

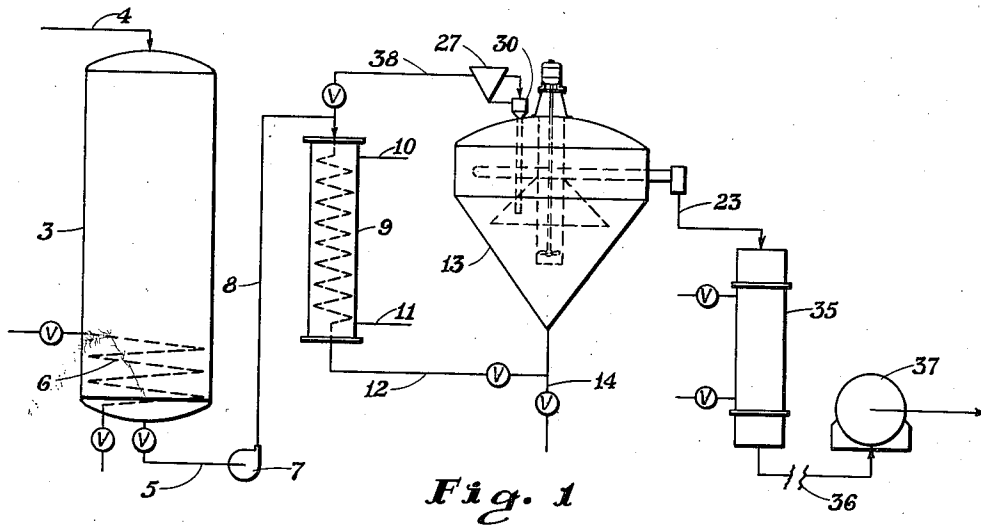
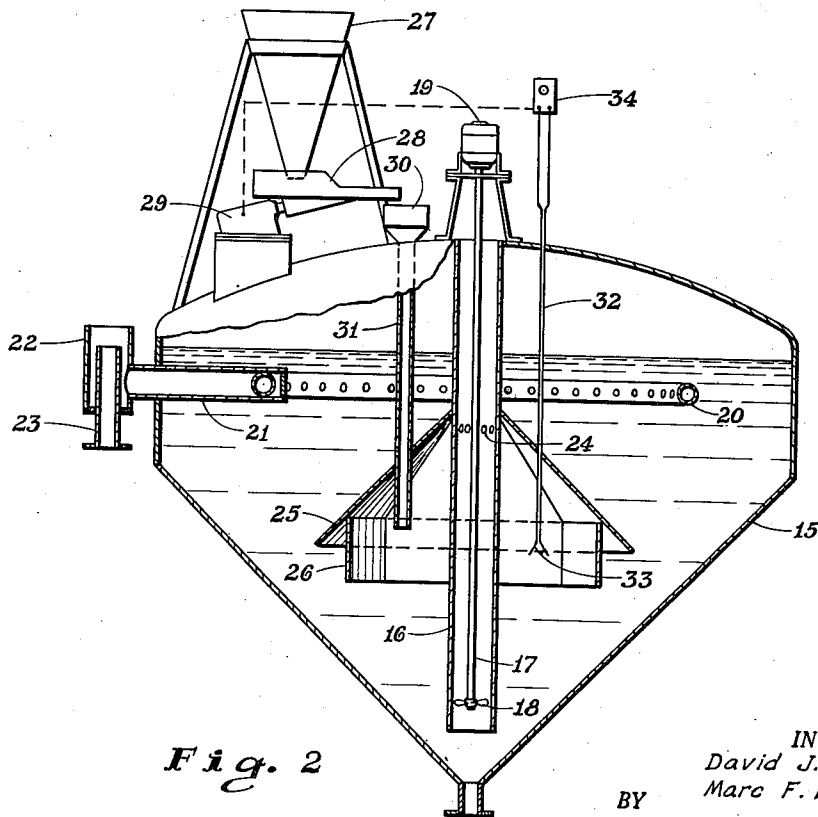
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D. J. PYE ET AL

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PURIFICATION OF CAUSTIC ALKALI

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INVENTORS
David J. Pye
Marc F. LeDuc
BY

Griswold & Burdick
ATTORNEYS

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PURIFICATION OF CAUSTIC ALKALI

David J. Pye, Pittsburg, and Marc F. Leduc,
Walnut Creek, Calif., assignors to The Dow
Chemical Company, Midland, Mich., a corpora-
tion of Michigan

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This invention relates to the purification of caustic alkali solutions, e. g. caustic soda or caustic potash, from chlorates contained therein. The invention is herein described with particular reference to the purification of caustic soda solutions, but it will be understood that it is similarly applicable to the treatment of caustic potash solutions.

In the manufacture of caustic soda by electrolysis of a sodium chloride solution, the common practice in working up the caustic cell liquors is first to concentrate them by evaporation to the point where the sodium chloride is substantially crystallized out, and after separation of the salt crystals to evaporate further the strong liquor or liquid caustic, which normally has a concentration of about 50 per cent NaOH, to produce solid caustic soda. Caustic cell liquors contain as an impurity small but significant amounts of chlorate, which for various reasons it is desirable to remove as far as possible. The presence of even a very small amount of chlorate in the liquor causes corrosion of the exposed nickel surfaces of the evaporators used in concentrating strong caustic liquors. The chlorate content of liquid caustic (50 per cent NaOH) varies somewhat, depending upon the type of electrolytic cell employed in its manufacture and other factors, but in general is on the order of about 500 to 2500 parts per million.

Various methods have been proposed for removing chlorate from caustic soda liquors, none of which in practice have proved wholly satisfactory, either for the reason that the chlorate is incompletely removed, or because other impurities are introduced as a result of the treatment. It has been proposed, for example, to reduce chlorates in electrolytic caustic soda liquors by treatment with ferrous hydroxide. One disadvantage of this method is that the ferrous hydroxide, being unstable if exposed to air and hence not available as an article of commerce, is formed by precipitation from a ferrous salt solution at the time of use, most conveniently by adding ferrous salt solution to the liquor to precipitate ferrous hydroxide in situ, thereby introducing an impurity corresponding to the anion, e. g. chloride or sulphate, of the ferrous salt. Furthermore the method requires a high molecular ratio of ferrous hydroxide to chlorate.

Attempts have been made to reduce chlorate in caustic soda liquors by treating with finely divided metallic iron. Under suitable conditions this method is capable of quantitatively reducing the chlorate, but, as heretofore employed, at the ex-

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pense of materially increasing the dissolved iron content of the liquor, thereby introducing or increasing another undesirable impurity.

It is an object of our invention to provide a process for purifying caustic alkali solutions from chlorate which successfully removes the chlorate without introducing other impurities. A particular object is to purify electrolytic caustic soda solutions from chlorate by means of finely divided iron without substantially increasing the iron content of the solution. Another object is to provide a process adapted for continuous operation, together with suitable controls for the same. Other objects and advantages will appear from the following description and annexed drawing.

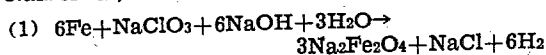
In the drawing, Fig. 1 is a flow sheet of the materials in the process; Fig. 2 shows in enlarged scale a form of treating tank for effecting the reduction of chlorate in caustic alkali liquors according to the invention.

We have discovered that, when powdered iron is used to reduce chlorates in hot caustic liquors, the dissolved iron in the solution is substantially in the trivalent (ferric) state at the end-point of the chlorate reduction. After the end-point is passed an excess of the iron powder reduces the dissolved trivalent iron compounds to the divalent (ferrous) state. As long as the ferrous compound is formed in the presence of existing ferric compound the two interact to form ferroso-ferric oxide (Fe_3O_4), which at first remains dissolved in a hydrated form, imparting a green color to the hot liquor, the appearance of which is an indication of the end-point of chlorate reduction. At the point of equivalence of the ferric and ferrous iron in the hot liquor, following the completion of the chlorate reduction, the dissolved iron is substantially in the form of the hydrated ferroso-ferric oxide, which separates after a time, particularly when the liquor is cooled to about normal temperature, as a black amorphous precipitate.

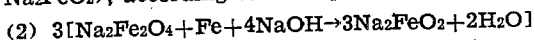
If the reaction between the caustic alkali and iron powder were stopped at such point of equivalence, the dissolved iron would be largely or almost wholly precipitated as the amorphous black oxide on cooling the liquor, which after filtration would be nearly if not completely free from iron. However, if the reaction between the caustic alkali and iron powder is allowed to continue, it proceeds with the formation of soluble ferrous compound, which does not precipitate, and the iron content of the liquor is progressively increased. The rationale of our invention, con-

sequently, is to remove the chlorate impurity from caustic liquors by treating the hot liquor with sufficient iron powder to cause complete and rapid reduction of the chlorate and then quickly separating the excess of iron powder from the hot liquor before continued solution of iron can occur. Thereafter, upon cooling the liquor, its dissolved iron content is largely or completely precipitated, either as black amorphous ferroso-ferric oxide or as alkali ferrite crystals, which are practically insoluble in the cold liquor. The reaction rate of powdered iron and chlorate in the hot caustic liquor is a function of the iron surface exposed to the chemical action, hence a substantial excess of the powder is required. Within limits, the larger the excess the more rapid is the reduction of the chlorate.

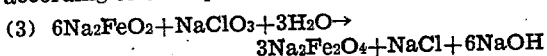
According to our observations the reduction of chlorate in caustic soda liquors by means of finely divided iron involves a number of reactions proceeding simultaneously. It is probable that the initial reaction is the direct reduction of chlorate by iron, accompanied by liberation of hydrogen and formation of sodium ferrite ($\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3$, or $\text{Na}_2\text{Fe}_2\text{O}_4$), according to the equation:



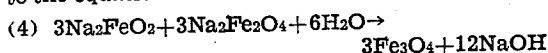
This reaction, however, occurs only to a limited extent, mainly at the beginning of the treatment. The hydrogen evolved corresponds to only a fraction of the total chlorate to be reduced. Sodium ferrite, in the presence of finely divided iron, is reduced to sodium ferrous ferrite ($\text{Na}_2\text{O} \cdot \text{FeO}$, or Na_2FeO_2), according to the equation:



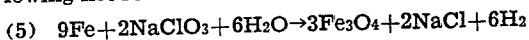
Sodium ferrous ferrite in turn reduces chlorate according to the equation:



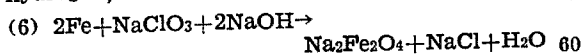
being thereby reoxidized to sodium ferrite. Sodium ferrous ferrite and sodium ferrite also react together to form ferroso-ferric oxide, according to the equation:



A summation of Equations 1 to 4 gives the following net result:



In addition to the foregoing series of reactions, wherein hydrogen is one of the products, finely divided iron also reduces chlorate directly in the presence of caustic soda without generation of hydrogen, according to the equation:



Reaction 6 is thought to proceed simultaneously with Reaction 5 when caustic soda liquors are treated with finely divided iron to reduce chlorates therein.

The theoretical equations developed above are somewhat speculative, due to the difficulty of verification where more than one reaction occurs at a time. However, our experimental results show good agreement with the theory. In Equation 5 the weight ratio of Fe/NaClO_3 is 2.36, and in Equation 6 the ratio is 1.05. We have determined in carrying out our process, wherein excess of metallic iron is quickly removed when the reduction of chlorate is complete, that the ratio of iron consumed to chlorate reduced can be

brought as low as 1.30, or lower, under preferred operating conditions. This value indicates that the proportionality between the reactions of Equations 5 and 6, respectively, under such conditions is on the order of 25:106, or approximately 1:4. In other words, about 20 per cent of the chlorate is reduced according to Equation 5, and about 80 per cent thereof according to Equation 6, when the weight ratio of iron consumed to chlorate reduced is 1.30. The foregoing theory has thus been found to agree well with our experimental results, but it will be understood that the invention is not limited by the theory.

The end products of the chlorate reduction remaining in the caustic soda liquor are sodium chloride, sodium ferrite and ferroso-ferric oxide. Ferroso-ferric oxide appears to exist initially in a soluble hydrated form which, as already mentioned, settles out after a time as an insoluble black precipitate that is readily separated by filtration. Sodium ferrite is somewhat soluble in hot caustic liquor, but is practically insoluble in the cold solution. Upon cooling a hot solution saturated with sodium ferrite the latter slowly crystallizes. It is probable that only part of such sodium ferrite is separated by crystallization under usual operation of our process, because in the absence of chlorate the sodium ferrite, while dissolved in the hot liquor, is in part reduced to the ferrous ferrite by the action of the suspended iron particles, and some of the remainder reacts with such ferrous ferrite to form ferroso-ferric oxide.

Continued contact of the liquor with the suspended iron particles, after the removal of sodium ferrite, will result in a progressive increase in the dissolved iron by reaction of the iron with the caustic soda according to the equation:



forming the soluble ferrous ferrite. It is important, therefore, to separate the iron particles from the liquor before Reaction 7 can take place to any material extent. The effectiveness of the process depends upon the speed with which this separation is carried out in the brief interval after completion of the chlorate reduction before the dissolved iron content begins to increase.

Since the amounts of chlorate is electrolytic caustic soda liquors, although significant, are in most cases relatively small, on the order of about 0.25 per cent or less, the quantitative reduction of the chlorate presents some special problems in establishing suitable conditions for carrying out the reduction. In our process the most important factors are temperature and surface area of iron exposed to reaction with the dissolved chlorate. These two factors are to a considerable extent reciprocal, in that at higher temperatures smaller amounts of iron can be used proportionally to the volume of liquor treated, and conversely.

The reduction of chlorate by finely divided iron, as herein described, can be carried out at temperatures from about 60° C. up to the boiling point of the caustic soda liquor. At the lower temperatures within the stated range the rate of reaction is relatively slow, so that it is preferred to operate at temperatures of 100° C. and above. In the case of liquid caustic of about 50 per cent strength the reduction proceeds quantitatively in a matter of seconds at temperatures of around 120° C. or higher, if sufficient iron powder is present. For such solutions a

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good working temperature range is about 115° to 135° C.

The quantity of iron particles to be used can be varied greatly, as well as the fineness thereof. Since the action of the iron depends upon a surface effect, the finer the particles within practical limits, the greater is the reducing power of a given weight of the particles. A fineness of 100 to 200 mesh is satisfactory for practical purposes, although the invention is not limited thereto. The iron particles may be made from carbon steel, cast iron, sponge iron or other form of iron. Commercial products of the types stated are available. For iron particles of any particular degree of fineness, the rate of the reduction of chlorate varies with the quantity or weight of the particles suspended in the liquor being treated, permitting the reaction rate to be controlled by varying the quantity of iron used. In practice the quantity of iron particles used to treat a given volume of caustic soda liquor will be considerably greater than the chemical equivalent of the chlorate to be reduced, but the excess removed after the reduction is complete is suitable for reuse.

In carrying out the process the caustic soda liquor to be treated is preheated, if necessary, to a temperature preferably between 115° and 135° C., but short of its boiling point, depending upon the strength of the solution, and introduced into a treating tank made of or internally lined with a material resistant to the action of hot caustic liquor, such as nickel, and provided with an agitator. Powdered iron of 100 to 200 mesh is added in amount of about two to five times the chemical equivalent of chlorate and held in suspension by agitation, while maintaining the temperature of the liquor, until reduction of chlorate is complete. The end-point of the chlorate reduction is conveniently determined by electrometric means, such as are described hereinafter. Upon completion of the reduction the treated liquor is at one drawn off and filtered to remove excess metallic iron. The hot filtered liquor is cooled to between room temperature and about 35° C. and allowed to stand for a time to permit separation of solid amorphous ferrous-ferrous oxide and to crystallize out sodium ferrite. The cooled liquid is then filtered to remove the precipitated solids.

By our process chlorate can be quantitatively removed from caustic soda liquors, but its success from a practical standpoint is complete only if the dissolved iron content of the treated liquor is held below the limits of commercial specifications. Effective control of the iron content, as already shown, requires complete separation of suspended iron particles from the liquor within a very short time interval following the end-point of chlorate reduction. When the treatment is carried out as a batch process there are physical limitations upon the speed with which the separation can be made, especially when handling large volumes of the liquor. Such limitations can be largely avoided by operating in continuous manner, taking advantage of the density of metallic iron which enables the suspended particles to be settled rapidly from the liquor when the chlorate reduction is complete. The liquor to be treated is passed continuously through a preheater, in which it is heated to the desired temperature, e. g. 120° to 130° C. The preheated liquor flows into a treating tank, in which iron powder is added in desired amount. The liquor in the lower part of the treating tank is agitated by a stirrer to keep the iron particles in suspen-

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sion while reduction of chlorate in the liquor takes place. In the upper part of the tank is an arrangement of baffles designed to damp the turbulence of the liquor rising in the tank from the agitated zone into the baffled zone. In the latter zone the suspended iron particles settle out and fall back into the agitated zone. Above the baffles the clear liquor overflows into a launder, whence it is conducted to a cooler where it is held until ferrous-ferrous oxide and sodium ferrite are precipitated, and finally the cooled liquor is filtered to remove the precipitate. The feed of iron powder is adjusted to the rate of flow of the liquor, so that the liquor passes from the agitated zone, wherein the reaction takes place, into the baffled zone at a point where reduction of the chlorate is complete and dissolved iron compounds present will be substantially precipitated on cooling. Variations in operation are compensated by varying the feed rate of iron powder, since the rate of chlorate reduction can be increased or decreased by corresponding increase or decrease in the amount of iron powder suspended in the reaction zone.

The drawing illustrates a preferred embodiment of the invention, including controls for maintenance of a proper balance of operating conditions. In Fig. 1, a storage tank 3 for caustic soda liquor is provided with a feed line 4 and an outlet line 5, as well as heating means, such as steam coil 6. Line 5 is connected to pump 7 which is connected by line 8 with preheater 9 having inlet 10 and outlet 11 for heating fluid. Discharge line 12 from the bottom of preheater 9 leads to the bottom of reactor 13, line 12 having a T branch 14 for draining the reactor.

Reactor 13, shown in detail in Fig. 2, is a circular tank having a conical bottom 15 and a rounded top. Centrally disposed in the tank is a draft tube 16 within which is a vertical shaft 17 carrying propeller 18 at its lower end, shaft 17 being directly connected to a motor 19. An annular launder tube 20, having perforations in its inner wall, is disposed concentrically in the vertical-walled section of the tank, and is connected by outlet pipe 21 to a basin 22 outside of the tank, in which is an overflow pipe 23. In draft tube 16 is a row of apertures 24 below the level of launder 20. An inverted conical apron 25 is attached to draft tube 16 at a level above apertures 24 but below launder 20. Sectoring the space beneath apron 25 surrounding draft tube 16 is a plurality of vertical baffle plates 26, which are cut off straight a short distance from the edge of apron 25 and depend therebelow. Each sector communicates with the interior of draft tube 16 through one or more of apertures 24. Disposed above the tank is a hopper 27, which delivers to a feeder plate 28 having a vibrator 29 attached thereto. Plate 28 is arranged to discharge into a funnel 30, the tubular extension 31 of which passes through the cover of tank 13 and extends also through apron 25 into one of the sectors between baffles 26. An electrode protection tube 32 depends through the cover of the tank into another of the sectors below apron 25, and encloses electrode couple 33, the bare tips of which protrude below the bottom of the tube. Electrode couple 33 is connected to a controller-recorder 34, which is also electrically connected to vibrator 29 in such way that variations of the E. M. F. of the couple are effective to vary the intensity of vibration of the vibrator.

Referring again to Fig. 1, overflow pipe 23 from

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reactor 13 leads to a cooler 35, which discharges through line 36 to a filter 37. The break in line 36 indicates a storage period during which the liquor is held for a time, e. g. two to three hours or more, in a tank or the like to complete the precipitation of iron compounds. A branch line 38 connects from line 8 to funnel 30 on the reactor 13.

In the operation of the foregoing apparatus, the caustic soda liquor to be purified enters storage tank 3 through line 4, and, if desired, may be warmed therein by means of steam coil 6. From tank 3 the warm liquor is forwarded by pump 7 through lines 5 and 8 to the preheater 9, in which it is heated to the temperature at which the treatment is to be carried out, or somewhat higher, e. g. 120° to 130° C. The preheated liquor then passes through line 12 into the bottom of the cone in reactor 13, where it fills the reactor to the level of overflow pipe 23. Reactor 13, as well as other apparatus, are of course provided with suitable heat insulation (not shown) to minimize heat losses.

The hot liquor in the lower conical section of reactor 13 is actively circulated therein by means of propeller 18, causing an upflow in draft tube 16 which discharges through apertures 24 into the sector chambers below apron 25. Powdered iron in hopper 27 is fed onto the vibrating feeder plate 28, which discharges into funnel 30, and thence through tube 31 into the circulating body of liquor beneath apron 25. To prevent the sticking of iron particles to the wall of tube 31, a small flow of liquor is diverted from line 8 through by-pass 38 into funnel 30 for washing the walls of the funnel and tube. In the space below apron 25 the iron particles suspended in the circulating liquor discharged into the sector chambers, as well as those in the fresh feed, settle toward the bottom where they are swept up and again suspended in the upflowing stream in the draft tube. The rate of feed of iron powder is adjusted to the rate of flow of the caustic soda liquor so as to maintain the oxidation-reduction potential at the electrodes 33 at a value slightly beyond that which corresponds to the end-point of chlorate reduction. Variations from the control point are compensated by either increasing or reducing the feed of iron powder, which is accomplished by varying the vibration of the feeder plate to increase or decrease the rate of feed through a control actuated by controller 34 in response to variations of the E. M. F. of the electrodes above or below the control point.

The end-point of the chlorate reduction is determined electrometrically by the inflection of the oxidation-reduction potential curve of $\text{Fe}^{++} \leftrightarrow \text{Fe}^{+++}$, which is sharply indicated. As already shown, the chlorate reduction end-point corresponds to the maximum concentration of Fe^{+++} ions in the liquor, Fe^{++} ions then being substantially absent. After the end-point, as long as metallic iron particles are present, the trivalent Fe ions are progressively reduced to divalent ions. The control point is set at the predetermined E. M. F. corresponding closely to an exact balance between Fe^{+++} and Fe^{++} ions, so that upon subsequent cooling the dissolved iron will precipitate largely as insoluble ferroso-ferric oxide, as already explained.

Any suitable electrode couple may be used to indicate the control point, which may be experimentally established for the operating conditions selected. We have found a Pt—Fe couple to be satisfactory for the purpose, Pt being the negative

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electrode, and have determined the proper control point to be 130 millivolts under the conditions as described, while the end-point is 145 millivolts. Any other suitable couple may be used, as will be evident to those versed in the art of electrometric control devices.

By the procedure described flow of liquor and feed of iron powder are adjusted so that the detention period of the liquor in contact with the suspended iron particles just suffices to reduce the chlorate without overshooting the selected control point. The liquor passes from the active zone upwardly into a quiescent settling zone in the space above, in which any remaining suspended iron particles rapidly settle out by gravity. The settled liquor then overflows through launder 20 and basin 22 and is conducted via line 23 to cooler 35, wherein it is reduced in temperature in one or more stages to about 35° C. or lower. From the cooler the liquor passes to storage to complete the precipitation of sodium ferrite crystals and ferroso-ferric oxide, and thence to filter 37 where the precipitate is separated.

As an example of the operation of our process, 50 per cent caustic soda liquor, containing 768 P. P. M. of sodium chlorate, was heated to 120° C. and passed at the rate of 200 pounds per hour through an apparatus similar to the one described. Iron powder of 170 mesh was fed to the liquor at a rate such as to maintain in the active zone of the reactor at the Pt—Fe control electrodes an E. M. F. of 130 millivolts, the calculated inventory of iron particles in the active zone being 1.17 pounds per cubic foot. The average detention time of the liquor in the reactor was 12.5 minutes. Chlorate was completely reduced with an iron consumption of 1.46 pounds per pound of NaClO_3 . Upon cooling and filtering the clear liquid had a dissolved iron content of less than 25 P. P. M.

For practical operation our process is most conveniently and economically applied to the treatment of strong caustic soda liquors of about 50 per cent NaOH concentration, such as are commonly produced at a stage in the manufacture of electrolytic caustic soda by present commercial processes, but the invention is not so limited. Chlorate can be completely reduced in caustic soda solutions having a concentration above 50 per cent and up to the saturation point at the temperature of treatment, as well as in solutions of less than 50 per cent concentration, in fact, as low as 10 per cent or lower. The presence of dissolved sodium chloride in the liquor does not affect the reduction of chlorate or control of dissolved iron in the treated liquor. For example, cell liquor from electrolytic caustic soda cells, containing on the order of about 9 per cent NaOH and 16 per cent NaCl, can be successfully treated to remove chlorate by our process. In working with caustic soda solutions containing less than 50 per cent NaOH the temperature of the treatment must be adapted to the boiling point of the weaker liquor, and should be held a few degrees below the boiling point. Otherwise, the agitation caused by boiling the liquor would interfere with the settling of iron particles in the settling zone.

Similar procedure is effective for removing chlorates from caustic potash liquors.

We claim:

1. A process of purifying caustic alkali solutions from dissolved chlorate which comprises heating the solution to a temperature above 100° C. but below the boiling point thereof, adding

powdered iron to the solution in excess of the amount chemically required to reduce the chlorate therein, passing the solution successively through a zone of agitation, in which the iron particles are suspended in the solution while reaction with chlorate occurs, and thence into a settling zone in which the particles settle out by gravity, the rate of flow through said zones being regulated so that the solution enters the settling zone when reduction of chlorate is substantially complete but before the dissolved iron content of the solution materially increases.

2. A process of purifying caustic soda solutions from dissolved chlorate which comprises heating the solution to a temperature above 100° C. but below the boiling point thereof, causing the solution to flow upwardly through a zone of agitation, in which powdered iron is added to the solution, and thence into a settling zone, in which the iron particles settle out by gravity, the rate of flow being so regulated that the solution enters the settling zone when reduction of chlorate is substantially complete but before a material increase in the dissolved iron content of the solution occurs, passing the settled solution through a cooling zone to reduce the temperature thereof below 35° C. and removing insoluble iron compounds precipitated from the cooled solution.

3. A continuous process of purifying caustic soda liquors from dissolved chlorate which comprises adding powdered iron to a stream of the hot liquor at a temperature above 100° C. but below the boiling point thereof, maintaining the iron particles in suspension therein until the chlorate is reduced, passing the stream into a free settling zone wherein the remaining particles are separated by gravity from the liquor, cooling the settled liquor to a temperature below 35° C. to precipitate iron compounds insoluble in the cooled liquor and removing the precipitate.

4. A continuous process of purifying caustic soda liquors from dissolved chlorate which comprises causing a stream of the hot liquor, at a temperature above 100° C. but below the boiling point thereof, to flow upwardly through a zone in which it is agitated and thence into a settling zone, adding powdered iron to the liquor in the agitated zone at a rate such that the liquor enters the settling zone after the chlorate is completely reduced, but before the dissolved iron content thereof has materially increased, cooling the settled liquor to a temperature below 35° C. and holding it at such temperature until insoluble iron compounds have precipitated therefrom, and separating the clear purified liquor from the precipitate.

5. In a process of purifying caustic alkali liquors from chlorate by treating the hot liquor with

powdered iron and removing the excess of iron particles by gravity separation when the chlorate is reduced, the step which consists in regulating the speed of reaction between the chlorate and the iron particles by adding the latter to a stream of the hot liquor at a rate varying in response to variations of the oxidation-reduction potential of the liquor from a predetermined value representing a point at which the concentrations of Fe^{++} and Fe^{+++} ions in the hot liquor are substantially equal.

6. In a process of purifying caustic alkali liquors from chlorate, the steps which consist in passing a stream of the hot liquor successively through a zone of agitation and a settling zone, adding powdered iron to the liquor in the agitated zone and removing residual iron particles in the settling zone, regulating the rate of addition of iron powder to the liquor in accordance with the oxidation-reduction potential of the same at the point where it passes from the agitated zone into the settling zone to maintain the potential at such point at a value corresponding substantially to equivalent concentrations of Fe^{++} and Fe^{+++} ions in the liquor.

7. In a process of purifying caustic soda liquors from chlorate, the steps which consist in passing a stream of the liquor at a temperature above 100° C. but below the boiling point thereof successively through a zone of agitation and a settling zone, adding iron powder to the stream in the agitated zone in amount varying in accordance with variations of the oxidation-reduction potential of the liquor entering the settling zone from a predetermined value representing approximately equal concentrations of Fe^{++} and Fe^{+++} ions in the liquor, and removing residual iron particles by gravity separation in the settling zone.

DAVID J. PYE.
MARC F. LEDUC.

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