

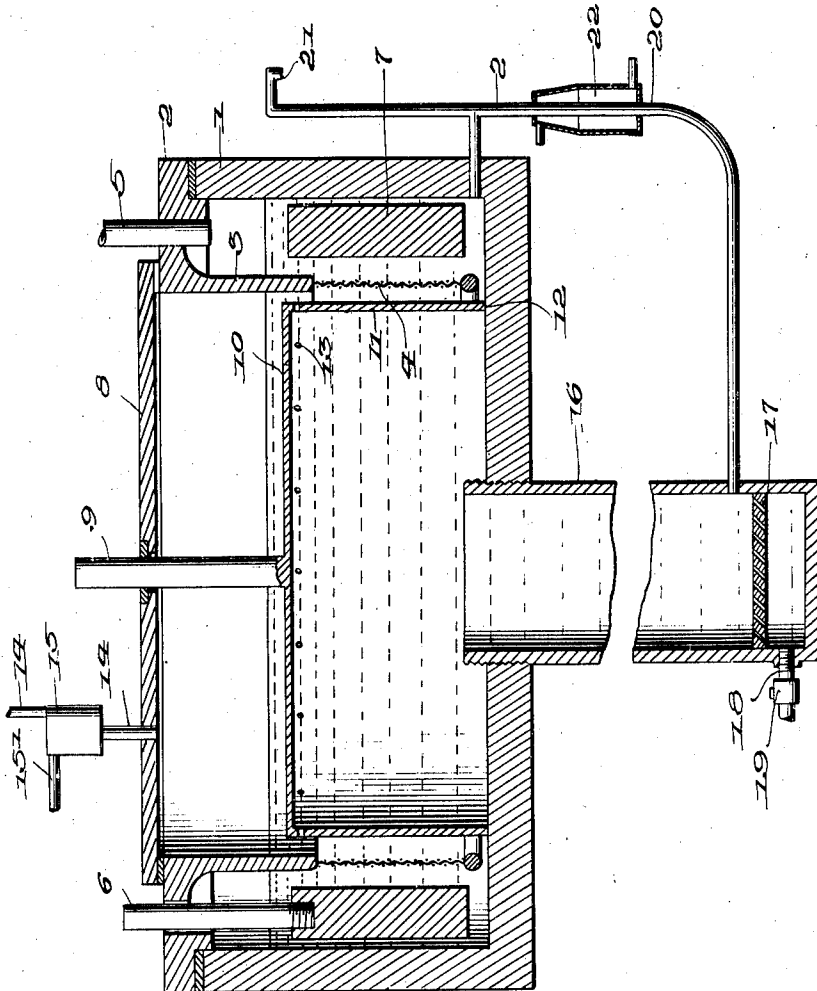
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MANUFACTURE OF CHLORINE

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UNITED STATES PATENT OFFICE

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MANUFACTURE OF CHLORINE

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This invention relates to the manufacture of chlorine; and it comprises a method of producing chlorine by electrolysis of a solution of hydrochloric acid (HCl) wherein a body of such solution is established and maintained between electrodes of opposed polarity in a suitable cell and the acidity replenished as it tends to disappear by addition of HCl gas to said body at a point below the electrode level; and it also comprises certain assemblages of apparatus elements useful in the said method; all as more fully hereinafter set forth and as claimed.

Chlorine is commercially made by electrolysis of solutions of salt; caustic soda in the corresponding amount being also produced. To secure good utilization of the salt and recover caustic soda from the cell liquor, extensive auxiliary apparatus is required and the process is one best operated on a large scale. There is, however, a demand for a method of producing chlorine which can be economically operated on a smaller scale and which is not coupled with the production of caustic soda. It is the object of the present invention to provide such a method.

In the present invention, chlorine is made by electrolysis of a solution of HCl (hydrochloric acid) replenished by additions of gaseous HCl. Formation of chlorine from HCl requires less energy than its formation from NaCl. The electrolytic operation is far simpler, since only gases (Cl_2 and H_2) are formed and there is no production of soluble byproducts in the cell liquor. The same body of electrolyte may serve indefinitely without removal from the cell, since the input of HCl gas is proportioned to the chlorine output, and but little attention is required. The operation of a cell becomes almost automatic.

The HCl gas used in replenishment may be made in any of the usual ways, as by the action of sulfuric acid on salt.

In the accompanying illustration, I have shown, more or less diagrammatically, an electrolytic cell within the present invention and useful in performance of my process. The view is in central vertical section.

As shown, element 1 is a casing of any suitable insulating and acid-proof material. It is shown as carrying a cap 2 having wing 3 depending below the normal liquid level of the electrolyte, forming an annular chlorine chamber. As shown, from the wing depends an annular screen member 4 of loosely woven asbestos or other pervious acid resistant material. It extends to a point just above the bottom. Through the cover for the anode compartment pass chlorine outlet pipe 5 and current lead 6, supplying current to anode 7. As shown, the anode is annular. It may be composed of graphite or other usual material. Supported by annular cap 2 is another cover element 8 for the axial cathode compartment. Through it passes current lead 9 taking current to a cathode immersed within the body of electrolyte. As shown, the cathode is drum-shaped, head 10 closing the axial compartment formed by annular member 11 which constitutes the cathode. Near the top, the wall 11 is provided with flow passages 13. Through the cover 8 passes hydrogen outlet 14. The whole system is run hot to reduce resistance and the electrolyte may be at the boiling temperature, although I find it better to work at a somewhat less temperature. The escaping hydrogen is therefore usually cooled to return entrained HCl and water vapor to the system. As shown, the hydrogen passes through a scrubber 15 provided with a water inlet 15'. The scrubber acts as a reflux condenser to return HCl and water. A similar reflux condenser may be provided for chlorine outlet 5 but is not really needed, since the chlorine goes through the usual purifying train (not shown). As shown, the casing 1 is provided with an axial depending well 16. The upper end of this well is somewhat above the bottom of 1. Near the base of the well is a perforated or foraminous plate 17, acting as a distributor for HCl gas. Below this distributor is inlet pipe 18 for HCl gas; this pipe being provided with check valve 19. Except in starting, this check valve is not necessary, for reasons later appearing. Liquid communication is established between the bottom of casing 1 and a low point in the well by circulating and equalizing pipe 20. This pipe serves to control the normal height of electrolyte in the cell

and is provided with outlet 21 through which excess of cell liquor may be removed. To aid in circulation, pipe 20 may be cooled by water jacket 22.

In normal operation, the axial chamber and well contain a hot strong solution of HCl; the temperature and strength depending somewhat on circumstances. A saturated solution, which is 20 per cent or thereabouts, boils at about 110° C. and it is desirable to have the temperature at least 10° lower. Actual ebullition is undesirable as carrying gaseous HCl into the cathode gas chamber. For the same reason, saturated solutions are not so desirable as those of somewhat less concentration. The less the HCl concentration, the easier it is to keep HCl in aqueous solution; but a rather high concentration, depending on the speed of flow between the electrode and the current density, must be maintained in the axial chamber to provide for the removal of HCl by electrolysis. If the acid passing between the electrodes is stripped too far, not only is there an increase in resistance, but oxygen evolution may tend to occur with formation of perchloric acid. It is generally safe to adjust conditions so that the return flow of acid in pipe 20 shall be not less than .015 per cent HCl and the axial concentration about 20 per cent. Hydrochloric acid gas entering through 18 passes upward through 17 as bubbles and is absorbed, for the most part, before it reaches the top of the well 16. Passages 13 prevent the top of the axial chamber becoming gas bound and permit outward flow of liquid. Imperforate top 10 may be replaced by a spider or open structure supported by 11 and carrying current from lead 9; but the imperforate disk 10 shown is generally more advantageous, as it prevents direct access of ascending HCl bubbles to the hydrogen chamber. The lower the chamber, the more advantageous is the use of disk 10. The absorption of the gas by the strong HCl solution in the axial chamber is not so rapid as to cause sucking back into pipe 18, so that check valve 19 rarely functions. In normal operation of the cell, the axial chamber contains strong HCl solution which passes upward and outward through vents 13, passing thence downward between the electrodes and back to the axial well via circulating pipe 20. HCl gas coming in through inlet 18 is sometimes rather hot, since it usually comes directly from the place of production. The gas may be precooled where this is desirable in any of the ordinary ways and by the ordinary apparatus. It may carry more or less water vapor. It is convenient to supply such further water as may be needed in the system through pipe 15 supplying the hydrogen scrubber.

In the assemblage of the apparatus shown, any of the usual structural materials resist-

ing the action of hydrochloric acid may be used. Cap 2 and cover 8 may be made of stoneware, molded glass or of concrete protected with bituminous cement or paint. The drum or bell cathode 10 may be made of graphite or any acid resistant metal. Silver, lead or lead-silver alloys will serve. It is protected by its polarity while the cell is in operation and with a lead cathode, a coating of PbCl₂ gives it resistance on shutdown. Screen 4 shown serves mainly to prevent mixing of gas bubbles and is not intended to retard ionic migration. Its use facilitates placing the cathode and anode in close approximation and thereby lessening resistance. The screen is advantageous, and particularly in tall types of cell, but not necessary.

Resaturation of the electrolyte can be done outside the cell proper, but the arrangement shown is better. It avoids handling acid solution and the use of pipe lines.

What I claim is:—

1. In the manufacture of chlorine, the process which comprises electrolyzing a body of aqueous solution of HCl between a pair of submerged electrodes and replenishing the HCl content by introduction of HCl.

2. In the manufacture of chlorine, the process which comprises electrolyzing a body of aqueous solution of HCl between a pair of submerged electrodes and replenishing the HCl content by introduction of HCl gas at a point below the level of the electrode.

3. In a chlorine cell, a casing, an annular anode therein, a annular cathode, an axial depending chamber in open communication with the chamber formed by the cathode and means for introducing HCl gas near the bottom of the depending chamber.

4. In the manufacture of chlorine, the process which comprises electrolyzing a bath composed of a solution of HCl between submerged electrodes with introduction of replenishing gaseous HCl near the bottom of said bath, the height of liquid column above the point of introduction being sufficient to effect substantially complete absorption by the bath of the gaseous HCl so introduced.

5. In the manufacture of chlorine, the process which comprises electrolyzing a continuously replenished bath of HCl solution, replenishment being by gaseous HCl.

In testimony whereof, I have hereunto affixed my signature.

FRANK S. LOW.