

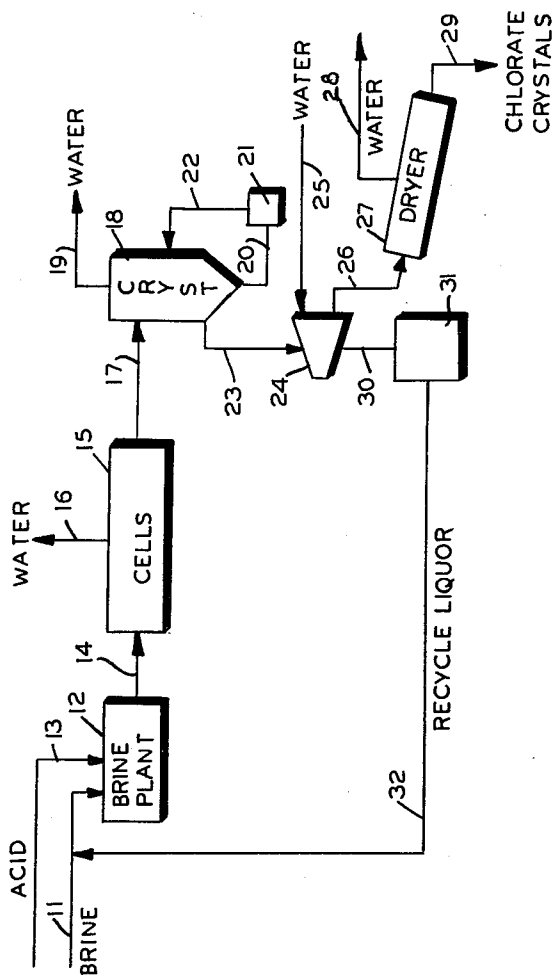
July 10, 1962

A. J. HOLMES

3,043,757

ELECTROLYTIC PRODUCTION OF SODIUM CHLORATE

Filed July 8, 1959



INVENTOR.

ARTHUR J. HOLMES

BY

Stanley J. Krownski

AGENT

1

3,043,757 ELECTROLYTIC PRODUCTION OF SODIUM CHLORATE

Arthur J. Holmes, Tonawanda, N.Y., assignor to Olin Mathieson Chemical Corporation, a corporation of Virginia

Filed July 8, 1959, Ser. No. 825,735
3 Claims. (Cl. 204—95)

This invention relates to improvements in the electrolytic manufacture of sodium chlorate from sodium chloride. More particularly it relates to a method of preparing electrolytically a cell liquor effluent of unusually high chlorate concentration from which the chlorate is crystallized directly as a first crop, advantageously simplifying the process of recovery of the solid chlorate.

Conventional sodium chlorate cells using steel cathodes and graphite anodes can be operated in the range of about 25° or lower up to about 70° C. At temperatures of 60° to 70° C. however, losses of graphite by oxidation become intolerably high and the usual temperature of operation is about 35° to 45° C. Were it not for the graphite losses, higher temperatures would be desirable because of the decreasing voltage requirements as the temperature increases.

Conventional sodium chlorate cells are usually equipped with cooling coils to maintain the temperature within the limits appropriate for use with graphite anodes. The cooling coils are an expensive part of the original cells and are expensive to maintain. Because of the heat produced as a by-product of the electrolysis, they are essential in conventional cells.

According to the process of the present invention, the electrolysis of sodium chloride to sodium chlorate is carried out at temperatures of about 105° to 123° C., the boiling range of the brine and preferably at about 105° to 115° C. Provision is made for removal of water as steam directly from the cells. The effluent liquor from the cell is cooled, advantageously by flashing off a further minor proportion of water from the liquor in the crystallizer. The crystals of sodium chlorate are separated and dried and the liquor is recycled.

The process of the present invention is carried out in simple cells with no provision for cooling. An outlet is arranged, suitably in the cell covers for removal of steam or water vapor. The electrodes are fabricated of titanium bearing superficially thereon a coating of platinum. Uncoated titanium used anodically in chloride brines is rapidly inactivated by the formation of a non-conducting, passive film thereon. Electrodes of titanium, however, do not form this passive film where they bear a superficial coating of platinum. The titanium electrodes bearing superficially a coating of platinum are used as anodes and may be used as cathodes, though separate cathodes of steel can be used. The electrodes may be arranged in any suitable monopolar or bi-polar fashion.

Suitable anodes may be prepared by the application of platinum metals to titanium base metal by the process described in Australian application 36,578 of 1958 by Jansen, opened to public inspection April 1, 1958 or by the process described in Australian application 49,837 of 1958 by Imperial Chemical Industries Ltd., opened to public inspection July 23, 1958 or by other suitable methods.

2

Using the electrodes as described above, the cells are operated at temperatures up to the boiling point of the brine saturated with both sodium chlorate and sodium chloride (123° C), suitably at about 105° to 115° C. Voltage requirement is reduced from about 4.2 volts to about 3.9 volts due to the increase in brine temperature from about 35° to 45° C. up to about 105° to 115° C. Current density is one ampere per square inch or higher compared to 0.13 to 0.35 ampere per square inch in the operation of conventional cells with graphite anodes.

By operating the electrolytic cells at temperatures of 105° to 115° C., it is possible to maintain the cell liquor at higher concentrations of chloride and considerably higher concentrations of chlorate than in cells operated at 35° to 45° C. The recycle cell liquor contains about 75 to 125 grams per liter of sodium chloride and 550 to 650 grams per liter of sodium chlorate. By the addition of about one volume of saturated sodium chloride brine feed to one volume of recycle liquor, the concentration of sodium chloride is brought up to about 150 to 225 grams per liter in the cell feed. The sodium chloride content of the effluent liquor from the cells is reduced by electrolysis to about 75 to 125 grams per liter and the chlorate content is raised by electrolysis and evaporation of water to about 675 to 800 grams per liter of sodium chlorate. By evaporative cooling of the effluent cell liquor of this concentration and removal of a portion of the sodium chlorate content which separates as the first solid phase, the recycle liquor contains about 80 to 125 grams per liter of sodium chloride and 550 to 650 grams per liter of sodium chlorate. Preferred concentrations lie within these ranges. For example, the recycle liquor suitably contains about 100 grams per liter of sodium chloride and 600 grams per liter of sodium chlorate when the crystals are separated at a temperature of about 45° C. The fortified liquor fed to the cells suitably contains about 200 grams per liter of sodium chloride and the effluent contains about 80 grams per liter of sodium chloride and 800 grams per liter of sodium chlorate.

In the more dilute liquors obtained by graphite anode cell operations containing about 160 grams per liter of sodium chloride and 400 grams per liter of sodium chlorate, sodium chlorate is recovered by cooling the liquor from 45° to 0° to -10° C. using expensive refrigeration. By an alternative method the cell liquor is evaporated to remove part of the water. As the solution becomes more concentrated, sodium chloride crystallizes and is separated and returned to the process. The residual solution is cooled to crystallize sodium chlorate which is removed from the solution. In contrast with these conventional processes, the present process obtains sodium chlorate in the first crystallization and unconverted salt remains in the liquor and is recycled to the cells. Only cooling water is required and the necessity of expensive refrigeration to lower temperatures is avoided.

A particular advantage of the operation of the process of the present invention is that all the evaporating, separating and handling of solid salt is eliminated as well as the refrigeration requirements. Instead, the present process utilizes the waste heat generated in the electrolysis step to evaporate water directly from the cells. The waste heat available at this point is ample to permit feeding brine instead of solid salt to the cells. In conventional operation, solid salt is either crystallized from

3

brine, separated and charged as solid salt to the cells or additional heat must be supplied in an evaporation step to remove excess water introduced as brine. It is thus a particular advantage of the operation of the process of the present invention that sodium chloride brine is an especially suitable feed. Advantageously the brine is saturated or substantially saturated, having a concentration of about 90 to 100 percent of saturation.

In conventional chlorate cells the operating pH is usually approximately 6.7 and generally is within the range of 6.5 to 7.0. Small proportions of chromates or bichromates are added to the electrolyte to prevent reduction at the cathodes. The addition of chromates in the present process using platinized titanium electrodes is also advantageous for the same reason.

In conventional chlorate cells with graphite anodes the current density can be up to about one ampere per square inch. Practically, the wear on the graphite anodes at such current density is intolerably high and limits actual operations to about 0.13 to 0.35 ampere per square inch. Decreasing the current density decreases the voltage drop across the cell and increases the size of the electrodes, cells and buildings required for a given tonnage per day of product. The present process advantageously makes possible high current densities without deleterious effect on platinum surfaced titanium anodes. The voltage drop across the cells is reduced from about 4.2 to about 3.9 volts and the current efficiency is significantly raised from about 80 to above 90 percent. This improvement in current efficiency is due primarily to the discharge of less hypochlorite ion at the anodes at the elevated temperatures. More hypochlorite is converted to chlorate and less decomposes to liberate oxygen. The oxygen liberation represents an inefficiency which is materially reduced in the present process. A further advantage of the present process is that a holding time and the tanks conventionally required for conversion of hypochlorite to chlorate are entirely avoided. The resultant savings in size of electrodes, cells, auxiliary equipment and buildings permits a material reduction in the cost per ton of chlorate.

In the flow sheet of FIGURE 1, sodium chloride brine introduced via line 11 is mixed with recycle liquor returning via line 32 and treated in brine plant 12 including particularly acidification by means of hydrochloric acid introduced via line 13. The treated brine flows via line 14 to cells 15 where a portion of the chloride content is converted to chlorate. Water is vaporized directly from the cells and removed via line 16. The cell effluent flows via line 17 to a crystallizer 18, removing additional water overhead via line 19. Liquor is recycled from the bottom of crystallizer 18 via line 20 using pump 21 to return the liquor via line 22 to crystallizer 18. A slurry of chlorate crystals and mother liquor passes via line 23 to centrifuge 24. The separated crystals are washed with water introduced by line 25 and transferred by line 26 to dryer 27. Water is removed via line 28 and the dry chlorate crystals are removed as product via line 29. Mother liquor from the centrifuge is transferred via line 30 to a surge tank 31 and recycled via line 32 to the brine plant.

Example I

Operating the process as described in the flow sheet of the attached figure, fresh brine is charged to the brine plant in the form of a 25 percent aqueous sodium chloride solution at the rate of 1840 pounds per hour together with a recycle liquor stream comprising 1080 pounds per hour of sodium chlorate, 181 pounds per hour of sodium chloride and 1260 pounds per hour of water. The mixed brine is treated with 10 percent hydrochloric acid to produce a feed which will maintain a pH of about 6.5 to 7 in the cells. Usually a pH of about 5 in the feed is satisfactory. The feed to the cell comprises 1080 pounds per hour of sodium chlorate, 640 pounds per hour of sodium chloride and 2640 pounds

4

per hour of water. During the electrolysis water is vaporized from the cells at the rate of 1340 pounds per hour. The effluent from the cells at a temperature of 112° C. comprising 1910 pounds per hour of sodium chlorate, 181 pounds per hour of sodium chloride and 1290 pounds per hour of water is charged to the crystallizer from which water is removed at the rate of about 200 pounds per hour. The slurry removed from the crystallizer at a temperature of 45° C. comprises 1080 pounds per hour of sodium chlorate, 181 pounds per hour of sodium chloride and 1090 pounds per hour of water. Wash water is used at the rate of 178 pounds per hour. The liquor is recycled to the brine feed tank and the crystals transferred from the centrifuge to the dryer comprise 840 pounds per hour of sodium chlorate, one pound per hour of sodium chloride and 13 pounds per hour of water. About 13 pounds per hour of water are removed in the dryer and the crystalline chlorate product comprises the 840 pounds chlorate containing only one pound of sodium chloride and about 0.25 pound of water.

Example II

A glass chlorate cell was constructed having a capacity of 4 liters. It carried a tight one inch thick "Lucite" cover carrying in turn leads for a pH controller, leads for a liquid level controller, leads for the principal electrodes and lines for the introduction of water, for the addition of dilute hydrochloric acid and for the removal of cell gas and water vapor. The line for the latter was connected to a condenser for the separation of the aqueous condensate from by-product gases. The liquid level controller was actuated by leads in the cell operating the valve on a water feed tank which replaced condensate and maintained constant level in the cell. The pH controller feeds one percent hydrochloric acid to the cell to maintain the pH of the cell contents at 7. The cell also contained a thermometer and provision for heating and stirring the cell contents. The principal electrodes suspended through the top cover comprised two titanium sheets each three inches square and one sixteenth inch thick welded to titanium rods and bearing a dull gray platinum coating 0.0001 inch thick. "Teflon" spacers maintained the electrode distance at one-eighth inch. Direct current was supplied to the electrodes at about 3.5 to 4.0 volts and 9 amperes giving a current density of about 1 ampere per square inch. The polarity of the cell was reversed periodically to remove any deposition of impurities on the cathodes tending to increase cell voltage. The cell liquor comprised an aqueous solution originally containing approximately 750 grams per liter of sodium chlorate, 100 grams per liter of sodium chloride and 2 grams per liter of sodium dichromate. The volume of the electrolyte was maintained at 2.5 liters. The cell contents were stirred and heated to the boiling point which varied from about 105 to 115° C. A sample of 200 milliliters of the cell liquor was removed at 24 hour intervals and replaced with approximately 80 grams of sodium chloride with sufficient water to bring the cell volume back to 2.5 liters. Sodium chlorate crystallized from the sample on cooling and was processed as described in Example I.

Hourly readings were taken of the amperage, voltage, temperature, pH, condensate volume and acid volume which were averaged over each 24 hour period. A sample of the gas was analyzed each 24 hours for chlorine, hydrogen and oxygen content. From these values and the average voltage and amperage, the current efficiency shown in column 9 of the table below was calculated by deducting from 100 percent the proportion of current consumed in the formation of chlorine and oxygen. Column 10 shows the current consumed, expressed as kilowatt hours per ton of chlorate produced. This is inversely proportional to the current efficiency except for minor variations in the voltage. The results for eleven days of continuous operation without current interruption, controller

failure or other interruptions are shown in the following table:

electrodes selected from the group consisting of steel and composite electrodes, at least the anodes being composite

Hours, Averaged (1)	Average Readings					Cell Gas Analysis		Current Efficiency, Percent (9)	Current Consumed ^b (10)
	Voltage (2)	pH (3)	Cell Temp., °C. (4)	Condensate, ml./hr. (5)	Acid Added ^a (6)	Chlorine, Percent (7)	Oxygen, Percent (8)		
18.....	3.86	7.1	106	13	32	0.4	6.2	87.2	6,100
6.....	3.90	7.0	106	13	13	0.2	4.6	90.0	5,900
18.....	3.88	7.0	104	8	14	0.2	5.1	89.5	6,000
6.....	3.92	7.1	110	39	29	0.5	2.4	94.7	5,700
6.....	3.85	7.0	110	32	62	0.8	2.7	92.8	5,370
24.....	3.90	7.3	111	11	50	1.6	1.7	94.6	5,700
18.....	4.00	7.2	111	13	55	1.0	2.9	93.2	5,930
24.....	3.91	6.8	110	12	13	0.4	5.7	88.2	6,100
5.....	3.97	6.6	111	12	9	0.3	5.65	88.4	6,200
20.....	4.02	6.8	111	13	15	0.7	2.4	94.5	5,850
4.....	3.98	6.8	110	4	7	0.8	2.9	93.4	5,860
66.....	4.19	6.8	109	12	13	0.2	1.6	96.0	5,750
6.....	3.99	6.8	112	4	97	7.0	1.92	91.1	6,070
24.....	3.52	7.0	111	6	26	2.3	0.9	95.5	5,060
24.....	3.73	7.2	111	3	40	1.3	1.8	94.9	5,200

^a Pounds of 36 percent hydrogen chloride per ton of sodium chlorate.
^b Kilowatt hours per ton of sodium chlorate.

The data of the above table are in striking contrast to the operation of conventional chlorate cells using graphite anodes. Although the art describes operation from room temperature to about 60° C. most conventional chlorate cells containing graphite anodes are operated at about 45° C. This temperature is a compromise between high graphite consumption at higher temperatures and low production rates and refrigeration requirements at lower temperatures. With conventional cells, current efficiencies vary from about 70 to 85 percent as contrasted with the above values of about 90 percent or better. Conventional current densities are in the range of about 0.13 to 0.35 amperes per square inch in contrast with the completely satisfactory current density of one ampere per square inch used above. The above-described run was continued for over 3000 hours with no visible change in the electrodes.

The process of the present invention is useful in batch or continuous operations or in any desired combination thereof. One cell may be charged with electrolyte and electrolyzed to suitable concentrations and the brine worked for sodium chlorate as described above. The mother liquor from the crystallization is charged with fresh brine to the next batch. In continuous operation, the electrolyte flows through a series of cells in which the concentration of chlorate in the electrolyte increases to the desired concentration. The electrolyte flows out of the last cell and is worked with recycle as described above.

What is claimed is:

1. In an electrolytic process for the production of sodium chlorate in which a chlorate brine containing sodium chloride and sodium chlorate is electrolyzed between

electrodes, said composite electrodes consisting of a core of titanium bearing platinum superficially thereon, the improvement which comprises electrolyzing at a temperature of about 105 to 123° C., simultaneously vaporizing and removing water from the chlorate brine to maintain a chlorate concentration in the chlorate brine of about 675 to 800 grams per liter, removing the chlorate brine from the zone of electrolysis, cooling to crystallize sodium chlorate from the electrolyzed chlorate brine and separating the crystals from the residual liquor, fortifying the residual liquor by adding sodium chloride brine and charging the fortified chlorate brine to the electrolysis

2. The process of claim 1 in which the residual liquor is fortified by the addition of sodium chloride brine to a concentration of about 150 to 225 grams per liter of sodium chloride.

3. The improvement of claim 2 in which the electrolyzed brine is cooled from a temperature in the range of 105 to 123° C. to a temperature above about 45° C. to crystallize sodium chlorate.

References Cited in the file of this patent

UNITED STATES PATENTS

50	1,143,586	Laib	June 15, 1915
	1,173,346	Gibbs	Feb. 29, 1916
	2,511,516	Schumacher	June 13, 1950

OTHER REFERENCES

55	Chemical and Metallurgical Engineering, vol. 45, No. 12, December 1938, pages 692-696.
	Chemical Age, January 3, 1959, page 9.
	Corrosion Technology, February 1959, pages 49-62.