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PROCESS OF ELECTROLYSIS OF AQUEOUS ELECTROLYTES

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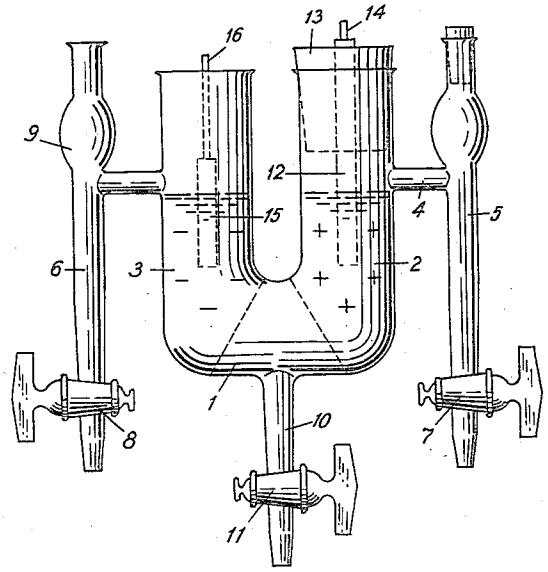


FIG. 1.

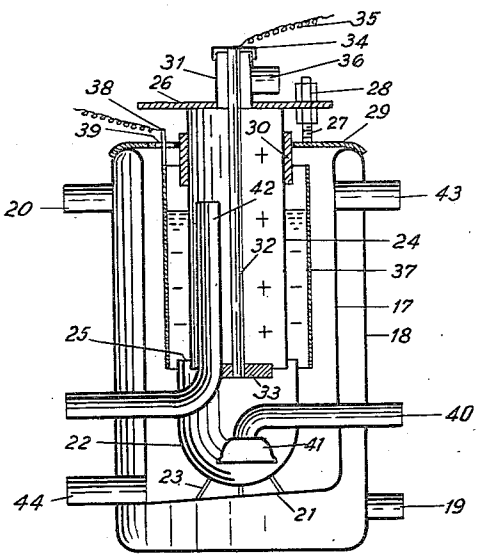


FIG. 2.

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PROCESS OF ELECTROLYSIS OF AQUEOUS ELECTROLYTES

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6 Claims. (Cl. 204—128)

This invention relates to the electrolysis of aqueous electrolytes for producing bromine or iodine by processes in which the products obtained at the anode and cathode, respectively, are apt to react with one another chemically if they are allowed to mingle in the aqueous medium.

Electrolytical processes in which none of the reaction products escapes in gaseous form but the reaction products have to be separated from one another in liquid form for the aforesaid reason, are hitherto carried out in cells provided with diaphragms. These cells are relatively costly, and in their operation there arise problems of corrosion and clogging. A diaphragm-less cell, the so-called bell-jar cell, is known for the manufacture of chlorine. In this cell the anolyte is separated from the catholyte by a neutral zone of the electrolyte located below the anode. The location of the neutral zone in the cell is not stable, as owing to the difference in the velocity of migration of the hydrogen and hydroxyl ions, respectively, the zone tends to be shifted towards the anode. In order to counteract this displacement the fresh brine is supplied to the cell from above into the region of the anode above the neutral zone which is thereby kept down. The chlorine escapes as a gas through an outlet provided above the anode. This known cell cannot be used for the production of bromine or iodine since, being heavier than water, these two elements would, at the moment of their formation, sink down, pass the neutral zone and react with the NaOH of the catholyte to form sodium hypobromite and sodium hypoiodite, respectively.

It is a primary object of the invention to provide a continuous electrolytical process for aqueous electrolytes containing bromine and iodine which can be carried out in a simple apparatus without diaphragm.

The invention has furthermore the object to provide a process for the electrolysis of bromide or iodide solutions containing both cations that form water-soluble hydroxides, and cations whose hydroxides are insoluble, wherein the whole or a substantial part of the hydroxide formed by the process can be removed from the apparatus as a sediment without interruption of the electrolysis. In particular, the invention provides a continuous electrolytical process for the production of pure magnesium hydroxide from aqueous bromide or iodide solutions in which magnesium is only one of the cations.

The invention consists in a continuous process for the electrolysis of aqueous bromide or iodide solutions substantially without formation of gaseous products of electrolysis at the anode and without separation of the anolyte from the catholyte by a diaphragm, wherein a stream of fresh electrolyte is fed immediately into the electrochemically neutral zone of the aqueous medium between the anolyte and catholyte.

Preferably, the current is made to pass between electrodes disposed mainly in the upper part of an electrolytic cell, both the anolyte and catholyte are withdrawn from the upper part of the cell and the fresh electrolyte

is fed into the electrochemically neutral zone below the reach of the electrodes and the anolyte and catholyte drains and is made to flow upwards so as to prevent the free halogen formed by the electrolysis from dropping into and through the neutral zone.

Where the electrolyte consists principally of alkali bromide or iodide, the product obtained at the cathode is alkali hydroxide which is apt to some extent to diffuse back into the neutral zone and further into the anode space, thus diminishing the current efficiency. It has, therefore, been found to be advantageous to admix the electrolyte with salts of metals whose hydroxides are insoluble or difficultly soluble in water, such as magnesium or calcium. Magnesium salts happen to be present anyway in many natural brines or residual industrial liquors which come into regard as sources for the production of bromine or iodine, such as sea-water, the water of some salt lakes such as the Dead Sea, or mother liquors remaining from the manufacture of sodium chloride from sea-water, the manufacture of carnallite from natural salt deposits or salt lakes, or the like. Where such liquors are subjected to electrolysis by the process according to the invention, the principal products are bromine on the one hand and a highly pure magnesium hydroxide on the other hand. The purity of the magnesium hydroxide thus obtained makes it even worthwhile to add magnesium salt, e. g. chloride, to alkali halide electrolytes with the main object of producing pure magnesium hydroxide.

Calcium hydroxide is more soluble in water than magnesium hydroxide, and the current efficiency is, therefore, lower in the case of precipitation of calcium hydroxide than in the case of magnesium hydroxide.

Where the process according to the invention serves for the preparation of bromine, the rate of inflow of brine can be so regulated that the anolyte is an aqueous bromine solution from which the bromine can be recovered in any suitable way, e. g. by solvent extraction. If the bromine is liberated by secondary reaction of the bromides of the brine with the chlorine set free from the chlorides of the brine by electrolysis, the brine inflow should be so regulated that about 2% of the bromides remain undecomposed, in order to avoid the formation of chlorine-bromine compounds.

The accompanying drawings show diagrammatically in axial section two cells for performing electrolytic processes according to the invention.

Fig. 1 shows a cell of small laboratory dimensions;

Fig. 2 illustrates a cell designed for commercial use.

The cell according to Fig. 1 consists essentially in an upright U-shaped glass vessel 1. The upright tube 2 of the vessel 1 is the anode space, the left-hand tube 3 is the cathode space. The tube 2 and 3 are provided each with overflows 4 which open into drains 5, 6, provided wtih cocks 7, 8, respectively. The upper ends of the drains merge into vents 9. A feeding pipe 10 provided with cock 11 opens into the horizontal bottom stretch of the vessel 1 substantially in the center thereof. The "plus" signs in the anode space, and the "minus" signs in the cathode space, indicate that the liquid in these spaces is not neutral electrochemically, the pH being clearly below 7 in tube 2, and above 7 in tube 3. The liquid in the bottom stretch of the glass tube, in which the supply pipe 10 opens, is electrolytically neutral, i. e. at a pH of 7 or in the vicinity of 7. The approximate boundaries of this neutral zone are indicated by dashed lines.

The anode space contains a graphite anode 12 which is a rod secured in an axially bored stopper 13 which tightly seals the tube 2. A current lead 14 is connected to the top end of the anode.

A cathode 15, e. g. an iron cylinder, is disposed in the cathode space, being freely suspended from any suit-

able support above the cell by means of the current lead wire 16.

Fresh electrolyte is supplied continually through pipe 10, and liquid flows out continually through both pipes 5 and 6. If, for example, sea-water or salt pan brine is the electrolyte, the anolyte flowing out through drain 5 is an aqueous solution of bromine, possibly containing some iodine, while the catholyte flowing out through the drain 6 contains alkali hydroxide. Besides, magnesium hydroxide separates in the tube 3 and gradually clogs the latter.

This cell is destined for experimental or demonstration purposes only, and it has been shown here merely because it illustrates the principle of the present invention in an especially simple way.

The electrolytic cell illustrated in Fig. 2 is designed for operation on a commercial scale. It comprises an upright cylindrical vessel 17 of stainless steel made integral with a jacket 18 which is provided with an inlet 19 and an outlet 20 for a coolant, e. g. water. The inclined bottom 21 of the vessel 17 supports the legs 23 of a cup-shaped receptacle 22 of stainless steel. A cylindrical chamber 24, also of stainless steel and co-axial with the receptacle 22 and the vessel 17, is disposed above the receptacle 22 and dips into the latter, and an annular passage 25 between the receptacle 22 and chamber 24 makes the interior of the chamber 24 (anode space) communicate with that of the vessel 17 (cathode space). The chamber 24 is secured, e. g. welded, to its lid 26 which is clamped between nuts 28 screwed on bolts 27. The latter are fixed to a cover 29 which rests unconnectedly on the common upper edge of the vessel 17 and jacket 18 and has in its middle a sleeve 30 for guiding the chamber 24. The latter can be raised and lowered relative to the receptacle 22 by a corresponding adjustment of the nuts 28, whereby the length of the passage 25 can be varied with a view to preventing the liquid contained in the anode space from mingling with that contained in the cathode space.

The lid 26 is provided with a tubular connection 31 co-axial with the chamber 24. A rod-shaped anode 32, e. g. of graphite, is fixed to a cap 34 which rests on the upper end of the tube 31 and is insulated electrically from the latter. The anode hangs down through the tube 31 into the chamber 24 and ends substantially flush with the bottom end of the chamber where it merges preferably with a disc 33 of the same material. A current lead 35 is connected to the cap 34. The tube 31 has a lateral extension 36 serving as a vent for the anode space.

The annular cathode space between chamber 24 and the wall of vessel 17 contains a cylindrical cathode 37, e. g. of iron, which is fixed in any suitable manner, e. g. suspended from a rod 38 which rises out of the cathode chamber through an opening 39 in the cover 29 and serves also as a current conductor.

A supply pipe 40 traverses from outside the jacket and cathode space and penetrates into the receptacle 22 which contains the electrochemically neutral portion of the liquid in the cell. A distribution head 41 may be provided at the downwards bent end of pipe 40.

The cell is provided with three outlets, namely, an anolyte overflow 42 comprising a vertical stretch within the anode space where its upper end defines the high-level of the anolyte, which is located in the upper part of the cell, while the lower part of the anolyte drain passes outwards through the receptacle 22, the cathode space and the jacket; a catholyte overflow 43 passing from the cathode space outwards through the jacket substantially at the level of the upper end of the anolyte overflow; and a sediment drain 44 connected to the deepest region of the cathode space. Control valves, which have not been shown, will be provided for the supply pipe and all the drains.

The surfaces of the cell liable to become corroded by contact with the products of the electrolysis, especially the inner surface of the anode space and the anolyte drain, are preferably coated with a corrosion-resistant matter, e. g. a layer of baked-on phenol-formaldehyde resin.

Owing to the fact that fresh electrolyte is fed into a zone below the reach of both electrodes and has to flow upwards in the cell, neither the free halogen formed in the anode space nor the metal hydroxides forming in the cathode space can drop into the neutral zone whose position within the cell thus remains stable. This stability of the neutral zone is also enhanced by the fact that both the anolyte and catholyte are drained from the upper part of the cell.

The invention is illustrated by the following examples to which it is, of course, not limited. In all these examples, a cell of the kind illustrated in Fig. 2 may be used, but the dimensions of the cell and the input of electrolyte and output of anolyte and catholyte are described on a small laboratory scale. For the figures given in the examples, a cell with a capacity of 250 ml. of total liquid is sufficient. Enlargement of the cell to dimensions suitable for the commercial performance of the process will entail a correspondingly larger input and output, but no alteration of principle.

Example 1

An electrolyte, being an aqueous solution containing per liter:

	Grams
$MgCl_2$	330
$CaCl_2$	110
$MgBr_2$	12
NaCl	10
KCl	10

is fed to the cell through the pipe 40 at a rate of 0.160 liter per hour. The current intensity is 0.5 amp., the voltage 4 volt, the temperature is maintained at 20–30° C. by the circulation of water through the jacket 18. The anolyte is withdrawn at a rate of 0.126 liter per hour, and catholyte at a rate of 0.034 liter per hour.

During the electrolysis, magnesium hydroxide precipitates, and owing to the slope of the bottom 21, the sediment collects in the deepest zone of the cell from which it can be removed from time to time by opening the valve controlling the drain 44. The magnesium hydroxide thus withdrawn has, after washing with water, a degree of purity of 99.5% and above.

The total quantity of 0.756 liter of anolyte withdrawn during 6 hours is shaken in a separating funnel with 30 ml. of ethylene dibromide, and the layers are separated. The solvent layer contains bromine in a concentration of 135 grs. per liter whereas the bromine concentration of the aqueous liquor has dropped to 4.8 grs. per liter. The extraction is repeated twice each time with 30 ml. of ethylene dibromide and again twice with 15 ml. each of ethylene dibromide.

About 8.3 grs. of bromine, viz. 98% of the total bromine produced, can be recovered from the combined extracts.

At the end of the same period the total weight of the magnesium hydroxide precipitate is 2.76 grs.

The anodic current efficiency is 95%, the cathodic current efficiency 85%.

Example 2

The electrolyte is composed as follows:

	Grams/liter
$MgCl_2$	130
$CaCl_2$	38
$MgBr_2$	4
NaCl	80
KCl	11

The other data are as in Example 1, but the rate of feed of the electrolyte is 0.500 liter per hour, the anolyte withdrawal is 0.370 liter per hour, the cathoylte withdrawal

0.130 liter per hour. Yield after 6 hours: 8.5 grs. of bromine, 2.76 grs. of $Mg(OH)_2$. The anodic current efficiency is 95%, the cathodic current efficiency 85%.

Example 3

The electrolyte is composed as follows:

	Grams/liter
NaCl	100
KBr	10
K_2CrO_4	2

The other data are as in Example 1, but the rate of feed of the electrolyte is 0.150 liter per hour, the anolyte withdrawal is 0.080 liter per hour, and the catholyte withdrawal 0.070 liter. With an anode current efficiency of 45%, a total amount of 4.0 grs. of bromine is obtained from 0.480 liter of anolyte after 6 hours.

Example 4

The electrolyte is composed as follows:

	Grams/liter
NaCl	100
$MgCl_2$	50
KBr	10

The other data are as in Example 1, but the rate of feed of electrolyte is 0.174 liter per hour, the anolyte withdrawal is 0.154 liter per hour, and the catholyte withdrawal is 0.020 liter per hour. The current efficiency is 80% at the anode and 80% at the cathode.

After 6 hours, 7.1 grs. of bromine can be recovered from 0.924 liter of anolyte, while the weight of magnesium hydroxide precipitate after 6 hours is 2.6 grs.

Example 5

The electrolyte is composed as follows:

	Grams/liter
NaCl	100
$CaCl_2$	100
KBr	10

The remaining data are as in Example 1, but the rate of feed of electrolyte is 0.150 liter per hour, the anolyte withdrawal is 0.108 liter per hour, and the catholyte withdrawal is 0.042 liter per hour.

After 6 hours, 5.4 grs. of bromine can be recovered from 0.648 liter of anolyte withdrawn. The anodic current efficiency is 60%.

Example 6

The electrolyte is composed as follows:

	Grams/liter
NaCl	100
$MgCl_2$	50
KI	1

The remaining data are as in Example 1, but the rate of feed of electrolyte is 2.442 liters per hour, the anolyte withdrawal is 1.642 liters per hour, and the catholyte withdrawal is 0.800 liter per hour.

At the end of 6 hours, 7.4 grs. of iodine can be recovered from 9.852 liters of anolyte withdrawn. The anodic current efficiency is 52%.

Example 7

End-brine from evaporation pans of ocean water was used as electrolyte. A partial analysis showed the following composition per liter:

	Grams
Ca^{++}	0.02
Mg^{++}	46.8
Cl^-	200.7
Br^-	2.1

The brine, like ocean water in general, has a pH above 7. An addition of acid is therefore required in order to prevent the formation of hypobromite. The acid may be added either to the incoming electrolyte or to the anolyte after electrolysis. If sulphuric acid is used, an addition of 0.85 gr. per liter of the above brine is sufficient. The other data are as in Example 1, but the rate of feed of the electrolyte is 0.80 liter per hour, the anolyte withdrawal is 0.750 liter per hour, the catholyte withdrawal 0.05 liter per hour. The total yield after 7 hours is 5.25 liters of anolyte containing 1.9 gr. of bromine per liter, and 0.35 liter of catholyte containing magnesium hydroxide. The quantity of bromine obtained corresponds to a current yield of 95%.

We claim:

1. A continuous process for the electrolysis in a diaphragm-less cell of aqueous brines containing at least one salt selected from the group consisting of alkali and alkaline-earth bromides and iodides, comprising setting up in the electrolyte, by the passage of current, an electrochemically neutral zone as well as an anolyte zone and a catholyte zone, both of these latter zones being located above the neutral zone and merging into it, continually feeding fresh electrolyte brine into the neutral zone, thereby producing a continuous upward flow of electrolyte brine from the neutral zone into the anolyte zone and a separate similar flow into the catholyte zone; and continuously withdrawing from the anolyte zone an aqueous liquor containing an elementary halogen of the group consisting of bromine and iodine, and spent liquor from the catholyte zone.

2. A process as claimed in claim 1, wherein the electrolyte brine contains magnesium chloride.

3. A process as claimed in claim 2, wherein the electrolyte contains alkali metal ions, magnesium ions in an amount at least equivalent to the alkali metal ions, chlorine and bromine ions, and the electrolysis is conducted at such a rate of flow of the electrolyte that the anolyte is an aqueous bromine solution and the major part of the alkali hydroxide formed at the cathode is converted into alkali halide with simultaneous formation of magnesium hydroxide.

4. A continuous process for the electrolysis in a diaphragm-less cell of aqueous brines containing at least one salt selected from the group consisting of alkali and alkaline earth bromides and iodides and in addition at least one chloride, comprising setting up in the electrolyte, by the passage of current, an electro-chemically neutral zone as well as an anolyte zone and a catholyte zone, both of these latter zones being located above the neutral zone and merging into it; continually feeding fresh electrolyte brine into the neutral zone, thereby producing a continuous upward flow of electrolyte brine from the neutral zone into the anolyte zone and a separate similar flow into the catholyte zone; and continuously withdrawing from the anolyte zone an aqueous liquor containing an elementary halogen of the group consisting of bromine and iodine, and spent liquor from the catholyte zone.

5. A process as claimed in claim 4, wherein the electrolyte contains chloride and bromide and the input rate of the brine is so regulated that the anolyte is an aqueous bromine solution.

6. A process as claimed in claim 4, wherein the electrolyte contains chloride and iodide and the input rate of the brine is so regulated that the anolyte is an aqueous iodine solution.

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