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PROCESS FOR COORDINATED OPERATION OF DIAPHRAGM AND MERCURY CATHODE ELECROLYTIC CELLS

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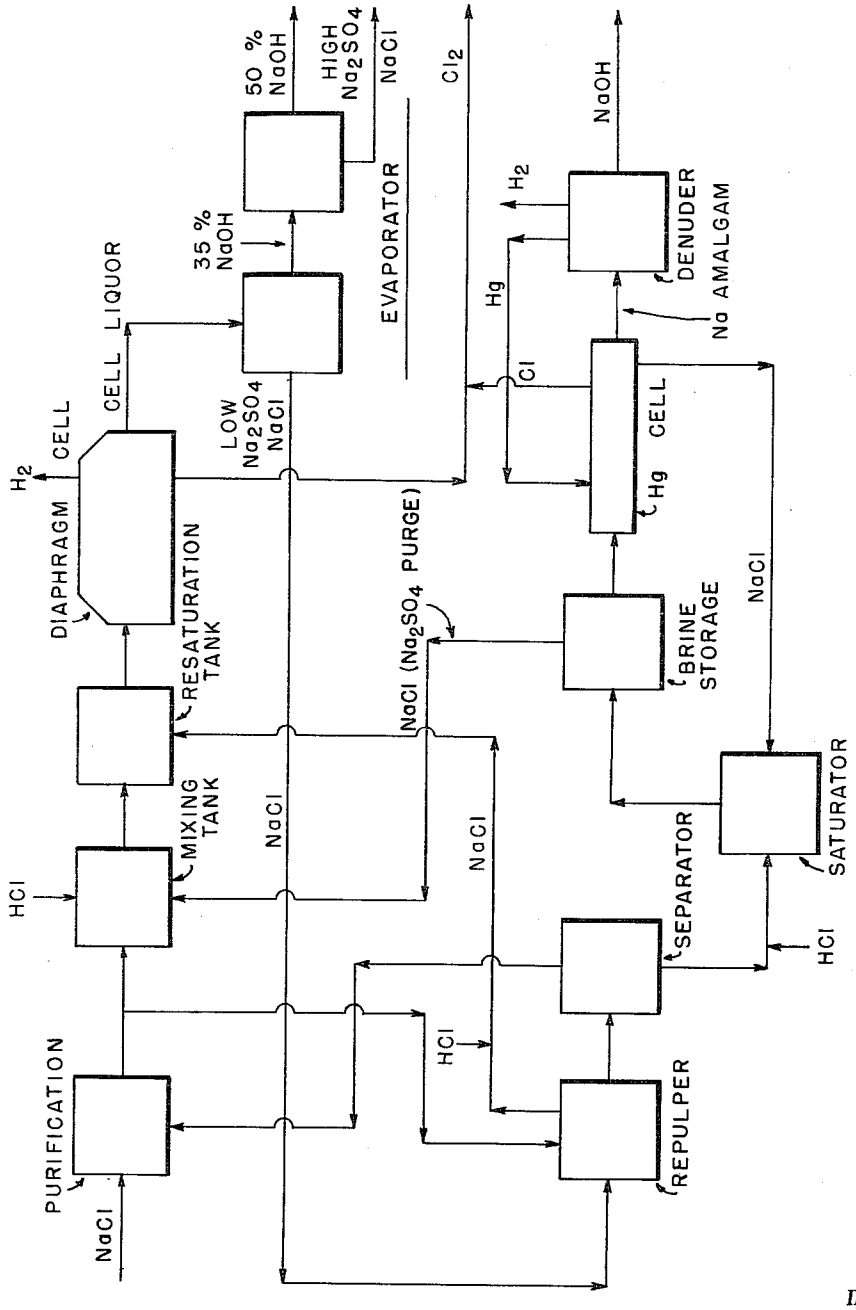

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PROCESS FOR COORDINATED OPERATION OF DIAPHRAGM AND MERCURY CATHODE ELECTROLYTIC CELLS

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This invention relates to a method for supplying alkali metal halide brines for use in industrial processes and, more particularly, relates to a method of supplying alkali metal halide brines for use in electrolytic cells for the production of chlorine and alkalies, and still more particularly, relates to a method for supplying alkali metal halide brines to such electrolytic cell systems which consists of both diaphragm cells and mercury cells.

Chlorine, for the most part, is produced commercially by the electrolysis of an alkali metal chloride brine, such as a sodium chloride brine, with the corresponding alkali metal hydroxide also being produced as a product of the electrolysis. In general, two different types of electrolytic cells are used to effect this electrolysis, i.e., diaphragm cells and mercury cells. Although in both types of cells, sodium chloride brine is electrolyzed using a carbon or graphite anode and chlorine and sodium hydroxide are recovered as the ultimate products, it is at this point that the similarity of the two types of cells ceases.

In the diaphragm cell, the cathode is generally of metal, such as iron, and is separated from the anode by a permeable diaphragm, generally of asbestos. Additionally, in the diaphragm cell, the sodium hydroxide is recovered at the cathode in admixture with sodium chloride and sodium sulfate, which mixture is referred to generally as the "cell liquor." This catholyte or "cell liquor" normally contains about 11% sodium hydroxide and 14 to 15% sodium chloride, which sodium chloride must be separated from the sodium hydroxide. This separation is effected by the evaporation of the "cell liquor" to a concentration of about 50% sodium hydroxide, at which strength the sodium chloride content ranges from about 0.8 to 2.0% depending upon the temperature of the sodium hydroxide solution. The above percentages as well as those noted elsewhere herein are percentages by weight, as is customary in the electrolytic chlorine-alkali industry with reference to percentages of components of solutions containing caustic soda.

In contrast, in the mercury cell, there is no diaphragm and the cathode is a moving film of mercury which passes through the cell. Additionally, the sodium produced by the electrolysis of the brine forms an amalgam with the mercury, from which amalgam sodium hydroxide is recovered in concentrations ranging up to 70% without the necessity for evaporation. In addition to these differences in the component parts of the diaphragm and mercury cells, as well as the difference in the form in which the product sodium hydroxide is initially recovered, these types of electrolytic cells also differ as to the purity of the alkali metal halide brine feed required by each.

In the diaphragm cell, substantially complete removal of the calcium and magnesium impurities in the brine feed is essential in order to prevent blockage of the diaphragms. Additionally, for efficient operation of the cell, it is desirable to maintain the sulfate content of the brine below about 5.0 g./l. Moreover, in diaphragm cell operation, it is necessary to provide a means for purging the sulfates from the system. On the other hand, for mercury cells, calcium impurities in the brine feed are not considered to be critical but magnesium impurities are especially bad so that substantially complete removal of these latter impurities is necessary. Additionally, substantially complete removal of the heavy metals, such as iron, nickel, vanadium, chromium and molybdenum, as well as aluminum, is essential inasmuch as these metals cause a break-down of the amalgam, thereby tending to cause a hydrogen discharge which leads to a dangerous concentration of hydrogen in the chlorine. As with the diaphragm cells, a sulfate content of only about 10 g./l. can be tolerated so that purging of the sulfate is likewise necessary. Moreover, in the operation of a mercury cell, where the brine is to be treated to remove impurities, it is necessary to dechlorinate the brine which has passed through the cell before treatment, resaturation and recycling of the brine to the cell.

Generally speaking, the installation costs of a mercury cell are slightly greater than those for a diaphragm cell. However, the mercury cell has an advantage in that the sodium hydroxide produced has a very low impurity content and is, thus, suitable for use in making rayon without further purification. In contrast, the sodium hydroxide from a diaphragm cell, being produced in admixture with at least about equal portions of sodium chloride, is recovered from the evaporator with as high as 1% sodium chloride contained therein. To be suitable for many uses, such as for making rayon, this sodium hydroxide must be further purified, which purification increases the cost of the diaphragm cell sodium hydroxide to at least that of the mercury cell.

Inasmuch as all consumers do not require sodium hydroxide of mercury cell quality nor are they willing to pay a premium price for such a product, it is apparent that there are definite advantages to be obtained from an operation combining both mercury cells and diaphragm cells. These advantages stem chiefly from the fact that by such an operation it is possible to supply sodium hydroxide of either mercury cell quality or diaphragm cell quality, depending upon which is desired, without the additional expanse incurred in purifying diaphragm cell sodium hydroxide to obtain caustic of useable quality.

In the coordinated operation of both diaphragm cells and mercury cells, the solid salt recovered from the diaphragm cells, by the evaporation of the "cell liquor" or catholyte, is used to saturate the circulating brine of the mercury cells, which brine is depleted in sodium chloride concentration in each pass through the mercury cell. In this manner, the salt recovered from the diaphragm cell can be utilized and there is a ready supply of solid salt for use in the mercury cells. However, as advantageous as such an operation might at first appear, difficulties therein have been encountered. Inasmuch as a high level of sulfate impurities cannot be tolerated in either the feed for the diaphragm cells or the mercury cells, in the past, it has been necessary to provide separate brine purification systems for both types of cells. Additionally, because of the detrimental effect of the chlorine which remains in the recycle brine on cell operation, dechlorination of this brine prior to treatment and recycle to the mercury cell has also been essential. It will be appreciated that the operation of separate purification facilities for both the diaphragm cell and mercury cell brine feed is expensive and tends to eliminate any cost advantage obtained by utilizing the solid salt recovered from the diaphragm cell to resaturate the mercury cell brine.

It is, therefore, an object of the present invention to provide an integrated brine supply and purification system for use in an installation utilizing both mercury cells and diaphragm cells, whereby the need of a separate purification system for the mercury cell brine supply is eliminated.

Another object of the present invention is to provide an integrated system as described above in which the need for dechlorination of the mercury cell brine prior to re-

saturation for recycle to the mercury cell is eliminated.

A still further object of the present invention is to provide an integrated system as described above, which system will be flexible enough to meet any change in operational demands of either the diaphragm cells or the mercury cells.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows:

The drawing, which is attached hereto and forms a part hereof, is a schematic flow diagram illustrating one embodiment of the integrated brine supply system of the present invention.

In the description of the invention and the claims which follow, the terms "alkali metal" and "halide" are intended to refer, respectively, to sodium, potassium, lithium, cesium, and rubidium and to the fluorides, chlorides, bromides and iodides. Additionally, the term "alkali metal" is also meant to include barium, which in this environment, has the properties of an alkali metal. However, because of its low cost and ready availability, sodium chloride is the preferred alkali metal halide and for this reason, primary reference will be made hereinafter to sodium chloride brines.

In the process for the coordinated operation of diaphragm and mercury cells wherein solid salt recovered from the evaporation of the diaphragm cell catholyte or "cell liquor" is used to resaturate the depleted brine in the mercury cells, the improved method of the present invention envisions evaporating the diaphragm cell catholyte or "cell liquor" to an alkali metal hydroxide concentration not substantially in excess of 35%, further evaporating the liquor to an alkali metal hydroxide concentration of about 50%, recovering precipitated solid alkali metal halide from each evaporation, utilizing only the recovered alkali metal halide from the first evaporation to resaturate the depleted brine in the mercury cell and purging a portion of the thus resaturated mercury cell brine feed to the diaphragm cell brine feed, the amount of said purged portion being sufficient to maintain the impurities in the mercury cell brine feed at a level which can be tolerated in the mercury cell.

It has been found that the alkali metal halide precipitated in the evaporation of the diaphragm cell catholyte to a concentration not substantially in excess of 35% alkali metal hydroxide is significantly lower in sulfate impurities than that precipitated in evaporating the catholyte from about 35% to 50% alkali metal hydroxide concentration. By using this first precipitated alkali metal halide, there is obtained a substantially pure, solid alkali metal halide for resaturating the mercury cell brine feed. It has been further found that by purging a portion of the mercury cell brine feed back into the diaphragm cell brine feed, which portion is sufficient to maintain the sulfate impurities in the mercury cell at a tolerable level, other undesirable impurities in the mercury cell brine feed are likewise maintained within tolerable limits. Thus, the need for treating this brine, to remove impurities, is eliminated and hence it is not necessary to dechlorinate the brine.

More specifically, in the present method, a brine containing about 295 g./l. NaCl is purified, particularly with respect to calcium and magnesium impurities. This purification can desirably be effected by adding to the brine solutions of caustic soda and soda ash and/or sodium bicarbonate, whereby the undesirable calcium and magnesium ions are precipitated as the insoluble carbonates and hydroxides, respectively. The thus-treated brine is then settled and filtered to remove the precipitated impurities and the sodium chloride concentration of the brine is increased to between about 318 to 325 g./l. by adding solid salt thereto. The pH of the brine is adjusted so as to be not substantially in excess of 10.2 by the addition of hydrochloric acid. The brine is then passed into the diaphragm cell wherein it is electrolyzed to produce chlorine gas, which is given off at the anode, and the cell liquor containing about 11% sodium hydroxide and 14% to 15% sodium chloride, which cell liquor is removed at the diaphragm cell cathode.

As the cell liquor is recovered from the cathode compartment of the diaphragm cell, it is introduced into a multi-stage evaporator, wherein it is evaporated to a sodium hydroxide concentration not substantially in excess of about 35%. At this sodium hydroxide concentration, solid sodium chloride precipitates from the solution and is removed in any convenient manner. The liquor is then further evaporated to a sodium hydroxide concentration of about 50%, during which evaporation additional solid sodium chloride is precipitated and removed. This latter sodium chloride, from the 50% sodium hydroxide concentration, is either discarded or recycled into the diaphragm cell brine feed stream to be used in the saturation of the raw brine from the brine wells. As this solid salt contains a high percentage of sodium sulfate, and additionally, has a relatively high sodium chloride to sodium sulfate weight ratio, i.e., about 4 to 5 parts by weight sodium chloride to 1 sodium sulfate, it is preferably discarded rather than reusing it in the diaphragm process, inasmuch as this can be done without loss of substantial quantities of sodium chloride. Alternatively, where salt costs are high, it can be further concentrated and treated so as to remove substantially all of the sulfate and then reused.

The solid salt from the first evaporation of the diaphragm cell catholyte is slurried with brine and a portion of this slurry is separated and returned to the brine feed system of the diaphragm cells, wherein it is used to resaturate the brine to increase its sodium chloride concentration from 295 g./l. to the desired 318 to 325 g./l. The remaining portion of the reslurried solid sodium chloride is passed into a separation apparatus, wherein the solid and liquid portions of the slurry are separated and the liquid portion returned to the diaphragm cell brine steam.

The solid portion of the slurry from the separator is added to the recycled brine stream from the mercury cell, the sodium chloride concentration of which brine stream, in passing through the mercury cell, has been depleted to about 280 g./l. from the desired 305 to 310 g./l. required for mercury cell operation. Sufficient of the solid salt recovered from the separator is added to the recycled brine stream until the desired concentration of about 305 to 310 g./l. is achieved and the pH of the brine is then adjusted to about 4.5 to about 5.5 by the addition of hydrochloric acid. After resaturation and prior to being returned to the mercury cell, a portion of the brine stream is purged back to the diaphragm cell brine system wherein it is added to the brine feed stream. The amount of this purge is sufficient to maintain the sulfate impurities in the mercury cell brine system at not substantially in excess of 10.0 g./l.

The remainder of the brine, at a sodium chloride concentration of 305 to 310 g./l., is passed into the mercury cell wherein it is electrolyzed to produce chlorine at the anode and a sodium amalgam at the mercury cathode, from which sodium hydroxide is recovered. In passing through the mercury cell, the sodium chloride concentration of the brine is depleted to about 280 g./l. so that the brine is recycled to the saturators wherein the sodium chloride concentration is increased by the addition of solid salt obtained from the evaporation of the cell liquor from the diaphragm cell, before being returned to the mercury cell.

It will be noted that in the method as described above, only one brine purification is required in order to obtain a brine feed of suitable purity for both the diaphragm and mercury cells. Moreover, by purging a portion of the mercury cell brine feed back into the brine feed for the diaphragm cell, the sulfate and other impurities in the mercury cell feed are prevented from building up to an intolerable level, thus eliminating the necessity for a

separate purification system for the mercury cell brine and hence the need for dechlorination of this brine.

Referring now to the drawing, as shown in the schematic flow diagram, raw sodium chloride brine from any convenient source, such as a brine well or reservoir (not shown) is passed through purification apparatus wherein the raw brine is purified, particularly with respect to calcium and magnesium impurities. Inasmuch as the precise mechanism of purification does not form a part of the present invention, no details of the purification step have been shown on the drawing. Suffice it to say that the calcium and magnesium impurities may conveniently be removed from the raw brine by adding thereto solutions containing sodium hydroxide and sodium carbonate, which materials cause the precipitation of these impurities so that they may be removed from the brine by settling and filtration. After the impurities have been removed from the raw brine, it passes into a mixing tank wherein hydrochloric acid is added to adjust the brine pH so as to not be substantially in excess of about 10.2. The brine is then saturated with solid sodium chloride to bring the sodium chloride concentration to within the range of 318 to 325 g./l., which sodium chloride concentration, is desired for the operation of the diaphragm cell. As will be explained in more detail hereinafter, the solid sodium chloride with which the purified brine is saturated may conveniently be a portion of that recovered from the diaphragm cell liquor.

The purified, saturated brine, having a sodium chloride concentration between 318 and 328 g./l., passes into a diaphragm cell wherein it is electrolyzed, chlorine gas being recovered at the anode and the cell liquor containing sodium hydroxide and sodium chloride being recovered at the cathode. This cell liquor is passed into a multi-stage evaporator wherein it is first evaporated to a sodium hydroxide concentration of about 35%, during which evaporation solid sodium chloride is precipitated from the cell liquor. The liquor having a concentration of about 35% sodium hydroxide is then further evaporated to a sodium hydroxide concentration of about 50%, during which evaporation additional solid sodium chloride is precipitated. This latter precipitation of sodium chloride, being high in sulfate impurities, is preferably discarded as waste material.

The solid sodium chloride precipitated in evaporating the cell liquor to a sodium hydroxide concentration of about 35%, passes to a repulping tank wherein brine is added so as to form a solid slurry of the sodium chloride. After adjusting the pH of this slurry to not substantially in excess of about 10.2, by the addition of hydrochloric acid, a portion of the slurry is returned to the diaphragm cell brine stream to be used in saturating the purified diaphragm cell brine to obtain the desired sodium chloride concentration of about 318 to 325 g./l. From the repulping tank, the remainder of the sodium chloride slurry passes into a separator wherein the liquid and solid portion of the slurry are separated. The liquid portion, which has a sodium chloride concentration of about 318 g./l., is returned to the purification portion of the diaphragm cell system to be used in making up the diaphragm cell feed stream.

The solid sodium chloride from the separator is then acidified with the hydrochloric acid to a pH within the rane of about 4.5 to 5.5 and passed into a saturator wherein it is contacted with the depleted brine recycled from the mercury cell. This depleted brine, which has a sodium chloride concentration of about 280 g./l., is saturated with the solid sodium chloride until a brine is obtained having a sodium chloride concentration of about 305 to 310 g./l., which sodium chloride concentration is desired in the operation of the mercury cell. This brine at the desired sodium chloride concentration, is then passed into the mercury cell, wherein it is electrolyzed to form chlorine gas, which is given off at the cell anode and sodium which combines with the flowing mercury film cathode to form a sodium amalgam. The sodium amalgam is directed into a denuder wherein the mercury is recovered and recycled to the cell and sodium hydroxide is formed and recovered as the second product of the electrolysis. As has been pointed out above, the brine in passing through the mercury cell, is depleted to a point at which the sodium chloride concentration is only about 280 g./l. Inasmuch as this sodium chloride concentration is insufficient for the operation of the mercury cell, after passing through the cell, the brine is recycled to the saturator so that the sodium chloride concentration can be increased to the desired level before the brine is returned to the mercury cell for electrolysis.

It will be appreciated that, in essence, the mercury cell brine system is a closed system, i.e., the brine passes through the cell and the sodium chloride concentration thereof is depleted, whereupon the brine is resaturated and then returned to the cell. In such a system, obviously, there will be a gradual build-up of impurities in the brine, such as sulfate, magnesium, and heavy metal impurities. To prevent these impurities from building up to an intolerable level, a stream of the resaturated brine is continuously removed and returned to the brine mixing tank in the diaphragm cell system. The impurities in this purged stream of brine are not sufficient to raise the impurity level in the diaphragm cell feed stream above that which can be tolerated.

It will, thus, be appreciated that the amount of brine which is purged from the mercury cell brine stream will depend upon the impurities which can be tolerated in both the mercury cell and diaphragm cell brine feeds. Therefore, the purged stream must be sufficiently large to maintain the mercury cell brine impurities at a tolerable level, but it must not be so large as to increase the impurities in the diaphragm cell brine stream to a level which cannot be tolerated.

It has been found, that by recycling a portion of the mercury cell brine feed at such a rate that the sulfate impurities are maintained at not substantially in excess of about 10.0 g./l., the other impurities therein, which are detrimental to mercury cell operation, will likewise be maintained at a tolerable level, without increasing the sodium sulfate content in the diaphragm cell brine feed above the upper limit of about 5.0 g./l. Inasmuch as the precise amount of this purge will, obviously, depend upon the rate of brine flow to both mercury and diaphragm cells, which factors will vary considerably depending upon the demands for chlorine and sodium hydroxide, no attempt will be made to set a precise rate of flow for this purge. It is believed that those skilled in the art can readily determine in each instance what this flow rate must be in order to maintain the sulfate impurities in the mercury cell brine at not substantially in excess of about 10.0 g./l., depending upon variations of the above-mentioned factors.

In actual operation, raw sodium chloride brine from brine wells at a sodium chloride concentration of 295 g./l. is pumped at the rate of 925 gallons per minute, representing a total of 4,964 tons per day of water, 1,640 tons per day of sodium chloride, 23.6 tons per day of calcium sulfate, and 0.315 ton of magnesium sulfate. This brine is then purified by adding thereto two streams of brine. The first brine stream at a sodium chloride concentration of 219 g./l. flows at the rate of 58 gallons per minute, representing a total of 314 tons per day of water, 80 tons per day of sodium chloride and 21.1 tons per day of sodium carbonate. The second brine stream, which is a mixture from the mercury cell repulping tank and the overflow from the separator, at a sodium chloride concentration of 315 g./l. is pumped at 195 gallons per minute, representing a total of 1,013.4 tons per day of water, 408 tons per day sodium chloride, 13.40 tons per day sodium sulfate, 1.808 tons per day sodium hydroxide and 1.534 tons per day sodium carbonate. After thor-

oughly admixing these two brine streams with the raw brine from the salt wells, the combined brine stream is reacted, settled and filtered to remove a total of 17.4 tons per day calcium carbonate and 0.15 ton per day magnesium hydroxide.

From the filter the brine stream passes to a mixing tank at the rate of 1,178 gallons per minute. The sodium chloride concentration in this brine stream is 301 g./l. This brine stream represents a total of 6,291.4 tons per day of water, 2,128 tons per day of sodium chloride, 1.599 tons per day of sodium hydroxide, 4.244 tons per day sodium carbonate, and 38.41 tons per day sodium sulfate. In the mixing tank, to the above is added the purged brine stream from the mercury cell brine feed system, which purged stream is pumped at a rate of 124.5 gallons per minute, representing a total of 655.6 tons per day of water, 231 tons per day sodium chloride, and 7.40 tons per day of sodium sulfate.

From the mixing tank, two brine streams are taken off, the first going to the resaturation tank for the diaphragm cell feed system and the second going to the mercury cell repulping tank. The first stream, to the resaturation tank, at a sodium chloride concentration of 301 g./l., flows at the rate of 1.068 gallons per minute, representing a total of 5,687 tons per day of water, 1,932 tons per day sodium chloride, 37.51 tons per day sodium sulfate, 3.474 tons per day sodium carbonate and 0.33 ton per day sodium hydroxide. The second stream to the mercury cell solid salt repulping tank, at a sodium chloride concentration of 301 g./l., flows at the rate of 235 gallons per minute, representing a total of 1,260 tons per day of water, 427 tons per day sodium chloride, 8.30 tons per day sodium sulfate, 0.77 ton per day sodium carbonate and 0.07 ton per day sodium hydroxide.

Within the diaphragm cell resaturation tank, the brine stream from the mixing tank is combined with a salt slurry from the mercury cell repulping tank, which stream is pumped at the rate of 49 gallons per minue, representing a total of 206 tons per day of water, 193 tons per day sodium chloride, 3.75 tons per day sodium sulfate, 0.40 ton per day sodium carbonate and 0.04 ton per day sodium hydroxide. From the resaturation tank the brine is pumped into the diaphragm cells at a concentration of 318 g./l. sodium chloride at the rate of 1,117 gallons per minute, representing a total of 5,893 tons per day water, 2,125 tons per day sodium chloride, 41.26 tons per day sodium sulfate, 3.874 tons per day sodium carbonate and 0.37 ton per day sodium hydroxide.

From the diaphragm cell, the cell liquor or catholyte, at a sodium hydroxide concentration of about 135 g./l. and a sodium chloride concentration of about 210 g./l., is recovered and sent to the evaporator. Within the evaporator, the catholyte is evaporated to a sodium hydroxide concentration of about 35%, during which evaporation, a low sodium sulfate content sodium chloride is recovered. The liquor is then evaporated to a sodium hydroxide concentration of about 50%, during which evaporation a high sodium sulfate content sodium chloride is recovered. About 90% to 95% of the salt is recovered in the first evaporation and about 5% to 10% is recovered in the second. The high sulfate salt from the second evaporation may be discarded or further processed to remove the sulfate and recover the salt, while the low sulfate salt from the first evaporation is directed to the mercury cell repulping tank.

From the diaphragm cell caustic evaporator to the mercury cell repulping tank is pumped 45 tons per day of water, 811 tons per day of sodium chloride, 16.25 tons per day of sodium sulfate, 1.68 tons per day of sodium carbonate and 3.258 tons per day of sodium hydroxide. To this substantially solid sodium chloride is added to the brine stream from the diaphragm cell mix tank as described above. Additionally, to the repulping tank are added 25.3 gallons per minute of water, representing 151.6 tons per day of water and the overflow at the rate of 131 gallons per minute, having a sodium chloride concentration of 318 g./l., representing a total of 694.3 tons per day of water, 249.5 tons per day sodium chloride, 10.12 tons per day sodium sulfate, 1.23 tons per day sodium carbonate and 1.38 tons per day sodium hydroxide.

From the repulping tank three streams are taken, one of which goes to the diaphragm cell brine purification, the second of which goes to the diaphragm cell brine saturation tank, both as described above, and the third going to the separator at the rate of 220 gallons per minute, representing a total of 931.5 tons per day of water, 886.5 tons per day of sodium chloride, 17.52 tons per day sodium sulfate, 1.75 tons per day sodium carbonate and 2.38 tons per day of sodium hydroxide. In addition to this latter stream, 71.4 gallons per minute of water, representing 444.6 tons per day of water, are also added to the separator.

The overflow from the separator is sent to the diaphragm cell purification tank while the underflow stream at the rate of 162 gallons per mintue, representing a total of 684.6 tons per day of water, 637 tons per day of sodium chloride, and 7.40 tons per day sodium sulfate goes to the mercury cell saturators. Within the mercury cell saturators this stream is admixed with the depleted brine from the mercury cell, which brine has a sodium chloride concentration of 280 g./l. and is pumped into the saturators at the rate of 1,570 gallons per minute, representing a total of 8,451 tons per day of water and 2,640 tons per day of sodium chloride. From the saturators, a brine stream having a sodium chloride concentration of 318 g./l. is pumped at the rate of 1,714 gallons per minute, representing a total of 9,135.6 tons per day of water and 3,277 tons per day of sodium chloride. To this stream is added depleted brine from the mercury cell at a sodium chloride concentration of 280 g./l. and a flow rate of 280 gallons per minute, representing a total of 1,520 tons per day of water and 478 tons per day of sodium chloride. The combination of these two brine streams gives a brine having a sodium chloride concentration of 310 g./l., which brine stream is pumped to the unfiltered mercury cell brine storage at the rate of 1,994 gallons per minute, representing a total of 10,655.6 tons per day of water and 3,755 tons per day of sodium chloride.

This brine is then filtered and pumped to the mercury cell filtered brine storage from where it is delivered to the mercury cell at a sodium chloride concentration of 310 g./l., at the rate of 1,870 gallons per minute, representing a total of 10,000 tons per day of water and 3,524 tons per day of sodium chloride. Aditionally, a portion of this filtered brine is purged back into the diaphragm cell system, as described above, at the rate of 124.5 gallons per minute, representing a total of 655.6 tons per day water, 231 tons per day sodium chloride and 7.40 tons per day sodium sulfate.

In operating the brine supply and purification system on both the mercury and diaphragm cells, as described above, it is found that the impurities in the mercury cell brine feed no not build up to such a level that the operation of the mercury cell is impaired, even though there is no provision made for a separate purification of the mercury cell brine. Additionally, it is found that inasmuch as no purification treatment of the mercury cell brine feed is required no provisions need be made for dechlorinating the mercury cell brine. It is, thus, seen by the method of the present invention, that a brine supply and purification system for use in the coordinated operation of diaphragm and mercury cells is provided, which system, by eliminating the need for a separate purification of the mercury cell brine and thus the need for dechlorination thereof, is considerably less expensive to operate than those processes used in the prior art.

While there have been described various embodiments of the invention, the methods 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 principle may be utilized.

What is claimed is:

1. In the process for the coordinated operation of diaphragm and mercury cathode electrolytic cells for the electrolysis of alkali metal halide brines, wherein solid salt recovered from the evaporation of the diaphragm cell catholyte is used to resaturate the depleted brine from the mercury cathode cells, the improvement which comprises evaporating the diaphragm cell catholyte to an alkali metal hydroxide concentration of about 35%, recovering the precipitated solid alkali metal halide resulting from such evaporation, adding the thus-recovered solid alkali metal halide to the depleted brine from the mercury cell so as to resaturate said brine to the alkali metal halide concentration required for mercury cathode cell operation and sending a portion of the resaturated mercury cathode cell brine back to the diaphragm cell brine feed, the amount of said portion being sufficient to maintain the impurities in the mercury cathode cell brine feed at a level below that which is detrimental to the operation of the mercury cell.

2. The method as claimed in claim 1 wherein the alkali metal halide is an alkali metal chloride.

3. The method as claimed in claim 2 wherein the alkali metal chloride is sodium chloride.

4. In the process for the coordinated operation of diaphragm and mercury cathode electrolytic cells for the electrolysis of alkali metal halide brines, wherein solid alkali metal halides recovered from the evaporation of the diaphragm cell catholyte is used to resaturate the depleted brine from the mercury cathode cells, the improvement which comprises evaporating the diaphragm cell catholyte to an alkali metal hydroxide concentration of about 35%, further evaporating the resulting liquor to an alkali metal hydroxide concentration of about 50%, recovering the precipitated solid alkali metal halide resulting from each evaporation, adding only the solid alkali metal halide recovered from the first evaporation of the catholyte to the depleted brine from the mercury cell, said quantity of solid alkali metal halide added being sufficient to raise the sodium chloride concentration of the depleted brine to the level required for mercury cathode cell operation, and sending a portion of the thus-resaturated mercury cathode cell brine back to the diaphragm cell brine feed system, the amount of said portion being sufficient to maintain the sulfate impurities in the mercury cathode cell brine feed below about 10 g./l.

5. The method as claimed in claim 4 wherein the alkali metal halide is an alkali metal chloride.

6. The method as claimed in claim 5 wherein the alkali metal chloride is sodium chloride.

7. In the process for the coordinated operation of diaphragm and mercury cathode electrolytic cells for the electrolysis of alkali metal chloride brine wherein solid alkali metal chloride recovered from the evaporation of the diaphragm cell catholyte is used to resaturate the depleted brine from the mercury cathode cells, an improvement which comprises evaporating the diaphragm cell catholyte to an alkali metal hydroxide concentration of about 35%, further evaporating the resulting liquor to an alkali metal hydroxide concentration of 50%, recovering the precipitated solid alkali metal chloride resulting from each evaporation, adding only the solid alkali metal chloride recovered from the first evaporation to the depleted brine from the mercury cathode cell so as to resaturate this brine to an alkali metal chloride concentration of about 305 to 310 g./l., and sending a portion of the thus-resaturated mercury cell brine back to the diaphragm cell brine feed, the amount of said purged portion being sufficient to maintain the sulfate impurities in the mercury cell brine at a level of about 10 g./l.

8. The method as claimed in claim 7 wherein the alkali metal chloride is sodium chloride.

9. A process for the coordinated operation of diaphragm and mercury cathode electrolytic cells wherein a sodium chloride brine is electrolyzed to produce initially a sodium chloride-sodium hydroxide catholyte solution, sodium amalgam, and chlorine respectively, which comprises resaturating that sodium chloride brine which is depleted in sodium chloride content in passing through said mercury cathode cell, with solid sodium chloride which is recovered in evaporating the catholyte of the diaphragm electrolytic cell, to a sodium hydroxide concentration of about 35% by weight, the amount of said solid sodium chloride added to said depleted brine being sufficient to resaturate it to the sodium chloride concentration required for operation of the mercury cathode cell, and sending a portion of the thus-re-saturated mercury cell brine back into the brine feed system for the diaphragm cell from which the solid sodium chloride is recovered, the amount of said portion being sufficient to maintain the impurities in the mercury cathode cell brine feed at a level below that which is detrimental to the operation of said mercury cell.

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