

#### 54 Electrolysis of aqueous salt solutions.

(f) An electrolysis process is disclosed in which an electrolyte, either anolyte or catholyte, is transferred serially from one cell, in a bank of a plurality of cells, to the corresponding electrolyte compartment of a succeeding cell in the bank. The transfer is accomplished by means of a gaslift in which gas, present in the compartment of the electrolyte to be transferred, rises through a confined space. The space is dimensioned such that the gas serves to lift the electrolyte upward to a point where the gas and liquid separate and the liquid electrolyte is allowed to fall freely to a collection point from which it is introduced into the corresponding electrolyte compartment of a succeeding cell.



N

đ

### BACKGROUND OF THE INVENTION

The electrolysis of aqueous salt solutions in permselective membrane electrolytic cells is well documented in the literature as are the advantages and disadvantages

- 5 associated therewith. It is known, for example, that when employing such cells for the production of sodium hydroxide (caustic soda) and chlorine from sodium chloride brines, the current efficiency decreases as the concentration of sodium hydroxide in the catholyte increases. It is of course desir-
- .0 able to be able to produce relatively concentrated caustic soda solutions without recourse to separate concentration procedures and with acceptable current efficiencies. One method for attaining this end is disclosed in U.S. Patent No. 4,057,474 wherein there is described a process involving
- .5 the flow of catholyte sodium hydroxide solutions exiting from one cell to the catholyte compartment of a succeeding cell in a bank. This "series catholyte flow" process results in the recovery of relatively concentrated sodium hydroxide solutions directly from the last of the cells in a
- 20 series and at the same time, the average current efficiency for the cells in the series is well within the acceptable range. German Offenlegungsschrift 2,437,783 also describes a series catholyte flow process.

While such series catholyte flow results in substantial improvement in current efficiency, certain problems have become apparent in operating a bank of cells with series flow. Some means must be provided for transferring

the catholyte from one cell to another. This can be accomplished with conventional pumps, but this requires additional equipment and, depending on how the cells are serially connected, a breakdown of just one pump could conceivably disrupt the whole operation. While the use of gravity flow has been postulated, commercial operation involves a large number of cells in a bank, and thus gravity becomes impractical because of design and/or operational problems associated with the necessity that succeeding cells connected together in series catholyte flow must necessarily

5

10

- 2 -

- be at lower elevations in order for flow from one cell to the next to occur. Additionally, when succeeding cells are at a different voltage, as in a filter press type bipolar cell stack or among individual monopolar cells connected via a series electrical circuit, the transfer of catholyte from
  - one cell to another should be done in such a manner as to insure electrical isolation of one cell from another. It is an object of this invention to provide a

process for operating a bank of electrolytic cells connected for series electrolyte flow. It is a further object of this invention to provide a process for transferring electrolyte from one cell to another which does not require external pumping means and which serves to substantially isolate the cells electrically. These and other objects will become apparent from the description which follows.

### SUMMARY OF THE INVENTION

In accordance with this invention there is provided an improved process for the electrolysis of an aqueous salt solution in a bank of a plurality of electrolytic cells wherein each cell has an anode electrolyte compartment and a cathode electrolyte compartment, the compartments being separated by a permselective membrane, and at least one electrolyte is transferred serially from one of the compartments of one or more cells to a corresponding electrolyte compartment of a succeeding cell. The improvement comprises effecting the transfer by means of a gas-lift in which gas present in the electrolyte compartment rises through the electrolyte solution in a confined space which is dimension-

ed such that liquid electrolyte is lifted by the gas up to a disengaging point at which the gas separates and is removed from the compartment, and the liquid is allowed to fall freely through a confined void space to a predetermined point at which it is collected and fed by gravity into the corresponding electrolyte compartment of a succeeding cell at approximately the same elevation as the preceding cell. In the electrolysis of an aqueous sodium chloride

5

10

30

35

cell.

solution in accordance with this invention, there is provided an improved process for operating a bank of a

plurality of electrolytic cells, wherein each cell has an anode compartment and cathode compartment, the compartments being separated by a cationic permselective membrane, and sodium hydroxide catholyte is transferred serially from the

- 15 cathode compartment of one or more cells to the cathode compartment of at least one succeeding cell in the bank. The improvement comprises effecting the transfer by means of gas-lift in which hydrogen, produced in the cathode compartment rises through the sodium hydroxide catholyte solution
- 20 in a confined space dimensioned to cause the hydrogen to lift the catholyte solution to a disengaging point at which the hydrogen is separated and catholyte solution is allowed to fall freely through a confined void space to a predetermined point wherein it is collected and fed by gravity to 25 the cathode compartment of a succeeding cell at approximate-
- ly the same elevation as the preceding cell.

This "gas-lift" method for transferring electrolyte serially from one cell to another results in a most advantageous method of operating a bank of cells. Auxiliary equipment is not required to transfer the electrolyte and the difficulties associated with the use of gravity alone, as outlined above, are avoided. Further, allowing the liquid electrolyte, as it separates from the gas, to fall freely through a confined void space to a collection point serves to electrically isolate the cells thereby preventing current from passing, via the electrolyte, to the succeeding

- 3 -

### BRIEF DESCRIPTION OF THE DRAWING

- 4 -

The drawing is a schematic flow diagram illustrating a bank of two permselective membrane cells employing series electrolyte flow in accordance with this invention.

5

15

20

DETAILED DESCRIPTION OF THE INVENTION The invention comprises a method for accomplishing

series electrolyte flow in a multi-compartment bipolar permselective membrane electrolyzer which utilizes the gas evolved in the electrode compartment for an autogenous gas-10 lift in order to transport the electrolyte from the electrolyte compartment of one cell to the electrolyte compartment of the next cell, and to establish a high electrical resistance in the stream of electrolyte between the exit of the preceding cell and the entrance of the succeeding cell so as to electrically isolate the electrolyte of the pre-

ceding cell from the electrolyte of the succeeding cell.

While the description which follows deals primarily with series catholyte flow in a bipolar permselective membrane electrolyzer producing chlorine and caustic soda by electrolysis of sodium chloride brine, the principle is applicable to both series catholyte and series anolyte flow in a variety of electrolytic processes.

Thus, series electrolyte flow can be advantageously applied to any electrolytic or any electrodialytic pro-25 cess in which it is desired to minimize the adverse effects of a high concentration of a particular ionic species generated in one or both of the electrolyte streams. For example, in the electrolysis of metal halide brines, high concentrations of hydroxyl ions in the catholyte tend to 30 reduce current efficiency by back-migration through the

membrane into the anode compartment. Hence, series catholyte flow can be advantageously applied to electrolysis of sodium chloride brine, and also to the electrolysis of potassium chloride brine and other metal halide brines in 35 which hydroxyl ions are generated in a catholyte according to the equation

> $H_2O + e \longrightarrow 1/2H_2 + OH^-$ . An example of a process in which series anolyte

- 5 -

flow can be advantageously applied is the anodic oxidation of sulfate to persulfate according to the equation

 $2SO_4^{=} + O + H_2O \longrightarrow S_2O_8^{=} + 2OH^{-}$ where the atomic oxygen is formed by the primary discharge of hydroxyl ion according to the equation

 $2 \text{ OH}^- - 2 \text{e} \longrightarrow 0 + \text{H}_2 \text{O}$ 

In this case, it is desired to minimize the adverse effects of high concentrations of the persulfate which result from its tendency to decompose, thus reducing current efficiency.

10

5

15

An example of a process in which series catholyte and series anolyte flow can be simultaneously applied to good advantage is the electrolytic splitting of a salt into its acid and base constituents in a cell employing both cationic and anionic permselective membranes. Thus, backmigration of hydrogen ion through one membrane and hydroxyl ion through the other membrane will both tend to reduce current efficiency.

Although the method of accomplishing series electrolyte flow described herein specifically contemplates an autogenous gas-lift effect which utilizes gas evolved at an electrode, series electrolyte flow can also be accomplished, for those processes which do not involve evolution of a gas, by the introduction of a gas from an external source into the bottom of the electrolyte compartment. Thus, the gas

- 25 may be unreactive to the various components of the electrolyte or, if so desired, the gas may serve a dual purpose by being chosen as a reactant. An example of a process in which a gas could be introduced to serve as motivating medium for the gas-lift and as a reactant would be the
- 30 oxygen depolarization of a chlorine/caustic soda permselective membrane electrolyzer. The cathodes in such an electrolyzer would possess an electro-catalytic coating to promote the reaction

 $2H^+ + 1/2O_2 + 2e \longrightarrow H_2O$ 

35 Thus, while suppressing the formation of hydrogen gas and accordingly reducing the cell operating voltage, the oxygen gas would also serve as the motivating gas to accomplish series catholyte flow according to this invention.

The present invention accomplishes series catholyte flow in an electrolyzer unit comprising a bank of a plurality of electrolytic permselective membrane cells in a manner which avoids the use of auxiliary equipment and also serves to electrically isolate the cells from each other.

- 5 serves to electrically isolate the cells from each other. For example, in the electrolysis of sodium chloride brine, the invention utilizes the hydrogen gas generated within the cathode compartment to raise the catholyte caustic soda liquid through a riser pipe from the top of a preceding
- 10 cathode compartment to a disengaging device wherein the hydrogen is separated from the catholyte, the catholyte then falls freely downward through a void confined space in a downcomer, to a level from which it flows, by gravity, into the bottom of a succeeding cathode compartment. The height
- 15 of the void space is dictated by the difference in the bulk density of the two phase system (catholyte liquid and hydrogen gas) in the preceding cathode compartment and the bulk density of the single phase (catholyte liquid) in the downcomer leading to the bottom of the succeeding cell.

20

The invention is more clearly illustrated by reference to the drawing wherein there are illustrated two cells 100 and 200 connected for series catholyte flow. Each cell has a cathode compartment 104 and 204, and an anode compartment 110 and 210 separated by permselective membranes

- 25 108 and 208, respectively. Each cathode compartment has a cathode 106 and 206. Lines 112 and 212 feed into the cathode compartments containing catholyte 102 and 202, respectively. The upper portion of each catholyte compartment is equipped with risers 114 and 214 through which the catholyte flows by
- 30 means of a gas-lift generated by gas bubbles 116 and 216. The gas and liquid separate at separation point 118 from which the gas flows upward into header 120 and the liquid drops through void space 220 to collection point 218. While the foregoing description of the drawing is based on series
- 35 catholyte flow, it will be readily recognizable that for series anolyte flow the feed would be to the anolyte compartment and the risers would be connected to the upper portion of the anolyte compartment. Also, for series anolyte

- 6 -

and series catholyte flow, both compartments would have similar feeds and risers. It should again be pointed out that while the description, for ease of illustration, will be directed to series catholyte flow in the production of caustic soda and chlorine from sodium chloride brine, it is not to be considered a limiting factor to the scope of the invention.

5

In operation of the process of this invention, water from an external source, or catholyte from a preceding cell, is fed via line 112 into cathode compartment 104. Regardless of the feed, water is electrolyzed at cathode 106 to produce hydroxyl ions and hydrogen gas which forms bubbles 116. Sodium ions from anode compartment 110 migrate through permselective membrane 108 into the catholyte

- 15 compartment to form aqueous caustic soda. The hydrogen gas bubbles and the aqueous caustic soda catholyte form a two-phase system which flows from the cathode compartment 102 through riser 114 up to separation point 118. At the separation point, the hydrogen gas passes into header 120
- 20 while the liquid caustic soda catholyte is allowed to fall freely through confined void space 220 to collection point 218. The dimensions of riser 114 and void confined space 220 are selected such that at separation point 118, the flowing liquid will occupy only a small portion of the
- 25 available cross section, thus preventing the entrainment of hydrogen gas in the liquid catholyte as it falls to collection point 218 and also to allow the liquid catholyte to fall freely, thus preventing electrical current from passing from cell 100 to cell 200. The liquid catholyte
- 30 flows from collection point 218, via gravity, through feed 212 into catholyte compartment 204 of the succeeding cell 200 wherein the water in the catholyte compartment is electrolyzed at cathode 206 resulting in a repeat of the process occurring in cell 100.
- 35 The difference between the height of the separation point 118 and the collection point 218 is designated in the drawing as ∆h and is approximately proportional to the difference between the effective density of the two phase

- 7 -

- 8 -

system in riser 114 (liquid catholyte and hydrogen gas) and the single phase system in feed 212 (catholyte liquid). This  $\Delta$ h will, of course, be a maximum for a no-flow condition and will be reduced to some extent by resistance to flow in 114 and 212. However, proper design of these lines will make the resistance to flow negligible at usual flow rates.

5

The extent of the difference in effective density between the catholyte-hydrogen mixture and the catholyte 10 falling through void space 220 to collection point 218 determines the effective gas-lift and it depends on the relative volumes of catholyte and hydrogen present in the cathode compartment. This, in turn, depends on the physical properties of the catholyte and hydrogen, the size of the 15 bubbles formed and the horizontal cross-sectional area of the cathode compartment. It is only this latter factor which can be controlled by the design of the electrolyzer and it will be evident that the cross-sectional area should be established within certain limits in order to assure 20 proper operation.

In the case where the horizontal cross-sectional area of the cathode compartment is very large, the hydrogen bubbles will occupy only a small fraction of the total cathode compartment volume and there will accordingly be

- 25 little difference in density between the contents of the cathode compartment and the liquid catholyte alone resulting in too small a gas-lift effect and too small a Ah to accomplish adequate electrical isolation between the cathode compartments. For the case where the horizontal cross-
- 30 sectional area of the cathode compartment is very small, the hydrogen bubbles will occupy a large fraction of the total cathode compartment volume, hence,  $\Delta h$  will be more than large enough to accomplish adequate electrical isolation. However, because the hydrogen will occupy such a large
- 35 fraction of the cathode compartment volume, the resistance to the flow of electrical current through the catholyte will be increased causing the cell to operate at too high a voltage.

Accordingly, in the preferred practice of this invention, the horizontal cross-sectional area of the cathode compartment should be confined within certain limits. The cathode compartment horizontal cross-sectional area required for satisfactory gas-lift effect will depend on the volumetric rate of hydrogen evolution. More specifically, it will be proportional to the product of the cathode area and the current density according to the equation

### $DW = KHWC_d$

10 wherein

5

D = depth of cathode compartment,

W = width of cathode compartment,

H = height of cathode compartment,

C<sub>d</sub>= current density on cathode,

15 K = proportionality constant.

Accordingly, the required depth of the cathode compartment, that is, the distance between the membrane and the back of the cell compartment, is given by the equation  $D = KHC_d$ .

It has been found, according to the present invention, that for operation at or near atmospheric pressure, producing caustic soda in concentrations of 7 to 20 weight percent at a temperature in the range of 30 to 90°C, the proportionality constant K should be in the range of 0.01 to 2.0, preferably, 0.05 to 1.0. At K values less than about 0.01 the cell will operate at an undesirably high voltage due to the large fraction of the catholyte compartment occupied by the hydrogen. At K values more than about 2.0, the rate of hydrogen evolution will be insufficient to create the necessary gas-lift effect.

### DESCRIPTION OF PREFERRED EMBODIMENTS

In the following examples, data were obtained from a three cell electrolyzer in which the individual cells were assembled together so that common end plates served to 35 separate the cathode compartment of one cell from the anode compartment of the adjacent cell. The cathode of each individual cell is electrically connected externally to the anode of the adjacent cell. As illustrated in the drawing,

- 9 -

the catholyte and hydrogen from the first cell exits from the top of the cell body into an external disengaging point from which the catholyte flows downward through a confined void space and thence into the bottom of the adjacent second

- 10 -

5 cell and so on from the second cell to the third cell. Caustic soda at the final concentration is withdrawn from the top of the third cell.

The anodes employed were constructed of titanium coated with rare earth metal oxides and available under the 10 trade name "DSA". The cathode was mild steel. The membrane was a cationic permselective membrane supplied under the trade name "Nafion". The current density employed was 0.25  $amps/cm^2$ The pressure within the anode compartment was maintained at about 7 inches of water, that within the 15 cathode compartment at about 1 inch of water.

Example 1 comprises the average result of two runs at approximately the same final caustic concentration, Example 2 is the average of 3 runs at approximately the same final caustic concentration, and Example 3 is the average of 2 runs at approximately the same final caustic concentration. The duration of each run was approximately 1 hour. The re-

20 sults are shown in the Table.

25

30

		TABLE		0002783	
	Operating Conditions		Example 1	Example 2	Example 3
	Feed Brine Concentration	(g/l)	322	317	312
	Brine Depletion (%)		11.4	10.8	10.6
5	Average Cell Temperature	(°C)	82	82	84
	E.M.F. Applied (volts)				
	Cell #1		4.2	4.2	4.0
	Cell #2		3.8	3.9	3.7
	Cell #3		4.2	4.4	4.3
10	Average		4.1	4.2	4.0
	Cell Efficiencies (% base	d on			
	NaOH pr	oduced)			
	Voltage efficiency		55.0	53.5	55.7
	Current efficiency		91.7	90.4	83.2
15	Power efficiency		50.0	48.4	46.3
	NaOH Concentration (weigh	t %)			
	Cell #1		6.0	4.6	8.5
	Cell #2		10.1	7.8	13.8
	Cell #3		13.5	10.9	17.8
20	Power Consumption (KWh/to	n NaOH)	2695	2800	2930
	For all of the	0 x1100	the walue	of V dia	waaad

- 11 -

0000707

For all of these runs, the value of K discussed above is calculated to be about 0.5 on the basis of H=10 cm,  $C_d = 0.25 \text{ amps/m}^2$ , and d=1.2 cm. In all the runs, the voltage was satisfactorily low. The difference in level

- 25 between the separation point and the collection point was, in all cases, in the range of 3 to 6 cm, quite satisfactory for electrical isolation between adjacent cathode compartments. For periods of operation at current densities less than 0.25 amps/cm<sup>2</sup>, it was observed that the difference in 30 catholyte levels between adjacent cathode compartments was diminished, but was still adequate (2-3 cm), at current
- densities in the range of  $0.12 \text{ amps/cm}^2$ , corresponding to a K value of about 1.0.

As compared to the alternative of a mechanical 35 pump for transporting the catholyte, the autogenous gas-lift method of this invention avoids increased complexity and cost, and decreased reliability of the electrolyzer. It also utilizes the energy generated by the buoyancy of the

hydrogen bubbles which would otherwise be wasted. As compared to the alternative of gravity flow for transporting the catholyte, the gas-lift method avoids the need for having adjacent cathode compartments at successively lower

- 5 positions which would seriously complicate the design and increase the cost of the electrolyzer. As regards the necessity for a high electrical resistance in the stream of catholyte for a series catholyte flow, the gas-lift method of this invention accomplishes this by creating a discontin-
- 10 uity in the catholyte stream where the stream falls freely through a confined void space created by the difference in head.

15

20

25

30

- 13 -

We claim:

 A process for electrolyzing an aqueous salt solution in a bank of a plurality of electrolytic cells, each cell having an anode compartment and a cathode
compartment, the compartments being separated by a permselective membrane and at least one electrolyte is transferred serially from one of the compartments of one or more cells to a corresponding electrolyte compartment of a succeeding cell, characterised by effecting the transfer

10 and maintaining electrical isolation between the cells by menas of a gas-lift in which gas present in the electrolyte compartment rises through the electrolyte solution in a confined space which is dimensioned such that liquid electrolyte is lifted by the gas up to a dis-

15 engaging point at which the gas separates and is removed from the compartment, and the liquid is allowed to fall freely through a confined void space to a predetermined point at which it is collected and fed by gravity to the corresponding electrolyte compartment of a succeeding cell.

20 2. A method according to claim 1 wherein the gas present in the electrolyte compartment is generated at the electrode.

3. A method according to either of claims 1 and2 wherein the electrolyte transferred is catholyte.

4. A method according to either of claims 1 and 2 wherein the electrolyte transferred is anolyte.

5. A process according to any one of claims 1 to 4 wherein the salt solution is an aqueous sodium chloride brine, the compartments are separated by a cationic perm-

30 selective membrane, and sodium hydroxide catholyte is transferred serially from the cathode compartment or one of more cells to the cathode compartment of at least one succeeding cell in the bank, and the gas-lift is effected by hydrogen produced in the cathode compartment which 35 rises through the sodium hydroxide catholyte solution

6. A method according to claim 5 wherein the hydraulic head generated by the presence of hydrogen gas in the catholyte solution and the hydraulic head required to feed the succeeding cell by gravity is equal to the difference in height between the separation point and the collection point.

