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Rapson

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[54] **REGENERATION OF CHLORINE DIOXIDE FOR PULP TREATMENT**

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[52] **U.S. Cl.** **162/30,** 162/89, 423/477

[51] **Int. Cl.** **D21c 11/00,** D21c 11/12

[58] **Field of Search** 162/29, 30, 31, 67, 162/88, 89; 423/475, 477, 499; 210/62, 63

[56] **References Cited**

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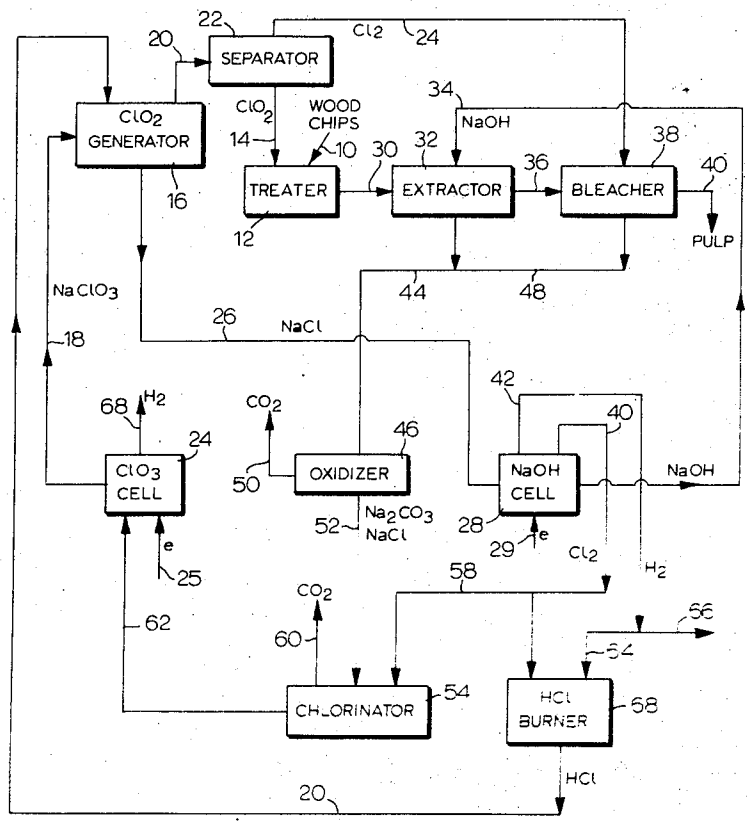
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[57] **ABSTRACT**

Alkali metal carbonate in aqueous solutions of alkali metal carbonate and alkali metal chloride is chlorinated using chlorine or hydrogen chloride. A typical aqueous solution is oxidized waste pulping and bleaching liquor from a process for pulping cellulosic fibrous material using a chlorine dioxide treatment followed by sodium hydroxide. Another typical aqueous solution is that formed from the precipitate of evaporation of a white liquor obtained in a Kraft recovery operation.

31 Claims, 2 Drawing Figures



2 Sheets-Sheet 1

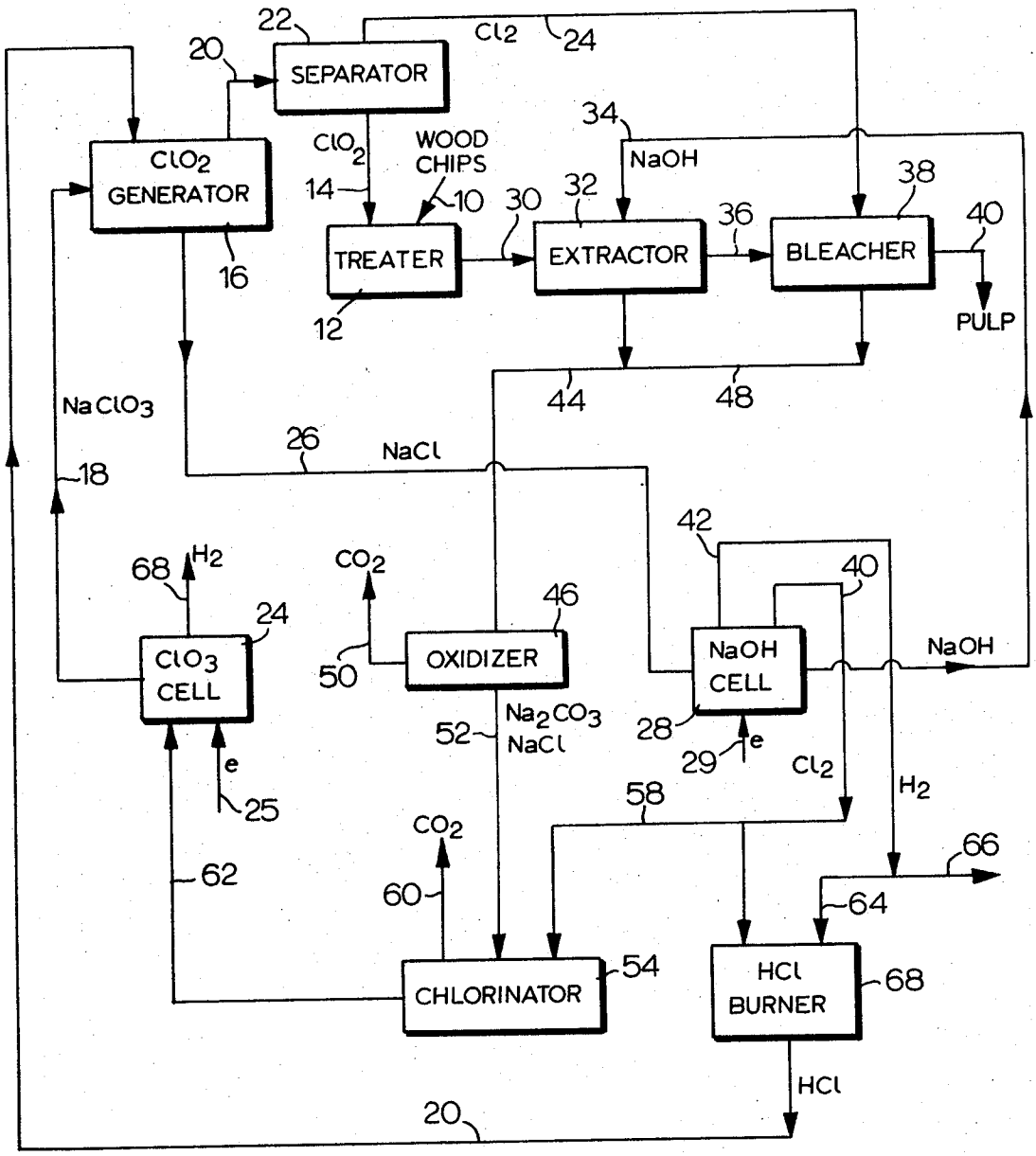


FIG. 1

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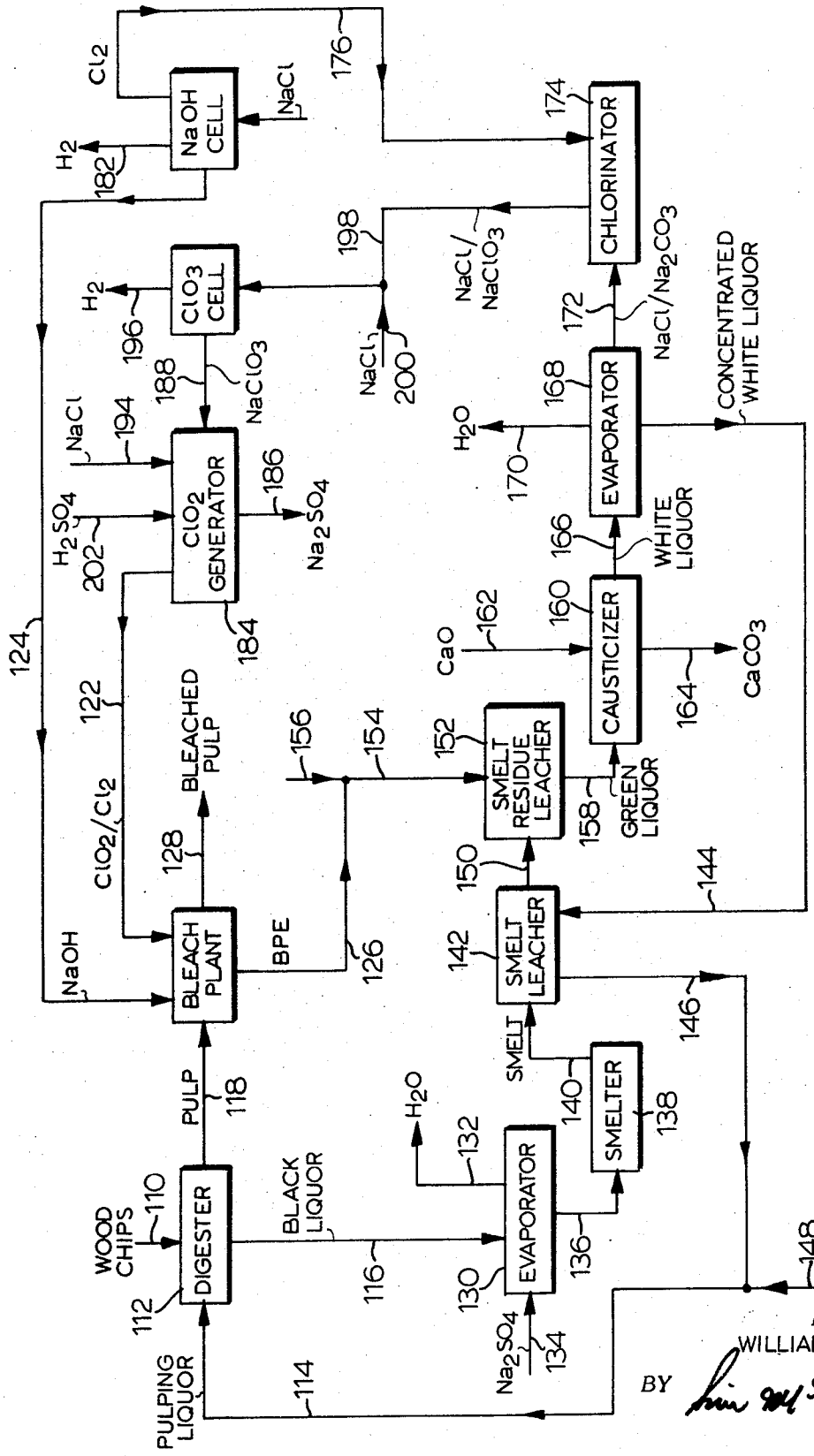


FIG. 2

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REGENERATION OF CHLORINE DIOXIDE FOR PULP TREATMENT

This invention relates to the production of pulp, more particularly to the formation of pulp of cellulosic fibrous materials, such as wood.

In the pulping of cellulosic fibrous materials, a number of different pulping chemicals have been employed. The present invention is concerned in one aspect with the so-called "holopulping process", which includes an initial treatment with chlorine dioxide followed by treatment with alkali.

The alkali treatment, or extraction, step usually is achieved with sodium hydroxide, which removes chlorine-containing materials and dissolves some organic matter from the cellulosic fibrous material.

The pulp, generally after intermediate washing, may be bleached, such as with hypochlorite, chlorine dioxide, peroxide, or peracetic acid.

The spent alkali extraction material, together with bleach plant effluents, consisting of alkali metal chloride and organic matter dissolved from the wood and any unreacted alkali, may be subjected to a recovery operation. This recovery operation generally consists of counter-current washing of successively bleached, extracted and unbleached pulp followed by evaporation and subjecting the concentrated material together with the spent materials to air oxidation, such as in a simple furnace or by the so-called "Zimmerman" wet oxidation process.

The oxidation step oxidizes the organic material to water and carbon dioxide which then may be discharged to the atmosphere without further treatment. Any alkali metal ions not combined with chloride will react with carbonate ions to form alkali metal carbonate.

The products of the oxidation step therefore are mainly alkali metal chloride and alkali metal carbonate. If the oxidation has occurred in a furnace, the products are recovered as a smelt or a solid mixture. If a wet oxidation process is adopted, then an aqueous solution containing these materials is recovered.

The alkali metal carbonate represents a loss of alkali from the system and it has been proposed to recover the alkali by subjecting a solution of the products of the oxidation, after settling of dregs, such as heavy metal ions, to crystallization to recover the bulk of the alkali metal chloride, and causticization of the alkali metal carbonate with lime to form alkali metal hydroxide. The precipitated calcium carbonate is roasted to provide more lime.

Such an operation involves the use of substantial amounts of equipment and energy. The present invention is concerned with the recovery of the alkali metal values of the alkali metal carbonate in readily usable form in a simpler and more economic manner than the causticization proposal discussed above.

In copending U.S. application, Ser. No. 100,669 filed Dec. 22, 1970 assigned to Electric Reduction Company of Canada, Limited here is described a process of providing a white pulping liquor which includes evaporation of the liquor to precipitate alkali metal chloride therefrom.

This process is applicable to many different pulping processes, but has particular applicability to the Kraft process.

In the pulping of cellulosic fibrous material using the Kraft process, wood chips or the like are digested in a "white liquor" containing sodium sulfide and sodium hydroxide. The pulp is separated from the resulting "black liquor" and the black liquor is subjected to a series of operations in a recovery system.

The black liquor first is concentrated by evaporation of water therefrom and the concentrated black liquor is burned in a furnace to yield a smelt containing sodium carbonate and sodium sulfide. The smelt is dissolved in water to yield a raw green liquor which then is clarified.

The clarified green liquor is causticized with slaked lime whereby the sodium carbonate is converted to sodium hydroxide and calcium carbonate is precipitated as a mud. The mud is washed with water and calcined to regenerate lime for further causticization. The causticized green liquor then is recycled as white liquor to the digester.

Make-up sodium sulfate is added to the recovery operation, generally to the black liquor before it is fed to the furnace. The sodium sulfate is converted in the furnace to sodium sulfide and sodium carbonate, the latter being converted on later causticization to sodium hydroxide. In this manner, the sodium hydroxide and sodium sulfide content of the white liquor is maintained at the desired level.

Sodium chloride finds its way into the regenerated white liquor in a number of ways. In coastal regions, logs from which the wood chips are formed are floated in sea water and the logs soak up a certain quantity of salts, especially sodium chloride. The sodium chloride is introduced into the pulping operation with the wood chips. While a certain amount of the sodium chloride may be removed by washing with fresh water, all is not removed so that some sodium chloride is inevitably introduced into the pulping system.

In addition, sodium chloride may be introduced into the recovery system by the use of well water and use of chloride containing make-up chemicals which are effluents of other plants.

The sodium chloride recycles in the liquor and constitutes a dead load. The quantity of sodium chloride builds up in the system with each recycle to a particular steady state concentration which depends on the efficiency of the recovery system.

In accordance with one of the processes described in the aforementioned U.S. Patent application, this sodium chloride content of the white liquor is reduced by evaporation of the white liquor to precipitate some of the sodium chloride. In the causticization step, not all of the sodium carbonate content of the green liquor is converted to sodium hydroxide and this unconverted sodium carbonate represents another dead load on the system.

Upon the concentration of the white liquor, some of the uncausticized sodium carbonate is precipitated along with the precipitated sodium chloride.

The present invention provides a process of reacting alkali metal carbonate in an aqueous solution containing the alkali metal carbonate and alkali metal chloride with gaseous chlorine or with gaseous hydrogen chloride or an aqueous solution thereof. This has the effect of converting the alkali metal carbonate to alkali metal chloride when hydrogen chloride or hydrochloric acid are used, thereby releasing carbon dioxide which may be vented to atmosphere.

Where chlorine is used, the nature of the products depends on the reaction conditions employed. When alkaline conditions generally above about pH 9 are used at room temperature, then the alkali metal carbonate is converted to alkali metal chloride and alkali metal hypochlorite. Where, however, the reaction occurs under neutral or slightly acidic conditions and/or at an elevated temperature, the products are alkali metal chloride and alkali metal chlorate. Generally it is preferred to form the alkali metal chlorate, but the reaction to produce the alkali metal chloride may be utilized. The following disclosure is concerned mainly with the formation of alkali metal chlorate, although it will be apparent that the formation of alkali metal hypochlorite also is possible and only minor modifications are necessary to the procedure.

The present invention may be incorporated into several processes, for example, to recover the alkali metal values of the alkali metal carbonate material in the processes mentioned above.

This reaction may form part of an integrated cyclic system in the holopulping process in which the only feed materials are water, cellulosic fibrous material and electric power and the only effluents are hydrogen, carbon dioxide and extracted pulp.

The chlorine dioxide utilized in part of the holopulping operation may be formed in a number of different ways, involving reduction of an alkali metal chlorate, generally sodium chlorate, in an acid solution. The reducing agents may be sulphur dioxide, chromic sulphate, methanol, alkali metal chloride, generally sodium chloride, or hydrochloric acid. The basic reaction in all such processes is that between chlorate and chloride in an acid solution to produce chlorine dioxide, chlorine and water, in accordance with the equation:

$$2H^+ + ClO_3^- + Cl^- \rightarrow ClO_2 + \tfrac{1}{2}Cl_2 + H_2O$$

When sodium chloride or hydrochlric acid is the reducing agent, chlorine is produced along with the chlorine dioxide. In the presence of other reducing agents, the chlorine is reduced to chloride in the reacting solution, so that the chlorine dioxide produced contains little chlorine.

The acid medium may be provided by sulphuric acid where the reducing agent is sodium chloride, and may be provided both by sulphuric acid and hydrochloric acid where the reducing agent is hydrogen chloride. The acid medium further may be wholly provided by hydrogen chloride also acting as the reducing agent.

Processes of forming chlorine dioxide from alkali metal chlorate utilizing alkali metal chloride and/or hydrogen chloride as reducing agent in the presence of sulphuric acid as acid medium are described in Canadian Pats. Nos. 543,589 issued July 16, 1957, 825,084 issued Oct. 14, 1969 and 826,577 issued Nov. 4, 1969, all to Electric Reduction Company of Canada, Limited.

A process of forming chlorine dioxide from alkali metal chlorate utilizing hydrogen chloride as both the reducing agent and the acid medium is described in copending Canadian Pat. No. 913,328 in the name of Electric Reduction Company of Canada, Limited.

It is preferred in the integrated operation to produce chlorine dioxide from alkali metal chlorate utilizing hydrochloric acid as acid medium and reducing agent, particularly by the process of the above-mentioned Canadian Pat. No. 913,328 . IN this latter process, water is evaporated from the reaction medium and removes the chlorine dioxide and chlorine from the generator. Generally, the generator is maintained under a reduced pressure and the reaction medium is maintained substantially at its boiling point. In this way, maximum evaporation of water from the reaction medium is achieved while maintaining the temperature of formation of the chlorine dioxide below the temperature above which substantial decomposition of that material occurs.

Generally, the generator is operated so that sufficient water is evaporated that the alkali metal chloride product is precipitated in the generator. This material may be removed and, after separation from any entrained liquor, recovered in substantially pure form.

As an alternative to this process of producing chlorine dioxide, it is possible to operate at room temperature. Under these circumstances a carrier gas, such as air, is used to remove the gaseous products from the reaction vessel. Since water is not evaporated from the reaction medium, it is necessary to remove aqueous solutions containing product alkali metal chloride, together with unreacted alkali metal chlorate and hydrochloric acid. This process had the advantage that it is unnecessary to heat the reaction vessel. The disclosure mainly refers to the evaporative process, but it will be readily apparent that this chlorine dioxide-making process may be utilized in equivalent or analogous manner in the integrated system.

The alkali metal chlorate utilized to form the chlorine dioxide, generally sodium chlorate, may be purchased as such, or, preferably in the integrated process, formed by electrolysis of acidic alkali metal chloride solution. The alkali metal chloride utilized for electrolysis as cell liquor may be formed from the alkali metal chloride recovered from the generator. The cell also produces hydrogen which may be vented, or burned with air to provide the water requirement of the system.

The alkali metal hydroxide, generally sodium hydroxide, used to pulp and to recover the chlorine values from the chlorine dioxide and chlorine after the chlorine dioxide initial treatment may be formed by electrolysis of an aqueous solution of alkali metal chloride. Gaseous by-products of this electrolysis are equimolar proportions of hydrogen and chlorine. In the integrated process, these gases may be burned to form the hydrogen chloride requirement of the chlorine dioxide generator.

As indicated above, in the pupling and bleaching operations, the alkali metal hydroxide forms alkali metal chloride with the chlorine values of the chlorine dioxide and the chlorine. The alkali metal chloride so recovered may be recycled in the integrated operation and utilized to form more alkali metal hydroxide or utilized to form alkali metal chlorate.

In accordance with the process of the present invention, the alkali metal carbonate present with the alkali metal chloride is reacted with chlorine, preferably in a manner to form alkali metal chlorate and alkali metal chloride. The alkali metal chlorate in the integrated process is utilized to make chlorine dioxide and chlorine in the generator, depositing an equivalent amount of alkali metal chloride. Such alkali metal chloride may be utilized to form the requisite amount of alkali metal hydroxide to react with the chlorine values of the chlorine dioxide and chlorine formed from the chlorate and chloride in the chlorine dioxide generator and used in the chlorine dioxide pulping process.

The chlorine utilized in the chlorination may be formed in the electrolysis of the alkali metal chloride to alkali. Hydrogen is formed as a by-product and may be vented to atmosphere or burned in air, if desired, to provide the water requirement of the system.

Alternatively, the alkali metal carbonate may be reacted with hydrogen chloride to form alkali metal chloride.

In the above-mentioned U.S. application No. 100,669 the mixture of sodium chloride and sodium carbonate precipitated from the white liquor is contacted with water so that the sodium carbonate and some of the sodium chloride are dissolved in the water. The remainder of the sodium chloride then may be utilized to form chlorine dioxide in a sulphuric acid based generator. Alternatively, it may be used to generate sodium chlorate by electrolysis. In one form of the process described in application Ser. No. 100,669, the aqueous solution of sodium carbonate and sodium chloride is recycled as part of the water requirement to form the green liquor from the smelt.

In accordance with the present invention, the sodium carbonate in the mixture may be reacted with chlorine, hydrogen chloride or hydrochloric acid. The mixture, or part thereof, may be dissolved in water. Reaction with chlorine generally is performed in a manner to convert the sodium carbonate to sodium chlorate and sodium chloride. Reaction with hydrogen chloride converts the sodium carbonate to sodium chloride.

The materials produced in these reactions, together with the sodium chloride in the mixture, may be utilized to manufacture sodium chlorate or as feed to a chlorine dioxide generator. Where the reaction with hydrogen chloride occurs, then the sodium chloride formed together with the sodium chloride of the mixture may be used to form sodium hydroxide.

The smelt used to form the green liquor may be fractionated to diminish the sodium sulphide content thereof and to provide a sulphide-lean green liquor. In accordance with the disclosure of the above-mentioned U.S. application Ser. No. 100,669 this fractionation may be achieved in a number of ways. For instance, the smelt may be contacted with water to leach sodium sulphide from the smelt to leave a solid mass which then is used to form the green liquor.

Alternatively, recycled white liquor, after concentration to deposit sodium chloride and sodium carbonate, may be utilized to leach the smelt, to thereby provide a white liquor containing sodium hydroxide and sodium sulphide.

Further, the smelt may be dissolved in water and the resulting solution evaporated to deposit therefrom a solid mass containing sodium chloride and sodium carbonate. The green liquor then may be made up from this deposited solid mass.

The invention now is further described by way of illustration with reference to the accompanying drawings, in which:

FIG. 1 is a flow sheet of an integrated holopulping process incorporating the present invention, and

FIG. 2 is a Kraft pulping operation incorporating the present invention.

Referring to FIG. 1, wood chips, or other finely divided cellulosic fibrous material, are fed by line **10** to a treater **12** wherein the wood chips are treated with aqueous chlorine dioxide solution fed by line **14**. The chlorine dioxide is formed in a generator **16** by reaction in an aqueous solution between an alkali metal chlorate fed by line **18** and hydrogen chloride fed by line **20**. The invention is described hereinafter with reference to sodium as the alkali metal, but the invention is not limited thereto.

The chlorine dioxide generator **16** preferably is operated at sub-atmospheric pressure induced by any convenient means. Further, the generator **16** preferably operates at the boiling point of the aqueous solution, whereby the maximum amount of water is evaporated from the reaction medium and this steam removes the chlorine dioxide and chlorine formed in the reaction from the generator. Sodium chloride is deposited from the aqueous solution.

The variables preferably are controlled to maintain a substantially constant level of reaction liquor in the generator. Any overflow liquor may be recycled to the sodium chlorate feed stream.

The gaseous mixture of chlorine dioxide, chlorine and steam is fed by line **20** to a separator **22**, wherein the mixture is condensed to provide an aqueous solution of chlorine dioxide containing some dissolved chlorine. This material then is fed to the pulper **12** by line **14**. The remaining gaseous chlorine leaves the separator **22** by line **24**. The sub-atmospheric pressure on the generator **16** may be provided through the gaseous chlorine line **24**.

The sodium chloride deposited in the generator **16** is removed and after washing to remove entrained reaction liquor is fed by line **26** as an aqueous solution to a caustic cell **28** wherein it is at least partially electrolyzed to sodium hydroxide. The provision of electrical energy input is indicated schematically by line **29**.

Following the chlorine dioxide treatment, the treated chips are passed by line **30** to an extractor **32**. The chips may be washed between the treater and the extractor. In the extractor **32**, the chips are contacted with sodium hydroxide solution fed through line **34** and the pulping operation thereby is completed. The extraction step additionally removes the chlorine values present in the pulp and also dissolves organic materials from the chips. The extraction may be carried out under conventional caustic extraction conditions.

The pulp leaves the extractor **32** through line **36** for further processing, such as bleaching in bleacher **38**. Chlorine in line **24** is fed to the bleacher as the bleaching agent, generally in the form of an aqueous solution.

A washing step may be included between the extractor and the bleacher. Additionally, the pulp leaving the bleacher through line **40** may be washed. Where such intermediate and final washing occurs, the spent wash water from the bleached pulp may be used as the wash water for the pulp, and that spent wash water may be used as the wash water for the treated chips leaving the treater. The spent wash water from washing the treated chips then may be fed to the oxidizer as discussed below. Alternatively, such counter-current washing may be omitted and each spent wash water passed separately to the oxidizer **46**.

The sodium hydroxide solution fed by line **34** is formed by electrolysis of the sodium chloride solution fed by line **26** in the caustic cell **28**. The off-gases from the caustic cell **28**, hydrogen and chlorine, leave respectively through lines **40** and **42**.

The spent liquid from the extractor **32** passes by line **44** to an oxidizer **46**. Spent liquid from the bleacher **38** passes by lines **48** and **44** to the oxidizer **46**. In the oxi-

dizer **46**, the organic materials are mainly oxidized to carbon dioxide which mainly vents to atmosphere through line **50**. Part of the carbon dioxide forms sodium carbonate with the appropriately excess amount of sodium hydroxide present in line **44**.

The oxidizer **46** may take the form of a furnace in which event the smelt or ash recovered is mainly sodium chloride together with a small amount of sodium carbonate and minor amounts of impurities. Alternatively, the oxidizer **46** may be one suitable for wet oxidation of the solution in line **44**, in which case, the product is a solution containing sodium chloride and some sodium carbonate, which may be clarified to remove heavy metal impurities. Where the wet oxidation process is used and wash water is added to the materials passed to the oxidizer, it is desirable to evaporate excess water prior to passing the solution to the oxidizer.

Where the treated chips, the pulp and bleached pulp are subjected to the washing steps indicated above and the spent wash water is fed to the oxidizer, it will be apparent that the chlorine and soda values present in the wash water are recovered in the oxidizer, thereby avoiding environmental pollution by discharge of the spent wash water.

Where the product of the oxidizer **46** is a smelt, this is dissolved in water and clarified to remove heavy metal ion contaminants. A clarified aqueous solution formed in a manner depending on the nature of the oxidizer **46** containing dissolved sodium chloride and sodium carbonate is passed by line **52** to a chlorinator **54**.

In the chlorinator **54**, the sodium carbonate-containing solution is contacted with gaseous chlorine in any convenient manner. The chlorine is fed through line **58** and is constituted by part of the chlorine off-gas from the caustic cell **28**. Alternatively, the chlorine used may be part of that in line **24**. The chlorination reaction generally occurs under neutral or slightly acid conditions at an elevated temperature.

The chlorination may be achieved if desired by using hydrogen chloride in place of chlorine. The chlorination with chlorine converts the sodium carbonate to sodium chlorate and sodium chloride, releasing carbon dioxide which may be vented to atmosphere through line **60**. Where hydrogen chloride is employed as the chlorinating agent, the sodium carbonate is converted to sodium chloride, and again carbon dioxide is released.

The resulting solution of sodium chlorate and sodium chloride is fed by line **62** to the chlorate cell **24**. The sodium chlorate in line **62** passes through the cell **24** and forms part of the chlorate feed to the generator. The sodium chloride in line **62** is partially converted to chlorate and this sodium chlorate combined with that sodium chlorate already in line **62** constitutes the chlorate feed to the generator **16** through line **18**. The provision of an electrical energy input to the chlorate cell **24** is indicated schematically by line **25**.

The hydrogen off-gas from the caustic cell **28** in line **42** is split into two streams, **64** and **66**. Part of the hydrogen is vented to the atmosphere through line **66**. Alternatively, this hydrogen may be combined with hydrogen off-gas from chlorate cell **24** in line **68** and the combined streams burned with air to form water for the operation. The remainder of the hydrogen is fed by line **64** to a hydrogen chloride burner **68**.

The chlorine off-gas from the caustic cell **28** in line **40** is split into two streams **58** and **70**. The stream **58** as previously indicated passes to the chlorinator **54**. The remainder of the chlorine passes by line **70** to the hydrogen chloride burner **68** wherein it is burned with the hydrogen fed by line **64** to form hydrogen chloride. The hydrogen chloride then may pass to the generator **16** through line **20**. It may be desirable to dissolve the hydrogen chloride in water, and pass the resulting hydrochloric acid to the generator **16**.

Where the reaction with chlorine occurs under alkaline conditions, for example, above about pH **9**, the sodium carbonate is converted to sodium chloride and sodium hypochlorite. This solution may be used as desired. It may be passed to the caustic cell **28**, wherein the hypochlorite is converted to caustic soda and chlorine is released. Alternatively, the solution is passed to the chlorate cell **24**. The initial step in the formation of sodium chlorate is the conversion of sodium chloride to sodium hypochlorite, so that the reaction is equivalent to that carried out in the process described above.

In the embodiment illustrated, all of the sodium chloride deposited in the generator **16** is formed into an aqueous solution and passed by line **26** to the caustic cell **28**.

It may be desirable to split the aqueous stream of sodium chloride to provide two feed streams, one of which passes to the caustic cell **28** and the other of which passes to the chlorate cell **24**.

Alternatively, all of the aqueous sodium chloride solution formed from the sodium chloride deposited in the generator **16** may be passed to the chlorate cell **24**.

The sodium chloride present in line **44** due to reaction between sodium hydroxide and the chlorine values in the pulp and the spent bleaching liquor may be partially recovered prior to passing to the oxidizer by evaporation of the aqueous solution. This recovered sodium chloride may be passed to the caustic cell **28** after formation into an aqueous solution. The sodium chloride present in the system may be utilized in several different manners.

As indicated above, the chlorine dioxide generator **16** may be operated at room temperature, using air to remove the chlorine dioxide and chlorine formed in the reaction. In that case, the material passing out of the generator **16** by line **26** is an aqueous solution containing product sodium chloride, unreacted sodium chlorate and unreacted hydrogen chloride in the form of hydrochloric acid. When this process is utilized, it is preferred to employ the oxidizer **46** in a form to produce a solid smelt from the solution in line **44**.

The solution in line **26** then is utilized to dissolve the smelt. In this way the sodium carbonate present in the smelt is converted to sodium chloride by reaction with the hydrochloric acid in the solution. The resulting solution may be recycled to the chlorate cell **24** or may be fed to the caustic cell **28**.

The integrated system described with reference to FIG. **1** has an input of water, wood chips and electrical energy and an output of bleached wood pulp, hydrogen and carbon dioxide. The hydrogen may be converted to part of the water requirement, if desired. The stoichiometry of the integrated system is apparent from the following equations for the formation of nominally 1 mole of chlorine dioxide and x moles of sodium carbonate:

Generator **16**: $(1+2x)\ NaClO_3 + (2+4x)\ HCl \rightarrow (1+2x)\ ClO_2 + (\frac{1}{2}+x)\ Cl_2 + (1+2x)\ H_2O + (1+x)$ NaCl

Treater, extractor and bleacher **12, 32** and **38**: $(1+2x)\ ClO_2 + (½+x)\ Cl_2 + (2+4x)\ NaOH \rightarrow (2+4x)\ NaCl + (1+2x)\ H_2O$

Line **44**: $(2+4x)\ NaCl + 2x\ NaOH$

Oxidizer **46**: $xCO_2 + 2xNaOH \rightarrow xNa_2CO_3 + xH_2O$

Chlorinator **54**: $xNa_2Co_3 + xCl_2 \rightarrow (x/3)\ NaClO_3 + (5x/3)\ NaCl + xCO_2$

Line **62**: $(x/3)\ NaClO_3 + (2+4x+(5x/3)\ NaCl$

Cell **24**: $(1+5x/3)\ NaCl + (3+5x)\ H_2O \rightarrow (1+5x/3)\ NaClO_3 + (3+5x)H_2$

Line **18**: $(1+2x)\ NaClO_3 + (1+4x)\ NaCl$

Line **26**: $(2+6x)\ NaCl$

Cell **28**: $(2+6x)\ NaCl + (2+6x)\ H_2O \rightarrow (2+6x)\ NaOH + (1+3x)\ Cl_2 + (1+3x)\ H_2$

Burner **70**: $(1+2x)\ Cl_2 + (1+2x)\ H_2 \rightarrow (2+4x)\ HCl$

Line **58**: xCl_2

Line **66**: $(3+6x)\ H_2$

It will be seen that the hydrogen formed may be burned in air to form the stoichiometric water requirement of the system.

The present invention, therefore, in one embodiment, provides an integrated holopulping process having no harmful effluents and which may be operated in ready and economic manner.

Turning now to FIG. **2**, wood chips or the like cellulosic fibrous material are fed by line **110** to a digester **112** wherein they are pulped using pulping liquor fed by line **114** and consisting of an aqueous solution of sodium sulphide and sodium hydroxide. Where the pulping process is other than the Kraft process, then appropriate modifications may readily be made. The spent pulping liquor, or black liquor, is separated from the resulting pulp and passed by line **116** to a recovery operation described below.

The pulp, after separation from the black liquor and generally after a washing step, is passed by line **118** to a bleach plant **120.** In the bleach plant the pulp is subjected to a series of steps involving, for example, bleaching of the pulp with chlorine dioxide, chlorine, or a mixture of the two fed through line **122,** followed by caustic extraction using a sodium hydroxide solution fed by line **124.** The pulp, after caustic extraction, is subjected to a further bleaching step with the chlorine dioxide, chlorine, or mixture of the two. The pulp then may be subjected to further caustic extraction and bleaching operations.

In a preferred sequence of steps in the bleach plant, the pulp is subjected to the successive steps of bleaching with a mixture of chlorine dioxide and chlorine, caustic extraction with sodium hydroxide solution, bleaching with an aqueous solution of chlorine dioxide, a further caustic extraction with sodium hydroxide solution and a final bleaching with an aqueous solution of chlorine dioxide. (This sequence of steps is known as the CEDED sequence).

The pulp preferably is washed after each bleaching step and each extraction step. The spent wash water from each succeeding washing step may be used as the wash water for the preceding washing step so that there is countercurrent flow of pulp and wash water through the bleach plant. The spent wash water from the first washing then is discharged from the bleach plant as bleach plant effluent (BPE) through line **126.** Where such countercurrent flow of wash water is not utilized, the individual spent wash waters from the various washing steps are combined to provide the BPE.

The finally bleached and washed pulp passes out of the bleach plant **120** through **128** for further processing.

The recovery operation for the black liquor in line **116** consists of the following steps. The black liquor first passes to an evaporator **130** wherein water is evaporated from the liquor. The water vapor so produced is vented through line **132** and may be condensed to provide part of the water requirement of the overall system.

Sodium sulphate is added by line **134** to the concentrated black liquor as make-up chemical for lost soda and sulphur values. The concentrated black liquor is passed by line **136** to a smelter **138** wherein the liquor is burned to leave a smelt residue containing sodium sulphide and sodium carbonate. The smelt additionally contains sodium chloride incorporated into the system with the wood chips, or otherwise, as discussed above.

The smelt is passed by line **140** to a smelt leacher **142** wherein at least part of the sodium sulphide content of the smelt is dissolved therefrom by concentrated sulphide-lean white liquor recycling in line **144.** There may be required several recycle loops of white liquor containing dissolved sodium sulphide for the sodium sulphide level therein to be sufficient to provide a liquor suitable for feeding by lines **146** and **114** as the pulping liquor to the digester **112.** It may be necessary to dilute the solution in line **146** by water fed by line **148** prior to use as pulping liquor.

The solid residue remaining after leaching of at least part of the sodium sulphide rich in sodium chloride and sodium carbonate is passed by line **150** to a smelt residue leacher **152** wherein the residue is dissolved in an aqueous medium fed by line **154.** The aqueous medium may be the bleach plant effluent **126** with extra water added if necessary through line **156.** By utilizing the bleach plant effluent to dissolve the smelt residue, the discharge of environmental pollutants from the bleach plant **120** is avoided.

The green liquor formed in the leacher **152** is passed by line **158** to a causticizer **160.** Lime is fed by line **162** to the causticizer **160** to convert most of the sodium carbonate present in the green liquor to sodium hydroxide. Calcium carbonate precipitates as a mud. The calcium carbonate is removed through line **164** and may be roasted to provide further lime. Not all of the sodium carbonate present in the green liquor is converted to sodium hydroxide, so that the white liquor leaving the causticizer **160** through line **166** is predominantly a sulphidelean sodium hydroxide solution having dissolved therein sodium chloride and sodium carbonate.

It is preferred to utilize a sulphide-lean green liquor to generate the sodium hydroxide, since smaller amounts of wash water are required to produce a given amount of sodium hydroxide as compared to green liquor formed from a non-fractionated smelt. Hydrolysis of sodium sulphide in conventional green liquor, thereby inhibiting the causticization reaction is substantially eliminated.

It is of course possible to form the green liquor in line **158** directly from the smelt without first fractionating the smelt to remove sodium sulphide values therefrom. The solution formed after causticization in that event contains both sodium sulphide and sodium hydroxide.

The white liquor in line **166** is passed to an evaporator **168** wherein, in accordance with the process dis-

closed in U.S. application Ser. No. 100,669, water is evaporated from the white liquor and the water vapor is removed through line **170.** Upon condensation of the water vapor, the resulting water may be used as part of the overall water requirement of the system.

The evaporation precipitates sodium chloride and sodium carbonate from the white liquor, and the resulting concentrated white liquor having a reduced sodium chloride-and sodium carbonate-content is passed by line **144** to leach sodium sulphide from the smelt.

The precipitated sodium chloride and sodium carbonate are formed into an aqueous solution and passed by line **172** to a chlorinator **174.** In the chlorinator, in accordance with the present invention, the sodium carbonate is reacted with chlorine fed through line **176,** preferably under conditions so that the sodium carbonate is converted to sodium chloride and sodium chlorate.

Alternatively, the chlorine may be replaced by hydrogen chloride, in which event the sodium carbonate is converted to sodium chloride. It is possible also to utilize mixtures of chlorine and hydrogen chloride to react with the sodium carbonate, in which case sodium chloride is formed, together with varying amounts of sodium chlorate. The quantity of sodium chlorate formed depends on the relative proportions of chlorine and hydrogen chloride.

The chlorine fed in line **176** to the chlorinator is the by-product of an electrolytic process of forming sodium hydroxide in a cell **178** from a feed of an aqueous sodium chloride solution fed through line **180.** Where hydrogen chloride is fed to the to the chlorinator **174,** this material may be formed in any convenient manner, such as by the reaction of hydrogen and chlorine, and the sodium chloride produced from the sodium carbonate together with the sodium chloride present in the solution in line **172** may be utilized as part of the sodium chloride requirement of the cell **178.**

The sodium hydroxide produced in the cell **178** is passed by line **124** to the bleach plant **120.** In addition to chlorine gas, hydrogen gas also is produced from the cell **178** and leaves the cell through line **182.** The hydrogen off-gas may be burned in air to provide part of the water requirement of the overall system.

Alternatively, where it is desired to feed hydrogen chloride to the chlorinator **174,** part of the hydrogen leaving the cell **178** may be reacted with part of the chlorine to provide the hydrogen chloride.

The quantity of chlorine in line **176** generally is in excess of that required to react with the sodium carbonate in solution fed by line **172** to the chlorinator **174.** The unreacted chlorine may be utilized in any convenient manner, such as, to form hydrogen chloride for use as feed to a chlorine dioxide generator **184,** or as bleaching material for the bleach plant **120.**

The chlorine dioxide generator **184** contains a chlorine dioxide-producing reaction mixture. In the enbodiment illustrated, the reaction mixture is an aqueous solution of sodium chlorate, a chloride, which is generally sodium chloride optionally together with some hydrogen chloride, if desired, and sulphuric acid. The chlorine dioxide and chlorine formed from the reaction mixture in the generator may be removed therefrom in any convenient manner, such as by the process described in Canadian Pat. No. 543,589 mentioned above. Preferably, however, the chlorine dioxide and chlorine are removed by water vapor evaporated from the reacting solution. Preferably, the reacting solution is maintained at its boiling point to achieve maximum evaporation of water vapor from the reacting solution. Further, the generator preferably is maintained under a reduced pressure to minimize decomposition of chlorine dioxide and to lower the heat energy requirements of the system. Under these conditions, sodium sulphate is precipitated from the reacting solution and removed from the generator through line 186.

The form of the sodium sulphate depends on the acidity conditions in the generator **184,** as can be seen from Canadian Pat. Nos. 825,084 and 825,577 referred to above.

The chlorine dixoide generator **184** alternatively may be one using hydrogen chloride as both the acid medium and reducing agent, such as that described in the above-mentioned Canadian Pat. No. 913,328, or an HCl-based system in which air is used to remove the product gases from the generator. In the latter case, the unreacted hydrochloric acid may be used to react with the sodium carbonate in line **172** to produce sodium chloride.

Sodium chlorate solution is fed to the generator **184** through line **188** from a sodium chlorate cell **190** wherein sodium chloride solution fed through line **192** is electrolyzed. The aqueous sodium chlorate solution contains unconverted sodium chloride and this latter sodium chloride constitutes part of the sodium chloride feed to the generator **186.** The remainder of the sodium chloride feed to the generator passes thereto by line **194.** Part of the sodium chloride fed to th generator **184** may be replaced by hydrogen chloride, if desired.

Hydrogen off-gas from the cell exits through line **196** and may be vented to atmosphere, or may be used to form part of the water requirement of the overall system.

The sodium chloride feed to the cell **190** may be constituted partially by the sodium chloride content of the aqueous solution leaving the chlorinator **174** through line **198.** The sodium chloride in line **198** includes the sodium chloride present in the aqueous solution fed by line **172** to the chlorinator **174** and the sodium chloride formed from the sodium carbonate in the chlorinator. The remainder of the sodium chloride requirement of the cell **190** is provided by a sodium chloride solution in line **200.**

The sodium chlorate in line **198** formed from the sodium carbonate passes through the cell **190** and constitutes part of the sodium chlorate feed to the generator **184** through line **188.**

Where the sodium carbonate is reacted with hydrogen chloride in chlorinator **174,** then the solution in line **198** does not contain any sodium chlorate.

Alternatively, the aqueous solution in line **198** may be fed directly to the generator **184** as part of the sodium chloride and sodium chlorate requirements of the generator.

Sulphuric acid is fed to the generator **184** by line **202.** Preferably the rate of evaporation of water from the reaction mixture and the rates of feed of the reactants are controlled to maintain a substantially constant level of reaction mixture in the generator **186.**

The sodium sulphate removed from the generator **184** may be used partly to provide the make-up sodium sulphate requirement fed by line **134** to the black liquor evaporator **130.**

The remainder or all, if desired, of the sodium sulphate may be converted to sodium chloride in accordance with the process described in copending Canadian patent application Ser. No. 072,527 filed Jan. 20, 1970 in the name of Electric Reduction Company of Canada, Limited. The sodium chloride so produced may be utilized as part of the sodium chloride content of the overall system. The other product of this reaction, namely, sulphuric acid, may be fed to the generator **184** as part of the sulphuric acid requirement.

The gaseous mixtures of steam, chlorine dioxide and chlorine leaving the generator **184** by line **122** generally is cooled to condense the steam and recover an aqueous solution of chlorine dioxide containing some dissolved chlorine, and providing a gaseous chlorine stream, which may be used in the bleach plant or in the chlorinator **176.** Alternatively, the chlorine may be converted to hydrogen chloride with the hydrogen offgases from one or the other or both of the cells **178** and **190,** and the hydrogen chloride so produced then may be used to convert the sodium sulphate in line **186** to sodium chloride and sulphuric acid.

Modifications are possible within the scope of the invention.

I claim:

1. In a process which comprises pulping a cellulosic fibrous material in a two-stage operation including an initial treatment with chlorine dioxide to provide a treated material and subjecting said treated material to alkali to remove residual chlorine values and soluble organic materials and to provide a pulp and a spent alkali solution, and oxidizing said spent alkali solution to form a material comprising alkali metal chloride and alkali metal carbonate, the improvement which includes subjecting said alkali metal carbonate to chlorination utilizing a chlorine-containing material selected from hydrogen chloride and chlorine thereby converting said alkali metal carbonate to alkali metal chlorate and alkali metal chloride or alkali metal hypochlorite and alkali metal chloride when said gaseous material is chlorine and converting said alkali metal carbonate to alkali metal chloride when said gaseous material is hydrogen chloride.

2. The process of claim **1** wherein said spent alkali solution is oxidized in a furnace to form a smelt containing alkali metal chloride and alkali metal carbonate and to form gaseous carbon dioxide, said smelt is dissolved in water, clarified and the alkali metal carbonate in the resulting aqueous solution is subjected to chlorination.

3. The process of claim **1** wherein said alkali treatment is accomplished utilizing an aqueous sodium hydroxide solution.

4. A process for the production of a pulp of cellulosic fibrous material which comprises contacting a cellulosic fibrous material with a chlorine dioxide-containing material to provide a treated material, subjecting said treated material to caustic extraction to provide a pulp and a spent extraction solution, bleaching said pulp to provide a bleached pulp and a spent bleaching solution, oxidizing at least one of said spent extraction solution and said spent bleaching solution to form a material comprising alkali metal chloride and alkali metal carbonate, and subjecting said alkali metal carbonate to chlorination utilizing a chlorine-containing material selected from hydrogen chloride and chlorine, thereby converting said alkali metal carbonate to alkali metal chlorate and alkali metal chloride or alkali metal hypochlorite and alkali metal chloride when said gaseous material is chlorine and converting said alkali metal carbonate to alkali metal chloride when said gaseous material is hydrogen chloride.

5. A process for the production of a pulp of a cellulosic fibrous material which comprises forming chlorine dioxide by reduction in aqueous acid solution of an alkali metal chlorate, treating a cellulosic fibrous material with said chlorine dioxide to provide a treated material, forming an alkali metal hydroxide solution and chlorine by electrolysis of an aqueous alkali metal chloride solution, contacting said treated material with said alkali metal hydroxide solution to remove residual chlorine values and soluble organic materials from said treated material and to provide a pulp and a spent alkali metal hydroxide solution, oxidizing said spent alkali metal hydroxide solution to form a material comprising alkali metal chloride and alkali metal carbonate, and subjecting said alkali metal carbonate to chlorination utilizing a chlorine-containing material selected from hydrogen chloride and chlorine.

6. The process of claim **5** wherein said chlorine dioxide is generated by reaction of an aqueous solution of an alkali metal chlorate and hydrogen chloride in a reaction zone while simultaneously evaporating water from said aqueous solution.

7. The process of claim **6** wherein chlorine dioxide and chlorine are formed by reaction in a reaction zone of an alkali metal chlorate with hydrogen chloride in an aqueous reaction medium while simultaneously evaporating water from said medium to remove said chlorine dioxide and chlorine from said zone and deposit alkali metal chloride from said medium in said zone.

8. The process of claim **7** wherein said alkali metal chlorate is formed at least partly by electrolysis of an aqueous solution of an alkali metal chloride.

9. The process of claim **8** wherein said alkali metal chloride is constituted at least in part by said alkali metal chloride deposited in said reaction zone.

10. The process of claim **9** wherein said alkali metal chlorate is sodium chlorate and said alkali metal hydroxide is sodium hydroxide.

11. The process of claim **5** wherein said chlorine dioxide is generated together with chlorine by reaction of an aqueous solution of an alkali metal chloride and hydrogen chloride in a reaction zone and said chlorine dioxide and chlorine are removed from said reaction zone as a gaseous mixture with an inert gas.

12. The process of claim **11** wherein said inert gas is air.

13. The process of claim **11** wherein a spent reaction liquor containing alkali metal chloride, unreacted alkali metal chlorate and unreacted hydrogen chloride is removed from said reaction zone and said unreacted hydrogen chloride is utilized to achieve said chlorination whereby said alkali metal carbonate is converted to alkali metal chloride.

14. The process of claim **5** wherein said gaseous material is chlorine and alkali metal chlorate and alkali metal chloride are formed in said chlorination reaction from said alkali metal carbonate, said alkali metal chlorate and alkali metal chloride so formed being utilized respectively to form chlorine dioxide and alkali metal hydroxide.

15. The process of claim **5** wherein said chlorination is achieved utilizing chlorine and said chlorine is

formed by said electrolysis of alkali metal chloride solution.

16. The process of claim 5 wherein said chlorination is achieved utilizing chlorine and alkali metal hypochlorite and alkali metal chloride are formed, said alkali metal hypochlorite and alkali metal chloride being utilized alternatively first to form alkali metal chlorate and subsequently to form chlorine dioxide, or to form alkali metal hydroxide.

17. A process for the production of a pulp of cellulosic fibrous material which comprises forming an aqueous solution of alkali metal chlorate and hydrogen by electrolysis of an aqueous alkali metal chloride solution, forming chlorine dixoide and chlorine by reaction in an aqueous solution of hydrogen chloride and an alkali metal chlorate in a reaction zone while simultaneously evaporating water from said solution to remove said chlorine dioxide and chlorine from said reaction zone and to deposit alkali metal chloride in said zone, said alkali metal chlorate being constituted partially by said alkali metal chlorate formed by electrolysis, removing said alkali metal chloride from said zone, forming an aqueous alkali metal hydroxide solution, hydrogen and chlorine by electrolysis of an aqueous solution of an alkali metal chloride, contacting a cellulosic fibrous material with said chlorine dixoide to provide a chlorine dioxide treated material, recovering residual chlorine values of said chlorine dioxide and removing soluble organic materials from said chlorine dioxide-treated material by contacting said chlorine dioxide-treated material with said alkali metal hydroxide solution to provide a pulp and a spent alkali metal hydroxide solution, oxidizing said spent solution to form carbon dioxide and a material comprising alkali metal chloride and alkali metal carbonate, forming an aqueous solution containing said alkali metal carbonate and said alkali metal chloride, subjecting said alkali metal carbonate to chlorination utilizing part of said chlorine to form alkali metal chlorate and alkali metal chloride, forming said hydrogen chloride by reaction between the remainder of said chlorine and part of said hydrogen formed in said electrolysis of alkali metal chloride to form alkali metal hydroxide, and passing said latter alkali metal chlorate and alkali metal chloride to said reaction zone.

18. The process of claim 17 wherein said alkali metal is sodium.

19. The process of claim 17 including the steps of washing said chlorine dioxide-treated material and said pulp and forwarding the spent wash water from said steps with said spent solution to said oxidizing step.

20. The process of claim 17 including the steps of washing said chlorine dioxide-treated material and said pulp, the spent wash water from washing said pulp being utilized as the wash water for said chlorine dioxide-treated material, and passing the spent wash water from washing said chlorine dioxide-treated material with said spent solution to said oxidizing step.

21. The process of claim 17 wherein said cellulosic fibrous material is wood.

22. A process for the production of a pulp of cellulosic fibrous material which comprises forming an aqueous solution of alkali metal chlorate and hydrogen by electrolysis of an aqueous alkali metal chloride solution, forming chlorine dioxide and chlorine by reaction in an aqueous solution of hydrogen chloride and an alkali metal chlorate constituted at least partially by said alkali metal chlorate formed by electrolysis, in a reaction zone while simultaneously evaporating water from said solution to remove said chlorine dioxide and chlorine from said reaction zone as a gaseous mixture with said evaporated water, and to deposit alkali metal chloride in said zone, removing said alkali metal chloride from said zone, forming an aqueous alkali metal hydroxide solution, hydrogen and chlorine by electrolysis of an aqueous solution of an alkali metal chloride, separating an aqueous solution of chlorine dioxide from said gaseous mixture, contacting a cellulosic fibrous material with said chlorine dioxide to provide a chlorine dioxide-treated material, washing said latter material with a first wash water to provide a first spent wash water, subjecting the resulting washed material to caustic extraction with said alkali metal hydroxide solution to remove residual chlorine dioxide values and soluble organic materials from said washed material and to provide a pulp and a spent extraction solution containing residual alkali metal hydroxide values, washing said pulp with a second wash water to provide a second spent wash water, bleaching said latter washed pulp with a bleaching agent constituted by chlorine from said gaseous mixture to provide a bleached pulp and a spent bleaching agent, washing said bleached pulp with a third wash water to provide a bleached and washed pulp and a third spent wash water, said third spent wash water constituting said second wash water and said second spent wash water constituting said first wash water, mixing said spent bleaching agent and said first spent wash water with said spent extraction solution whereby chlorine values in said first spent wash water and said sepnt extraction solution react with part of said residual alkali metal hydroxide to provide a waste liquor, oxidizing said waste liquor to form carbon dioxide and a material comprising alkali metal chloride and alkali metal carbonate, forming an aqueous solution containing said alkali metal chloride and alkali metal carbonate, subjecting said alkali metal carbonate to chlorination utilizing part of said chlorine formed by electrolysis of alkali metal chloride to form alkali metal hydroxide to convert said alkali metal carbonate to alkali metal chlorate and alkali metal chloride, and forming said hydrogen chloride by reaction between the remainder of said chlorine and part of said hydrogen formed in said electrolysis of alkali metal chloride to form alkali metal hydroxide.

23. In a process of forming a white liquor, including the steps of forming a green liquor from a solid mass containing sodium carbonate and sodium chloride and an aqueous material, causticizing said green liquor to form a white liquor containing sodium hydroxide, sodium chloride and uncausticized sodium carbonate, and concentrating said white liquor to deposit therefrom sodium chloride and sodium carbonate and to provide concentrated white liquor, the improvement which comrpises forming an aqueous solution from the deposited sodium chloride and sodium carbonate, and reacting said sodium carbonate in said aqueous solution with a chlorine-containing material selected from chlorine and hydrogen chloride.

24. The process of claim 23 wherein said solid mass additionally contains sodium sulphide and said green liquor contains said sodium sulphide.

25. The process of claim 23 wherein said solid mass is formed by fractionating a smelt containing sodium sulphide, sodium chloride and sodium carbonate to

separate said sodium sulphide from said smelt, said smelt being formed in the recovery of spent chemicals from the pulping of cellulosic fibrous material.

26. The process of claim **25** wherein said fractionation is achieved by contacting said smelt with said concentrated white liquor to dissolve said sodium sulphide from said smelt into said white liquor.

27. The process of claim **25** wherein said fractionation is achieved by contacting said smelt with water to dissolve preferentially sodium sulphide from said smelt.

28. The process of claim **25** wherein said fractionation is achieved by dissolving said smelt in water, and evaporating the resulting solution to deposit said solid mass containing sodium chloride and sodium carbonate therefrom.

29. A process for the production of a pulp of a cellulosic fibrous material which comprises pulping said cellulosic fibrous material with a pulping liquor, separating pulped material from spent pulping liquor, forming a sodium chloride- and sodium carbonate-containing smelt from said spent pulping liquor, forming a sodium chloride- and sodium carbonate-containing white liquor from said smelt, concentrating said white liquor to deposit therefrom sodium chloride and sodium carbonate, forming an aqueous solution of the deposited sodium chloride and sodium carbonate, reacting said sodium carbonate in said aqueous solution with a chlorine-containing gaseous material selected from chlorine and hydrogen chloride thereby forming a reaction product consisting of sodium chlorate and sodium chloride when said gaseous material is chlorine and sodium chloride when said gaseous material is hydrogen chloride, forming sodium chlorate by electrolysis of an aqueous solution of sodium chloride, forming an aqueous solution in a reaction zone of sodium chlorate, sodium chloride and sulphuric acid, generating a gaseous mixture of chlorine dioxide and chlorine from said aqueous solution and removing said mixture from said reaction zone, subjecting said pulp after removal of said spent pulping liquor to a bleaching operation which includes bleaching with one or more of said gaseous mixture of chlorine dioxide and chlorine, and utilizing said reaction product of said sodium carbonate and said chlorine-containing gaseous material and said deposited sodium chloride in at least one of the formation of said sodium chlorate and the formation of said gaseous mixture of chlorine dioxide and chlorine.

30. The process of claim **25** wherein said aqueous solution in said reaction zone is maintained at its boiling point and said reaction zone is subjected to a subatmospheric pressure, whereby said gaseous mixture of chlorine dioxide and chlorine is removed from said reaction zone by steam formed from said aqueous solution.

31. The process of claim **25** wherein spent chemicals are recovered from said bleaching operation and wherein said sodium chloride- and sodium carbonate-containing white liquor is formed by dissolving said smelt in an aqueous material including said spent chemicals to provide a green liquor and causticizing a substantial proportion of the sodium carbonate content of said green liquor.

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