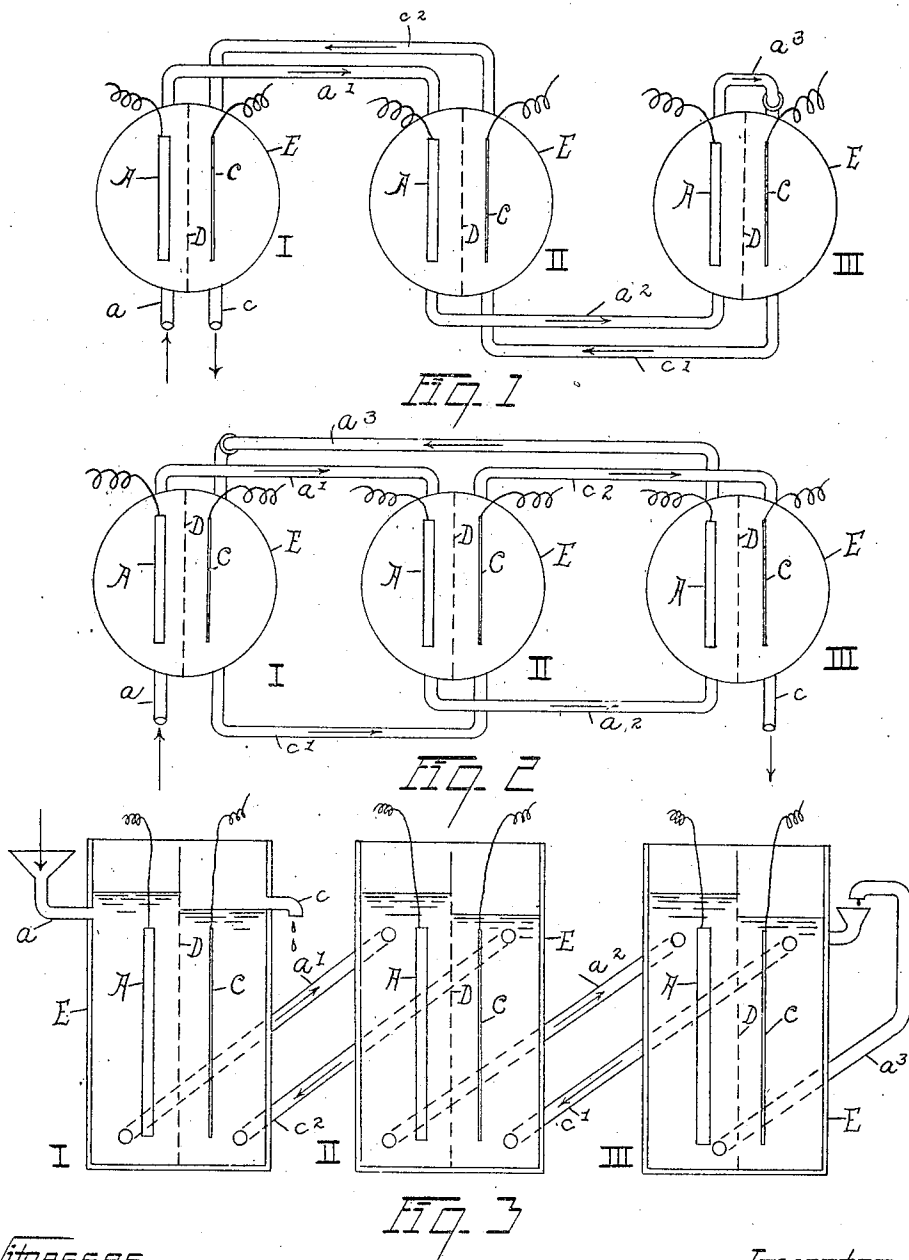


H. H. DOW.
 PROCESS OF AND APPARATUS FOR ELECTROLYTIC PRODUCTION OF CAUSTIC ALKALI.
 APPLICATION FILED AUG. 12, 1915.

1,284,618.

Patented Nov. 12, 1918.

2 SHEETS—SHEET 1.



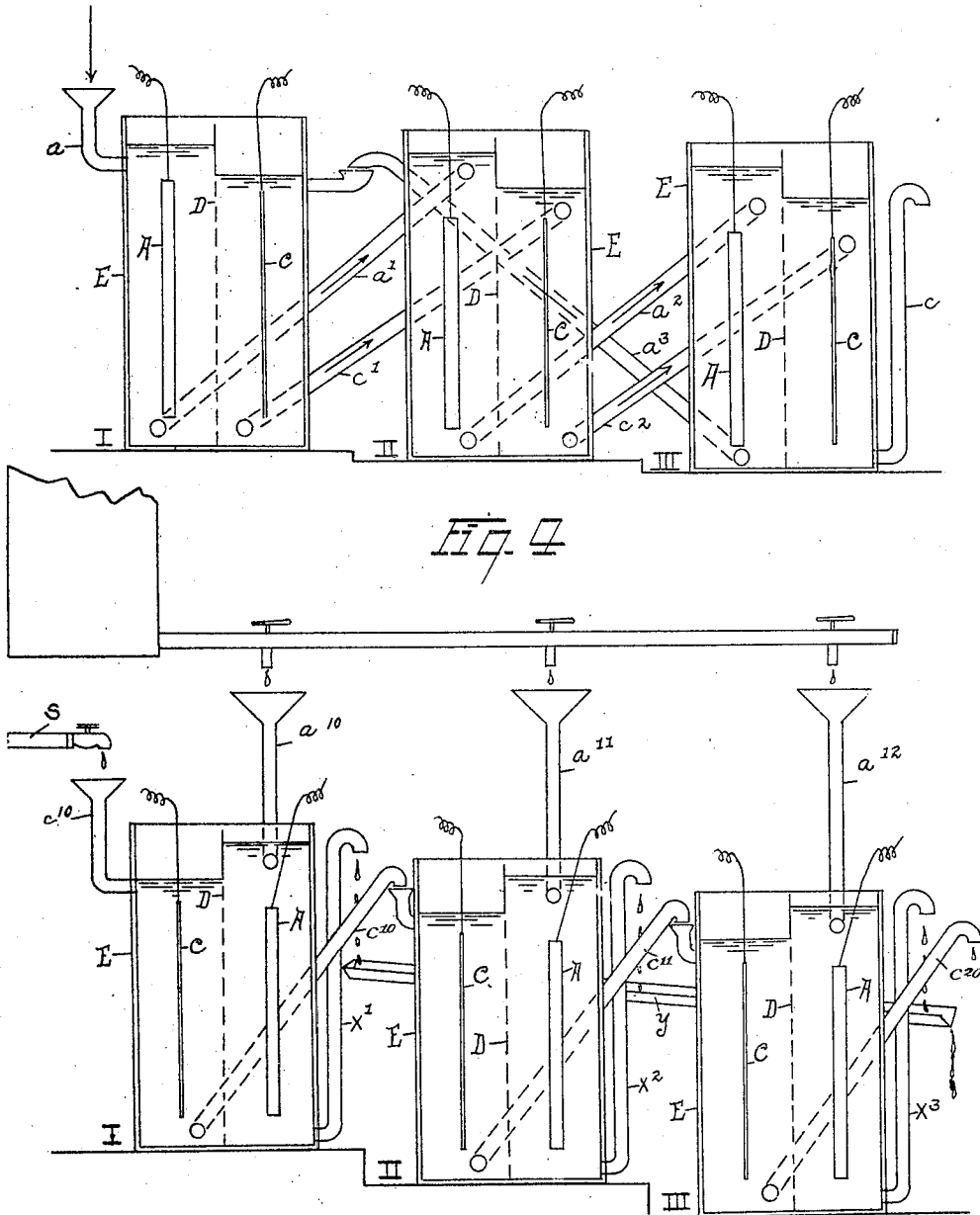
Witnesses
 H. C. Small
 H. B. McMill

Inventor
 Herbert H. Dow,
 By Hull & Smith, Attys.

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Fig. 5

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UNITED STATES PATENT OFFICE.

HERBERT H. DOW, OF MIDLAND, MICHIGAN, ASSIGNOR TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF MICHIGAN.

PROCESS OF AND APPARATUS FOR ELECTROLYTIC PRODUCTION OF CAUSTIC ALKALI.

1,284,618.

Specification of Letters Patent.

Patented Nov. 12, 1918.

Application filed August 12, 1915. Serial No. 45,097.

To all whom it may concern:

Be it known that I, HERBERT H. DOW, a citizen of the United States, residing at Midland, in the county of Midland and State of Michigan, have invented a certain new and useful Improvement in Processes of and Apparatus for Electrolytic Production of Caustic Alkali, of which the following is a full, clear, and exact description, reference being had to the accompanying drawings.

This invention relates to the art of electrolyzing liquids and has for its object the provision of a method and apparatus whereby the power consumption may be rendered more efficient, whereby the liquid effluent may be obtained in a more pure state and with fewer by-products and impurities than heretofore, and whereby the cell destruction, particularly the anode erosion, may be decreased. While the improvements hereinafter described may be of value in other relations, they have been especially perfected for the purpose of electrolyzing alkali chlorids for the production of chlorin and caustic, and the following description will be based upon the electrolyzation of common salt for the production of chlorin and caustic soda, although it will be understood that the same is applicable wholly without change for the electrolysis of any halid salt whose base yields a hydroxid soluble in water, and may be available for other uses in addition, wherefore I do not limit myself except as particularly stated in the claims hereto annexed.

The principle of my invention consists in this, that the electrolysis is conducted in a series of cells, the catholyte being also advanced from cell to cell so as to receive an increment in its causticity in each succeeding cell. The advantage of this method is that the average causticity of the catholyte is maintained at a lower point than would be the case if the separate cells were operated individually and the complete reduction performed in each cell; for example, in case all the cells were fed with catholyte liquor in parallel. According to my improved process the causticity of the catholyte liquor varies progressively from the first to the last cell of the series, the average causticity being materially less than

that of the final effluent. In other systems of working with which I am familiar the final causticity is obtained in every cell so that the average causticity and the final causticity are substantially or exactly the same thing. It is well settled, both theoretically and practically, that in the electrolysis of a halid solution for halid and caustic, the presence of strong caustic liquor in the cathode compartment of the cell serves both to diminish the current efficiency and to impair the purity of the caustic product. The theoretical explanations of this condition are somewhat abstruse and possibly not definitely settled, but the existence of the fact is well established. It is known that at low causticities and small concentrations the current efficiency is comparatively high and the contamination of the effluent with secondary reduction products is very small, but practical considerations do not permit the full utilization of these conditions since the cost of evaporating such a large quantity of liquid, and the extremely large plant required to handle a commercial business necessitates the employment of a higher concentration.

As one means for diminishing such secondary reactions, it has heretofore been proposed to provide each cell with a porous diaphragm located between the anode and cathode, and to maintain a higher static pressure of the anolyte than of the catholyte, thus mechanically opposing the diffusion or migration of ions from the cathode to the anode, and increasing the current efficiency and the purity of product. The porosity of the diaphragm permits a slow percolation of the electrolyte from the anode compartment to the cathode compartment, and in some systems this percolation is depended upon for the maintenance of catholyte during electrolysis.

I have discovered that in case the catholyte be withdrawn from each cell after having been electrolyzed a certain amount and be added to the cathode chamber of a succeeding cell, and be there electrolyzed a certain amount and afterward transferred to a third cell, and so on, the efficiency of the cell system may be considerably improved, and the contamination of the final product and the average destruction of the anodes much

reduced. This results from the fact that in the first cell the liquids upon the opposite sides of the diaphragm are very nearly alike and the catholyte of extremely low causticity; in the next succeeding cell the difference in the composition of the liquid is somewhat greater, though both the composition difference and the catholyte causticity are still small; and only in the last cells of the series does the composition difference and the catholyte causticity reach its maximum, and with it the tendency to produce the unfavorable results mentioned. Thus the average inimical effect of these operations is reduced over what would be the case if all the cells were run in parallel as heretofore, since with the parallel arrangement there is present a maximum difference of liquid composition in all of the cells; also with this arrangement I am enabled to employ a less pervious diaphragm, and one which by its mechanical construction is better constituted to prevent the diffusion heretofore mentioned. In order to secure the requisite electrolytic effect it is probably necessary to employ a diaphragm of such porosity that some percolation will take place, although the feeding of the catholyte chamber by percolation as has been common in previous methods has necessitated the employment of a more porous diaphragm than is required for the electrical purposes of the apparatus. According to my invention the major part of the catholyte is derived from a preceding cell, and only a minor portion of the same by percolation through the diaphragm. The working of my invention does not depend to any degree upon the derivation of the catholyte liquor from the anode side of the cells at any point of the cell series; even though, as a result of diaphragm porosity, a certain amount of anolyte should pass to the catholyte at each cell, this is entirely apart from the merits of the present invention. It is the essence of this invention that the catholyte be derived mainly, and preferably entirely, from the cathode compartment of a preceding cell, to the end that the composition difference between the anolyte and catholyte, and the catholyte causticity may vary progressively from one end of the series to the other, which result would be obtained in its greatest efficiency in case the diaphragm percolation could be wholly eliminated.

It is wholly immaterial to this invention how the anode chambers of the various cells are maintained. They may be fed separately or in parallel; they may be fed in series, one from the other; if fed in series, the direction of flow may be either parallel or opposite to that of the catholyte flow; the spent liquor from the anode compartments may be resaturated with halid and

returned as anolyte feed, or it may be employed for the catholyte liquor. As a matter of convenience I prefer to return through the cathode chambers the anode liquor which has previously passed through the anode chambers, owing to the fact that in composition, concentration, temperature, conductivity, and the like respects it is fully suitable and because it is present in the right quantities and at a convenient place, but this is wholly a matter of choice.

In the drawings accompanying and forming a part of this application I have illustrated certain apparatus whereby the methods and objects of this invention may be realized, although it will be understood that these drawings are merely diagrammatic, and that they are not intended to be exhaustive of all the arrangements, connections, or systems whereby the principle of my invention may be utilized. In said drawings each figure illustrates diagrammatically an arrangement of cells by which the principle of my present invention may be utilized. Figures 1 and 3 illustrate an arrangement in which the flow of the anolyte and catholyte are in opposite directions; Figs. 2 and 4 an arrangement in which the anolyte and catholyte flow in the same direction; and Fig. 5 an arrangement in which the anolyte and catholyte are entirely distinct from each other.

Each figure of the drawings shows three cells, indicated by I, II and III, although it will be understood that the number could be continued to any length desired, and will ordinarily in practice be extended to much greater length so that when the cells are connected in series electrically, a convenient commercial voltage may be utilized while affording each cell the E. M. F. necessary to its most efficient performance. However, so far as the present invention is concerned, it is wholly immaterial whether the electrodes be connected in series or in parallel or even whether they are fed from the same current source or different sources.

In each of the views of the drawing the cell container is indicated at E, the anode at A, the cathode at C and the diaphragm at D. In the apparatus illustrated in Figs. 1 to 4 inclusive the raw brine is admitted by the conduit *a* to the first anode chamber, and thence by conduit *a'* *a''*, etc., to the succeeding anode chambers, being then transferred by a conduit *a'''* to a cathode chamber, whence it is transferred by conduits *c'*, *c''*, etc., to the remaining cathode chambers of the series, being ultimately discharged at the outlet *c*. The liquid upon the anode side of each cell is shown at a slightly higher level than that on the cathode side of that cell so as to induce the percolation through the diaphragm heretofore mentioned. In Fig. 4

I have illustrated the successive cells as placed at different levels so as to provide the gradient necessary to the free flow of liquid from chamber to chamber. In this instance it will be noted that the total difference in the height of the cells is less than the difference in height between the anolyte and catholyte, so that liquid from the last anode chamber can flow directly into the first cathode chamber. In case the series of cells were longer or the difference in height greater, a suitable elevating device could be introduced in the pipe a^3 , such as a pump or worm.

In Fig. 5 I have illustrated an arrangement wherein the anode chambers are fed independently of each other as by the inlets a^{10} , a^{11} , and a^{12} , the effluent therefrom being conveyed away by the outlets x^1 , x^2 , x^3 to a conduit y and discarded or otherwise utilized, the various cathode chambers being fed independently from a source s and the catholyte passing from cell to cell by conduits c^{10} , c^{11} , etc., as before, and finally appearing at the outlet c^{20} . In case the same liquid be fed to both anode and cathode cells in this arrangement, the operation is exactly the same as that above described, with the possible advantage that with the arrangement in Fig. 5 the anode cells all contain liquid of the same composition and conductivity, while in Figs. 1 to 4 inclusive the anolyte is slowly being drained of its halid content. In order to prevent the undue impoverishment of the anolyte with the arrangement shown in Figs. 1 to 4 inclusive, it is necessary in the case of a long series of cells to introduce raw brine at intervals into the anolyte stream. However, the expedient of reducing the halid content of the anolyte before introducing this liquid into the cathode chambers is sometimes advantageous, both as reducing the total concentration of the catholyte and diminishing the amount of halid to be removed from the solution.

I have already pointed out that my improvements are independent of the derivation of catholyte by percolation of anolyte through the cell diaphragm, although it is necessary to make provision for some such percolation since the same may be expected to some degree in practice. It can be proved, both by theoretical deduction and practical demonstration, that by the employment of a series electrolysis such as herein described and claimed, the difference in electrolyte composition between different cells is greater and the average concentration and causticity for the whole system is lower in a case where the percolation is everywhere small than in a case where the percolation is everywhere large. However it may be assumed that in all practical embodiments of my improved method the catholyte in any given cell will

be derived from two sources, namely by percolation through the diaphragm of that same cell, and by accretion from the cathode chamber of the preceding cell.

From one aspect it may be stated that my invention comprehends reducing the former increment to its lowest practical value, and increasing the latter increment to its highest practical value.

It will be understood that I have shown only a few out of many forms of apparatus with which my improved process can be carried out, and described only a part of the benefits to be derived therefrom, and considered only a part of the uses to which such process and apparatus can be put.

Having thus described my invention what I claim is:

1. Apparatus for producing an alkali hydrate and chlorin from an alkali chlorid by electrolysis, comprising a series of electrolytic cells each having a diaphragm of limited permeability to liquid whereby the cell is divided into an anode compartment and a cathode compartment, each compartment of each cell having an inlet and an outlet, the outlet of each catholyte compartment communicating with the inlet of a succeeding catholyte compartment, until the last of the series is reached, means for delivering halid solution to the anode inlets, means for maintaining the level of the anolyte in each cell at a point above that of the catholyte of that cell, and means for delivering to the first cathode inlet the effluent from the anode outlets.

2. Apparatus for producing an alkali hydrate and chlorin from an alkali chlorid by electrolysis, comprising a series of electrolytic cells each having a diaphragm of limited permeability to liquid whereby the cell is divided into an anode compartment and a cathode compartment, each compartment of each cell having an inlet and an outlet, the outlet of each catholyte compartment communicating with the inlet of a succeeding catholyte compartment, until the last of the series is reached, the outlet of each anode compartment communicating with the inlet of a succeeding anode compartment until the last is reached, the outlet from the last anode compartment communicating with the inlet of the first cathode compartment, means for maintaining the level of the anolyte in each cell above that of the catholyte of that cell, and means for delivering halid solution to the first anode compartment.

3. In a method of electrolyzing an alkali halid solution for caustic and halid, the step which consists in passing the solution first through the anode compartments of a plurality of diaphragm cells and then passing the same solution successively through the cathode compartments of said cells.

4. The process of electrolyzing an alkali halid solution for halid and caustic alkali which consists in adding to the anode chamber of a diaphragm cell a greater quantity
5 of solution than said diaphragm can transmit by percolation, drawing off the excess of such liquid and passing it into the cathode chamber of the same or a similar cell by a separate passage, and thereafter passing said
10 liquid through the cathode chambers of a plurality of similar cells until the desired causticity is attained.

5. The process of electrolyzing alkali halid solution for halid and caustic alkali
15 which consists in adding to the anode chambers of a plurality of separate electrolytic cells of the diaphragm type, a quantity of solution greater than the diaphragms can transmit by percolation, drawing off the
20 excess of such solution after treatment in such anode chambers and passing it successively through all the cathode chambers of the series.

6. The process of electrolyzing alkali
25 halid solutions for halid and caustic alkali which consists in adding to the anode chambers of a plurality of separate electrolytic cells of the diaphragm type, a quantity of solution greater than the diaphragms can
30 transmit by percolation, drawing off the excess of such solution after treatment in such anode chambers and passing it successively through all the cathode chambers of the series, and meanwhile maintaining in each
35 said cathode chamber a pressure of liquid less than that in the corresponding anode chamber.

7. Apparatus for electrolyzing alkali halid solution to produce halid and caustic
40 alkali, comprising two electrolytic cells of

the porous diaphragm type, the anode compartments being connected in series so as to permit the flow of liquid from one to the other, the cathode chambers being also connected in series so as to permit the flow of
45 liquid from one to the other, and the last anode chamber being connected to the first cathode chamber so that the spent anolyte may pass through the cathode chambers.

8. A series of electrolytic cells of the porous diaphragm type, the anolyte being fed
50 into the anode compartment through a suitable passageway and withdrawn from the anode compartment through the porous diaphragm and another suitable passageway,
55 the catholyte being fed into each compartment through a suitable passage and also through the pores of the diaphragm and withdrawn through a passage connected
60 with the cathode compartment of another cell of the series, the effluent from the last anode compartment of the series flowing to a cathode compartment and from thence to each cathode compartment in succession.

9. The method of electrolyzing an alkali
65 halid solution for caustic and halid which consists in first passing the halid solution successively through the anode compartments of a plurality of independent electrolytic cells of the diaphragm type, and
70 second returning the same liquid successively through the cathode compartments of the same cells in reverse order.

In testimony whereof, I hereunto affix my signature in the presence of two witnesses. 75

HERBERT H. DOW.

Witnesses:

JAMES T. PARDEE,
A. W. SMITH.