

SOME OBSERVATIONS RESPECTING THE RELATION OF STABILITY TO ELECTROCHEMICAL EFFICIENCY IN HYPOCHLORITE PRODUCTION.

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Any person referring to Herr Viktor Engelhardt's encyclopædic monograph on hypochlorite production,* and examining in detail any of the tables or curves, cannot but be struck by the fall in the yield of available

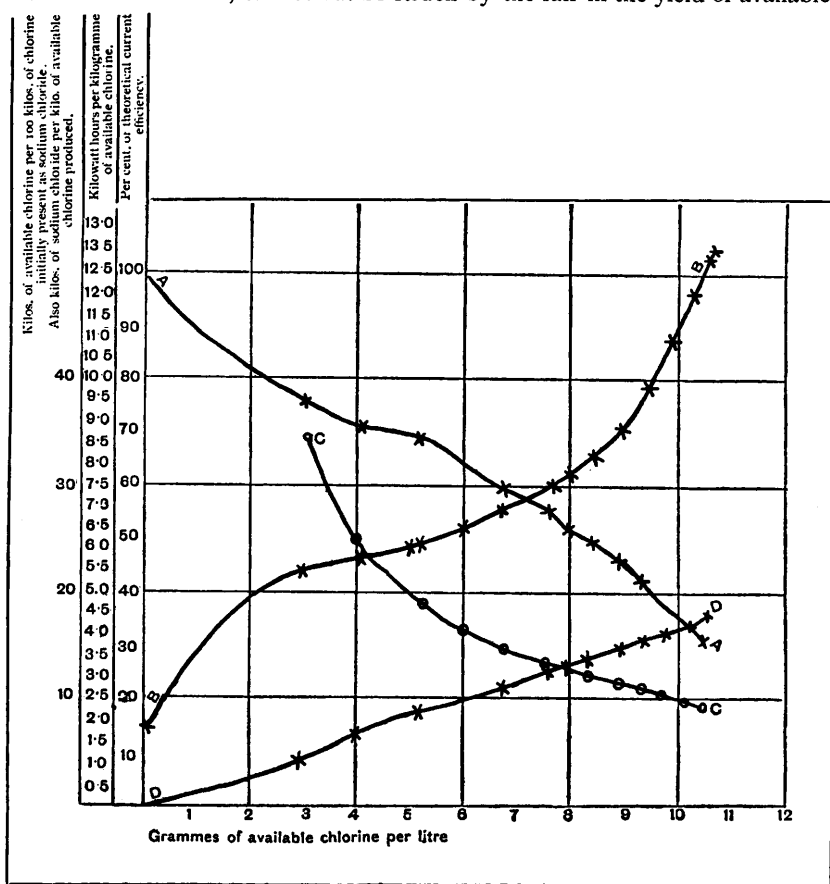


DIAGRAM I.

chlorine per kilowatt hour as the amount of available chlorine in the solution increases. Diagram No. 1 is a reproduction of a typical instance.† Curve A represents the falling current efficiency in percentages of the theoretic yield ;

* Hypochlorite and Electrische Bleiche von Viktor Engelhardt.

† Ibid. page 132, Table XII.

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curve B represents the energy efficiency, in kilowatt hours per kilogramme of available chlorine ; while curve C represents the salt consumption in kilogrammes of sodium chloride per kilogramme of available chlorine.* To these curves the writer has added the curve marked D, which, for the given solution, shows the percentage between the chlorine present in the solution as sodium chloride, and the smaller quantity which has been converted into available chlorine in the form of sodium hypochlorite. This curve depicts an obviously unsatisfactory state of affairs, when one considers that at the finish of the run only 17.48 per cent. of the chlorine initially present has been converted into hypochlorite.

Examinations of other tables show that the fall in current efficiency for the same apparatus, with the same specific gravity of solution, varies with the difference of potential between anode and cathode, or in other words with the distance between the electrodes if these remain constant in area. A particular example occurs on page 136 of Engelhardt's book, where in fig. 147, with a 24.5 per cent. sodium chloride solution the current efficiency falls to 50 per cent., when the available chlorine present has reached 9 grammes per litre the voltage being 4.0. By increasing the voltage to 5.5 the current efficiency does not fall below 50 per cent. until the available chlorine amounts to 15.2 grammes per litre. Raising the voltage still further to 6.5, the current efficiency remains above 50 per cent. until a strength of 17 grammes per litre is reached.

One hypothesis to account for this state of affairs would be that, other factors being constant, the amount of available chlorine produced from a sodium chloride solution depends upon the relation which the amount of unconverted sodium chloride actually present between the electrodes bears to current density. In support of this view, the succeeding diagram in Herr Engelhardt's book may be referred to. In this is shown the effect of keeping the voltage constant, at 5.5 volts, and increasing the amount of salt in the solution. The following figures are abstracted from that diagram.

Percentage NaCl in Solution.	Strength attained in Grammes of available Chlorine per litre before Current Efficiencies fall to 50 per cent.	Percentage of Chlorine in Solution as Sodium Chloride converted into Hypochlorite.
6.0	2.9	7.9
10.0	8.2	13.6
17.0	11.5	11.1
24.5	15.3	10.4

A comparison of the first and second columns shows that by regarding 50 per cent. as the critical point in the fall of the current efficiency, the maximum strength in available chlorine which can be attained before this point is reached increases with an increase in the density. The third column shows that a further explanation of the falling efficiency is necessary as in the four cases cited, the percentage of the salt converted into hypochlorite is by no means constant. A partial explanation may be afforded by a study of the stability of the solution, and in a consideration of the ratio of the volume of the electrolyte to the amount of electrical energy required per hour.

* This curve may be read against the index to curve D, the values then representing kilogrammes of salt per kilogramme of available chlorine.

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The factors which go to produce a really stable solution of sodium hypochlorite, such as a solution which, kept in a dark amber-coloured glass-stoppered bottle, will only lose 5 per cent. of its strength per annum, or which, when standing in an open tank exposed to the air, will only lose one-half of 1 per cent. of its strength in 28 days, are numerous. Of these, temperature during manufacture is of supreme importance. The writer has

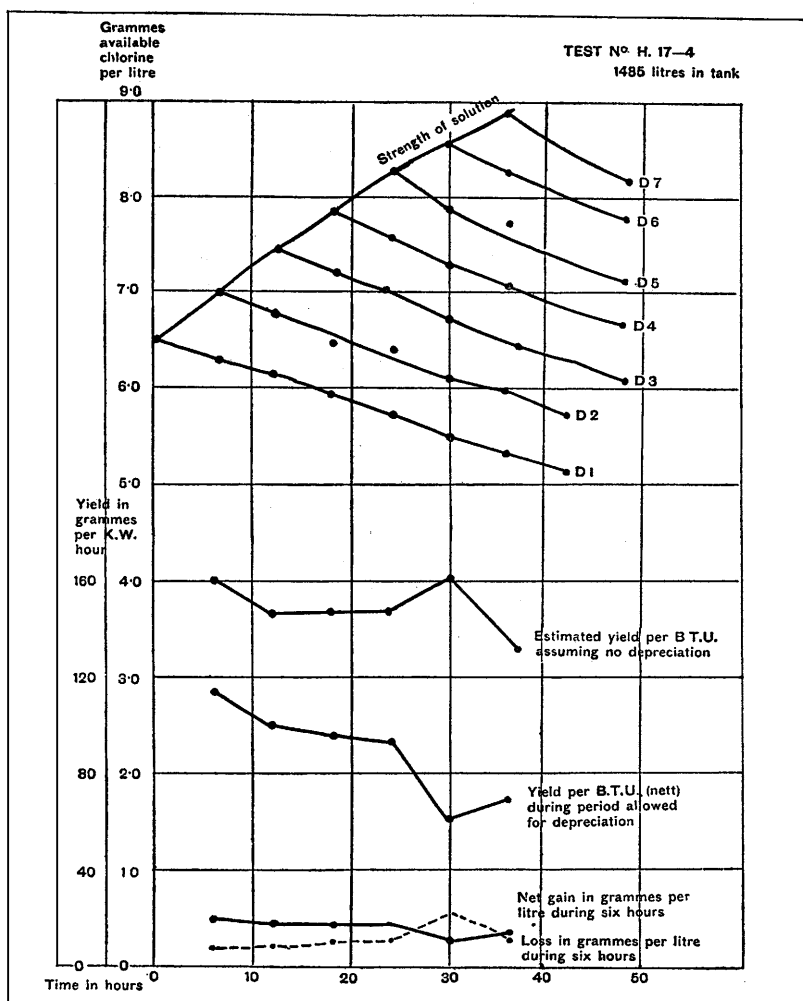


DIAGRAM II.

also found it generally advisable to sacrifice a large part of a possible high electro-chemical efficiency, and work with lower efficiencies when desiring to produce stable solutions. In cases, however, where the solution produced can be supplied almost immediately, as in the sterilisation of sewage effluents, or in the bleaching of the materials used in paper-making, a small percentage of instability is practically immaterial so long as the ratio of storage capacity to the dynamo output remains small, say five times the

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hourly quantity of solution produced. If, as in a case recently investigated, the storage capacity represented from fifty to seventy times the average output, a depreciation in itself relatively small, absolutely prevents the commercial production of solutions containing 7 or 8 grammes of available chlorine per litre.

Attention was called to this matter by the fact that on one run with 2,250 litres of saline solution of a specific gravity of 1.086, it took four hours to increase the strength from 7.847 grammes of free chlorine per litre to 7.867 grammes, during which time 4.688 kilowatt-hours were supplied to the electrodes in the tank. This amounted to a nett increase of 45 grammes, or less than 10 grammes of free chlorine per Board of Trade Unit. A sample taken at the commencement of the four hours was found to have lost .337 grammes per litre in four hours. Nearly the whole of the electrical energy supplied was therefore required to balance this total loss, 758.25 grammes in the tank. The real electrical efficiency (assuming that no depreciation had taken place) would thus have been in the neighbourhood of 171 grammes per kilowatt-hour. Subsequent analysis showed this abnormal rate of depreciation (of nearly 1 per cent. per hour) to be due to the presence of certain metallic impurities in the electrolyte, and special precautions were taken to reduce the amount of these in the succeeding trials of this type of electrolyser. If, however, the ratio of storage to hourly output had been within the limits suggested by the writer, this depreciation would not have proved an insuperable bar to the obtaining of a 10 or 15 gramme solution on a commercial scale.

For working under the conditions ruling when the writer was conducting his tests, it became necessary to take special precautions to remove such impurities from the electrolyte. These precautions were fairly effective, but did not by any means eliminate the deterrent effect of the depreciation on the economic production of solutions containing from 7 to 10 grammes of available chlorine per litre.

The following Table gives the observations taken during six-hour intervals on test No. H. 17-4. Certain of the results are depicted on Diagram No. 2. The upper part of the diagram shows the gradual increase in the amount of available chlorine present per litre, and the curves set off from this, D 1, D 2, &c., the strength at succeeding six-hour intervals of samples taken.

TEST NO. H. 17-4.

1,485 Litres in Tank.

Power supplied in B.T.U. during period.	Grammes of available chlorine per litre present in solution.		Net grammes of available chlorine produced, <i>i.e.</i> , gained during period.		Grammes of available chlorine lost, <i>vide</i> depreciation test in period.		Estimated production assuming no depreciation.		Time between Tests.
	At start of period.	At end of period.	Total quantity. Grammes.	Net gain per kilowatt hour. Grammes.	Grammes per litre.	Total grammes in tank.	Total grammes per litre.	Yield in grammes per kilowatt hour.	
6.48	6.5	7.0	742.5	114.6	0.20	297.0	0.70	160.4	6 hours
6.48	7.0	7.44	653.4	100.8	0.20	297.0	0.64	146.6	6 hours
6.54	7.44	7.86	623.7	95.3	0.23	341.5	0.67	147.5	6 hours
6.54	7.86	8.27	608.8	93.0	0.26	386.1	0.67	147.5	6 hours
6.60	8.27	8.54	400.9	60.7	0.45	668.2	0.72	162.0	6 hours
6.60	8.54	8.85	460.3	69.8	0.28	415.8	0.59	132.7	6 hours

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These were placed in bottles, which were suspended in the electrolysing tank in order that they might be subject to the same conditions of temperature, &c., as the main volume of the electrolyte. It may be mentioned that the temperature of the electrolyte remained constant at 13.5°C., while the temperature of the surrounding atmosphere varied from 17° to 20°C.

The next Table, together with Diagram No. 3, gives details of another run in which a larger volume of electrolyte was used, amounting to 2038.5 litres. In this case the figures are given from the start of the run instead of for the end portion, as shown in Diagram 2. The depreciation tests were taken at twelve-hour intervals. Owing to the precautions mentioned, the electrolyte contained fewer impurities, and the solution generally was more stable; owing, however, to the greater volume of the electrolyte the nett gain per kilowatt hour was in the latter stages greatly inferior.

TEST No. H. 21-4.

2,038.5 Litres in Tanks.

Power supplied in B.T.U. during period.	Grammes of available chlorine per litre present in solution.		Nett grammes of available chlorine produced, i.e., gained during period.		Grammes of available chlorine lost <i>vide</i> depreciation test in period.		Estimated production assuming no depreciation.		Time between Tests.
	At start of period.	At end of period.	Total quantity.	Nett gain per kilowatt hour. Grammes.	Per litre.	Total grammes in tank.	Total grammes per litre.	Yield in grammes per kilowatt hour.	
12.08	nil	1.50	3,058	253.1	—	—	—	253.1	{ 12 hours from start.
12.48	1.50	2.90	2,854	228.6	0.03	61.0	1.43	233.5	12 hours.
12.48	2.90	4.18	2,600	200.3	0.05	102.0	1.33	208.5	12 hours.
12.30	4.23	5.20	1,977	152.6	0.04	81.4	1.01	162.5	12 hours.
11.06	5.20	6.14	1,915	160.0	0.10	203.8	1.04	177.1	12 hours.
12.50	6.14	6.91	1,854	148.3	0.21	428.0	0.98	166.5	12 hours.
12.48	6.91	7.59	1,386	111.0	0.20	408	0.88	143.7	12 hours.
12.48	7.59	8.08	998	80.0	0.40	816	0.89	145.3	12 hours.
12.40	8.08	8.54	938	76.0	0.33	672	0.79	129.8	12 hours.

In Diagram No. 3, which illustrates the above Table, a break occurs at the 36th hour owing to the stoppage at the week end. As stated, the samples set aside for measuring the depreciation were examined at 12-hour intervals, the curves D 1, D 2, &c., indicating the loss in available chlorine of these. The effect of loss of strength of the electrolyte in the tank is appreciable when the strength of the solution has arisen to 4.18 grammes per litre. The margin between the actual efficiency and the estimated efficiency had the electrolyte remained unchanged in regard to its available chlorine contents is then about 4 per cent. The effect of the loss of strength, when the solution contains 8 grammes of available chlorine to the litre, adversely influences the yield per kilowatt hour by over 60 per cent. as against the yield had the electrolyte remained stable, and no loss through depreciation needed to be made good.

In this case the tank temperatures varied from 13 C. to 16.5° C., and the temperatures in the room from 19.5° C. to 23.5° C.

From his experience on these trials the writer is of the opinion that no test of the efficiency of any apparatus for the electrolytic production

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of the hypochlorites can be regarded as complete without an estimation of the losses through instability, and a mention of the volume of the contents of the electrolysing tank. While stability of solution does not greatly affect

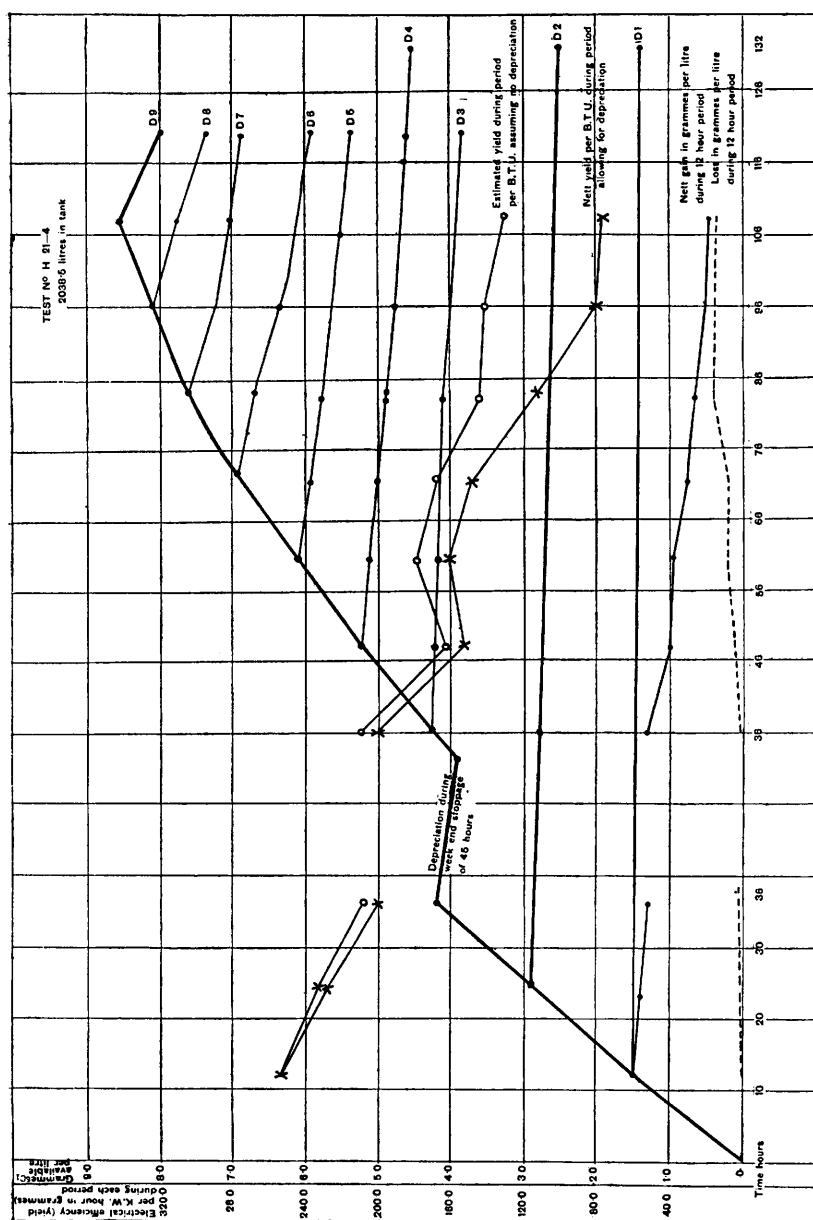


DIAGRAM III.

the efficiency of any continuous type of apparatus (in which the sodium chloride solution is fed in at one end, and drawn off at the other end ready for use), it will materially affect the efficiency in any non-continuous

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apparatus such as that tested by the writer, or in any of the cases in which the electrolyte is circulated through an external cooling tank and returned to the electrolyser to be further worked up. The relation between the amount of chlorine present as sodium chloride, and the amount of chlorine in the form of hypochlorite is unsatisfactory in most of the cases which have been chronicled by various investigators. Instability is one cause of this. But even allowing for this, the fall in efficiency is in no way proportional to the decrease in the amount of unconverted sodium chloride present in the solution. The factors which produce a markedly unstable solution are numerous, and further investigation is necessary. When the writer first considered the question of the relation of stability to efficiency, he thought it would have been possible to plot a curve indicating once and for all the probable amount of depreciation per hour for different strengths of available chlorine per litre. He has found that, even with a cool electrolyte, a difference of 1 part of iron in 100,000 parts of water in the solution affects the depreciation curve to a marked degree. During the experiments to which reference has been made, it was found impossible to keep the percentage of iron present at an even figure, and on this account no figures are given in these pages. It can only be said that during the run depicted on Fig. 3, the presence of iron was much less marked than in the run depicted in Fig. 2.

In conclusion, the writer desires to express his indebtedness to Mr. F. Ernest Pollard for valuable assistance rendered during the tests; in particular, for localising certain ferric chlorides as one of the disturbing factors, which limited the economic production of solutions containing from 8 grammes and upwards per litre of available chlorine.