CATHOLYTE RECIRCULATION IN DIAPHRAGM CHLOR-ALKALI CELLS

Original Filed Sept. 23, 1968

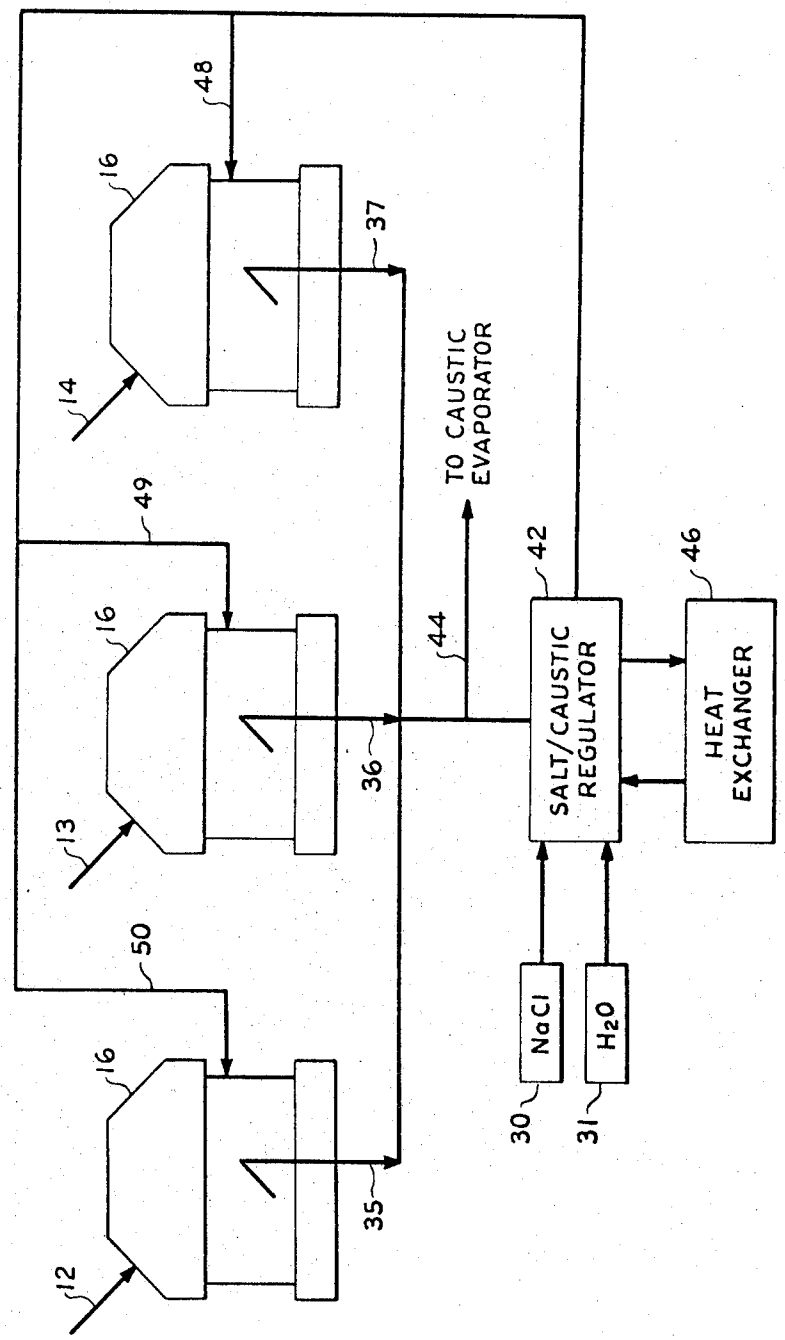


Fig. 1

CATHOLYTE RECIRCULATION IN DIAPHRAGM CHLOR-ALKALI CELLS

Original Filed Sept. 23, 1968 3 Sheets-Sheet 2

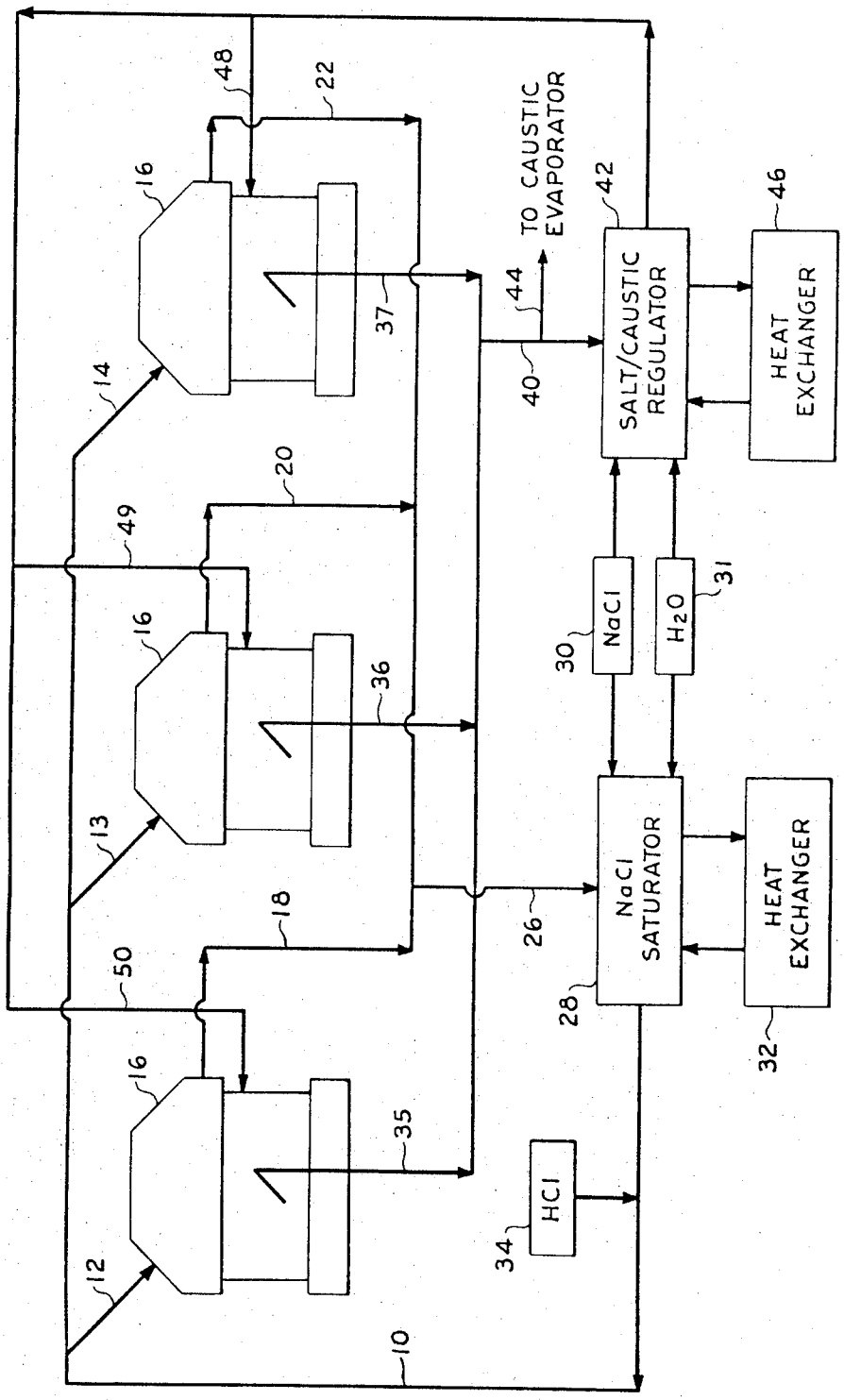


Fig. 2

CATHOLYTE RECIRCULATION IN DIAPHRAGM CHLOR-ALKALI CELLS

Original Filed Sept. 23, 1968 3 Sheets-Sheet 3

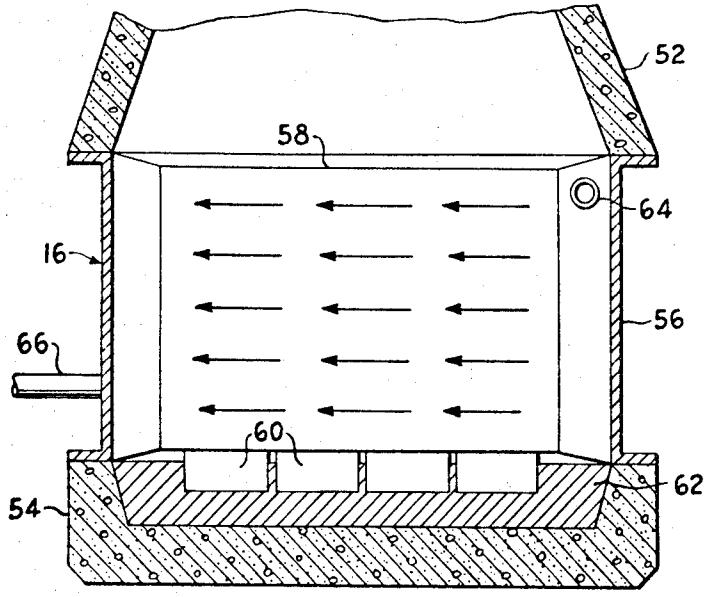


Fig. 3

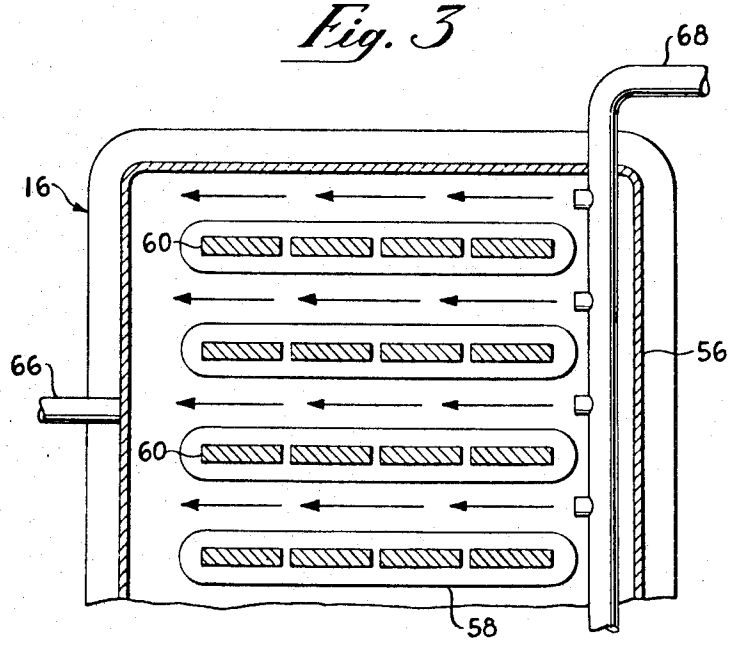


Fig. 4

United States Patent Office 3,723,266 Patented Mar. 27, 1973

3,723,266

CATHOLYTE RECIRCULATION IN DIAPHRAGM CHLOR-ALKALI CELLS

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Original application Sept. 23, 1968, Ser. No. 761,752. Divided and this application Nov. 12, 1970, Ser. No. 89,102

Int. Cl. C01d 1/06

U.S. Cl. 204—98 7 Claims

ABSTRACT OF THE DISCLOSURE

The caustic concentration, and salt-caustic ratio of catholyte is requlated by addition of an alkali metal chloride and/or water to withdrawn cell liquor. The temperature of the cell liquor is regulated as desired and an amount of the idealized cell liquor is returned to the cathode compartment of the cell which is approximately one-third to ten times the volume of catholyte withdrawn in the absence of recirculated catholyte. The cell liquor treatment and recycle may be employed in conjunction with anolyte recycle or as an independent means for cell control. Catholyte recirculation increases the cell efficiency and/or produces a cell liquor with a higher caustic concentration than is obtained conventionally.

This is a division of our parent application, S.N. 761,752, filed Sept. 23, 1968 now Patent No. 3,616,328.

This invention relates to chlor-alkali diaphragm cells and more particularly to a method of operating chlor-alkali diaphragm cells alone or in groups under controlled conditions of catholyte salt and caustic concentration and temperature, to thereby increase the efficiency of such cells, to reduce anode consumptions, to control the ratio of caustic to chloride produced in the cell liquor, to produce a cell liquor of increased caustic soda content, to improve diaphragm life, and to effect numerous other improvements in cell operation as herein disclosed.

Chlor-alkali diaphragm cells are normally operated in circuits consisting of groups of 50 to 150 or more cells. Each cell running independently of the other cells. The product from these cells are combined into three major effluent streams so that the total group of cells produces an effluent stream of chlorine, an effluent stream of hydrogen and an effluent stream of cell liquor. The cell liquor is usually a mixture of 9% to 12% caustic and 10% to 18% salt, by weight.

With each cell in a series running individually, only very limited operational control can be achieved through changes in the decomposition voltage and regulation of the brine concentration and feed rates which in turn depend largely on the porosity and flow rate through the diaphragm. This results in each cell operating at different efficiencies and under different conditions of temperature, catholyte concentration, anolyte concentration, pH and so forth. As for example, cells having diaphragms whose porosity has been partially reduced by deposits of impurities from the brine tend to operate at higher voltages, temperatures and higher caustic strengths. The higher caustic strength results when it becomes necessary to throttle back on the brine feed to the cells; this results in higher operating temperatures, greater hydroxyl migration through the diaphragm to the anode compartment which in turn causes excessive loss of current efficiency.

The major items of expense in operating diaphragm cells are (1) power, (2) cell renewal and (3) caustic evaporation. All of these items are directly related to the cell operation in (1) current efficiency, (2) cell voltage, (3) anode life, (4) diaphragm life and (5) cell liquor

caustic and salt concentration. If the current efficiency and cell voltage could be advantageously controlled to reduced power costs and extend the anode life, and if the diaphragm life could also be extended, two of the major cost items in operating diaphragm cells would be reduced. Further, if in advantageously controlling the first four factors enumerated above, the cell liquor caustic and salt concentrations could be changed to a more advantageous ratio, then all three of the major cost items in operating diaphragm cells could be reduced, thereby greatly improving chlor-alkali diaphragm cell operation.

In addition if the current density could be increased on a cell or circuit of cells, greater production would result without a compensating increase in investment and the overall economics of chlorine, caustic, and hydrogen production could be improved. One of the major limiting factors in the operation of diaphragm chlor-alkali cells as they are presently operated is the generation of such quantities of heat that the solutions in the cell begin to boil, resulting in evaporation of a significant proportion of the anolyte and catholyte. When this happens, large quantities of gas develop throughout the electrolyte. The electrolyte is thrown out of the cell into the gas collection headers and the current conducting path between the electrodes is replaced with a large portion of gas which results in very high voltages across a particular cell. Once started, this action will continue until the cell goes dry and conduction stops.

It is an object of this invention to provide a method whereby the current efficiency of chlor-alkali diaphragm cells is improved. It is another object of this invention to provide a method whereby chlor-alkali cell voltages are advantageously improved to operate at the most efficient level. A further object of this invention is to provide a method whereby the anode life of chlor-alkali diaphragm cells is extended. Yet, another object of this invention is to provide a method of operation whereby the porosity of the diaphragm becomes less critical, so that the diaphragm life can be extended to equal the anode life. Another object of this invention is to improve the salt/caustic concentration ratio in the cell liquor. Another object is to produce a higher concentration of caustic in the cell liquor. Another object of this invention is to control the cell temperature at an optimum point whereby cells can be operated without flashing of the water to vapor occurring to an extent that the process is out of control. A further object is to provide a method whereby a cell can be operated at higher current densities. A further object is to operate a bank of cells closely to the saturation limits found in the cell liquor thereby reducing the water necessary to be evaporated for the production of concentrated caustic. A further object is to produce more uniform operation, more uniform anode wear, a more uniform diaphragm life thus enabling better prediction of renewal requirements and easier scheduling. These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

In accordance with the invention, a process is provided for operating a group of chlor-alkali diaphragm cells comprising imposing a decomposition voltage across the electrodes of a group of chlor-alkali diaphragm cells, feeding a solution of brine to the cells, maintaining a head on the anolyte compartment sufficient to maintain flow through the diaphragm into the catholyte compartment, withdrawing the catholyte cell liquor from the individual cells, combining the cell liquor from a group of cells, withdrawing a portion of the combined cell liquor and feeding it to the evaporation system, controlling the temperature of the remaining portion of the combined cell liquor and controlling the ratio of salt to caustic by adding solid NaCl, water or bine and returing the remaining portion of the resultant solution back into the catholyte

compartment of the cells. Advantageously the amount of cell liquor returned to the cells compared with the amount withdrawn is in the range of one-third to ten times by volume. Preferably, between about one to three times the volume of cell liquor withdrawn from a cell is returned to the cathode compartment. In addition, cell temperatures may be maintained at a predetermined optimum of from about 90° C. to 105° C. by controlling the temperature of the resaturated cell liquor prior to its return to a cell. The salt-caustic ratio of the catholyte within the cathode compartments is maintained between about 0.5 and 2.0 and preferably between 0.7 to 1.5.

The catholyte recirculation method of the present invention provides improved control of the catholyte liquor concentrations thereby controlling the hydroxyl ion migration from the catholyte compartment to the anolyte compartment which results in achieving the highest operating efficiencies. The process can be operated with a group of cells thereby establishing controlled conditions of temperature and cell liquor concentration which in turn tend to control anolyte composition, pH and the like. This method of operation, in which the catholyte conditions are made substantially the same in all cells, effectively controls all or nearly all of the cells under the most desirable conditions.

Caustic concentration is the single most influential parameter affecting current efficiency. High caustic concentrations results in high hydroxyl ion migration through the diaphragm into the anolyte compartment; these OH ions are electrolyzed at the anode producing oxygen and carbon dioxide, thus consuming current and graphite. In a group of cells it is not unusual to find a broad range of caustic concentrations. Because of the non-linear relationship between caustic concentration and current efficiency, the cells with high caustic concentration cause greater inefficiency than is compensated for by the cells with low caustic concentration. The overall result is a drop in efficiency from that anticipated from the average caustic concentration of a cell series.

By recirculating the catholyte, and bringing all catholyte concentrations closer to the average of all cells, in a series, the average current efficiency increases for the series. An aqueous caustic solution from a source extraneous to the electrolytic cell catholyte may be fed to the cathode compartments in addition to excess cell liquor to aid in the production of more concentrated catholyte caustic.

The process of the present invention can be used in the electrolysis of any alkali metal chloride. However, because sodium chloride is preferred and is normally the alkali metal chloride used, the description hereinafter is directed more particularly to sodium chloride. It is to be understood that other alkali metal chlorides may be used, particularly potassium and lithium chlorides.

The present invention presents a method of controlling more closely the catholyte conditions; this system combined with the recirculated anolyte system as disclosed in application S.N. 510,225, filed Nov. 29, 1965 now U.S. 3,403,083, gives complete control over anolyte and catholyte of a single cell or group of cells.

The anolyte salt concentration has an affect on the current efficiency. Normally, increasing the chloride concentration in the anolyte compartment results in benefits of higher current efficiency, purer chlorine, lower voltage, lower graphite consumption, higher caustic concentration and less chlorate in the cell liquor so that it is normally preferred to operate at the highest salt concentration. However, the solubility of sodium chloride in the feed brine limits the amount of sodium chloride which can be practicably fed to a normally operated cell.

Since both chlorine and sodium ions are being removed from the cell at the electrodes, the bulk anolyte solution becomes depleted of salt to such an extent that a normal cell has an anolyte salt concentration considerably below the saturation point, even though the brine was fed to the cell as a nearly saturated solution. Typically, a normal diaphragm cell was fed with a brine solution containing about 310 to 330 grams per liter of sodium chloride (a saturated solution at about 90 degrees centrigrate contains about 333 grams per liter) but has an anolyte sodium chloride concentration of only about 270 grams per liter. Better cell operation is obtainable at higher anolyte salt concentrations.

It was found that by the anolyte recirculation method, the advantages of higher sodium chloride concentration in the anolyte compartment can be realized by feeding a stream of brine to the anolyte compartment at a rate faster than the brine can pass through the diaphragm into the catholyte compartment. Thus, it is possible to increase the sodium chloride concentration in the anolyte compartment by continuously adding concentrated brine and removing depleted anolyte solution. The excess brine is withdrawn from the anolyte compartment and is resaturated with sodium chloride. Also, it is preferred to adjust the temperature to the desired operating range and to add HCl to an amount to obtain the desired anolyte pH prior to returning the brine to the anolyte compartment. The practical over-all result is that a leveling effect is obtained in all of the cells and the sodium chloride concentration in the anolyte compartment is increased to a level higher than that previously obtainable. By the anolyte recirculation method, the sodium chloride concentration in the anolyte compartment can be maintained at any level up to the saturation concentration and particularly may be maintained within the preferred range of 260 to 330 grams per liter of sodium chloride. Because the recirculation of anolyte liquor without an enrichment of sodium chloride results in substantial improvements in the operation of chlor-alkali cells, the process can also be operated with lower NaCl concentrations, such as about 130 to 260 grams per liter of NaCl.

It was found that catholyte salt concentration and the catholyte caustic concentration have an effect on the hydroxyl ion migration through the diaphragm thus affecting the cells current efficiency. Normally increasing the catholyte chloride concentration results in benefits of higher current efficiency, lower graphite consumption, and less chlorate in the cell liquor so that it is normally preferred to operate at the highest salt concentration. Also the caustic concentration in the cell liquor is the single most important factor that controls hydroxyl ion migration through the diaphragm which effects current efficiency.

Typically a normal diaphragm cell operates with a caustic concentration in the cell liquor of from 120 to 160 grams per liter NaOH. At a typically 140 grams per liter NaOH concentration there will be approximately 200 grams per liter NaCl.

It has been found that the present catholyte recirculated method of optimum conditions of cell liquor concentrations and temperatures can be controlled on all cells to achieve the optimum overall process economics for the specific plant under consideration. The caustic concentration can be controlled so that the cost of evaporating the water and the cost relating to the inefficiency at the anode can be reduced to a minimum.

Conventionally, as the cell series is placed in operation, a constant brine feed rate is employed with each individual cell. The feed brine contains a uniform sodium chloride concentration. Since the current efficiency and temperature of operation varies from cell to cell as a result of the specific anode age, electrode alignment, diaphragm permeability or weight uniformity and a similar idiosyncrasies of a specific-cell the caustic concentration in the catholyte varies markedly. As the caustic concentration of a specific cell increases, back migration of hydroxyl ion is to the anode results in a decreased current efficiency. Hence, in a cell series, the production of a uniform caustic concentration throughout the series will produce an average current efficiency which is higher than that of a circuit operating at the same average cell liquors

strength with individual cells operating at a wider variance from the average caustic strength. Therefore, removal of catholyte, production of the desired caustic concentration in return of cell liquor to the individual cells produces the higher current efficiency by lowering the caustic strength in the cells with high sodium hydroxide concentration and raising the sodium hydroxide concentration in the cells with low sodium hydroxide concentrations.

If desired, a higher current density may be employed in cells operating on the principle of recirculated catholyte without incurring the undesirable high temperature and excess evaporation of water from the electrolyte, by cooling the cell liquor before return to the cathode.

The amount of sodium chloride which may be added to the caustic cell liquor is governed by that concentration at which sodium chloride will crystallize and precipitate. The temperature of the cell liquor of course is a governing parameter for sodium chloride solubility. Solid sodium chloride or brine may be added to the returning cell liquor to regulate the salt/caustic ratio after the cooling step in a high current density cell series. This results in a higher sodium hydroxide concentration and a lower sodium chloride to sodium hydroxide ratio at a higher cell efficiency than would be normally obtainable. The operation to produce higher caustic concentrations in a cell liquor is at no sacrifice to normal current efficiency, when recirculated catholyte is practiced.

The invention will be further described by reference to the drawings in which:

FIG. 1 is a partially schematic flow sheet illustrating the present invention, particularly as it relates to operation of a group of cells;

FIG. 2 is a partially schematic flow sheet illustrating the process of the present invention in conjunction with anolyte recirculation, particularly as it relates to operation of a group of cells;

FIG. 3 is a schematic side elevation of a cathode finger in the recycled catholyte of this invention flows as indicated by the arrows;

FIG. 4 is a top view of an electrolytic cell operated under the instructions of this invention so that catholyte is directed via manifold means to flow across the cathode face.

The process of this invention is effected, as illustrated in FIG. 1, by feeding a stream of feed liquor to a group of chlor-alkali diaphragm cells **16** by means of feed lines **12, 13** and **14**. The brine in the anode compartment permeates the asbesos diaphragm passing into the cathode compartment. The catholyte exits the cells and is fed by lines **35, 36** and **37** to a salt/caustic regulator **42** after sending a portion of the cell liquor to a caustic evaporator via line **44**. In salt/caustic regulator **42**, the ratio of salt to caustic is controlled as well as the temperature of the liquor and the caustic concentration. Additional sodium chloride **30**, water **31**, or mixtures thereof, are mixed with the cell liquor in **42**. Furthermore, heat exchanger **46** maintains the cell liquor at the proper temperature for optimum cell performance. The modified cell liquor is then returned to the cathode compartment of the several cells via lines **48, 49** and **50**.

The process of the present invention if effected, as illustrated by FIG. 2, by feeding a concentrated stream of feed liquor **10** to a group of chlor-alkali diaphragm cells **16** by means of lateral feed lines **12, 13** and **14**. The group of series of cells may be 2 to 150 or more cells from which anolyte liquors are withdrawn and combined for recirculation. The feed rate of brine to the cells **16** by means of the lateral lines **12, 13** and **14** is at a rate greater than the amount of liquor which flows from the anolyte compartment through the diaphragm in the chlor-alkali cell into the catholyte compartment and more preferably, the brine feed rate is 1.5 times up to about ten times the flow through the diaphragm. The most preferred flow rate averages, for a group of cells, is about two to five times that flowing through the diaphragm. The excess feed liquor is withdrawn from the cells **16** via lines **18, 20** and **22**. These lines are combined and returned to salt saturator **28** via line **26**. Cell liquor is withdrawn from the catholyte compartments of the cells via lines **35, 36** and **37** and combined in line **40** using suitable withdrawal means.

In salt saturator **28**, additional sodium chloride **30** and water **31**, or mixtures thereof, are mixed with the brine to the anolyte compartments of the cells **16** via line **10**. Normal salt saturation techniques are used in the salt saturation step. In addition to resaturating the withdrawn anolyte liquor, sufficient additional brine is prepared or mixed with the anolyte liquor to replace brine which passes through the diaphragm in the electrolytic cell.

Another variable which affects the anode current efficiency is the anolyte temperature. The provisions for heat exchange means **32** associated with brine saturator **28**, as shown, or other heating means, provide for maintaining the cells at the most efficient operating temperatures. Heat exchange means **32** maintains the saturator **28** at the proper temperature for saturating the recirculating anolyte solution so that the maximum practical salt concentration is supplied to the cells. Normally, saturated brine fed to the cells contains about 26 to 27 percent NaCl by weight or about 327 grams per liter of NaCl, which is the saturation concentration at about 65 degrees centrigrade. Additional heat is provided after the saturator to heat the brine to a temperature of approximately 75 to 80 degrees centigrade to prevent the deposition of salt crystals in the feed lines to the cells. This latter temperature is regulated so that the temperature of the anolyte in the cell is maintained between about 85 and 100 degrees centrigrade by the additional heat provided by the electrochemical reaction taking place in the cell.

Alternatively, the saturator can be operated at a higher temperature, such as 75 to 80 degrees centigrade, and a small stream of unsaturated brine or water may be added after the saturator to reduce the salt concentration in the brine to about 327 grams per liter to prevent salt drop out in the lines to cell. Again it is preferred that the temperature of the saturated brine be regulated so that the operating temperature in the anolyte compartment of the cell is maintained at the most preferred temperature of about 93 to 100 degrees centigrade.

In an operating group of electrolytic cells, the amount of heat required by heat exchanger **32** varies primarily with the requirements to heat the additional water or brine added in the salt saturator **28**. The heating of brine prior to feeding it to the cell is not in itself, new. However, the effect of rapid anolyte turnover and the mixing of the anolyte effluents from a group of cells produces a cumulative heat exchange effect which results in all of the cells operating at more efficient temperatures independent of the cell age, electrode decomposition, particular cell characteristics and the like factors which previously dictated the individual cell operating temperature.

As a result of the changes effected in the anolyte compartment by means of the present anolyte recirculation method further beneficial changes result in the entire cell operation. It was previously known that the addition of hydrochloric acid to a chlor-alkali diaphragm cell having a porous asbestos diaphragm resulted in a tightening of the diaphragm and a restriction of liquid flow through the diaphragm when the anolyte pH dropped to too low a level. When this occurred, the liquid level in the anolyte chamber increased and often the cell would have to be removed from service due to the high level. Because of the variations in porosity of deposited diaphragms and the changes effected by acid additions, the flow rates through the diaphragms varied with each cell such that previously the brine feed had to be individually controlled in each cell to maintain the desired cell liquor strength to compensate for the added acid. To regulate the anolyte pH within the most desirable pH range of 2 to about 4 while maintaining a proper cell level was indeed, a diffi-

cult task. To further complicate the matter, changes in the flow through the diaphragm affect the back migration of hydroxyl ions which changes the acid requirement for each cell. Thus, as a practical matter, large acid additions have not previously been feasible in large scale operations.

The method of anolyte recirculation substantially reduces the need for individual cell attention due to changes in diaphragm porosity, hydroxyl ion back migration, and the like. The rapid anolyte turnover or flow rate produces a leveling effect in all the cells, whereby the desired pH range is maintained independent of the particular porosity of the diaphragm and back migration. In addition, the effects of a restricted diaphragm are of lesser importance because the anolyte recirculation method maintains the same anolyte liquid level independent of the flow through the diaphragm.

In a preferred embodiment of the present invention, hydrogen chloride **34** is added to the saturated or nearly saturated brine withdrawn from salt saturator **28** via line **10**. When HCl is added, it is added in an amount sufficient to maintain an anolyte pH within the range of about 0.2 to about 4.5 and more preferably about 1.5 to 4. The most preferred pH range is about 2.0 to 3.0. The lowest pH values are best used with a diaphragm material other than asbestos, such as chlorinated polyvinyl chloride, polypropylene, and the like. The amount of HCl required for this adjustment varies with the particular operating conditions and can be in an amount up to about 20 percent HCl, by weight, based on the amount of chlorine liberated at the anode; that is, 20 percent of the chlorine produced is from the HCl addition. With greater amounts of HCl being added, the pH of the brine fed to the cell can be as low as about 0.2. When no HCl is added, the pH of the brine fed to the cell is as high as about 7, because the recirculated anolyte lowers the brine pH from the normally alkaline pH of about 9 to a neutral or slightly acidic pH. The HCl added can be added either as a gas or as an aqueous solution.

The pH of the anolyte has been found to be important in establishing high current efficiencies in the cell, and especially in attempting to improve the efficiency of already highly efficient cells. In normal cell operations, the back migration of the hydroxyl ions into the anolyte results in an increase in the anolyte pH while the chlorine evolved therein lowers the pH. Cells running individually will vary widely in anolyte pH. Normally, a low anolyte pH is obtained in cells with new diaphragms and a high anolyte pH is found in cells with older diaphragms. As the mechanism of back migration of hydroxyl ions is presently understood, the migration increases for any particular diaphragm as the concentration of caustic in the catholyte cell liquor increases. In turn, the concentration of caustic in the catholyte cell liquor increases because of a decrease in the flow of brine into the catholyte chamber as a result of a decrease in the porosity of the diaphragm. The decrease in the diaphragm porosity results from the deposition of calcium and magnesium compounds and other substances in the diaphragm pores during use. Thus, over-all brine quality and the nature of the diaphragm are factors which bear significantly on the changes in anolyte pH and its attendant lower cell efficiency.

In normal cell operation, when the anolyte pH increases for any reason, there is no built-in compensating affect to keep it at its proper value. The present invention provides the means for maintaining anolyte pH within the desired range by (1) recirculating the anolyte from a group of cells to obtain the cumulative effect of the anolyte pH of all of the cells so as to result in the cells operating at a pH which is the average thereof and/or by (2) the addition of HCl to the brine feed, with anolyte recirculation. Thus, the cell can always be kept operating at the most effective pH for peak efficiency substantially independently of the porosity of the diaphragm and the concentration of the caustic in the catholyte chamber.

Being able to use a tight diaphragm or a diaphragm of lower porosity has the added benefit of enabling cell operating at higher caustic concentrations in the catholyte compartment. Whereas previously the catholyte solution (cell liquor) contained about 9 to 12 percent to about 22 percent in the catholyte cell liquor or about 145 to 270 grams per liter of NaOH, while the desired anolyte pH is maintained. As will be readily realized, the process can also be operated to obtain normal cell liquor strengths of about 110 to 150 grams per liter of NaOH. By controlling the anolyte pH at the desired efficient operating level, such as by increasing the recirculation rate and/or using brine with enough HCl dissolved in it to compensate for increased back migration of the hydroxyl ion, the former limiting factor of the hydroxyl back migration is mitigated. By operating the cells to increase the caustic concentration in the catholyte compartment a higher ratio of caustic to sodium chloride in the cell liquid is obtained. Thus, over twice the normal caustic concentration can be obtained in the cell liquor, thereby greatly reducing the evaporation and concentration costs normally otherwise incurred.

In order to very accurately control the catholyte characteristics, the cell liquor is combined from an entire cell series in salt/caustic regulator **42** after sending an amount of cell liquor equal to that which passes through the diaphragms of all the cells in the cell series to a caustic evaporator via line **44**. In salt/caustic regulator **42**, the ratio of salt to caustic is controlled as well as the temperature of the liquor and the caustic concentration. Additional sodium chloride **30**, water **31**, or mixtures thereof, are mixed with the cell liquor in **42**. Furthermore, heat exchanger **46** maintains the cell liquor at the proper temperature for optimum cell performance. The modified cell liquor is then returned to the cathode compartment of the several cells via lines **48**, **49** and **50**.

As shown in FIGS. 3 and 4, the individual cells **16** within a cell series are composed of a cell top **52**, a cell bottom **54**, side walls **56**, cathodes **58**, and anodes **60**, embedded in a mastic covered lead base **62**. The cell liquor **40** is returned to the cells via line from the salt/caustic regulator. The cell liquor enters the cathode compartment of each cell via inlet **64**, sweeps across the face of the cathode **58** and exits the cell via outlet **66**. The inlet **64** may be advantageously in the form of a manifold device **68** which uniformly supplied catholyte to all surfaces of the cathode **58** as shown in FIG. 4.

EXAMPLE 1

A group of 50 Hooker Type S–1 cells is operated in the normal method by feeding brine to the anolyte compartments of each cell at a feed concentration of 310 grams per liter of NaCl. The brine feed is at a pH of 9, which is the normal brine pH of feed liquor. A decomposition voltage of about 4 volts at about 12,000 amperes per cell is passed through the cell in the normal manner thereby producing gaseous chlorine at the anode and hydrogen and caustic soda (cell liquor) at the cathode. The caustic soda is withdrawn from the catholyte compartment of each cell as cell liquor. The group of cells is continuously operated for several weeks, during which time the operating conditions of the cells are noted. The brine feed rate during the period of operation averages 2.7 liters per minute per-cell which corresponds to the flow through the diaphragm of each cell. The average current efficiency of the cells for this period is 95.7 percent and that the anolyte temperature within the cells varies from cell to cell within the range of 92 degrees centigrade to 104 degrees centigrade, the average being about 95 degrees centigrade. The corresponding temperature of the catholyte averages 92 degrees centrigrade. The brine strength within the anolyte compartments averages 260 grams per liter of sodium chloride. Caustic concentration in catholyte compartments averages 133 grams per liter at a flow rate of 2.6 liters per minute.

A similar group of 50 Hooker Type S–1 cells is operated in accordance with the present invention. The cells are fed a liquor recirculation stream from the main caustic header to the catholyte compartments. The catholyte recirculation rate is adjusted so that the catholyte overflow is an average of 5.2 liters per minute. As with other groups, these cells are fed a brine solution of 310 grams per liter concentration sodium chloride at the normal 2.7 liters per minute rate. The average temperature of the anolyte compartment remains at 95 degrees centigrade with a catholyte temperature of 91.5 degrees centigrade. Average caustic concentration is 135 grams per liter. After extended operation, the group of cells using the catholyte recirculation method of the present invention exhibit improved current efficiencies compared to the cells operated in the conventional manner. The average current efficiency of the cells operating by the cathodlyte recirculation method is 96.1 percent.

EXAMPLE 2

A group of 50 Hooker Type S–1 cells is operated in accordance with the present invention as described in Example 1. The cells are fed a liquor recirculation stream from the main caustic header into the catholyte compartments. The catholyte recirculation rate is adjusted so that the catholyte overflow is an average of 7.9 liters per minute. These cells are fed a brine solution of 310 grams per liter at a rate of 2.7 liters per minute. The average temperature of the anolyte and catholyte compartments is 95 degrees centigrade and 91 degrees centigrade respectively. Average caustic concentration is 130 grams per liter. The average current efficiency of thte cells operating in this manner is 96.3 percent.

TABLE NO. 1.—OPERATION DATA

	Example 1		Example 2
	Normal operation	Catholyte recirculation	Catholyte recirculation
Recirculation rate, percent	0	100	200
Cell liquor, g.p.l. NaOH	133	132	130
Cell voltage	4.00	3.99	4.00
Anolyte temperature, ° C	95	95	95
Catholyte temperature, ° C	92	91.5	91
Anode current efficiency, percent	95.7	96.1	96.3
Percent cells operating in optimum range [1]	42	64	76

[1] 120–140 g.p.l. NaOH caustic catholyte concentration.

In comparing the 50 cells operating in the normal manner to those with caustic recirculation (i.e. double and triple catholyte overflow, it may be seen that improved operation is obtained with catholyte recirculation. The preceding table demonstrates that the current efficiency increases with catholyte recirculation. For an overflow double the normal volume the increase is 0.4 percent current efficiency and for triple overflow it is 0.6 percent.

This is reflected in an increased production of about 0.0042 to 0.0063 percent at the same voltage and current. This could also have been expressed as a reduction in lower cost per ton product.

Having disclosed the invention, it will become obvious to those of average skill in this art that various modifications may be made which do not differ in spirit from the true nature and scope of this contribution.

What is claimed is:

1. A process for operating a chlor-alkali diaphragm cell which comprises feeding a solution of brine to the anolyte compartment of the chlor-alkali diaphragm cell and a solution of an alkali metal chloride and alkali metal hydroxide to the catholyte compartment of the chlor-alkali diaphragm cell while imposing a decomposition voltage across the electrodes of said cell, withdrawing the cell liquor from the catholyte compartment, the amount of alkali metal chloride-alkali metal hydroxide solution fed to the catholyte compartment being from about ⅓ to 10 times the volume of cell liquor withdrawn, feeding to a caustic evaporator a portion of the cell liquor withdrawn and recycling the excess cell liquor to the catholyte compartment as at least a portion of said said alkali metal chloride-alkali metal hydroxide feed solutions.

2. The process of claim 1 in which said excess cell liquor is cooled before return to said cathode compartment.

3. The process of claim 1 in which the salt-caustic ratio of said excess cell liquor is regulated by the addition of a member of the group consisting of solid alkali metal chloride, an aqueous solution of an alkali metal chloride and water.

4. The process of claim 1 in which the salt-caustic ratio of the catholyte within said cathode compartment is between about 0.5 and 2.0.

5. The process of claim 1 in which the salt-caustic ratio of the catholyte within said cathode compartment is between about 0.7 and about 1.5.

6. The process of claim 1 in which the temperature of said excess cell liquor is adjusted so as to obtain a catholyte temperature of about 90 to 105 degrees centigrade.

7. The process of claim 1 in which the amount of cell liquor fed to said caustic evaporator is approximately equal to the amount of electrolyte flowing through the diaphragm.

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