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Rapson et al.

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[54] **RECOVERY OF SODIUM CHLORIDE FROM SPENT PULPING LIQUORS**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **162/17,** 162/30, 423/207

[51] **Int. Cl.** **D21c 3/00,** D21c 11/12

[58] **Field of Search** 162/17, 30, 82, 45; 23/48, 66, 134; 423/207

[56] **References Cited**

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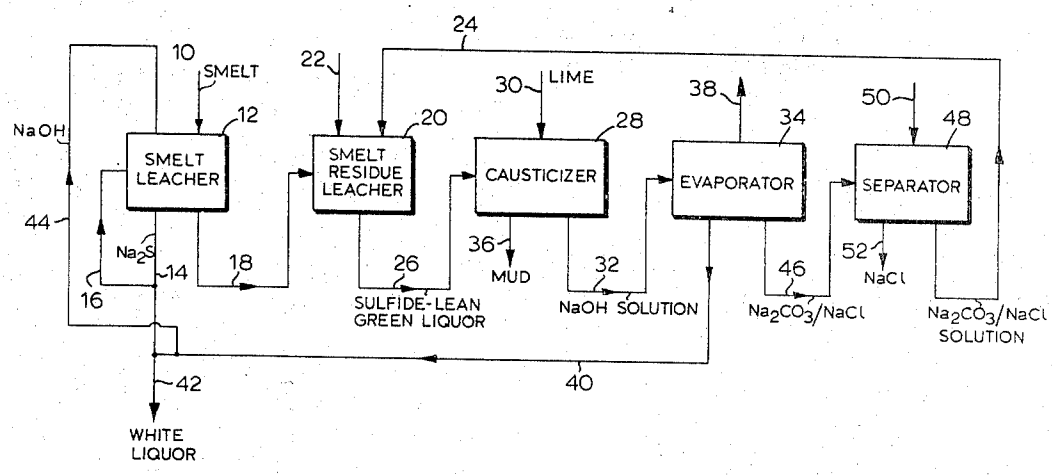
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[57] **ABSTRACT**

A sodium sulfide and sodium chloride-containing smelt formed from waste pulping liquor is fractionated to separate the sodium sulfide from the sodium chloride.

6 Claims, 2 Drawing Figures



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SHEET 1 OF 2

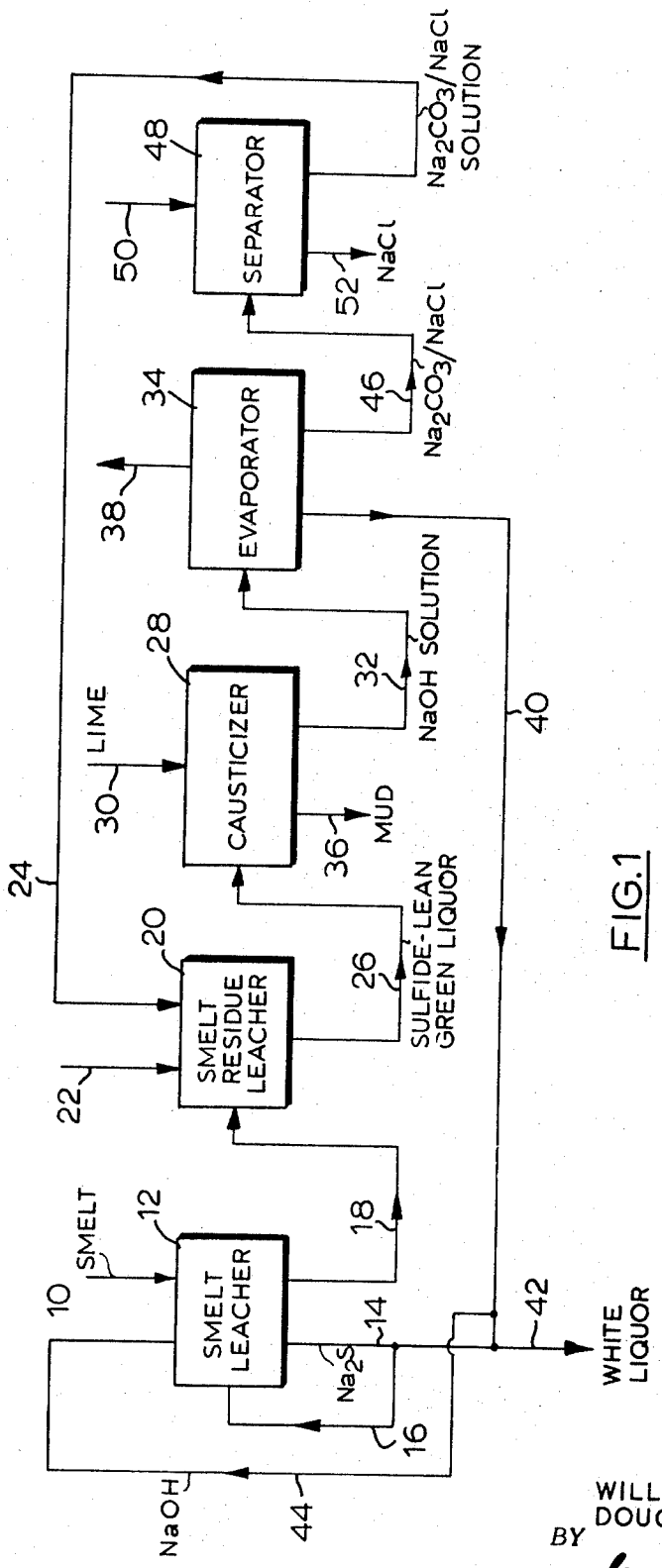


FIG. 1

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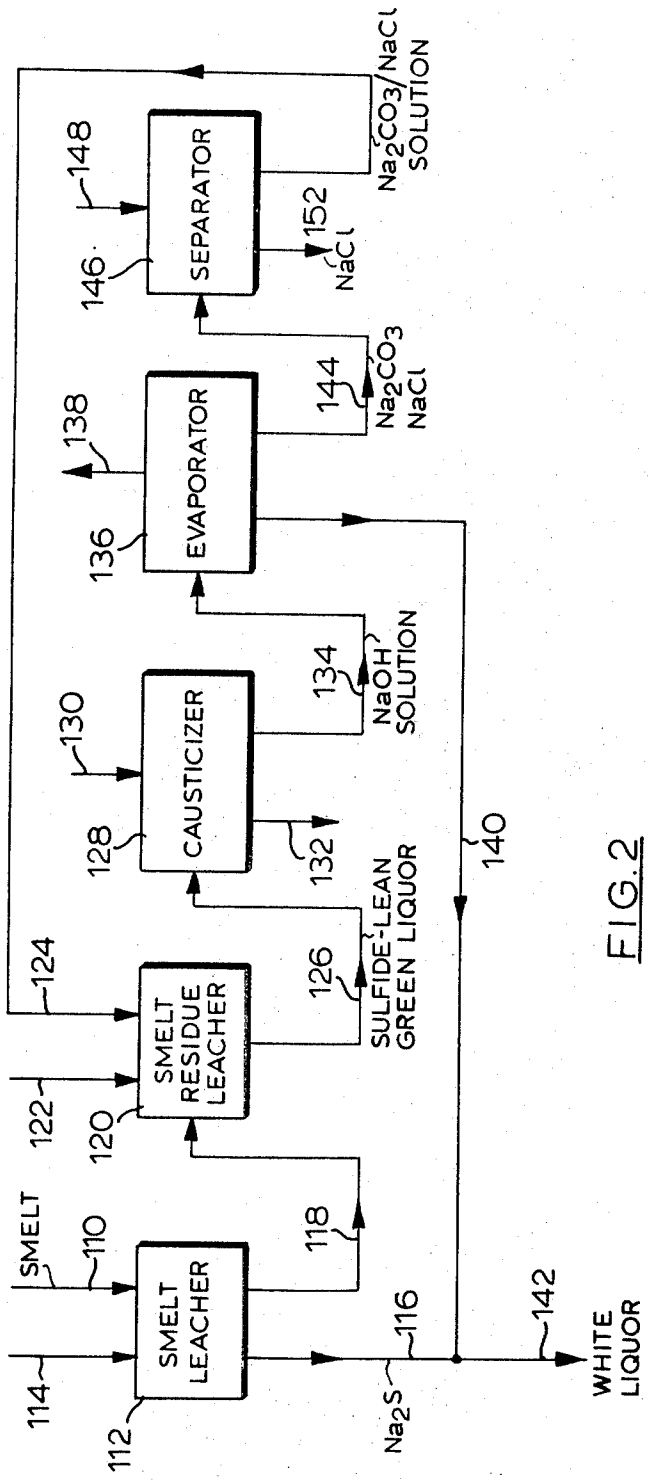


FIG. 2

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RECOVERY OF SODIUM CHLORIDE FROM SPENT PULPING LIQUORS

This invention relates to the recovery of chemicals from the pulping of cellulosic fibrous material and more particularly to improved efficiency in the operation of pulp mills.

The invention will be described particularly with reference to the Kraft mill process but the invention is not limited thereto. The operations described below readily may be integrated with other pulping processes, for example, the alkafide, sodium base — sulfite, cold alkali refining prehydrolysis kraft, soda, polysulfide and holopulping processes.

In pulping operations, the raw cellulosic fibrous material, generally wood chips, is digested in a pulping liquor, generally known as a "white liquor". This latter term is used in this specification generally to refer to liquors containing dissolved sodium hydroxide. After the digestion step, the pulp is separated from spent pulping liquor, known as "black liquor".

In the normal Kraft process, the cellulosic fibrous material, generally wood chips, is digested by heating with a white liquor containing sodium sulfide and sodium hydroxide to dissolve from the wood chips a substantial part of the hemicelluloses and lignin therein. The fibrous material so produced is separated from the resulting black liquor, washed in a brown stock washer, and, thereafter, may be passed to a bleaching process.

The black liquor is subjected to a series of operations in a recovery system. The black liquor first is concentrated by evaporation of water and the concentrated black liquior 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 dregs resulting from the clarification, generally consisting of insoluble salts of metal cations other than sodium and potassium, are washed with water.

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. The wash water from the dregs and the mud usually is used as water for dissolving the smelt.

Sodium sulfate is added to the recovery operation to provide make-up sodium and sulfur values to the system. Generally the sodium sulfate is added to the balck liquor before it is fed to the furnace. The sodium sulfate forms in the furnace sodium sulfide and sodium carbonate, the sodium carbonate being converted to sodium hydroxide on later causticization. In this manner, the sodium hydroxide and sodium sulfide content of the white liquor is maintained at the desired level.

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, it is not possible to remove all of the sodium chloride by such washing, 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. In a preferred aspect of the present invention, sodium chloride also is introduced into the recovery system with bleach plant effluent.

The sodium chloride passes without change through the black liquor recovery operations and recycles in the white liquor, and, therefore, constitutes a dead load in the system. 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.

The present invention provides a process wherein a sodium sulfide- and sodium chloride-containing smelt is subjected to fractionation to obtain an aqueous solution of sodium sulfide and to leave a solid deposit containing sodium chloride.

The smelt may be of any convenient type containing sodium sulfide and contaminating sodium chloride. Preferably, the smelt is one formed in a Kraft mill black liquor recovery system and, therefore, in addition to sodium sulfide and sodium chloride, contains sodium carbonate. In that event, the residue remaining after leaching the sodium sulfide from the smelt contains sodium chloride and sodium carbonate. The invention is hereinafter more particularly described with reference to such a smelt.

The fractionation of a smelt may be achieved in a number of different ways. For example, the smelt may be leached with water, or recycled sodium sulfide solution to dissolve preferentially sodium sulfide and leaving solid sodium carbonate and sodium chloride. Small amounts of the sodium chloride and the sodium carbonate generally also are dissolved in the solvent.

Fractionation of the smelt may be achieved in other manners. In one such alternative, aqueous sodium hydroxide solution for example, in the form of recycling sodium sulfide-lean white liquor, after concentration to precipitate sodium chloride therefrom, may be utilized to fractionate the sodium sulfide-containing smelt, to thereby form a sodium hydroxide- and sodium sulfide-containing white liquor, which may be used, optionally, after dilution, as pulping liquor in a Kraft mill. The sodium sulfide-lean white liquor concentrated in accordance with the above-mentioned process is saturated with respect to both sodium chloride and sodium carbonate and hence upon contact with the sodium sulfide-containing smelt, sodium chloride and sodium carbonate are deposited from the sulfide-lean white liquor as the sodium sulfide is dissolved in the white liquor.

The contact of a sodium sulfide-containing smelt by a relatively concentrated sodium hydroxide solution constitutes the invention of copending application Ser. No. 100,083 filed concurrently herewith.

The smelt also may be fractionated by contact with a dilute aqueous sodium hydroxide solution or a dilute sulfide-lean white liquor, thereby forming pulping liquor which may be used in a Kraft mill. Unless the solvent is already saturated with respect to sodium chloride and sodium carbonate, then some sodium chloride and sodium carbonate also are dissovled from the smelt.

The smelt which is fractionated in accordance with this invention may be in several alternative physical forms, for example, the smelt may have been crushed after solidification, or comminuted while molten, i.e.

"wooled" by using high velocity steam jets. The comminuted solidified smelt then is fractionated as described above.

Another manner of fractionating the sodium sulfide from the smelt in accordance with this invention is to prepare the green liquor in the conventional manner and then evaporate water therefrom to precipitate the sodium carbonate and sodium chloride.

The leaching of the sodium slufide by the above-described methods may be conducted over a wide range of desired temperatures, generally from about 25°C to about 130°C.

Where the fractionation of the smelt occurs using water or recycled sulfide solution to form an aqueous solution of sodium sulfide, it is preferred to carry out the fractionation to provide a sodium sulfide solution having a concentration of about 20 to 35 wt.% Na_2S. Where such fractionation is carried out by leaching using recycled relatively concentrated sodium hydroxide solution, then it is preferred taht the concentration of Na_2S + NaOH in the resultant solution be about 25 to 50 wt.%.

When fractionation of the smelt is achieved using sodium sulfide solution or water, then the resulting sodium sulfide solution may be combined with sulfide-lean white liquor, preferably a white liquor which has been concentrated in accordance with the invention of the above-mentioned process to precipitate sodium chloride therefrom to provide a pulping liquor, which may require dilution prior to use in a Kraft mill operation.

The solid mixture of sodium carbonate and sodium chloride remaining after leaching of the sodium sulfide from the smelt may be subjected to several operations, similar to those employed in the formation of pulping liquor for a Kraft mill. Thus, the mixture may be dissolved in water to provide a green liquor. This green liquor may contain residual quantities of sodium sulfide not leached from the smelt in accordance with the invention and is termed "sulfide-lean" green liquor for this reason. The sulfide-lean green liquor is causticized to convert substantially the sodium carbonate-content thereof to sodium hydroxide to thereby provide a white liquor after removal of precipitated calcium carbonate.

The green liquor may be clarified prior to causticization to remove "heavy dregs" of the smelt. The "light" dregs of the smelt may be removed from the sodium sulfide solution.

The resulting white liquor containing sodium hydroxide may be recycled to contact more smelt to dissolve the sodium sulfide therefrom, or may be utilized in a bleach plant operation. In accordance with a preferred embodiment of the invention, however, the white liquor is concentrated to precipitate part of the sodium chloride content therefrom.

The resulting sulfide-lean and sodium chloride-lean white liquor may be combined with the sodium sulfide solution obtained in accordance with this invention as set forth above by leaching the smelt to provide concentrated white liquor, which may require dilution prior to recycle to the digester. Alternatively, the white liquor may be used to fractionate the smelt in accordance with this invention and a specific embodiment of the invention of copending application Ser. No. 100,083.

The provision of a sodium sulfide-lean green liquor in a Kraft mill recovery operation has certain advantages as compared to the provision of a green liquor directly from the smelt in accordance with the conventional recovery operation, such green liquor, therefore, containing the sodium sulfide content of the smelt as well as the sodium carbonate and sodium chloride content.

One advantage is that smaller volumes of water are required to form the green liquor in the case of a sulfide-lean green liquor provided in accordance with the present invention, to produce a given amount of sodium hydroxide. In this regard, it can be shown that the formation of a sulfide-lean green liquor may reduce the volume of liquor required to produce a given volume of sodium hydroxide to approximately 70 percent of that required for conventional green liquor.

In conventional green liquor, some hydrolysis of the sodium sulfide content to sodium hydroxide occurs and the presence of this sodium hydroxide inhibits the causticization reaction. By the use of a sulfide-lean green liquor, this hydrolysis with consequent inhibition of the causticizing process is eliminated.

Generally, not all of the sodium carbonate is converted to sodium hydroxide upon the causticization of a green liquor, even in the case where the green liquor is sulfide-lean, although the efficiency of the causticization is improved in this case as noted above. The unconverted sodium carbonate remaining after the causticization step represents a dead load in the system and may recycle with the sodium chloride through the system, if the sulfide-lean white liquor resulting from the causticization step, after mixing with the aqueous sulfide solution, or after being utilized to fractionate the smelt, is recycled to the digester.

In accordance with a preferred embodiment of the invention, the white liquor is concentrated, so that the unconverted sodium carbonate is partially deposited from the white liquor along with sodium chloride.

In order to separate pure sodium chloride from the mixture of sodium carbonate and sodium chloride precipitated upon concentration, preferably evaporation, of the white liquor the precipitated mixture may be leached with water whereby all of the sodium carbonate is dissolved together with part of the sodium chloride, thereby leaving pure sodium chloride.

Alternatively, the white liquor may be subjected to a two-stage evaporative crystallization. In the first stage pure sodium chloride is precipitated, and, as the evaporation continues, in the second stage a mixture of sodium carbonate and further sodium chloride is precipitated. This mixture may be dissolved in water to provide a solution of sodium carbonate and sodium chloride.

Any sodium sulfate which may be present in the white liquor may coprecipitate with the sodium chloride and sodium carbonate.

The solution of sodium carbonate and sodium chloride, formed by leaching of a precipitated mixture or from the precipitate of the second stage of a two-stage evaporative crystallization, may be recycled to dissolve the solid mixture of sodium carbonate and sodium chloride separated from the smelt by the fractionation process of the present invention, or to dissolve the smelt in the case where there is no initial fractionation of the smelt. Such recycle constitutes the invention of copending application Ser. No. 100,082 filed concurrently herewith. In this way, while the concentration of sodium chloride in the white liquor, prior to evapora-

tion, is increased as compared to the concentration in the white liquor without recycle, such further sodium chloride does not contaminate the remainder of the plant since it is precipitated on concentration of the white liquor.

As indicated above, the white liquor, after concentration to deposit part of the sodium chloride and sodium carbonate, may be fed to the smelt leacher to dissolve the sodium sulfide therein. Since the white liquor is saturated with respect to sodium chloride and sodium carbonate and sodium sulfide has a higher solubility than these materials, contact of the white liquor with the smelt causes not only sodium sulfide to dissolve but also sodium carbonate and sodium chloride to precipitate from the white liquor. The recycle of the sodium hydroxide solution as leach water for the smelt reduces the quantity of water required to be evaporated in the system and thereby reduces the cost per ton of pulp. In this way, the white liquor sent to the pulping operation contains less sodium chloride and sodium carbonate than after the evaporation, without the necessity of increased evaporation. The sodium chloride and sodium carbonate precipitated upon leaching of the smelt forms green liquor with the remainder of the smelt.

The Kraft mill operation may be integrated in accordance with a preferred embodiment of this invention with a bleach plant to eliminate liquid effluents from such plants. Bleach plants generally subject pulp to a series of operations to provide a bleached pulp suitable for use in the formation of end-products, such as paper. Typically, such series of operations includes one or more bleaching steps and one or more caustic extraction steps. Usually, the pulp is washed after each of these operations, so that spent wash water contains dissolved chemicals, including sodium chloride, and fibrous material removed from the pulp.

It has generally been the case that this spent wash water has been discharged to water bodies, such as streams, rivers, lakes and oceans, without any attempt to recover the chemicals, although in some instances solid particle recovery operations are included. However, one of the main reasons that no attempt has been made to recover these chemicals is because they are very dilute. The spent wash water is harmful to aquatic and marine biotia and polluting from the point of view of containing fibres and materials consuming oxygen present in the water. It is desirable to avoid such environmental pollution and this is achieved in accordance with this embodiment of the invention in the manner described below.

A particular bleach plant operation which has been employed involves an initial bleaching of the pulp with an aqueous solution containing chlorine and chlorine dioxide, an intermediate washing, a caustic extraction using aqueous sodium hydroxide solution, a further washing, a bleaching with an aqueous solution of chlorine dioxide, another washing, a further caustic extraction using aqueous sodium hydroxide solution, an additional washing, a final bleaching with aqueous chlorine dioxide solution and a final washing. This is the so-called CEDED operation. Alternatives of this operation are known and may be employed. It is preferred to provide a flow of wash water through the bleach plant which is countercurrent to the flow of the pulp. In such countercurrent operation spent wash water from one washing step is utilized as the wash water for the preceding washing step. The spent wash water from the washing of the pulp after the first bleaching step constitutes the bleach plant effluent (known as BPE).

The environmental problems posed by discharge of bleach plant effluent to water bodies are eliminated by using the effluent to provide at least part, preferably all, of the overall water requirement of the system of conversion of smelt to white liquor. Thus, the bleach plant effluent may be used to dissolve the smelt residue after removal of sodium sulfide to form green liquor or to dilute already formed sulfide-lean green liquor. Further, the effluent may be used to leach the precipitated mixture of sodium chloride and sodium carbonate from the concentration of the white liquor where such is carried out, to dissolve the sodium carbonate and part of the sodium chloride. In addition, such effluent may be used to wash the calcium carbonate mud deposited in the causticization step, and to wash dregs. Further, the effluent water may be used to dilute the concentrated white liquor prior to recycle to the digester.

In this way the chemicals contained in the bleach plant effluent are retained within the mill and the pollutant effect of these materials is eliminated. In addition, fresh water requirements of the mill and the cost of water treatment are reduced.

The addition of water such as bleach plant effluent to the sulfide-lean green liquor increases causticizing efficiency. This in turn improves any sodium chloride recovery carried out, since the amount of sodium carbonate to be recycled is reduced. Water is evaporated during the concentration step and the condensed water may be returned to the bleach plant as wash water.

The sodium chloride recovered in the above-described operations may be used to generate chlorine dioxide and chlorine by reacton with sodium chlorate and sulphuric acid. It also may be used to generate sodium hydroxide or sodium chlorate by electrolysis.

The present invention will be further described, by way of illustration, with reference to the accompanying drawings, in which,

FIG. 1 is a schematic flow sheet of part of a Kraft pulp mill recovery system embodying the present invention; and

FIG. 2 is a schematic flow sheet of part of an alternative Kraft pulp mill recovery system embodying the present invention.

There have been omitted from the drawings separators, washers, etc. in order to simplify the matter appearing therein.

With reference to FIG. 1, smelt from a furnace of a Kraft mill recovery system, including sodium sulfide, sodium chloride and sodium carbonate, is fed by line **10** to a smelt leacher **12**. The smelt, which may be "wooled" by the action of steam, is leached with recycled sodium hydroxide solution to fractionate the smelt. The leaching of the smelt with recycled sodium hydroxide solution constitutes the invention of copending application Ser. No. 100,083. Where such leaching is carried out with sulfide-lean white liquor concentrated in accordance with the process described above, and recycled by lines **40** and **44**, then as the sodium sulfide is dissolved from the smelt, more sodium chloride and sodium carbonate are deposited from the liquor and these deposited slats are forwarded with the material remaining from the smelt after leaching.

Liquid effluent from the leacher **12** exits through line **14** and consists of white liquor where the leaching occurs with recycled sodium hydroxide solution alone or

both recycled sodium hydroxide solution and sodium sulfide solution. The liquid effluent from the smelt leacher **12** may be recycled through line **16** to the smelt leacher **12.**

A solid residue consisting of substantially sodium carbonate and sodium chloride and any undissolved sodium sulfide, is fed from the smelt leacher **12** by line **18** to a smelt residue leacher **20.**

The sodium carbonate and sodium chloride may be separated from the sodium sulfide by the alternative procedure outlined above, i.e. formation of green liquor in the normal way from the smelt followed by evaporative crystallization of sodium carbonate and sodium chloride.

The smelt residue is contacted in leacher **20** by water fed through line **22** and a recycled solution of sodium carbonate and sodium chloride fed through line **24.**

Such recycle of sodium carbonate and sodium chloride solution constitutes the invention of copending application Ser. No. 100,082.

The water fed through line **22** may be at least partially and for economic reasons preferably is partially bleach plant water effluent. Calcium carbonate mud wash water also may form part of the water feed. Preferably, the water fed through line **22** consists partially of bleach plant water effluent and partially of mud wash water. As indicated below, the mud wash water preferably is bleach plant effluent, and, therefore, in effect, the water in line **22** in this preferred embodiment is all bleach plant effluent.

The resulting sulfide-lean green liquor is fed through line **26** to a causticizer **28.** The green liquor is causticized with lime fed through line **30.** The sodium carbonate thereby substantially is converted to sodium hydroxide and calcium carbonate precipitates as a mud.

Dregs from the residue leacher **20** may be fed to a dregs washer (not shown) and washed therein. The remaining solids may be passed to a sewer as a slurry. The wash water fed to the dregs washer may be effluent water from a bleaching plant.

The reaction between the lime and the sodium carbonate is incomplete and therefore the sodium hydroxide solution formed contains unreacted sodium carbonate in addition to sodium chloride.

The calcium carbonate mud leaves the causticizer **28** by line **36,** is washed, preferably with bleach plant effluent, and reconverted to lime in conventional manner. The mud wash water then may be fed to the smelt residue leacher **20** as described above.

The sodium hydroxide solution formed in the causticizer **28** is fed by line **32** to an evaporator **34.** In the evaporator **34,** the sodium hydroxide solution is subjected to concentration and the resulting water vapor leaves by line **38.** The evaporator may be maintained under a reduced pressure to lower the boiling point of the solution. Such water vapor is condensed and may be used as wash water in a bleach plant, so that part of the spent wash water from the bleach plant is substantially purified and returned to the bleach plant as fresh wash water.

This evaporation is continued to induce crystallization of at least part of the sodium chloride and sodium carbonate contents of the sodium hydroxide solution. Such crystallization may be carried out in a single step, in which case a mixture of sodium carbonate and sodium chloride is precipitated, or in two steps in which case pure sodium chloride first is precipitated and then a mixture of sodium carbonate and sodium chloride is precipitated. In the single step case, sodium chloride first is precipitated and subsequently a mixture but no attempt is made to recover the sodium chloride first precipitated.

The white liquor so produced, having a reduced sodium chloride content, is fed from the evaporator **34** by line **40** to admix with sodium sulfide solution from the smelt leacher **12** to form a white liquor containing sodium hydroxide and sodium sulfide, which is fed by line **42** to a digester (not shown). It may be necessary to dilute this latter white liquor prior to feed to the digester. Bleach plant effluent may be used to achieve such dilution. Alternatively, at least part of the sodium hydroxide solution may be used to leach the smelt and is fed by line **44** to the smelt leacher **12** for this purpose.

The crystallized sodium chloride and sodium carbonate mixture is fed from the evaporator **34** by line **46** to a separator **48.** In the case where the evaporation of the sodium hydroxide solution occurs in two stages, the pure sodium chloride is first removed from the evaporator and then the mixture of sodium chloride and sodium carbonate passed to the separator **48.**

In the separator **48,** the mixture of sodium chloride and sodium carbonate is contacted with water fed through line **50.** The sodium carbonate and part of the sodium chloride are preferentially dissolved leaving substantially pure sodium chloride which is removed from the separator through line **52** as a cake for further purification and later use, such as in the formation of chlorine dioxide and chlorine, the formation of sodium chlorate or the formation of sodium hydroxide by electrolysis.

The resulting aqueous solution of sodium carbonate and sodium chloride is recycled by line **24** to the smelt residue leacher **20.**

The water fed by line **50** to the separator **48** may be bleach plant effluent, usually as part of the wash water used to wash the lime mud.

Other minor refinements of the operation just described may be made, and such refinements lead to water economy. For example, the effluent from the smelt leacher **12** consists of a slurry of sodium chloride and sodium carbonate in sodium sulfide. After separation of the sodium sulfide, the resulting solids may be subjected to displacement washing by water. Such water may be bleach plant effluent and preferably is part of the spent dregs wash water and part of the water obtained from calcium carbonate mud dewatering. Where such dregs and mud wash waters are bleach plant effluent, then the BPE is providing the source of a further water requirement of the system.

Calcium carbonate mud precipitated in causticizer **28** may be mixed with part of the spent dregs wash water and passed to a storage area. In the storage area, the mud may be repulped by admixture with bleach plant effluent water, and the slurry so obtained passed to a mud dewaterer wherein water is recovered from the slurry. The resulting thick slurry then is passed to a roaster to reform the lime. The carbon dioxide and water vapor formed in the roaster may be vented to atmosphere.

The water recovered in the mud dewaterer may be used partially as already described as part of the feed water in line **22** and to slurry the sodium carbonate and sodium chloride. In addition, such water may be partially used in other refinements of the operation. Thus,

the solution formed in the evaporator **34** may be removed as a slurry of sodium carbonate and sodium chloride in sodium hydroxide. The solids are separated and the sodium hydroxide solution passed for further use as described above. The solids may be washed by displacement washing with part of the wash water from the mud dewaterer.

It will be seen that a combination of these refinements leads to economic utilization of water and fully integrates the operation with effluent water from a bleach plant, using as the only water supply bleach plant effluent and completely eliminating the discharge of harmful pollutants from the bleach plant.

In an alternative embodiment of the form of the invention shown in FIG. **1**, the white liquor having a reduced sodium chloride content in line **40** may be used to prepare caustic extraction and sodium hypochlorite solutions for the bleach plant. Further, the sulfide-lean green liquor in line **26** may be employed to prepare sodium hydrosulfite from zinc hydrosulfite.

Turning now to the embodiment of FIG. **2**, this is similar to FIG. **1**, except that the sodium chloride-lean white liquor is not utilized to fractionate the smelt. Smelt from a furnace of a Kraft mill recovery system containing sodium sulfide, sodium chloride and sodium carbonate, is fed by line **110** to a smelt leacher **112.** The smelt, which may be wooled initially by the action of steam, is leached with water fed through line **114.** Liquid effluent, generally consisting of an aqueous solution of sodium sulfide exits through line **116.** It may be necessary to recycle the sodium sulfide solution in line **116** to the leacher to build up the sodium sulfide content to the desired level.

The water fed through line **114** may be at least partially and preferably is bleach plant effluent.

A solid residue consisting of substantially sodium carbonate and sodium chloride, together with any undissolved sodium sulfide, is fed from the smelt leacher **112** by line **118** to a smelt residue leacher **120.** The smelt residue is contacted in leacher **120** by water fed by line **122** and a recycled solution of sodium carbonate and sodium chloride fed through line **124.**

The water fed through line **122** preferably is bleach plant effluent. The bulk of the bleach plant effluent used in line **122** is passed directly to the smelt residue leacher, and the remainder is passed thereto after being utilized as calcium carbonate mud wash water.

The resulting sulfide-lean green liquor is fed through line **126** to a causticizer **128.** The green liquor is causticized with lime led through line **130.** The sodium carbonate thereby substantially is converted to sodium hydroxide and calcium carbonate precipitates as a mud.

The calcium carbonate mud leaves the causticizer **128** by line **132,** is washed, preferably with bleach plant effluent, and reconverted to lime in conventional manner.

The sodium hydroxide solution produced in the causticizer contains some unreacted sodium carbonate since the reaction between the lime and the sodium carbonate is incomplete.

The sodium hydroxide solution is fed by line **134** to an evaporator **136.** In the evaporator **136,** the sodium hydroxide solution is subjected to concentration in accordance with the present invention and the resulting water vapor leaves by line **138.** This water vapor is condensed and the water may be used as wash water in a bleach plant.

The evaporation concentrates the sodium hydroxide until crystallization of sodium chloride and sodium carbonate occurs to the extent required. The white liquor produced having a reduced sodium chloride content is fed from the evaporator **136** by line **140** to mix with the sodium sulfide solution in line **116** to provide a white liquor in line **142** suitable for use as pulping liquor in a Kraft mill digester (not shown), optionally after dilution. Where such dilution occurs, it is preferably achieved by using bleach plant effluent.

The crystallized sodium chloride and sodium carbonate mixture is fed from the evaporator **136** by line **144** to a separator **146.** In the separator **146,** the mixture of sodium chloride and sodium carbonate is contacted with water fed by line **148,** preferably the mud wash water. The sodium carbonate and part of the sodium chloride are dissolved preferentially leaving substantially pure sodium chloride which is removed from the separator **146** through line **150** as a cake for further purification and later use.

As in the embodiment of FIG. **1**, the evaporation in evaporator **136** may have been conducted in such a manner to recover part of the sodium chloride in substantially pure form.

The resultant solution of sodium carbonate and sodium chloride passes from the separator **146** by line **124** to smelt residue leacher **120.**

A number of modifications and minor refinements are discussed above with reference to FIG. **1** and these modifications and minor refinement as applicable, may be utilized with this embodiment.

The invention is illustrated further by the following Examples:

EXAMPLE I

Utilizing experimental observations of solubility a mass balance for a typical arrangement was arrived at for the embodiment of the invention illustrated in FIG. **1.** All quantities are pounds weight per theoretical ton of pulp. In the following calculation, perfect solid phase/aqueous phase separation is assumed for convenience.

A typical Kraft mill recovery system smelt contains 195 lb. Na_2S, 225 lb. NaCl and 808 lb. Na_2CO_3. The sodium chloride is 120 lb. from recycle and 115 lb. from bleach plant effluent. In arriving at this mass balance, it is assumed, for the sake of convenience, that the bleach plant effluent has been added to the black liquor and hence the sodium chloride content of the effluent appears in the smelt. This material is leached with sodium hydroxide solution fed by lines **40** and **44,** and as will become apparent, this solution contains 1870 lb. water, 600 lb. NaOH, 249 lb. NaCl and 61 lb. Na_2CO_3. It has been observed experimentally that this solution is saturated at 50°C with respect to both sodium chloride and sodium carbonate. Upon contact of this solution with the sodium sulfide containing smelt, sodium sulfide is dissolved from the smelt and an equivalent quantity of sodium chloride and sodium carbonate are deposited from the solution, so that the resulting pulping liquor contains 1735 lb. water, 600 lb. NaOH, 195 lb. Na_2S, 110 lb. NaCl and 13 lb. Na_2CO_3. This latter solution has been found experimentally to be saturated with respect to both sodium chloride and sodium carbonate.

The smelt residue fed by line **18** to the smelt residue leacher **20** contains 364 lb. NaCl, 856 lb. Na_2CO_3 and

135 lb. water as water of crystallization of the sodium carbonate. The residue is contacted with 2640 lb. water fed by line **22** and recycle solution in line **24** containing 624 lb. water, 147 lb. NaCl and 134 lb. Na_2CO_3. The recycle solution has been observed experimentally to be saturated with respect to sodium chloride at 30°C. The resulting green liquor in line **26** contains 3400 lb. water, 511 lb. NaCl and 990 lb. Na_2CO_3. This solution was found to be unsaturated at 30°C.

Assuming 80 percent efficiency in causticization, the white liquor in line **32** formed by causticization of the green liquor contains 3592 lb. water, 600 lb. NaOH, 511 lb. NaCl and 197 lb. Na_2CO_3. The increase in the quantity of water in line **32** as compared to line **26** is water gained from mud washing and is included for convenience. This solution was found to be unsaturated at 50°C. This solution is boiled under reduced pressure to evaporate 1700 lb. water therefrom and thereby precipitate 262 lb. NaCl and 134 lb. Na_2CO_3. This precipitated material passes to separator **48** together with 23 lb. of water as water of crystallization of sodium carbonate. Therefore, the solution recycled by line **40,** as already indicated, contains 1870 lb. water, 600 lb. NaOH, 249 lb. NaCl and 61 lb. Na_2CO_3.

To the sodium chloride and sodium carbonate mixture in the separator was added 601 lb. water to form a solution of sodium carbonate and sodium chloride containing as indicated previously, 624 lb. water, 147 lb. NaCl and 134 lb. Na_2CO_3, leaving 115 lb. NaCl which is recovered through line **52** for further use.

It is apparent, therefore, that 115 lb. of sodium chloride introduced to the smelt other than by pulping liquor recycle is removed from the system.

EXAMPLE II

A mass balance for a typical arrangement was arrived at for the embodiment of FIG. **2,** utilizing experimental observations. As in the case of Example **1,** for convenience, perfect solid phase/aqueous phase separation is assumed.

A typical Kraft mill recovery operation smelt containing 195 lb. Na_2S, 235 lb. NaCl and 815 lb. Na_2CO_3 is contacted with 690 lb. water fed by line **114** to leach sodium sulfide and part of the sodium chloride and sodium carbonate from the smelt to yield a solution in line **116** containing 550 lb. water, 195 lb. Na_2S, 35 lb. NaCl and 7 lb. Na_2CO_3. This solution was found to be saturated with respect to both sodium chloride and sodium carbonate at 50°C.

The residual solid mixture contains 200 lb. NaCl, 808 lb. Na_2CO_3 and 140 lb. water as water of crystallization of the sodium carbonate. After passage by line **118** to the smelt residue leacher **120,** the mixture is contacted with 2522 lb. water fed by line **122** and a recycle solution of sodium chloride and sodium carbonate containing 848 lb. water, 200 lb. NaCl and 182 lb. Na_2CO_3 fed by line **124.** This latter solution has been found to be saturated with respect to sodium chloride at 30°C.

This provides a green liquor containing 3510 lb. water, 400 lb. NaCl and 990 lb. Na_2CO_3. This solution was found to be unsaturated with respect to either sodium chloride or sodium carbonate at 30°C. After causticization at 80 percent efficiency, in causticizer **128,** and separation of the calcium carbonate mud formed thereby, the resultant white liquor contains 3703 lb. water 600 lb. NaOH, 400 lb. NaCl and 197 lb. Na_2CO_3. The increase in the quantity of water is due to water gained from mud washing.

The white liquor is evaporated in the evaporator **136** to remove 2482 lb. of water from the liquor and to deposit therefrom 315 lb. sodium chloride and 182 lb. sodium carbonate. The resulting concentrated white liquor contains 1190 lb. water, 600 lb. NaOh, 85 lb. NaCl and 15 lb. Na_2CO_3 and this solution was observed experimentally to be saturated with respect to both sodium chloride and sodium carbonate at 50°C.

The concentrated white liquor was passed through line **140** to mix with sodium sulfide solution in line **116** to provide a pulping liquor in line **142** containing 1740 lb. water, 600 lb. NaOH, 195 lb. Na_2S, 120 lb. NaCl and 22 lb. Na_2CO_3. It was found that this solution was supersaturated with respect to sodium chloride and sodium carbonate at 50°C and therefore in this operation it is necessary either to dilute the white liquor in line **140** prior to mixing the sodium sulfide solution, or to mix the two solutions and remove precipitated sodium chloride and sodium carbonate prior to use a pulping liquor.

The residue from the evaporator **136** consisting of 315 lb. NaCl, 182 lb. Na_2CO_3 and 31 lb. of water as water of crystallization of sodium carbonate is passed to a separator **146** wherein it is contacted with 817 lb. water to form the recycle solution in line **124.** One hundred fifteen lb. of sodium chloride is recovered through line **152.**

In this way, a considerable quantity of sodium chloride introduced into the system with the smelt is removed and is not recycled with the pulping liquor to the digester.

By reducing the quantity of sodium chloride in the recycling white liquor in the manner described above, exposure of the digester, the black liquor evaporator and the furnace to high concentrations of chloride is avoided.

The integrated system outlined above is extremely flexible and modifications may be made thereto to suit individual requirements without departing from the scope of the invention.

Comparison of the quantities of water to be evaporated in the examples indicates the increased efficiency of the process of Example I over the process of Example II.

We claim:

1. A process for the pulping of cellulosic fibrous material, including the steps of contacting said cellulosic fibrous material with a pulping liquor consisting substantially of an aqueous solution of a sodium sulfide, separating pulped material from spent pulping liquor, forming a smelt from said spent pulping liquor consisting substantially of sodium sulfide and sodium chloride, fractionating the components of said smelt to provide a substantially sodium chloride-free aqueous solution of sodium sulfide and a solid material consisting substantially of sodium chloride, and recycling said latter aqueous solution of sodium sulfide to said contacting step as at least part of said pulping liquor.

2. The process of claim **1** wherein said smelt is fractionated by contact with water to dissolve preferentially said sodium sulfide.

3. The process of claim **1** wherein said latter aqueous solution of sodium sulfide is utilized to fractionate said smelt to preferentially dissolve said sodium sulfide from further smelt prior to recycle to said contacting step.

4. The process of claim 1 wherein said smelt is subjected to the action of steam to provide said smelt in a wool-like form prior to fractionation.

5. The process of claim 1 including introducing to said spent pulping liquor a sodium chloride-containing aqueous medium whereby said smelt contains sodium chloride.

6. The process of claim 5 wherein said sodium chloride-containing aqueous medium is bleach plant effluent.

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