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OPERATION IN ELECTROLYTIC ALKALI CHLORINE CELLS

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Our invention relates to a method of materially decreasing formation of chlorate in electrolytic alkali chlorine cells of the diaphragm type, resulting from back migration from the cathode compartment through the diaphragm to the anode compartment of the cell, and contamination of the products and attack upon the anodes resulting therefrom.

In electrolytic cells of this type, the anode compartment is separated from the cathode compartment by a permeable diaphragm. Alkali metal chloride brine is introduced into the anode compartment, where it comes into contact with the anodes, and is caused to percolate through the diaphragm into the cathode compartment, where it comes into contact with the cathodes. When electric current is passed between these electrodes, chlorine is liberated at the anodes and alkali metal hydroxide formed at the cathodes, with liberation of hydrogen. In order to minimize voltage drop in the cell, the cathodes are placed as close to the diaphragm as possible; and in fact, in practice the diaphragm is generally a thin sheet of fibrous material, preferably of asbestos, overlying and supported by cathodes of woven iron wire screen. The cathode compartment may be occupied by hydrogen, but in best modern practice, it is allowed to fill up with caustic alkali solution to a level at which the diaphragm is largely submerged, and to overflow from the cell at that level. In any case, the surface of the cathodes in contact with the diaphragm is wet with catholyte.

Chlorine, as such and as hypochlorous acid, is more or less soluble in brine, depending on the temperature thereof, and some chlorine inevitably passes through the diaphragm in solution in the percolating brine. Coming into contact with the caustic alkali in the cathode compartment, this chlorine reacts with the alkali to form alkali metal hydrochlorite, in accordance with the following equations:

$$2NaOH+Cl_2\rightarrow NaClO+NaCl+H_2O \quad (1)$$

$$NaOH+HClO\rightarrow NaClO+H_2O \quad (2)$$

This, of course, represents a loss of both chlorine and caustic alkali as useful product; hence, a loss of current efficiency. However, at the temperature at which such cells are operated, according to best modern practice, namely about 90° C., the solubility of chlorine in the brine is so low that the formation of hypochlorite in this manner is not serious. A far more serious loss comes about through back migration from the cathode compartment of the cell, or face of

the cathode itself, through the diaphragm to the anode compartment, chiefly of negatively charged hydroxyl ions seeking their way to the positive anode. Hydroxyl ions reaching the anodes as such are there discharged, liberating oxygen. However, at normal anolyte pH, which is about 4, hypochlorous acid may be formed, by reaction with the chlorine.

Hypochlorous acid is quite unstable in the anolyte and tends to form chlorate, and in doing so to liberate more oxygen, at the anode. The liberation of oxygen results in contamination of the chlorine thereby; also, since the anodes are of carbon, some of the oxygen attacks the anodes, slowly consuming them, which results in contamination of the chlorine with carbon dioxide. Furthermore, since the hydroxyl ions carry a negative charge, which is discharged at the anode, their back migration represents a loss of current efficiency.

The chlorate formed in the anode compartment passes through the diaphragm in the percolating brine. This is the chief source of chlorate in the cathode compartment. However, the hypochlorous acid which escapes decomposition also passes through the diaphragm and reacts with the caustic alkali in the cathode compartment, forming more hypochlorite and chlorate. In presence of a great excess of alkali, the chlorate is quite stable. It therefore tends to persist in the cell effluent and pass on through to the evaporators in which the caustic alkali is concentrated. During such concentration a part of the chlorate is decomposed by heat, liberating oxygen, which attacks the walls of the evaporator, contaminating the product with the metal of which the evaporator is composed, generally iron or nickel. A part of the chlorate survives the evaporation and remains in the final product, where it constitutes a highly objectionable contaminant.

One way by which formation of chlorate has heretofore been prevented is by feeding hydrochloric acid to the anode compartment with the brine.

This lowers the pH and opposes formation of hypochlorous acid and chlorate and liberation of oxygen at the anode. It also tends to neutralize the negative charge of the hydroxyl ions, and thus decreases loss of current efficiency from this cause. However, there are serious practical objections to supplying acid to the cells, such as attack upon any metals with which it may come into contact, necessitating the use of acidproof equipment in the brine feed system; also, the addition of acid tends to precipitate the chloride and clog the brine feed system.

Our invention therefore has for its object materially to decrease formation of hypochlorous acid and chlorate, and liberation of oxygen, in the anode compartment, thereby raising the purity of the caustic alkali and chlorine and prolonging the life of the anodes, and to do this without the necessity of using acid proof equipment. In the pursuance of these objectives, we add to the anolyte an agent having itself an alkaline reaction, which will react with water, in presence of chlorine to liberate hydrochloric acid. Such an agent we find to be sulphur, in oxidizable form, i. e. either unoxidized or incompletely oxidized.

Sulphur reacts with water, in presence of chlorine as follows:

$$S+3Cl_2+4H_2O \rightarrow H_2SO_4+6HCl \qquad (3)$$

The HCl of Equation 2 lowers the pH and acts as above described.

However, because of the practical difficulty of supplying ordinary elemental sulphur to the cell, we prefer to use it in colloidal form, or as a compound having a reducing reaction in the cell, which reacts with chlorine and water in the same way as sulphur, to liberate hydrochloric acid. This may be demonstrated by the effect of such compounds on the pH of the solution.

Example I

To a solution saturated with sodium chloride and chlorine at 90° C. were added various compounds of sulphur to the amount of 0.1 per cent based on the weight of brine, with observation of the effect on the pH.

The results were as follows:

Sulphur compound added:	pH
None	4.0
$Na_2S_2O_5$	.8
Na_2SO_3	.72
Na_2S	.50
Na_2S_4	.08

This shows that the compounds highest in sulphur and lowest in oxygen are to be preferred. In fact, the effect is proportional to the number of sulphur atoms in the compound and the extent to which they are susceptible of further oxidation. This comparison clearly shows that Na_2S_4 is the best material for our purpose of those tested.

Sodium tetrasulphide reacts with chlorine and water as follows:

$$Na_2S_4+13Cl_2+16H_2O \rightarrow Na_2SO_4+3H_2SO_4+26HCl \qquad (4)$$

It will be seen that the acid products of Equation 4 contain 32 hydrogen ions; hence, one molecule of sodium tetrasulphide will neutralize 32 hydroxyl ions, whereas one molecule of hydrochloric acid will neutralize only one hydroxyl ion; therefore, the sodium tetrasulphide of our process is 32 times as effective per molecule as the acid of the prior art.

It might be thought that the sodium sulphate resulting from the use of sulphur would present a removal problem; but as a matter of fact, sodium sulphate is always present in naturally occuring sodium chloride, and its removal is standard practice. The sulphate is precipitated with the chloride in the evaporator and separated therefrom, which is a routine purification step. The presence of the sulphate therefore presents no additional removal problem.

Example II

The following table gives the results obtained in the operation of cells of the type illustrated in Patent No. 1,866,065, with brine saturated at 60° C. and containing about 310 grams of NaCl per liter, to which various percentages of Na_2S_4, based on the weight of the brine, had been added:

Na_2S_4 in brine, per cent by weight	NaOH in effluent, g. p. l.	pH of Anolyte	Chlorate in effluent, lbs./M NaOH
None	147	3.37	1.5
0.02−	154	3.60	0.92
0.02	151	2.60	0.60
0.02+	150	2.60	0.54
0.04	150	1.43	0.30

It should be noted that the variations in concentration of the caustic effluent have no significance as an effort was made to keep this factor constant; but that even 148 grams per liter is a much higher concentration than standard practice, which averages about 138 grams per liter. This high concentration of caustic alkali was a factor which would ordinarily be very unfavorable to the production of caustic alkali of low chlorate content; but in spite of this, even when the Na_2S_4 added was as little as 0.02 per cent, the chlorate content was remarkably low, as measured by ordinary practice.

Example III

A group of 46 cells of the same type were operated with sodium chloride brine saturated at 60° C. and containing about 310 grams of salt per liter. The caustic effluent from this group showed an average of 150 grams of NaOH per liter and 1.5 lbs. of $NaClO_3$ per 1,000 lbs. of NaOH. The chlorine showed an average content of oxygen, as such and as CO_2, of 1.5 per cent by volume.

To the brine feed of this group of cells was added sodium tetrasulphide to the amount of 0.03 per cent, based on the weight of brine. During the next three months the caustic effluent from this group of cells showed an average of 0.5 lb. sodium chlorate per 1,000 lbs. of caustic soda, which could have been accounted for almost entirely by passage of chlorine through the diaphragm dissolved in the brine. During the same period the chlorine contained oxygen, as such and as carbon dioxide, amounting to 0.5 per cent.

Although in Example I, we have listed a number of sulphur compounds that we consider suitable for our purpose, we do not wish to be limited thereto, as any compound of sulphur having at least a slight solubility in water and containing incompletely oxidized sulphur, or having a reducing action under the conditions of use, comes within the scope of our invention, the extremely small quantity required making it possible to use materials of very low solubility. Among the compounds of sulphur suitable for our purpose are the alkali metal sulphides, polysulphides, hydrosulphides, sulphites, hyposulphites, thiosulphates, pyrosulphites, etc.

Neither do we wish to be limited to the proportions of sodium tetrasulphide or other reducing compounds of sulphur given in the examples, as the addition of as little as .01 per cent is useful and the addition of as much as 1.0 per cent is not necessarily harmful.

Although we have hitherto spoken only of back migration of hydroxyl ions, we wish it understood that other ions may form in the cathode compartment and migrate thence back through the diaphragm to the anode compartment. The expression "back migration" is understood to comprehend migration of hydroxyl ions, hypochlorite ions, chlorate ions, or even molecules of caustic alkali, or any other ions not at present identified, which may operate to produce hypochlorous acid or liberate oxygen in the anode compartment or lower current efficiency.

We claim as our invention:

1. In the method of decomposing alkali metal chlorides in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing sulfur in oxidizable form into the anolyte in the cell in quantities between about 0.01 and about 1.0 per cent by weight of the aqueous chloride fed to the cell.

2. In the method of decomposing alkali metal chlorides in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing colloidal sulfur into the anolyte in the cell in quantities between about 0.01 and about 1.0 per cent by weight of the aqueous chloride fed to the cell.

3. In the method of decomposing alkali metal chlorides in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing sulfur as an alkali metal compound containing sulfur in oxidizable form into the anolyte in the cell in quantities between about 0.01 and about 1.0 per cent by weight of the aqueous chloride fed to the cell.

4. In the method of decomposing alkali metal chlorides in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing sulfur as an alkali metal sulfide into the anolyte in the cell in quantities between about 0.01 and about 1.0 per cent by weight of the aqueous chloride fed to the cell.

5. In the method of decomposing alkali metal chlorides in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing sulfur as an alkali metal compound containing a plurality of sulfur atoms to the molecule in oxidizable form into the anolyte in the oil in quantities between about 0.01 and about 1.0 per cent by weight of the aqueous chloride fed to the cell.

6. In the method of decomposing alkali metal chlorides in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing sulfur as an alkali metal polysulfide into the anolyte in the cell in quantities between about 0.01 and about 1.0 per cent by weight of the aqueous chloride fed to the cell.

7. In the method of decomposing alkali metal chlorides in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing sulfur as sodium tetrasulfide into the anolyte in the cell in quantities between about 0.01 and about 1.0 per cent by weight of the aqueous chloride fed to the cell.

8. In the method of decomposing alkali metal chloride brines in electrolytic alkali chlorine cells of the diaphragm type: the step of introducing into the brine fed to the anode compartment of the cell, between about 0.01 and about 1.0 per cent by weight of sulfur as alkali metal polysulfide.

9. In the method of decomposing alkali metal chloride brines in electrolytic alkali chlorine cells of the diaphragm type: the step of introducing into the brine fed to the anode compartment of the cell, between about 0.01 and about 1.0 per cent by weight of sulfur as alkali metal sulfide.

10. In the method of decomposing sodium chloride brine in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing into the brine fed to the anode compartment of the cell, between about 0.02 and about 0.1 per cent by weight of sulfur as sodium tetrasulphide.

11. In the method of decomposing sodium chloride brine in electrolytic alkali chlorine cells of the diaphragm type, the step of: introducing into the brine fed to the anode compartment of the cell, between about 0.02 and about 0.1 per cent by weight of sulfur as sodium sulfide.

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The following references are of record in the file of this patent:

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