The Production of Caustic Alkali and Bleach*

A Review of Recent Developments

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THE most important advances made in late years in the technical electrolysis of alkaline chlorides for the production of caustic alkali and chlorine are perhaps due to Dr. Jean Billiter, privatdozent in the University of Vienna. Some years back he designed a diaphragm cell which is being exploited by Siemens & Halske, and recently he has invented a modified form of the well known bell-jar cell, which is undoubtedly, taken all in all, one of the most efficient cells now operated technically. The Billiter-Siemens diaphragm cell I propose to mention briefly only, as full accounts of it are available elsewhere, and shall devote most attention to the Billiter "membrane" cell, the first installation of which started work early this year.

BILLITER-SIEMENS CELL.

Most diaphragm cells in technical use have vertical diaphragms (e. g., Hargreaves-Bird, Townsend, Finlay). Billiter, however, has returned to the use of horizontal diaphragms such as were formerly employed by Le Sueur and by Carmichael. He has compared elsewhere the relative advantages and disadvantages of the vertical and horizontal arrangements.

A horizontal diaphragm is more slowly attacked chemically, as it remains more or less saturated with the alkali which migrates upward from the cathode situated immediately underneath. This is particularly important when making strong alkaline liquors. Further, the hydrostatic pressure on it is uniform at all points, not varying with the height as in vertical diaphragms. This means a more uniform flow of liquid through, and consequently a more efficient checking of the movement of the OH ions toward the anode.

There are corresponding structural disadvantages. The floor-space needed is greater. Further, the insides of the cells are less easily accessible and the anodes are necessarily of more complicated construction.

The active diaphragm material in the Billiter-Siemens cell consists of a mixture of asbestos wool and BaSO₄, spread out evenly on top of a sheet of woven asbestos cloth, which in its turn rests on the ironwire net-work which constitutes the cathode. The function of the asbestos cloth is merely to support the BaSO₄ mixture and to prevent its being displaced by the lively hydrogen evolution. The cathode makes contact with the iron bottom of a trough, the sides of which are lined with cement, and the anode chamber is formed by a non-conducting bell-jar, which is securely cemented around the edges of the diaphragm. An important feature of the cell is the arrangement for heating the electrolyte by means of earthenware pipes through which hot liquids run, these being immersed in the brine at the top of the bell-jars.

Cells have been made carrying up to 3,000 amperes at a current density of 4 to 6 amperes per square decimeter. Working at 89 to 90 degrees, 12 to 16 per cent NaOH or 18 to 20 per cent KOH can be made at a 95 per cent cathodic efficiency, employing 3.5 volts.

An interesting laboratory study of the Billiter-Siemens cell has been recently published by Muhlaus. He finds that the BaSO₄ used for the diaphragm is best precipitated hot. No change of size of grain when in the hot liquors of the Billiter cell is then likely to take place, and a regular and uniform flow is thus assured.

The highest current density permissible is about 6 to 7 amperes per square decimeter.

Above this limit, disintegration sets in. Using 30 to 32 per cent brine at ordinary temperatures, the following figures were obtained:

Concentration of Alkali.	Current Efficiency, Per Cent.
3n.....	98-99
4n.....	95-97
5n.....	80-85
6n.....	75

The chlorine gas fell in purity from 99.5 per cent to 92 per cent as the alkali concentration was increased. The oxygen produced exceeded the amount of CO₂. The solid caustic resulting contained considerable quantities of NaClO₂ if pro-

duced from liquors stronger than 4n. The best results on the whole were given when making 4n. NaOH at a current density of 4 amperes per square decimeter. Raising the working temperature to 70 to 80 degrees improved both energy efficiency and purity of alkali.

The Billiter-Siemens process is now operated as follows:

(a) In Aschersleben, Saxony, by the Kaliwerke Aschersleben A. G. Ten 2,000-ampere units.

Fig. 1.—Section of Billiter-Leykam cell.

(b) In Höchst, by the Farbwerke Höchst.

(c) In Brückl, Bosnia, by the Bosnische Elektrizitäts A. G. Sixty-four 2,500-ampere units.

(d) In Krumau, Bohemia, by Ignaz Spiro and Söhne. Thirty-two 500-ampere units.

(e) At Niagara Falls, by the Niagara Alkali Company. A 1,000-kilowatt installation of 3,000-ampere units.

A number of plants are also being installed or enlarged. The Niagara Alkali Company (which has succeeded the old Roberts Chemical Company) is at present increasing the size of its plant from 1,000 to 3,000 kilowatts. It has also been made known that a new factory for caustic alkali and bleach is being erected, commencing with 78 2,000-ampere units, and that a textile factory is installing twenty-four 100-ampere units.

BILLITER-LEYKAM CELL.

In this cell Billiter has successfully modified the bell-jar process, placing the cathodes (hooded to collect the hydrogen) immediately underneath the bell-jar, and not around its sides, as in the Aussig cell. Similar constructions had been formerly suggested by Richardson and by Bein, but had achieved no technical success.

By doing this, Billiter gains an important advantage. In the ordinary bell-jar, both flow of liquid and flow of current change in direction at the

Fig. 2.—Section of Billiter-Leykam cell.

lower edge of the bell-jar. This results in non-uniformity of current density and liquid flow in the different parts of the bell-jar section. At some points liquid will be flowing more quickly than is necessary to overcome the OH⁻ migration toward the anode, at other points the contrary will be true; the movement of the OH⁻ ions will predominate, and the current efficiency will fall. This last statement particularly holds for those parts of the bell-jar section farthest removed from the walls, where the current of liquid is exceedingly slow. The larger the bell-jar, the greater proportionately is this disturbance. It also increases rapidly with current density. The consequence is that the units (bell-jars) at Aussig are very small, and can only be worked at a low current density,

furnishing weak alkali. Such a plant requires much floor space for its output and the labor charges are high.

In the Billiter cell, this change of direction and the resulting irregularities are avoided, the motion of the brine being directly opposed to that of the current lines until it has passed the cathodes. The consequence is that high current densities can be used, stronger caustic liquors produced, high current efficiencies obtained, and large units constructed. At the same time, the advantage of the bell-jar cell, the absence of diaphragms, is essentially retained. For, though the current must all pass through the hoods which cover the cathodes, this is not true of the electrolyte. Most of it passes directly through the spaces between neighboring cathodes, and is charged with caustic by diffusion from the concentrated alkali which fills the cathode hoods. Not only does this alkali protect the hood material (in practice, woven asbestos) against chemical action of chlorine compounds, but suspended matter present in the brine is not filtered out, as happens in diaphragm cells, and it is not necessary to purify the brine in any way. The asbestos hoods are made of as coarse a structure as is consistent with their function of leading off the hydrogen gas, and affect the voltage to a very slight degree only. Finally, the cell is heated in a similar fashion to the Billiter-Siemens cell, and the voltage thus lowered.

The essential parts of the Billiter-Leykam cell are shown diagrammatically in Figs. 1 and 2. A is the bell-jar inverted in the cement trough B, and provided with anode outlet for chlorine, inlet for brine and heating arrangement. The cathodes C are arranged below the bottom level of A and consist in practice of T-iron. They are inclosed separately in long woven asbestos tubes which are suitably braced in order to avoid deformation by the evolved hydrogen, and are slanted sufficiently to allow the gas to stream away readily. These cathodes project out into a side compartment of the cell as shown, from which the hydrogen can, if necessary, be collected.

The causticized brine flows off through D.

The Austrian rights to the Billiter bell-jar cell have been purchased by the paper manufacturers Leykam-Josefsthäl A. G. The first plant has been erected in their mill at Gratwein, a village on the Austrian Southern Railway, a few miles from Graz, has been in continued operation since early 1912, and has given every satisfaction. Some 1,700 to 1,800 kilos of active chlorine are produced daily, and the whole plant uses about 400 P. S.—350 P. S. for the cells and 50 P. S. for auxiliary pumps, fan, etc. Power is purchased from a company at 150 kr. (\$31.25) per P. S. year. After converting into direct current, and reckoning all losses in leads, etc., the cost comes to 180 kr. (\$37.50) per P. S. year.

The plant consists of 561,200-ampere units, 50 of which were working at the time of my visit last July.

The cells are 5.5 meters long, 1.1 meters broad (internal measurements), and about 1.3 meters high. The side walls commence to slope inward about 70 centimeters below the top of the cell. They are built of reinforced concrete, the upper part being lined with earthenware bricks set in cement.

They are provided with three cement lids, each of which carries eight anodes.

The anodes are of Acheson graphite (1.0×0.18×0.05 meter), each being led through its lead by means of two graphite rods. The lids are cemented on to a shallow shelf cut out of the wall of the cell by means of ordinary putty, which stands the action of chlorine very well and always remains fairly soft. Putty is also used at the points where the anodes pass through the lids, as the weight of the anodes is not borne by the latter, but by the copper leads above. Each anode takes 50 amperes at a current density, assuming lower and side surfaces to be active, of about 1.6-1.7 amperes per square decimeter.

The cathodes are of T-iron and inclosed in woven asbestos tubes. These taper down slightly toward their closed lower ends, and the whole is braced by the insertion of a wedge-shaped strip of asbestos cement. The tubes pass through holes in the

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dividing wall into the side compartment of the cell as indicated in Fig. 1. Two iron rods attached to each T-iron cathode take the current to the copper leads above. The hydrogen is allowed to escape. The cathodes are, of course, about 1 meter in length, and the mean breadth of the asbestos tubes is about 5 centimeters. Between each tube there is a space of 5 to 8 millimeters. The upward slope of these tubes is about 2 centimeters per meter.

The brine (moving from a reservoir under gravity) is led to a distributing box situated above the cells. From this it proceeds by way of a series of short capillary tubes (1.5 millimeters bore) to 22-inch tubes, which pass through the cell lids, and is thus fed in between the anodes. Regulation of the main supply to the cell is effected by means of a rubber tube and clip. This arrangement acts on the whole very satisfactorily, though the capillaries sometimes get stopped up. The causticized brine is drawn off from one side of the cell by means of siphon overflows. Three are provided, but one only is used in practice.

The heating arrangement used by Dr. Billiter in his diaphragm cell, though available for all other installations of his "membrane" cell, cannot be used at Gratwein. (The patent rights are not there available). The cells are, therefore, provided with a heating arrangement which employs steam, the details of which, however, I cannot divulge here. When I was at Gratwein, the cells were being mostly worked at room temperature, while those few which were being heated were working at a temperature of 65 deg. Cent. to 70 deg. Cent.

The cells are arranged in four rows, two rows being worked in series, and are insulated by glass resting on concrete supports. Beneath the cells are arranged the chlorine and brine pipes, and a channel for the caustic liquors. The chlorine pipeline is constructed of cement, junctions being made by covering the ends with a cement box and filling up with asphalt. The current leads are of copper, those connecting the cells of circular cross-section and 3 centimeters in diameter. They are all painted with a composition stable against chlorine

and acid fumes, as are also the tin tubes and rubber connections referred to above. The cells are worked under slightly reduced pressure ($\frac{1}{2}$ centimeter of water), and, as a matter of fact, no smell of chlorine was noticeable. Ventilation can be effected, if necessary, by blowing air in through the agency of a fan driven by a horse-power motor. A traveling-crane is provided to facilitate lifting off the tops of cells, etc.

Saturated brine is used, prepared in the simplest way. A long cement trough is filled with large lumps (20 to 40 centimeters) of crude salt. Waters enter continuously at one end, and saturated brine leaves at the other. It is not purified, and can be sent straight to the cells. The average cathode liquors produced contain 12 to 13 per cent NaOH and about 20 per cent NaCl. By decreasing the rate of flow of brine, 16 per cent NaOH can readily be made. Up to 350 liters of brine per cell are causticized in 24 hours. The liquors are first evaporated in two vacuum pans, furnished by the Skodawerke A. G., Pilsen, and similar to those used in sugar refineries. In these they are successively brought to 30 deg. B $\acute{e}$. and 40 deg. B $\acute{e}$. Then by means of a Kaufmann rapid evaporator they are brought to 50 deg. B $\acute{e}$. before going to the melting-house. The final product, which will probably be later somewhat improved upon, contains 97 per cent NaOH, 1.2 per cent Na $_2$ CO $_3$, and 1.8 per cent NaCl. The chlorine is diluted and absorbed in milk of lime.

Cells which are worked at room temperature take about 4 volts. Those I saw working at 65 to 70 degrees require 3.4 to 3.5 volts. Long continued experiments carried out with a 250-ampere unit have shown that at the normal working temperature of 85 degrees the voltage falls to 3.1 volts (plus in all cases the voltage drop in the leads). The cathodic current efficiency is about 92 per cent for 3n to 4n alkali.

It remains to be added that wear and tear in the cells are very small. Under normal working conditions the anodes lose about 1 millimeter in thickness at their bottoms and sides in two months. Suspended matter in the brine settles on the bottom of the cells, and the asbestos hoods remain unaffected. Finally, when once matters are adjusted,

the whole system works automatically. The actual cell-room in Gratwein is worked by shifts of one workman only, whose duty it is to adjust the rates of flow in the different cells. Moderate fluctuations in rate of flow of brine or in current density result in a change in the alkalinity of the liquors produced, and in a corresponding small change in current efficiency. The cells at Gratwein work at a current density between the electrodes of about 2 amperes per square decimeter only. With cells working at 85 degrees the most convenient figure, according to Billiter, is 4 to 6 amperes per square decimeter; but, by suitably varying the other conditions, 14 amperes per square decimeter can be employed.

The withdrawal of 350 liters of catholyte per cell per 24 hours corresponds to a movement of the brine of about 0.00007 centimeter per second. The OH ions in that part of the catholyte between the electrodes will have a velocity anodeward of just about the same magnitude. (E. g., assuming the cell to work at room temperature, the conductivity of the electrolyte would be about 0.5 reciprocating ohm per cubic centimeter, the velocity of the OH ion at a voltage gradient of 1 volt per centimeter, 0.0018 centimeter per second, and the actual velocity $0.02 \times 0.0018 \div 0.95 = 0.000072$ centimeter per second). This close approximation between the two opposing velocities, with the consequent straying of OH ions toward the anode, is of course the chief cause of the 8 per cent deficiency in current efficiency, as the amount of chlorine which dissolves in the concentrated brine, and which would thus tend to be carried to the cathode, is very small.

In conclusion, I will again emphasize the chief characteristics of the Billiter-Leykam cell. They are:

- (1) Freedom from diaphragm troubles.
- (2) Use of impure brine.
- (3) Automatic working, great adaptability, and low attendance charges.
- (4) Alkali (3n to 4n) strong compared with most other non-mercury cells.
- (5) With heated cells, lowest energy consumption per ton of product of any of the electrolytic cells now working on a large scale.

Regulation of the Heat of the Body in Hot Climates*

In all temperate climates and, if certain exceptional cases are noted, in almost all climates in which mankind is engaged in the usual activities of life, the temperature of the human body is higher than that of the environment, so that there is a tendency toward continuous loss of heat from the surface of the body. Except in so far as it is prevented by the insulating devices of clothing, this loss takes place in part by convection, that is, by warming the layers of air in contact with the body, as well as by radiation whereby there is an exchange of heat between the surface of the body and that of surrounding cooler objects. When there is occasion for the removal of a larger amount of heat, this is accomplished through the function of perspiration. In the evaporation of sweat a large amount of heat becomes latent and is removed from the body. The chief factor which may interfere with this procedure is the impeding of the evaporation by the presence of an atmosphere already saturated with water vapor so that the sweat can no longer be converted into the gaseous phase.

Few persons realize that there are, nevertheless, inhabited regions in which the temperature of the surrounding air is not lower than that of the body. In parts of India, for example, during the hot weather in March, April and May, the maximum temperature is daily seldom under 38 deg. Cent. (100.4 deg. Fahr.), and in some places it rises to over 43 deg. Cent. (109.4 deg. Fahr.) for long periods. Usually such habitable areas experience a very low percentage of moisture in the air. Wet heat is not usual, since with the rains the weather becomes cool.

It is well known that the body temperature can be maintained at its normal height in an atmosphere much higher than 37 deg. Cent. (98.6 deg. Fahr.), in spite of the fact that the production of heat is still going on in the organism. It is said that a man can stand exposure to a temperature of 90 deg. Cent. (194 deg. Fahr.) or even 120 deg. Cent. (248 deg. Fahr.) for a considerable time provided that the air is dry. If the outside temperature be above that of the body, heat is actually added instead of lost; and this additional heat is greatly increased by exposure to a very hot sun or wind. Inasmuch as radiation and conduction are available as cooling agencies only when the outside temperature is below that of the body, it is a matter of no little moment to understand what the organism is called on to

do in order to prevent any marked rise of internal temperature. That an adjustment does take place is assured from the fact that during extremes of dry heat no great discomfort is felt by healthy persons; and it is stated on good authority that fairly hard physical work is possible in the sun, even with a "shade" temperature of 43 deg. Cent. (110 deg. Fahr.) or more. Here the organism must depend solely on evaporation as a cooling agent; and this function must be sufficient to remove all the heat added from external sources as well as the heat due to internal metabolism. In a Turkish bath the loss of weight, represented almost entirely by water, may be at the rate of at least two pounds every hour.

Dr. E. H. Hunt, medical officer to the N. G. S. Railway, who resides in Deccan, India, where extremes of heat like those mentioned prevail, has furnished interesting data as to how one becomes adjusted to the physiologic and hygienic conditions thus created.¹ The heat contributed by the combustion of the ordinary food-supply sufficient to maintain nutritive equilibrium may be judged from its fuel value. If this is put at 3,500 calories for an active working man, a calculation shows that the amount of water the evaporation of which will absorb this heat at body temperature is 6 liters (about 6 quarts). Water must therefore be taken into the body in food and drink to supply this requirement in addition to what is lost by excretion, is wasted by inefficient perspiration, or is needed to remove the heat actually added to the body from without, in the hot climates referred to.

Such hypothetical estimates have been compared by Dr. Hunt in India with actual observations made during an exceedingly hot and very dry period when, for some hours at midday, the lowest temperature which could be secured in tents under trees was 42.8 deg. Cent. (109 deg. Fahr.). All dry objects were as hot as this or hotter and were uncomfortable to handle. The mercury in the thermometer fell at once when a hand was placed near it, or if it were breathed on. Until about midday the party of investigated healthy Europeans remained in the sun with no shade whatever, a considerable amount of physical exercise being taken. Such a life, we are told, is led by hundreds of Europeans in India, customarily with a gain rather than a loss of health. When health suffers it is usually through the incidence of infectious disease. None of the party, using strict moderation, consumed less than three gallons of liquid

per day. When the activity and considerable exposure to the extremes of heat are taken into account in this experience, which probably represents an approach to the limit of comfort, the fluid intake is not far removed from the hypothetical estimate, based on the many data at hand.

It is obvious that in such extremes of dry heat any failure of perspiration must lead to instant and grave risk. This failure may result from an insufficiency of drinking-water. It may equally result, as Dr. Hunt maintains, from pathologic processes incident to slight malaria, early typhoid, or any other process by which heat regulation is upset. He adds that he has not come across any case of pure "heat-stroke" or sunstroke in a proved healthy person. A man might suffer from but slight fever while indoors and might be unaware that he was ill; yet his whole regulation might completely fail if he were at work in the sun under the numerous conditions which involve an extreme effort even for the healthiest.

The main regulation of heat loss takes place by the control of the nervous system over the cutaneous circulation and the sweat-glands. When this fails, the temperature must speedily rise above the normal in these hot climates. General excitability is evinced and metabolism is stimulated so that a "vicious circle" is established. There is not even any compensation by lessened heat production. In "wet heat" the limit of safety is speedily reached. When the air is already more or less saturated with moisture, as indicated by high wet-bulb thermometer readings, evaporation is slow and inefficient, and danger ensues even during rest. The excess of sweat secreted and any increase in the amount of water consumed under such conditions merely increase discomfort rather than facilitate the proper heat regulation of the body.

The large amount of water absolutely required and actually consumed by men in these hot climates has not been appreciated adequately in any quantitative sense. Experiments by Hunt have demonstrated that a healthy man carries in his body a large reserve of water mainly stored in muscle and so readily available that the percentage of water in the blood is not appreciably diminished even when several liters of water have been lost by sweating. If, however, it is extensively drawn on, replacement seems to occupy many hours, and this delay is an important factor, forming a strong argument against any restriction of drinking which would cause undue or needless use of the stored water of the human body.

* Reproduced from the *Journal of the American Medical Association*.

¹ Hunt, E. H.: The Regulation of Body Temperature in Extremes of Dry Heat, *Jour. Hyg.*, 1912, xii, 479.