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ON-OFF OPERATION OF CHLOR-ALKALI DIAPHRAGM CELLS

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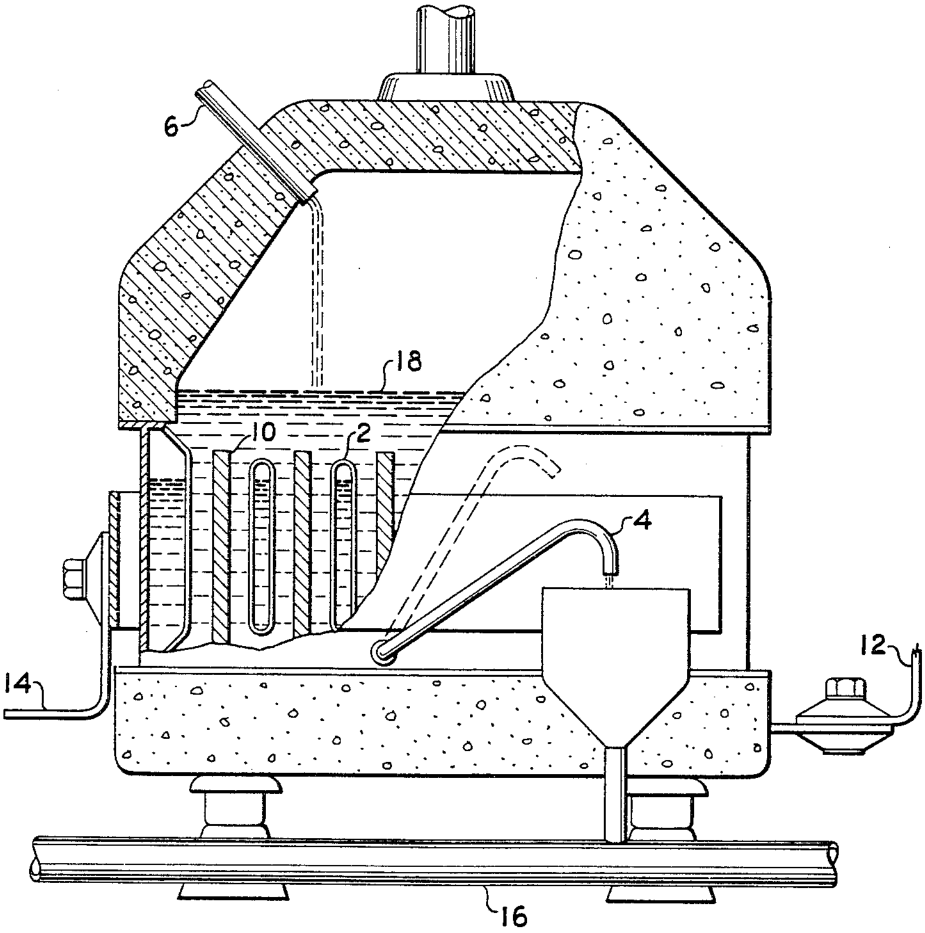

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ON-OFF OPERATION OF CHLOR-ALKALI DIAPHRAGM CELLS

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ABSTRACT OF THE DISCLOSURE

There is provided a process for the intermittent operation of chlor-alkali diaphragm cells wherein, during part or all of the time the cell is shut down, it is flushed with brine, said cell being periodically shut down and started up. The cell current efficiencies provided by this process are excellent.

About 14,000 tons of chlorine and 15,500 tons of caustic are produced every day in the United States by chlor-alkali diaphragm cells. These cells, which have been in commercial use for about 60 years, produce approximately 70 percent of all the chlorine made in the United States.

Several thousand kilowatt-hours of power are needed to produce each ton of chlorine from these cells. If the cost of each unit of power required for these cells could be cut approximately 15 percent, a cost savings running into tens of millions of dollars would result.

In many areas of the country, "off-peak" power is available at rates considerably lower than those for "firm" continuous power. In general, "off-peak" power is approximately 20 percent cheaper than "firm" power. If a process could be devised wherein said chlor-alkali diaphragm cells could be run during only that period of the day which "off-peak" power is available, substantial cost-savings in the operations of said cells would result.

Though "off-peak" power has been available for many years, hitherto no known attempt has been made to intermittently operate said cells thereon. Though this may appear to be incongruous, especially in view of the vast economies which are afforded by the use of "off-peak" power, there is an explanation as to why said attempt was never made—it was believed that chlor-alkali diaphragm cells had to be run continuously for even reasonably good cell efficiencies to be obtained, that the starting up and shutting down of said cells which is necessitated by the use of "off-peak" power would result in catastrophic cell efficiencies.

It is an object of this invention to provide an efficient, economical process for the on-off operation of chlor-alkali diaphragm cells. In accordance with this invention, there is provided a process for the intermittent operation of chlor-alkali diaphragm cells wherein, during part or all of the time the cell is shut down, it is flushed with brine, said cell being periodically shut down and started up. The current efficiencies in the cells operated by this process are excellent, being substantially the same as those obtained when said cells are run continuously.

In the practice of the process of this invention, said chlor-alkali diaphragm cells are periodically shut down and started up. In general, this shut down-start up cycle will occur at least once a day inasmuch as "off-peak" power is generally available during one or more periods of the day. It is to be understood that the present invention is applicable to processes wherein said cycle occurs once during a period of days, weeks, or even months. To best utilize the economic advantages offered by the present invention, however, it is preferred that said cycle occur at least about 4 times a month, it is more preferred that said cycle occur at least 30 times a month, and it is even more preferred that said cycle occur at least 60 times a month. Said cycle may, however, occur as frequently as 120 times a month.

The process of the present invention is useful with all chlor-alkali diaphragm cells. For the sake of convenience, said process will hereinafter be described with reference to Hooker S cells (these are chlorine-caustic cells with foraminous cathodes and asbestos diaphragms deposited thereon. An interesting discussion thereof is presented in "Chlorine, Its Manufacture, Properties and Uses," J. S. Sconce [Rheinhold, New York: 1962], pp. 94–97), it being understood that said process is operative with every chlor-alkali diaphragm cell.

The term "brine" refers to a solution comprised of a large amount of alkali metal salt. It is preferred that said alkali metal salt be sodium chloride, and that the brine contain from about 75 to about 98 percent of the amount of sodium chloride which would result in saturation (it being understood that the saturation level of the brine varies with temperature); it is even more preferred that said brine contain from about 90 to about 95 percent of the amount of sodium chloride which would result in saturation.

The figure is a partial sectional view of the Hooker S cell. When the cell is operating, a voltage differential is maintained between anode bus connector **12** and cathode bus connector **14**, brine is fed in through brine inlet **6**, asbestos covered cathode **2** and graphite anode **10** are immersed in electrolyte, and cell liquor is withdrawn from the cell through caustic outlet **4** and header **16**. When the cell is shut down it is desirable to have an alkaline medium surrounding the asbestos covered cathode inasmuch as said cathode is comprised of steel and is corroded by an acidic environment. To render the anolyte **18** basic after shut down, caustic outlet **4** may be raised ton an almost vertical position, thereby insuring that virtually no cell liquor will flow therethrough into the header and that all or part of said cathode will be covered with caustic liquor. It is to be understood that other means may be used to decrease the acidity of said anolyte. Thus, e.g., in chlor-alkali diaphragm cells which do not have movable caustic outlets, the caustic outlets may be plugged by some suitable means so that no caustic can flow therethrough. Alternatively (or in conjunction with the aforementioned techniques), the cell may be flushed with alkaline brine.

It is preferred to decrease the flow of caustic from the cell shortly after the power has been shut off. Thus, e.g., with the Hooker S cell the caustic outlet should be raised from about 0 to about 10 minutes after the power has shut off, though it is preferred to raise said outlet from about 0 to about 5 minutes after power shut-off, and it is even more preferred to raise said outlet almost immediately after power shut-off, within from about 0 to about 60 seconds. The caustic outlet should be raised to an almost vertical position. When this is done, percolation ceases in the cell, and the cathode becomes surrounded by caustic liquor.

Once the cell power is shut off, hydroxyl ion back migrates through the asbestos diaphragm covered cathode **2** into the anolyte compartment. Prior to start up of the cell, the concentration of the hydroxyl ion in the anolyte must be lowered, for if the cell is operated with a high hydroxyl ion concentration in the anolyte the graphite anode **10** will be oxidized at a higher rate, and poor cell efficiencies will result. Thus, the cell is flushed with brine during part or all of the time it is shut down. In the practice of the process of this invention, the cell is flushed just prior to start-up thereof, brine being fed through brine inlet **6** and cell liquor coming out of caustic outlet **4**. Said flushing prior to start-up may, however, be accompanied by a flushing just prior to shut-down.

When, in conjunction with brine flushing prior to start-up, the cell is flushed just prior to shut-down, it is preferred that said brine flushing be begun from about 0 to about 30 minutes before power shut-off, though it is more preferred that it be begun from about 5 to about 20 minutes before power shut off, and it is even more preferred that it be begun from about 10 to about 15 minutes before power shut-off. The brine flushing after shut-down is continued until the desired anolyte pH is obtained. It is preferred that said anolyte pH be above about 5, and it is even more preferred that said pH be above about 8. One may flush after shut-down with brine which has a pH of from about 7 to 12, though it is preferred to use brine with a pH of from about 9 to about 11, and it is even more preferred to use brine with a pH of about 10.

Flushing with unsaturated alkaline brine prior to shut-down serves a two-fold prupose: it prevents "salting" the brine feed lines by replacig the saturtaed brine therein with unsaturated brine; it increases the pH of the anolyte, thereby decreasing some of the corrosive forces the cathode is subjected to; and it dilutes the cell liquor, thereby decreasing the hydroxyl ion concentration thereof, the back migration of said hydroxyl ion, and the anolyte pH which exists just prior to start-up. The anolyte pH is acidic when the cell is in operation. As soon as the current is shut-off, back migration of hydroxyl ion occurs, and the pH of the anolyte gradually increases. Flushing with alkaline brine after power shut-off increases the rate at which anolyte pH increases—but it also dilutes the cell liquor. At approximately that point at which the pH of the anolyte is equal to that of the feed brine the flushing may be stopped (in general it is desirable when flushing either after shut-down or prior to start-up to continue said flushing until it is approximately equal to that of the feed brine). While the cell is shut down, the anolyte pH will gradually increase further because of further back-migration of hydroxyl ion until an equilibrium is established; the amount of said further increase in anolyte pH, however, is inversely proportional to the amount of dilution of the cell liquor which occurs as a result of said flushing after shut-down. Prior to the time the cell is started up again, however, the pH of anolyte should be reduced until it is at least about as low as the pH of the feed brine. Thus, brine flushing is again resumed until the desired pH is obtained, at which point the cell may be started up. Soon after the cell is in operation, an acidic environment is generated in the anolyte, and the pH thereof decreases.

Brine which is saturated with sodium chloride may be used for brine flushing either before shut-down or prior to start-up, though it is preferred to use unsaturated brine inasmuch as the use of the former does not prevent "salting" of the brine feed lines. When using unsaturated lines brine, it is preferred that it contain at least about 90 percent of the sodium chloride which would result in saturation thereof at that temperature at which the brine is at (the saturation level being a function of temperature), and it is even more preferred to use a brine containing at least 95 percent of the amount of sodium chloride which would cause saturation.

The rate at which brine is flushed through the cell and the amount of brine to be used in said flushing will vary from cell to cell, being largely dependent upon the size of the cell. For the Hooker S-3 cell, for example, from about 1.1 to about 1.7 gallons of brine per minute are fed into the cell for from about 5 to about 30 minutes prior to start-up, though it is preferred to flush from about 10 to about 20 minutes prior to start-up, and it is even more preferred to flush about 10 to about 15 minutes prior to start-up.

The pH of the brine used for flushing prior to start-up should be as acidic as possible, and to this end one may acidify the brine so that the use thereof will more readily reduce anolyte pH. When the brine is to be acidified, a suitable acid such as hydrochloric acid may be used. It is preferred to use the most concentrated hydrochloric acid available, such as anhydrous hydrochloric acid, so that the cell liquor is diluted as little as possible. When the brine is to be acidified, it is preferred to adjust the pH thereof to from about 2.5 to about 4.5, and it is even more preferred to adjust the pH thereof to from about 3 to about 4.

When it is inconvenient to acidify the feed brine, one may use an unadulterated feed brine with a pH of from about 7 to about 12, though it is preferred to use said feed brine with a pH of from about 7 to about 10, and it is most preferred to use said feed brine with a pH of from about 7 to about 8. In general, brine of about pH 2.5 to about pH 12 may be used.

In the practice of the process of this invention, chlor-alkali diaphragm cells will be run from about 1,000 to about 100,000 amperes, although with most of said cells from about 10,000 to about 60,000 amperes are used. It is to be understood that the amperage required for the operation of said cells will vary with the size of said cells. In general, however, enough current will be applied to said cells so that a current density of from about 70 to about 150 amperes per square foot of cathode exists, though it is generally preferred to work with a current density of from about 75 to about 135 amperes per square foot, and it is even more preferred to work with a current density of about 100 to about 125 amperes per square foot.

In general, a voltage differential of from about 3.2 to about 4.5 volts will exist between the anode and cathode, though it is preferred to work with a voltage differential of from about 3.4 to about 4.2 volts, and it is even more preferred to work with a voltage differential of about 3.4 to about 3.9 volts.

Cells operated by the process of this invention require from about 2,800 to about 3,800 kilowatt hours of power for every ton of chlorine they produce. When conditions are optimized, however, from about 2,900 to about 3,400 kilowatt hours of power are required per ton of chlorine.

It is to be understood that the process of the present invention may be used in the electrolysis of electrolytes other than sodium chloride. Thus, for example, the process of the present invention is operative in the electrolysis of potassium chloride with a diaphragm cell.

When cells are operated by the process of the present invention, the current efficiencies thereof are excellent, usually being in excess of 95 percent and ranging from about 95 to about 98 percent.

The following example illustrates one of the preferred embodiments of the invention and is not to be deemed limitative thereof, it being understood that applicant's process may also be used with other chlor-alkali diaphragm cells.

EXAMPLE

A circuit of 96 Hooker S-3 cells was intermittently operated for 36 days on about 30,000 amperes and 3.5 volts. On days 1-5, 8-12, 15-19, 22-26, and 29-33, and 36 the cells were shut down for three hours and then started up; on days 6-7, 13-14, 20-21, 27-28, and 33-35 the cells were operated continuously. About 15 minutes prior to the time the cells were shut down unsaturated feed brine (with about 95 percent of the amount of sodium chloride required to cause saturation) was fed to the cells. About eight minutes after the power was shut off, the caustic outlet pipes were raised to full height. About nine minutes after the power was shut off, the feed brine was shut off. About 15 minutes prior to the time the power was to be turned on, the brine feed was resumed. Within about eight minutes of the time the power was to be turned on, the caustic outlet pipes were lowered to their normal operating positions. One minute after the power was turned on saturated brine was again fed to the cells.

The current efficiency of the cells was up to about 95 percent within about 20 minutes of start up, and this efficiency was maintained while the cell was operating.

About 15 gallons of brine were used to flush each of the cells after shut-down, and about the same amount of brine was used to flush each of said cells before the start-up.

Little or no foaming was observed when said cells were restarted. When other chlor-alkali diaphragm cells with foraminous cathodes are operated via the process of the present invention, similarly good results are obtained. Similarly, when other chlor-alkali diaphragm cells are operated via the process of the present invention, excellent current efficiencies are obtained.

While there have been described various embodiments of the invention, the methods and elements described are not intended to be understood as limiting the scope of the invention, as it is realized that changes therewithin are possible, and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principles may be utilized.

What is claimed is:

1. A process of intermittently operating a chlor-alkali diaphragm cell having a catholyte compartment and an anolyte compartment separated by a liquor permeable diaphragm, said catholyte compartment containing an aqueous catholyte liquor and a cathode susceptible to corrosion in an acidic solution, said anolyte compartment containing an aqueous anolyte liquor and a consumable anode, comprising the steps of:

(a) maintaining a voltage differential between the anode and the cathode of said cell, thereby operating said cell;
(b) ceasing to maintain said voltage differential between said anode and cathode, thereby shutting down said cell;
(c) immersing said cathode in caustic liquor after said cell ceases to operate;
(d) flushing said cell with brine having a pH of from about 7 to about 12 during part of the time it is shut down to produce an anolyte having a pH of about 5 or greater;
(e) causing said voltage differential to be maintained between said anode and said cathode, thereby starting up said cell; and
(f) repeating steps (a) through (e) at least 4 times a month.

2. The process of claim **1**, wherein virtually no catholyte liquor is allowed to flow out of said cell, thereby immersing said cathode in caustic liquor.

3. The process of claim **2**, wherein the brine used for flushing prior to start-up is unsaturated with sodium chloride, and wherein said brine contains about at least about 90 percent of the amount of sodium chloride it would contain if it were saturated.

4. The process of claim **3**, wherein up to about 30 minutes prior to the time said cell is started up it is flushed with brine.

5. The process of claim **4**, wherein steps (a) through (e) repeated at least 30 times a month.

6. The process of claim **5**, wherein said brine contains at least about 95 percent of the amount of sodium chloride it would contain if it were saturated.

7. The process of claim **6**, wherein said brine flushing occurs from about 5 to about 20 minutes prior to start-up.

8. The process of claim **7**, wherein the pH of the brine used for flushing prior to start-up is from about 7 to about 10.

9. The process of claim **8**, wherein said brine flushing occurs from about 10 to about 15 minutes prior to start up.

10. The process of claim **9**, wherein the pH of the brine used for flushing is from about 7 to about 8.

11. The process of claim **5**, wherein the brine is acidified to a pH of from about 2.5 to about 4.5 prior to being used.

12. The process of claim **11**, wherein said brine is acidified with hydrochloric acid.

13. The process of claim **12**, wherein the brine is acidified to a pH of from about 3 to about 4.

14. The process of claim **5**, wherein brine flushing occurs prior to both the shut-down and start-up of said cell.

15. The process of claim **14**, wherein up to about 30 minutes prior to said shut-down and up to about 30 minutes prior to said start-up, said cell is flushed with brine whose pH is from about 7 to about 12.

16. The process of claim **15**, wherein:

(a) said brine contains at least about 95 percent of the amount of sodium chloride it would contain if it were saturated;
(b) from about 10 to about 15 minutes prior to said shut-down and from about 10 to about 15 minutes prior to said start-up, said cell is flushed with brine, the pH of the brine used for flushing prior to shut-down being about 10, the pH of the brine used for flushing prior to start-up being from about 7 to about 8.

17. The process of claim **16**, wherein the brine used for flushing prior to start-up is acidified to a pH of from about 3 to a bout 4 by the addition of hydrochloric acid thereto before it is used.

18. The process of claim **5**, wherein the said cell has a foraminous cathode with an asbestos diaphragm deposited thereon.

19. The process of claim **18**, wherein the pH of the brine used for flushing is from about 7 to about 12, said brine contains at least about 90 percent of the amount of sodium chloride it would contain if it were saturated, and the brine flushing occurs from about 5 to about 20 minutes prior to start up.

20. The process of claim **19**, wherein the pH of the brine used for flushing is about 7–8 said brine contains at least about 96 percent of the amount of sodium chloride it would contain if it were saturated, and the brine flushing occurs from about 10 to about 15 minutes prior to start-up.

21. The process of claim **21**, wherein from about 10 to about 15 minutes prior to the shut-down of the cell it is flushed with brine with a pH of about 10 which brine contains at least about 95 percent of the amount of sodium chloride it would contain if it were saturated.

22. The process of claim **20**, wherein the brine used for flushing prior to shut-down is acidified with hydrochloric acid to a pH of from about 2.5 to about 4.5 before it is used.

23. The process of claim **21**, wherein the brine used for flushing prior to shut-down is acidified with hydrochloric acid to a pH of from 3 to 4.

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