a result as the others, or rather that the efficiency becomes less as the strength is higher—a point generally observed on these plants. The fact that a run at 17 amp. gives worse results than at 16 is not easily accounted for, unless it was due to stable conditions not having been reached on the 17-amp. run. Another run at 17 amp., not plotted, practically coincided with the run at 16 in grammes per litre, but must obviously be worse as regards efficiency. The temperature differences were 17°C. (30°F.) for the 17, and 19°C. (34°F.) for the 16-amp. run.

The high temperatures at which some of the samples have been made are interesting, in view of the widespread belief that the hypochlorite solution deteriorates rapidly if made under such conditions. Samples were taken from solutions made and bottled during the warm weather of last summer with the following results:—

STABILITY TABLE. I.*

Temperature difference between Tank and Final Liquid.	Temperature of Final Liquid when made.	Loss in Grammes per Litre.	Time between Making and Re-testing.
(1) 15 ° C. 27° F.	40° C. 104° F.	0·5	6 weeks.
(2) 14·5° C. 26° F.	40° C. 104° F.	0·2	4 „
(3) 15 ° C. 27° F.	40° C. 104° F.	0·1	6 „
(4) 14·5° C. 26° F.	34° C. 93° F.	0·1	6 „

* The liquid tested had been kept in ordinary dark glass bottles, corked.

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While on the question of stability the following tables will be of interest ; the liquids in question were kept in carboys, not in small bottles :—

II.

1.		6.	
Made 13/3/06.	c.c. NaOH 300, tem. 76.	Made 23/2/06.	c.c. NaOH 200, tem. 74.
13/3/06	4'184	23/2/06	5'30
3/5/06	4'184	28/2/06	5'30
19/9/06	3'975	2/3/06	5'129
		3/5/06	5'129
		19/9/06	4'818
2.		7.	
Made 13/3/06.	c.c. NaOH 300, tem. 76.	Made 23/3/06.	Temp. 72.
13/3/06	4'297	27/3/06	4'297
3/5/06	4'297	3/5/06	4'297
19/9/06	4'184	19/9/06	3'975
3.		8.	
Made 23/3/06.	Temp. 72.	Made 29/3/06.	c.c. NaOH 300, tem. 78
27/3/06	4'297	30/3/06	4'818
3/5/06	4'297	10/4/06	4'676
19/9/06	3'975	3/5/06	4'676
		19/9/06	4'297
4.		9.	
Made 26/2/06.	Temp. 74.	Made 12/2/06.	c.c. NaOH 225.
5/3/06	4'416	12/2/06	3'785
3/5/06	4'416	3/5/06	3'785
19/9/06	3'975	19/9/06	3'613
5.			
Made 29/3/06.	c.c. NaOH 300, tem. 76.		
30/3/06	4'968		
26/5/06	4'968		
19/9/06	4'416		

The specimen made on October 2nd at a temperature of $104^{\circ}\text{F.} = 40^{\circ}\text{C.}$ and a strength of 5.4 grammes per litre, was tested three hours later to see if immediate depreciation took place in the hot liquids, but it was found to be unaltered, practically. The test gave 5.3 for the whole carboy, which contained more 5.3 than 5.4 liquid.

The principal conclusions to be drawn from the working of this plant appear to be the following :—

- The manufacture of hypochlorite solutions can be carried on by a process which is practically automatic.
- For an output of 200 gals. per eight hours at 4 grammes per litre the capital cost, including buildings and fittings, should not exceed £500.
- Where continuous current is available the series system of electrolysis is the most suitable. Where alternating current only is to be had, and a motor-generator must be installed, fewer cells may be employed. In the Poplar plant about 1 gramme per litre is added for every ten cells.
- That a warm climate would not affect the manufacture at any rate of the magnesium hypochlorite.

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In conclusion, the author wishes to acknowledge his indebtedness to Dr. Alexander, the Medical Officer of Heath for Poplar, for giving him every facility for inspecting and testing the plant, and for the use of blocks, for illustrations appearing in the Paper. The improvements suggested by Dr. Alexander which have been introduced in the plant in question are numerous, and it is largely due to them that the running has become the simple process described.

APPENDIX A.

NOTES ON THE HISTORY OF THE HYPOCHLORITE PROCESSES.

The basis of the electrolytic hypochlorite processes has been well defined as producing chlorine at the anode, and the hydrate of the base (sodium or magnesium) at the cathode.

In 1851 Charles Watt patented a simple electrolysing cell, in which hypochlorite could be produced. In the description the use of this substance for bleaching is suggested.

About 1884 the Hermite electrolysing cell was introduced. The early forms used a revolving kathode. The plant at Poplar is an improved form by the same inventor. The objection formerly urged against this process, viz., that the product was unstable, does not now hold.

Woolf's electrolyser appeared about the same time as the Hermite. It consisted of zinc and platinum electrodes suspended in a tank; originally sea-water was used as the electrolyte, but found to give unstable liquid.

The reasons for the slowness of the solution to come into commercial use appear to be: Heavy initial outlay caused by the necessity for using platinum for the anode; instability in the early liquids; and general lack of confidence in the working plants due to insufficient trials and constant improvements and alterations.

APPENDIX B.

CHEMICAL ACTION.

Dr. W. R. Hodgkinson says: " $\text{Mg}^{\text{OCl}}_{\text{OCl}} \text{MgCl}_2$ is a somewhat unstable substance even at low temperatures in the presence of water. Although produced in the presence of sodium chloride during electrolysis, the tendency to combine with it is not so great as when the sodium chloride is formed in contact with it, or in a so-called nascent state.

"Thus, when sodium hydrate is added to the $\text{MgO}_2\text{Cl}_2\text{MgCl}_2$ solution, the following change takes place—

The magnesium-sodium double salt being considerably more stable than the corresponding magnesium one."

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APPENDIX C.

VALUE OF THE FLUID.

The practical value of hypochlorite solutions of a certain strength (2 grammes per litre and over) as deodorants and disinfectors has been frequently proved.

The Riker's Island example, in which the fluid was used to deodorise an enormous garbage heap near New York (1895), is well known.

Sir H. E. Roscoe investigated the Hermite process (as it then was) in the same year, and came to the conclusion that a solution of as low a strength as 0.25 grammes per litre would destroy non-sporing organisms, but would not affect *bacillus subtilis*. Also that the 0.25 g.p.l. solution was an excellent deodoriser.

Prof. Kanthack, in 1898, in inspecting the plant at Maidenhead for sterilising sewage effluent by means of this fluid, found that satisfactory sterilisation was effected by a 2-gramme solution used in the proportion of 2 gallons of solution to 1,000 gallons of sewage. In 1904 similar experiments were made at Guildford under Dr. Rideal, and the sterilisation effected was found to be satisfactory.

APPENDIX D.

RUNNING COSTS.

From the figures given it will be seen that in an ordinary run of eight hours the electricity consumed will be—

$$8 \left\{ \frac{240 \times 15}{1,000} = 3.6 \text{ units per hour} \right\} = 28.8 \text{ units.}$$

At 1d. per unit this will cost 2s. 5d.—say 2s. 6d.—per 200 gallons of the fluid.

With sodium chloride at 40s. per ton, and magnesium chloride at £5 per ton (high prices), 185 gallons (omitting the first carboy drawn off, 15 gallons, the bulk of which has only been through one row of cells) can be produced for—

	s.	d.
(NaCl) salt	1	6
Magnesium chloride	1	0
Electricity	2	6
Attendance and labour, say	4	0
	<hr/>	
	9	0
Interest on £500 at 4½ per cent., say 2s. per run ...	2	0
	<hr/>	
Total	11	0

Reductions in the price of salt could be obtained by buying in bulk. If the disinfectant plant were made an adjunct to the borough electrical generating station the cost of attendance could be reduced. Probably, including bottling and depreciation of plant, ¾d. per gallon is a fair estimate for the smaller sizes of plant.

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APPENDIX E.

TITRATION TEST EMPLOYED FOR TESTS AT POPLAR REFERRED TO.

Five cubic centimetres of arsenious acid are run into a dish, and a drop of indigo added. The liquid to be tested is then allowed to flow into the coloured arsenious acid until the colour disappears. The amount of liquid required to bleach out the indigo being known, the chlorine intensity can be read from a table.