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PROCESS FOR REDUCING LOSSES OF MERCURY IN THE ALKALI METAL CHLORIDE ELECTROLYSIS ACCORDING TO THE AMALGAMATION PROCESS

Martin Krieg, Gerathofen, Germany, assignor to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Bruning, Frankfurt am Main, Germany

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3 Claims

ABSTRACT OF THE DISCLOSURE

Losses of mercury arising during filtration in the electrolytic production of chlorine according to the amalgamation process with electrolyte cycle and alkaline filtration of the electrolyte are reduced by adding hypochlorite to the electrolyte before the filtration.

This application is a continuation of application Ser. No. 806,678 filed Mar. 12, 1969 and now abandoned.

The present invention relates to a process for reducing losses of mercury in the alkali metal chloride electrolysis according to the amalgamation process.

Chlorine and alkali metal hydroxide solutions, particularly sodium hydroxide solution and potassium hydroxide solution, are produced to an increasing extent by electrolysis of the corresponding chloride solutions according to the amalgamation process. The electrolysis plants generally use an electrolyte cycle, the necessary increase in the concentration of alkali metal chloride being brought about at least in a partial stream of the electrolyte coming from the electrolysis cells by the addition of a salt containing alkali metal chloride to the electrolyte which has become poor in alkali metal chloride. As the salts containing alkali metal chloride do not, in general, consist of a 100% alkali metal chloride, the electrolyte absorbs, in addition to the alkali metal chloride, also soluble and insoluble foreign matter during this dissolving process. The foreign matter must be prevented from penetrating into the electrolysis cells and must therefore be removed from the electrolyte. This is generally achieved by precipitation in an alkaline medium and subsequent alkaline filtration.

In alkali metal chloride electrolysis plants operated according to the above method, losses of mercury arise which, in view of the relatively high cost of mercury, render the process less economic. Attempts have therefore been made to reduce the losses of mercury as far as possible by using additional process stages. Processes have been proposed, for example, for the recovery of mercury from the alkali metal hydroxide solutions and the hydrogen gas.

By far the largest losses of mercury arise in the above electrolysis process in the electrolyte cycle. The electrolyte solution which flows off from the electrolysis cells and is called "thin brine" always contains mercury, generally from 1 to 20 milligrams Hg per liter of thin brine. After increasing the concentration with alkali metal chloride, subsequent precipitation in an alkaline medium of the impurities and following alkaline filtration, the electrolyte which is now called "pure brine" contains only a fraction of the initial content of mercury. The loss of mercury in the electrolyte cycle can be exactly calculated from the difference between the mercury content of the thin brine and that of the pure brine. Most of the lost mercury is present in the filter residue of the alkaline

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filtration. Since an economic process for the recovery of mercury from these filter residues has not so far been known, the said filter residues are rejected in the form in which they are obtained. This does not only lead to losses of mercury, but also creates an industrial-hygienic problem.

Processes have also been proposed for reducing the losses of mercury in the electrolyte cycle. In all these processes the mercury is first removed from the electrolyte and then returned to the electrolysis cells, optionally after a work-up. It has been proposed, for example, to precipitate the mercury from the electrolyte in the form of the sulfide thereof or to adsorb it on a strong basic anion exchange resin. The cathodic separation of the mercury from the electrolyte by the application of an electromotive force has also been proposed. However, these processes are so complicated that they are not suitable for use in large-scale alkali metal chloride electrolysis plants.

Now I have found that losses of mercury in the electrolyte cycle can be reduced not by removing the mercury from the electrolyte, but by maintaining it as quantitatively as possible in the electrolyte when carrying out the alkaline precipitation and the separation of impurities from the electrolyte.

The present invention provides a process for reducing losses of mercury in alkali metal chloride electrolysis plants operated according to the amalgamation process with electrolyte cycle and alkaline filtration of the electrolyte, which comprises adding such an amount of hypochlorite to the electrolyte before subjecting it to the alkaline filtration that it still contains hypochlorite ions after the filtration.

It was surprising that the process of the invention enables the mercury contained in the electrolyte coming from the electrolysis cells to be maintained completely or almost completely in the electrolyte cycle and thus to be returned to the electrolysis cells in a simple manner. As compared with the known method using no or too little hypochlorite in the electrolyte, the losses of mercury in the electrolyte cycle are within the range of from 0 to at most 10% by weight of the amount that would be lost without the application of the process of the invention, and the filter residue obtained in the electrolyte filtration which is consequently free from or contains only traces of mercury can be rejected without hesitation as regards industrial hygiene.

To carry out the process of the invention with success and obtain an optimum effect it is essential that the entire filtration process be carried out in the presence of hypochlorite. This means that the pure brine leaving the filtration should contain at least about 1 gram ClO⁻ per cubic meter. The concentration of hypochlorite is therefore advantageously adjusted before the filtration in a manner such that the concentration is not only reliably prevented from dropping below this minimum value but that a somewhat larger amount of hypochlorite, advantageously 1 to 30 grams, and preferably 3 to 10 grams, of ClO⁻ per cubic meter is always present in the pure brine leaving the filtration. It is also possible to use considerably higher concentrations of hypochlorite, but this does not offer any advantages.

The concentration of hypochlorite to be adjusted depends on numerous factors, for example, the residence time between adjustment and filtration, the temperature of the electrolyte, the quality of the salt used for saturating the electrolyte, and the materials with which the electrolyte comes into contact. In general, a hypochlorite concentration within the range of from 10 to 100 grams ClO⁻ per cubic meter brine is necessary.

The temperatures in the electrolyte cycle which, for example for sodium chloride or potassium chloride elec-

trolyses, are generally within the range of from 40 to 90° C. are of no importance for the balance of mercury in the process of the invention.

It is immaterial in which place in the electrolyte stream before the alkaline filtration the required hypochlorite concentration is adjusted. It may be adjusted before, during or after raising the concentration of alkali metal chloride in the brine. As the hypochlorite undergoes a pronounced decomposition in the hot electrolyte solution and the hypochlorite-containing electrolyte is somewhat more corrosive than electrolyte free from hypochlorite, the required hypochlorite concentration is advantageously adjusted, as regards time and space, only shortly before the alkaline filtration, preferably for example shortly before or simultaneously with the alkaline precipitation of the impurities contained in the electrolyte.

The required hypochlorite concentration may be adjusted in several chemical ways. Advantageously a finished hypochlorite solution is added. It is advantageous to use the alkali metal hypochlorite solution with the alkali metal of which the hydroxide solution is produced by the electrolysis. For a sodium chloride electrolysis, a sodium hypochlorite solution is therefore preferably used. Such solutions designated "bleaching liquors" are available at a low price in alkali metal chloride electrolysis plants or are obtained as undesirable by-products in the absorption of chlorine-containing waste gases. The use of hypochlorite solutions has the advantage that exactly measured-out quantities can be used with only little expenditure.

The required hypochlorite concentration may also be adjusted by the reaction of chlorine with hydroxyl ions according to the following scheme



in the electrolyte itself. It is not necessary in this case that the alkalization agent, which in a sodium chloride electrolysis is advantageously sodium hydroxide solution, be added in the same place of the electrolyte stream as the chlorine. As chlorine there may be used pure gaseous or pure liquefied chlorine as well as waste chlorine gas diluted with air. Especially the latter is preferably used for industrial electrolysis plants because such mixtures of chlorine and air are generally obtained as waste gases, for example, in the dechlorination of the thin brine and in other places.

In a special form of the last mentioned process the required hypochlorite concentration may be adjusted by leaving such an amount of chlorine in the electrolyte when dechlorinating the acid thin brine that the necessary amount of hypochlorite is formed in the subsequent alkalization. In this mode of executing the process it is necessary, because of the decomposition of hypochlorite in the hot electrolyte solution already mentioned above, to adjust the electrolyte solution to a considerably higher initial concentration of hypochlorite, which in turn increases the corroding property of the electrolyte. This fact must already be taken into consideration in process stages of the electrolyte cycle for which correspondingly corrosion-resistant materials have not generally been used, for example the salt dissolution plant.

The following example serves to illustrate the invention, but is not intended to limit it.

EXAMPLE

Through a sodium chloride electrolysis plant operated according to the amalgamation process, 500 cubic meters electrolyte solution were passed per hour in uniform flow. The thin brine flowing off from the cells at a temperature of about 80° C. contained, in addition to small amounts of sulfate, chlorate and chlorine, also an average of 275 kilograms sodium chloride and 3.85 grams mercury per cubic meter. The brine was adjusted to a pH of about 2 by the addition of hydrochloric acid and freed from the major part of the dissolved chlorine in a vacuum dechlorination plant. The residual chlorine was subsequently expelled by

blowing in air. The brine was then adjusted to a pH of 9.5 by adding sodium hydroxide solution and pumped into a salt dissolution plant where the concentration was increased to an average of 310 kilograms NaCl per cubic meter by contacting with natural rock salt. The brine was then passed through so-called precipitation vessels where the alkaline earth ions and the sulfate were converted to a large extent into a difficultly soluble precipitate by the addition of soda and barium carbonate. To separate these salts and remove other substances causing turbidity which originated from the rock salt, the brine was filtered, whereby the salts and substances causing turbidity accumulated as a filter cake on filter cloths of synthetic fabric. The filtered pure brine was returned to the electrolysis cells via buffer vessels. The pure brine contained an average of only 2.05 grams mercury per cubic meter. Consequently an average of 1.80 grams mercury had been lost per cubic meter of brine. Calculated on the production of chlorine of 10.4 tons per hour, the loss of mercury was 87 grams per ton of chlorine produced. In a fully continuous operation about 7.88 tons mercury per year were lost in this manner. The lost mercury was almost completely contained in the filter cake of the alkaline filtration. The filter cake which had been dried at 130° C. contained, on an average, 1.4 kilograms mercury per ton of dry substance.

In the same electrolysis plant 180 liters of a sodium hypochlorite solution containing, per liter, 120 grams NaClO were added to the brine (mercury content 3.85 grams per cubic meter) in accordance with the invention shortly before the brine entered the precipitation vessels. This solution, designated "waste bleaching liquor" had been formed in an absorption plant for chlorine-containing waste gases. Instead of the waste bleaching liquor, 23.4 kilograms NaOH in the form of caustic soda or sodium hydroxide solution and 20.7 kilograms chlorine could be added to the brine per hour. The chlorine could be used in the gaseous or liquid form or in the form of waste chlorine gas diluted with air. In each case the brine was first adjusted to a hypochlorite content of about 30 grams ClO⁻ per cubic meter. The hypochlorite content of the filtered pure brine was within the range of from 3 to 10 grams ClO⁻ per cubic meter and the average content of mercury was 3.78 grams per cubic meter. The loss of mercury was therefore on an average only 70 milligrams per cubic meter brine, that is it had been reduced to about 4% of the original value. The specific loss of mercury in the electrolyte cycle was only 3.4 grams per ton of chlorine produced and the annual loss arising from this source had been reduced to about 0.3 ton mercury. No mercury could be traced in the filter cake of the alkaline filtration and the filter residues were consequently harmless from the viewpoint of industrial hygiene.

What is claimed is:

1. A process for electrolysis of alkali metal chloride brine in electrolytic flowing mercury cathodic cells which comprises

- (a) introducing a substantially saturated aqueous solution of an alkali metal chloride brine into the flowing mercury cathodic cells
- (b) electrolyzing said brine in said cells to produce chlorine and alkali metal amalgam, thereby depleting the alkali metal content in the brine
- (c) removing the thus depleted brine from the cells, which brine contains mercury impurities picked up from the flowing mercury cathodes
- (d) adding caustic alkali to the brine
- (e) resaturating the brine with alkali metal chloride
- (f) adding to the resaturated brine soda and barium carbonate to precipitate the alkaline earth ions and the sulfate ions, and then filtering the brine, and
- (g) adding such an amount of hypochlorite to the brine, prior to the filtration, that the brine still contains at least one gram of hypochlorite ions per cubic meter after the filtration, whereupon the filtered and resaturated brine is fed back into the electrolytic cells.

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2. The process of claim 1 wherein the required concentration of hypochlorite is adjusted by the addition of an alkali metal hypochlorite.

3. The process of claim 1 wherein the required amount of hypochlorite is formed in the brine from the calculated amounts of chlorine and alkali metal hydroxide.

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3,115,389	12/1963	Deriaz	204—99
3,213,006	10/1965	Crain et al.	204—99
3,691,037	9/1972	Updyke	204—99

5 ALLEN B. CURTIS, Primary Examiner
H. A. FEELEY, Assistant Examiner

References Cited

UNITED STATES PATENTS

2,248,137	7/1941	Taylor et al.	204—99
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