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[54] **CONDITIONING DIAPHRAGMS IN CHLOR-ALKALI CELLS**

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[52] **U.S. Cl.** **204/98**
[51] **Int. Cl.** **C01d 1/06**
[58] **Field of Search** 204/98

[56] **References Cited**

UNITED STATES PATENTS

3,630,863	12/1971	Jeffery et al.	204/98
2,569,329	9/1951	Osborne	204/98
2,954,333	9/1960	Heiskell et al.	204/98
3,403,083	9/1968	Currey et al.	204/98
3,485,730	12/1969	Virgil, Jr.	204/98
3,471,382	10/1969	Grotheer	204/98

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[57] **ABSTRACT**

An improved process is described for the production of alkali metal hydroxides and elemental chlorine which comprises passing substantially saturated sodium chlorine brine solutions through a diaphragm type chlor-alkali cell consisting essentially of a cell enclosure, an anode having an electrically active surface on an electrically conductive substrate metal, and a formaminous metal cathode, the anode and cathode being separated by porous diaphragm containing asbestos wherein the brine solution has been acidified to a pH of less than 2 and continuing the passage of the acidified brine into the cell at least until the hydrogen content of the chlorine produced at the anode is less than 0.5 percent by weight. The improved process results not only in purer chlorine product, but also higher current efficiencies and maintainance of the desired head of anolyte liquor of more readily accomplished.

6 Claims, No Drawings

CONDITIONING DIAPHRAGMS IN CHLOR-ALKALI CELLS

BACKGROUND OF THE INVENTION

This invention relates to improvements in the production of alkali metal hydroxide and elemental chlorine in diaphragm type chlor-alkali cells equipped with anodes having an electrically active surface on a electrically conductive substrate metal. It is known that chlorine, and aqueous alkali metal hydroxide, can be produced readily by electrolysis of alkali metal chloride brine in a diaphragm type cell. Such cells consist essentially of a cell enclosure and an anode of a chlorine resistant electro conductive material such as platinum, platinum coated titanium or the like, or graphite and a foraminous cathode usually made of iron within the enclosure.

The anolyte compartment and the cathode compartment are separated by means of a porous diaphragm usually of asbestos or like material.

It has been found that in such cells having metal or dimensionally stable anodes that is difficult to maintain the necessary head of anolyte liquor without using an excessive brine feed rate. This condition results in the production of chlorine gas containing a high content of hydrogen and excessive back migration of caustic soda into the anolyte through the asbestos diaphragm.

Diaphragm type chlor-alkali cells equipped with graphite anodes do not, in general, exhibit such problems of back migration of caustic alkali and hydrogen. Such cells usually operate at an anolyte pH within the pH range of about 3 to about 4. On start-up using a new graphite anode, anolyte pH values of less than 3 have been observed. However, using normal brine feed rates and brine feed having a pH of about 6.5 the anolyte pH quickly increases to within the desired operating range of between about 3 to about 4.

It is thus a problem, especially on start-up of chlor-alkali cells equipped with chlorine resistant electro-conductive metal anodes and using freshly prepared asbestos diaphragm material, to maintain the desired head of the anolyte liquor and to prevent the caustic alkali as well as hydrogen produced at the cathode from diffusing into the anolyte compartment.

It is known is such cells to substantially prevent or limit the back migration of hydrogen and caustic alkali through the freshly prepared diaphragm by diapersing elemental carbon particles throughout the diaphragm in a more or less uniform manner. By this means the cell may be operated at a lower voltage and the flow of brine therethrough is sufficient to substantially prevent the back migration of hydrogen and caustic alkali from the cathode compartment into the anode compartment. However, the use of carbon and like materials in the asbestos diaphragm often weakens the fibrous character of the diaphragm and results in the rapid disintegration of the diaphragm in use.

BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention an improved process for the production of alkali metal hydroxides and elemental chlorine is provided which process comprises passing a substantially saturated sodium chloride brine solution through a diaphragm type cell consisting essentially of a cell enclosure, an anode having an electrically active surface on an electrically conductive substrate metal, and a cathode of a foraminous

metal, the anode and the cathode being separated by a porous diaphragm containing asbestos, wherein the brine solution has been acidified to a pH of less than 2 and continuing the passage of the acidified brine solution into the cell until the hydrogen content of the chlorine produced at the anode is less than about 0.5 percent by weight. It has been discovered that the diffusion of hydrogen and caustic alkalies from the catholyte into the anolyte compartments of a diaphragm type chlor-alkali cell equipped with anodes which present an electrically active surface on electrically conductive substrate material can be substantially prevented and the required anolyte head using the normal brine feed rate can be maintained by the addition of sufficient hydrochloric acid to the brine feed to reduce the pH thereof to below 2. By "normal brine feed rate" it is meant that necessary to maintain caustic strength in the catholyte liquor in the range of about 140–150 grams per liter NaOH. In conventional operation, this normal brine feed rate will depend on the current load and the size of the cell, and may vary between about one and about 5 gallons per minute. By this improved process, the chlorine produced in the anode compartment is characterized by extremely low contents of hydrogen and the electrolysis is operated with higher current efficiency especially during the initial phases, i.e., start-up.

It is known, when using diaphragm type chlor-alkali cells equipped with graphite electrodes to utilize acidified brine feed solutions. For example, it has been disclosed in U.S. Pat. No. 3,403,083 to improve the overall performance of the cell by feeding brine solution to the cell at a rate in excess of that which flows through the diaphragm. The excess brine solution is withdrawn from the anolyte compartment, the withdrawn solution is replenished with an additional amount of sodium chloride and the pH of the resultant solution is adjusted to within the range of 2 to 4 prior to being recycled back into the cell.

It has been found, however, that in diaphragm type chlor-alkali cells equipped with chlorine resistant metal anodes, that acidified brine feed solutions having pH values within the range of 2 to 4 are without effect to permitting the obtention of the required anolyte head using the normal feed brine rate and thus to prevent the substantial back migration of hydrogen and caustic alkali from the cathode compartment through the diaphragm into the anode compartment.

The diaphragm type chlor-alkali cells useful in the present invention are those equipped with anodes which present an electrically active surface on an electrically conductive substrate material. By substrate metal, it is intended to encompass those metals and metal alloys which become passivated when polarized anodically and remain passive beyond the anodic potential needed to convert a chloride ion to chlorine. The phenomenon of passivity in this connection is discussed in an article by Green appearing in the Apr., 1962 issure of Corrosion National Association of Corrosion Engineers, pages 136*t* to 142*t* wherein reference may be made to FIG. 1 which describes a typically active-passive transition of a metal toward a corrosive medium. The metal substrate employed in the electrodes applicable in this invention will not pass into the transpassive range until a potential is reached which is considerably higher than that needed to produce chlorine from the chloride ion. Hence, the substrate metal remains passive during the operation of the electrolytic cell. Illustrative of the substrate metals in a generic sense are the "valve" metals (with the exclusion of certain metals which obviously are inapplicable such as aluminum, zirconium, and the like). Titanium, tantalum or niobium are acceptable substrate metals. The titanium employed is normally of a commercially pure grade of titanium of intermediate strength. Alloys of titanium may be employed as long as the alloy meets the criterion of acidity set forth in the above, for example, titanium alloys of aluminum, vanadium, paladium, chromium or tin may be employed in which the latter metals are present as less than about 10 percent of the alloy.

The surface of the substrate metal is made active by various methods. For example, a conductor such as a noble metal (preferably platinum) may be desposited on the surface of the substrate metal by methods known in the art. Mixtures of other noble metals and platinum may be used to activate the surface of the metal substrate. The preferred surface metal mixture or alloy is one containing more than about 50 percent platinum. Likewise, noble metal oxides may be used alone or in combination with the noble metals to form the active electrode surface. By noble metal, it is intended to include the platinum and palladium triads of the periodic table with the exclusion of osmium. Thus, ruthenium, rhodium, palladium, iridium and platinum represent noble metals which are especially applicable in their metallic form, alloys thereof and as oxides.

With specific reference to platinum-titanium electrodes or plantinized titanium electrodes, the titanium substrate used the commercially pure grade of intermediate strength or a titanium alloy of aluminum, vanadium, palladium, chromium, or tin in which about 90 percent or more of the alloy is titanium. The platinum-titanium or noble metal oxide-titanium electrodes are acceptable as well as the platinum or noble metal oxide surfaced titanium or titanium clad copper electrodes wherein the titanium or tantalum is applied to the copper core by mechanical coating or with electrically conductive adhesive materials.

The anodes may be assembled within the diaphragm type chlor-alkali cell in any manner known to the art. The anode current conductor connections may be isolated from the corrosive contents of the electrolytic cell by bituminous materials such as mastic or synthetic resin sealants. In this regard, one typical anode assembly is that disclosed by M. P. Grotheer in U.S. Pat. No. 3,563,878, issued Feb. 16, 1971, wherein an anode assembly is disclosed which is applicable to monopolar and bipolar chlor-alkali cell operation. The anode assembly provided therein is a unitary electrode assembly which involves a metallic (preferably steel) base plate or backer plate to which spacer bars of an electrically conductive material such as platinized-titanium, aluminum alloys and preferably copper is attached by welding or tinning to the steel at predetermined intervals based upon the desired pitch of the anodes. When the spacer bar is constructed from platinized titanium, the use of sealants may be dispensed with as protective means against attack by the corrosive materials which contact it. The spacer bar is disposed in such a manner that the attached anodes will be aligned with abutting edges vertically situated within the cell unit. The spacer bar contains holes through which pass the bolts running parallel to the base plate. The holes through the spacer bars are preferably slotted, at an angle downwardly extending from the vertical bar surface. The number of anodes that may be attached to the spacer bars by pressure bars depends upon the designed height of the cell where the anodes are horizontally attached to the spacer bar in a vertically disposed bank of anodes, or the cell width where the anodes are vertically attached to the spacer bar in a bank extending across the cell.

The pressure bars, one being drilled and countersunk, the other being provided with threaded holes, act, in conjunction with the bolt running through them, the anode and spacer bar, as an electrode clamping device. In the clamped position, the electrical resistance through the anode-spacer bar contact is a function of the pressure developed at the contacting surfaces. Hence, the resistance developed through the clamped connection of anode and spacer bar may be controlled by regulating the pressure applied by the clamping bolts. Consideration must also be given to the thermal expansion of the spacer bar during operation of the cell in which temperatures above 95°C., are common. In practice, the bolts may be of a suitable metal or metal alloy to compensate for the expansion of the spacer bars and pressure bars. Likewise, the pressure bars may be made of any suitable material such as steel.

Any corrosion resistant sealant known to the art may be placed over the connecting members between each electrode. For example, natural or synthetic rubbers may be employed by themselves, in combination or in conjunction with other resins. Bituminous materials may be employed if desired and the phenol-formaldehyde resins and polyester resins are acceptable sealants. Especially good sealants may be derived from the reaction of a polyhydric alcohol with a Diels-Alder adduct of hexahalocyclopentadiene and an alpha, beta unsaturated dicarboxylic acid, such as are disclosed in U.S. Pat. No. 3,216,884. The sealants employed in this invention may be advantageously highly filled with such materials as sand, SiO_2, graphite particles, or other inert materials.

The electrolytic cells contemplated by this invention are those conventionally used in the electrolysis of sodium chloride solutions. The electrolytic cell comprises a cell top, a cell bottom, sidewalls, an anode compartment and a cathode compartment separated by a porous diaphragm which may be of deposited asbestos. The brine is fed into the anode compartment from which it flows through the diaphragm into the cathode compartment. Chlorine and hydrogen are withdrawn from the anode and cathode compartments, respectively. The cell liquor containing sodium hydroxide, sodium chloride and other impurities is withdrawn from the cathode compartment.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention a saturated brine containing from about 250 to about 320 grams per liter of sodium chloride is adjusted to a pH below about 2 and preferably below about 1.5 and especially between about 1.2 and about 1.3 is fed to a conventional chlor-alkali cell which consists essentially of a cell enclosure, an anode of a chlorine resistant electro conductive material, and a foraminous cathode having attached thereto a diaphragm of asbestos or like material. The pH adjustment of the brine feed is preferably carried out with hydrochloric acid. The brine feed is adjusted through the cell under head of about 3 to 30 inches of saturated brine and preferably from about 3 to 18 inches. In conventional chlor-alkali cells the concentration of the brine and the feed rate are adjusted to control the caustic alkali strength of the catholyte. During the operation of the cell, the head of the brine liquor in the anolyte compartment increases with time to maintain a uniform flow through the diaphragm. In chlor-alkali cells wherein the anolyte liquor is continuously recirculated, it is preferred to introduce the brine feed into the cell at a rate higher than that of the flow through the diaphragm while recycling the excess brine with make-up brine. The advantages of recycle are to maintain a relatively constant anolyte chloride concentration and pH. In operation, the electrolytic cell may be efficiently operated within the temperature range of about 80° centigrade up to the boiling point of the brine (which depends upon the brine concentration). The anode current density of the operating electrolytic cell is preferably greater than 0.8 amperes per square inch.

It is preferred that the electrolysis be operated at least in the initial stages with the highly acidified brine. The pH of the brine may be gradually increased during the electrolysis to the normal levels, i.e., pH about 4 either by following the hydrogen content of the chlorine gas produced at the anode or by monitoring the head of the liquor in the anolyte compartment. When the hydrogen content of the chlorine is reduced to less than 0.5 percent by weight or when an anolyte head of greater than 3 inches can be maintained at the desired flow rate, e.g., the normal brine feed rate, the pH of the circulating brine may be increased to normal level e.g., about 4.

The following examples will illustrate the process of the present invention.

EXPERIMENT 1

A conventional diaphragm type chlor-alkali cell equipped with platinum coated titanium anode, a steel cathode having deposited thereon an asbestos diaphragm was charged with brine containing about 300 grams per liter ("gpl") of sodium chloride at about 98° centigrade, to a head of about four inches in the anolyte compartment. The current load was maintained at 95 KA and the caustic strength of the catholyte was maintained between 145 and 150 gpl NaOH by controlling the brine feed rate to the anolyte compartment. The pH of the anolyte liquor during the first three days of operation varied between 3.7 and 4.0 and the head of anolyte liquor varied between about 3.25 and 4.5 inches. After about 1.5 days of operation, the pH of the anolyte liquor was reduced to 1.2 by the addition of aqueous hydrochloric acid for about 24 hours. The head of anolyte liquor increased within one day to 9 inches and remained constant for the duration of the run at that level.

EXPERIMENT 2

The above described run was repeated with the following exceptions.

1. The electrolysis was initiated with a current load of 85 KA, which after one day of operation was increased to 90 KA.
2. The pH of the anolyte liquor varied between 4.1 and 4.4 during the first 9 days of the run.

The head of anolyte liquor was initially 3 inches and dropped within 24 hours to about 1 inch. The head varied between about 1 and 3 inches during the first 9 days of cell operation. On the ninth day, the pH of the anolyte was decreased to about 2 and maintained for about 20 hours by the addition of aqueous hydrochloric acid. Thereafter the pH increased to about 3.7. The anolyte head increased slightly to about 3.2 inches but quickly leveled off to about 3 inches for the balance of the run. The hydrogen content of the chlorine was originally 1.0 percent and after the period of acid addition varied between about 0.4 and 0.8 percent throughout the duration of the run.

EXPERIMENT 3

A chlor alkali cell equipped with a side entry platinum coated titanium anode and a steel cathode, the anode and cathode being separated by a deposited asbestos diaphragm was charged with brine of about 300 gpl NaCl concentration and at about 98° centigrade to an initial head in the anolyte compartment of 11 inches. The current load was initially 53 KA and was gradually increased to 60 KA after 7 days, to 70 KA on the eighth day and to 80 KA on the ninth day. The cell was operated at 80 KA for the balance of the run. The caustic strength of the catholyte was maintained at 90–95 gpl NaOH for the first day and at 145 to 155 gpl NaOH on the second through ninth day, then permitted to rise as high as 190 gpl NaOH on the final, twelfth day.

The pH of the anolyte was adjusted to 1.3 by the addition of aqueous hydrochloric acid to the brine feed at the start-up of the electrolysis and continued for about 20 hours. The pH of the anolyte increased to 4.4 after 24 hours after start-up and varied between 4.3 and 4.8 thereafter.

The head of the anolyte liquor increased rapidly to 29 inches after about 20 hours and varied between about 18 and 28 inches throughout the run. After cessation of the acid addition, the head decreased from a maximum of 29 inches (20 hours) to 18 inches (4.5 days) and then increased to 28 inches (8 days), varying thereafter between about 24 and 28 inches. The hydrogen content of the chlorine was about one percent at the beginning of the run but fell to about 0.6 percent on the first day and from the second day to the completion of the run, varied within the range of 0.1 to 0.4 percent.

What is claimed is:

1. In a process for the production of alkali metal hydroxides and elemental chlorine which comprises passing a substantially saturated sodium chloride brine solution through a diaphragm type chlor-alkali cell consisting essentially of a cell enclosure, an anode having an electrically active surface on an electrically conductive substrate metal, and a cathode of a foraminous metal, said anode and said cathode being separated by a porous diaphragm containing asbestos, the improvement which consists of initially utilizing as the brine feed one which has been acidified to a pH of less than 2 and continuing the passage of such an acidified brine into the cell until the hydrogen content of the chlorine produced at the anode is less than about 0.5 per cent by weight, thereafter increasing the pH of the brine feed to at least about 4, and containing the passage of said brine of increased pH into the cell.

2. The process of claim 1 wherein the anode is formed of platinum coated titanium.

3. The process of claim 1 wherein the brine feed is maintained at a rate sufficient to produce a catholyte liquor containing at least about 90 grams per liter of sodium hydroxide.

4. The process of claim **3** wherein the brine feed rate is maintained at a rate sufficient to produce a catholyte liquor containing between about 140 and about 155 grams per liter of sodium hydroxide.

5. The process of claim **1** wherein the initial brine feed is adjusted to a pH of below about 1.5.

6. The process of claim **5** wherein the initial brine feed is acidified to a pH of between about 1.2 and about 1.3.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,755,103 Dated August 28, 1973

Inventor(s) Morris P. Grotheer et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the ABSTRACT, last line "of" should read ---is---; Col. 1, line 22, after "that" insert ---it---; line 35 "feed" should read ---feeds---; line 47, " diapersing" should read ---dispersing---; Col. 2, line 59, "issure" should read ---issue---; Col. 3, line 16, "desposited" should read ---deposited---; line 32, after "used" insert ---is---; line 38, "titanuim" second occurrence should read ---tantalum---. Claim 1, Col. 6, line 61, "containing" should read ---continuing---. Col. 1, line 45, "is", second occurrence, should read -- in --.

Signed and sealed this 22nd day of January 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents