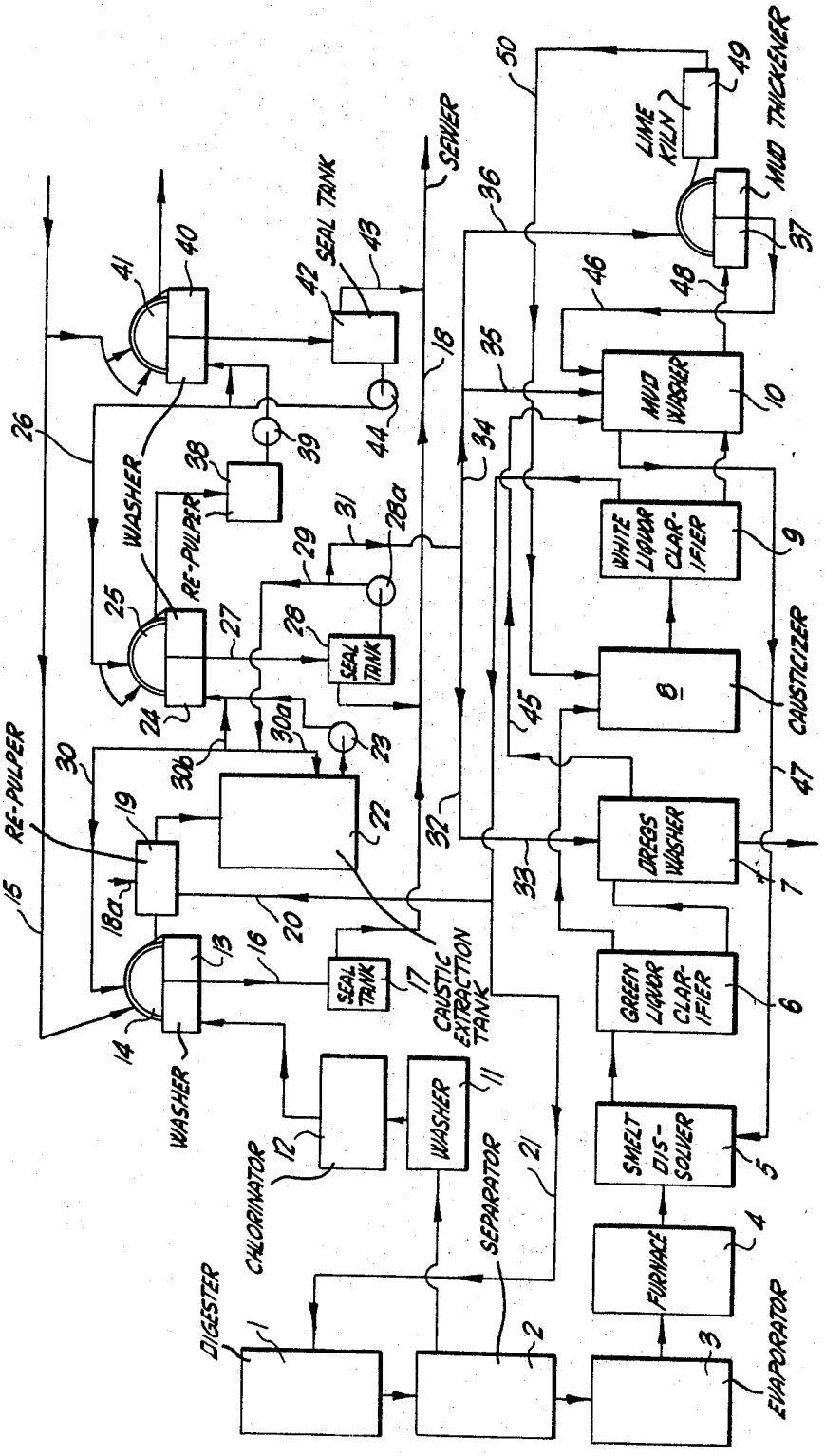
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PULPING AND BLEACHING PROCESS WHEREIN EFFLUENT LIQUOR FROM ALKALINE EXTRACTION OF BLEACHED PULP IS USED TO DISSOLVE SMELT

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PULPING AND BLEACHING PROCESS WHEREIN EFFLUENT LIQUOR FROM ALKALINE EXTRACTION OF BLEACHED PULP IS USED TO DISSOLVE SMELT

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ABSTRACT OF THE DISCLOSURE

A pulping and bleaching process is provided wherein, after fibrous cellulosic material is digested and the waste liquor produced by said digestion is separated from the pulp and evaporated and burned to form a smelt, the pulp is partially bleached and extracted with an alkali metal hydroxide solution and effluent liquor from said alkali metal hydroxide extraction is then used to dissolve the smelt.

The present invention relates to the production of bleached cellulosic fibrous pulp. More particularly, the present invention relates to a method of producing bleached fibrous cellulosic pulp in which the chemical compounds contained in the effluent liquors from a caustic extraction stage in a bleaching sequence are recovered and reused in the digestion of the raw cellulosic material.

In the conventional Kraft process for the production of bleached cellulosic fibrous pulp, the fibrous cellulosic material such as grasses, straw, bagasse and particularly wood chips, is heated in a digestion stage with a "white liquor" which contains sodium sulfide and sodium hydroxide. This digestion stage serves to dissolve from the cellulosic material a substantial part of the hemicelluloses, the lignin and other extractible organic materials contained therein. The fibrous pulp so produced is separated from the resultant "black liquor." The black liquor is subsequently sent to a recovery stage and the separated pulp is washed and sent to a bleaching stage.

In the recovery stage, the black liquor 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 quenched with water to form a raw green liquor which is clarified. Insoluble salts of metal cations other than sodium or potassium form the dregs from the clarification which are separated and washed with water. The clarified green liquor is then causticized with lime to convert the sodium carbonate present in the liquor to sodium hydroxide. During this conversion, calcium carbonate is precipitated and subsequently separated therefrom as a mud, washed with water and calcined to regenerate the lime for further causticization. The washings from the dregs and the mud are usually used as the water for quenching and dissolving the smelt from the furnacing of the black liquor. The causticized green liquor becomes the white liquor which is recycled to the digestion stage. In order to maintain the concentration of sodium hydroxide and sodium sulfide in the recycled white liquor, sodium sulfate is added to the recovery stage, usually to the black liquor before furnacing thereof, which on reaction with the carbon in the black liquor forms sodium carbonate and sodium sulfide. Sodium hydroxide is generated from the sodium carbonate on causticization.

In the "Alkafide process" which is a modified form of the Kraft process, the digestion liquor for the fibrous cellulosic material contains principally sodium sulfide. In the recovery stage sodium carbonate is separated from the green liquor to provide a solution rich in sodium sulfide which is subsequently recycled as make-up liquor to the digestion stage.

In the conventional Soda process, the digestion liquor for the fibrous cellulosic material contains only sodium hydroxide and as such, the addition of "salt cake," e.g., sodium sulfate, is omitted in the recovery stage.

The pulp separated from the black liquor is washed with water and then partially bleached in a first bleaching step with an aqueous solution which normally contains chlorine and desirably some chlorine dioxide. The partially bleached pulp is washed with water and passed to a caustic extraction stage in which it is mixed with a sodium hydroxide solution and heated to remove the colored organic impurities oxidized in the first bleaching step. The extracted pulp is washed with water and passed to one or more further bleaching steps to complete the bleaching using one or more bleaching agents such as additional chlorine, peroxides or preferably, chlorine dioxide.

The effluent from the caustic extraction step, that is, the effluent obtained when the extracted pulp is washed with water, in addition to containing residual unreacted sodium hydroxide, also contains sodium salts of inorganic acids such as sodium carbonate, sodium sulfide, sodium sulfate and sodium chloride, as well as sodium salts of organic acids derived from the small fraction of organic matter which is extracted from the partially bleached pulp in the extraction step. Heretofore, this effluent has usually been sent to waste, contaminating public water systems as well as losing valuable chemical compounds from the over-all process. The possibility of evaporating the effluent to recover the chemical compounds for reuse in the process, e.g., by addition to the black liquor, and for recovery of the heat of combustion of the organic matter has been considered but because of the very low concentration of solids in the effluent, evaporation and combustion of the effluent have appeared to be relatively uneconomic and this has not been effected heretofore on a commercial scale. Another possibility is the concentration of the effluent by a suitable countercurrent washing system but the equipment required involves a large capital investment and the operating technique is difficult to control.

It is an object of the present invention to provide an improvement in a process for the production of bleached fibrous cellulosic pulp in which the solids from the effluent of the caustic extraction step are recovered and are reused in the process in a simple step which does not require the extensive evaporation of water as in previous recovery processes. It is another object of the present invention to reduce the water requirements of pulping operations such that very little additional water is incorporated into the process. A further object of the present invention is to markedly and economically reduce stream pollution by recovering and reusing products previously passed as waste from pulp bleaching processes.

In accordance with the invention, a cellulosic pulping and bleaching process is provided comprising using the effluent liquor from a caustic extraction of partially bleached pulp as an aqueous medium for dissolving smelt formed from the digestion of cellulosic pulp. More specifically, a process is provided for the bleaching of pulp comprising digesting a fibrous cellulosic pulp material in an aqueous medium containing a compound selected from the group consisting of alkali metal hydroxide, alkali metal sulfide and mixtures thereof, separating the fibrous pulp from said medium, evaporating and burning said medium to form a smelt, bleaching the separated fibrous pulp, extracting it with aqueous alkali metal hydroxide

solution using at least part of the resulting caustic extraction solution as an aqueous solution for dissolving the smelt and reusing at least part of said dissolved smelt in said digesting of said cellulosic pulp.

The present invention involves the discovery that the effluent liquors from the caustic extraction step of partially chlorinated and partially bleached pulp is admirably suitable as the solution for quenching the smelt from the furnacing of the black liquor to dissolve the same. Also, in using such a process, numerous benefits such as reduced chemical requirements and lessening of water pollution are obtained.

In a preferred embodiment of the present invention, an improvement is made in the process wherein a bleached pulp is produced by heating in a digestion stage a fibrous-cellulosic material in an aqueous solution containing sodium hydroxide or sodium sulfide or both to dissolve a large proportion of the lignin and hemicelluloses contained therein, separating the fibrous pulp from the solution, sending the solution to a recovery stage which includes evaporating said solution, burning said concentrated solution to form a smelt, dissolving said smelt in water, causticizing the solution so produced, separating the precipitate so formed from the solution and recycling at least a portion of said solution to the digestion stage, and sending the fibrous pulp to a bleaching stage which includes partially bleaching the pulp in a first bleaching step with an aqueous solution of chlorine or chlorine dioxide or both, extracting the partially bleached pulp in a caustic extraction step with hot aqueous sodium hydroxide solution and further bleaching the pulp in at least one more bleaching step. The improvement comprises using the effluent from the caustic extraction step at least partially and preferably completely as the water for the quenching and dissolution of the smelt from the furnacing of the solution in the recovery stage.

It will be seen that by using the effluent from the caustic extraction step to quench the smelt from the furnacing of the black liquor instead of using the washings from the dregs and mud in the recovery stage, essentially no additional water is added to the recovery stage and the solids dissolved in the effluent are introduced into the green liquor and thus subsequently into the white liquor for the digestion stage. Further, after digestion, the black liquor so formed in evaporated and burnt to remove the organics and as such, the heat of combustion of the organic material in the effluent is recovered in addition to the dissolved salts which are recovered in the form of sodium carbonate and sodium sulfide.

In the present invention, the proportion of caustic extraction liquor used in dissolving the smelt can vary widely but preferably the extraction liquor is used in an amount of about 10 percent to 100 percent of the total liquor used in dissolving the smelt.

The term "smelt" as used herein means the pyrolyzed product formed by heating the pulp digesting liquors at a temperature and time sufficient to burn and decompose substantially all of the organics contained therein. The resulting smelt, when sodium salts are used, is primarily sodium carbonate, sodium sulfide and sodium hydroxide. The composition and concentration of the green liquor formed in dissolving the smelt can vary widely depending on the particular digestion process used. The preferred composition and concentration for a given process is readily provided by adjusting the amount of quenching and dissolving liquor used and by the addition of further amounts of alkali metal hydroxides and/or sulfides as required. The sulfides are normally added as sulfates prior to the burning of the digestion liquor. Normally, the resulting green liquor has a chemical content of about 100 to 500 or more grams per liter of the described chemicals.

The employment of the effluent liquor from the caustic extraction step in the formation of the green liquor does not depend on the precise form of the sodium hydroxide solution used in the caustic extraction step of the partially bleached pulp. Thus, it is possible to use for the caustic extraction step either green liquor containing sodium sulfide and sodium carbonate or white liquor containing sodium hydroxide and sodium sulfide, these liquors being suitably obtained from the recovery stage. However, when these liquors are used in the caustic extraction step, in view of the presence of sodium sulfide therein and the effect this has on the subsequent bleaching step, particularly with chlorine dioxide, it is very desirable to remove the sodium sulfide completely from the pulp before it passes to these further bleaching stages. To this end, an extra washer, i.e., two washers after the caustic extraction are provided and desirably, the effluent from the second washer is partially recycled for use as washing water in the first washer.

While the effluent from the caustic extraction step may be used directly to quench and dissolve the smelt from the furnacing of the black liquor, it is preferred to use the effluent before such quenching to wash the dregs from the clarification of the green liquor and the mud from the clarification of the causticized green liquor whereby to recover the chemical values therefrom in a similar manner to the water used in the conventional Kraft process.

In general, the dissolved solid additionally introduced into the recovery stage by the present invention amounts to about 6 percent dead-load on the over-all process which generally requires a slight, on the order of 6 percent, additional evaporation of water therefrom and thus, it is possible, for a very small additional process operating expense, to recover valuable chemicals from the effluent from the cautsic extraction step for reuse in the process, particularly in the digestion of the cellulosic material and, at the same time, avoid pollution of the public water system with these chemicals. Further, the heat of combustion from the organic material in said effluent is retained in the process.

The present invention will be further illustrated by way of the accompanying drawing which is a partial schematic and flow sheet representing a preferred embodiment of the process of the present invention.

Referring to the drawing, wood chips are digested in a digestor **1** in a white liquor comprising an aqueous solution of sodium hydroxide and sodium sulfide. After digestion of the wood chips by the above-described processes, which are known in the art, the pulp mixture is passed to a separator **2** in which the pulp is separated from the black liquor so obtained and the black liquor is passed to an evaporator **3**, where it is concentrated. To the concentrated black liquor is added make-up sodium sulfate. The concenrtated liquor containing the sodium sulfate dissolved therein is burnt in a furnace **4** to obtain a smelt containing sodium carbonate and sodium sulfide. The smelt is then passed to a smelt dissolver **5** where it is quenched with an aqueous solution, as herein described. The green liquor so formed is passed to a green liquor clarifier **6** and the dregs obtained therefrom are passed to a dregs washer **7**. The clarified green liquor is then passed to a causticizer **8** in which it is mixed with lime causticized to convert the carbonates to hydroxides thereby forming white liquor. The causticized liquor is passed to a white liquor clarifier **9** wherein calcium carbonate, precipitated in the causticizing reaction, is removed therefrom as a mud. The mud is passed to a mud washer **10** for washing.

The fibrous pulp separated in separator **2** is washed with water in washer **11** and then passed to a first bleacher, preferably a chlorinator **12** in which it is partially bleached with an aqueous solution of chlorine, chlorine dioxide or both. From chlorinator **12**, the partially bleached pulp passes to washer **13** where it is passed as a mat over a wire mesh on the periphery of rotating drum **14** and washed with water which passes thereto via line **15**. The effluent from the washer **13** is drawn through line **16** by a vacuum pump (not shown) to a seal tank **17** and then to sewer via line **18**. From washer **13**, the fibrous mat passes to a

repulper **19** in which it is mixed with steam which enters via line **18***a* and recycled white liquor which enters via line **20** from the white liquor clarifier **9**. The remainer of the white liquor from the white liquor clarifier **9** passes via line **21** to the digester **1** for digestion of fresh wood chips. The hot mixture of fibrous pulp and white liquor then passes to a caustic extraction tank **22** in which the impurities are dissolved and the mixture pumped therefrom by a pump **23** to a washer **24** in which the pulp is taken up as a mat on the wire mesh periphery of a rotating drum **25** whence it is washed by water passing through line **26**. The effluent is drawn from washer **24** through line **27** by a vacuum pump (not shown) and passed to a seal tank **28** from which a portion thereof is pumped by pump **28***a* for recycle via lines **29** and **30** to the surface of the wash mat on drum **14** of washer **13** and a further portion thereof is passed through the lines **31**, **32** and **33** to the dregs washer **7** and through the lines **31**, **34** and **35** to the mud washer **10**. If desired, this water can also be passed through the lines **31**, **34** and **36** to the mud thickener **37**. Some of the effluent passing through line **30** is taken off through lines **30***a* and **30***b* to the caustic extraction tank **22** and the washer **24**, respectively. The washed fibrous pulp mat from the washer **24** is then passed to a repulper **38** and pumped by means of pump **39** to washer **40** wherein it forms a mat on the wire mesh periphery of rotating drum **41**. The pulp mat thereon is washed by water from the line **15**. The effluent liquor drawn from the washer **40** by a vacuum pump (not shown) to seal tank **42** is partially passed to the sewer through lines **43** and **18** and partially recirculated as wash water to washer **24** through line **26** by means of the pump **44**.

The wash water passing through the line **33** to the dregs washer **7** is subsequently passed through the line **45** to the mud washer **10** and the wash water passing through line **36** to mud thickener **37** is subsequently passed to mud washer **10** through the line **46**. The wash water exiting from the mud washer **10** passes through the line **47** to smelt dissolver **5** where it is used to dissolve the smelt from the furnace **4**.

The mud is supplied to the mud thickener **37** from mud washer **10** via the line **48** where it is thickened and subsequently passed to a lime kiln **49** in which the mud is calcined to regenerate lime which is then returned through the line **50** to the causticizer **8** for further causticization of the green liquor.

From the washer **40**, the extracted pulp is passed to further bleaching steps with bleaching agents such as chlorine dioxide, chlorine, hypochlorite, peroxide, and the like.

Although sodium is the normally preferred cation of the alkali metal hydroxide and sulfide used, other alkali metal hydroxides and sulfides can be used, particularly those of lithium, potassium, cesium, and the like.

The invention will be further described by the following examples. Unless otherwise indicated, all temperatures are in degrees centigrade and all parts are by weight.

EXAMPLE 1

This example illustrates tests conducted to determine whether there would be any adverse effects in using recovered caustic extraction liquor from a pulp bleaching step as the quenching and dissolving liquor for smelt and particularly whether suitable green liquor could be prepared which could satisfactorily be converted to white liquor.

Two green liquor compositions were prepared, the first composition by dissolving 211.7 grams of a smelt material in sufficient distilled water to produce one liter of solution and the second composition by dissolving an equal amount of the same smelt material in sufficient caustic extraction liquor from a Kraft mill operation to form one liter of solution. The smelt material had a composition comprising 29 parts of Na_2S, 22.7 parts of NaOH and 160 parts of Na_2CO_3.

200 milliliters of each of the prepared green liquor solutions were treated with 22.4 grams of solid calcium hydroxide, heated to 80 degrees centigrade and stirred for two hours. After stirring was stopped, the settling rate was observed. Both liquors settled at virtually the same rate, indicating that the dissolved matter in the caustic extraction liquor had no adverse effect on the settling rate, which is a very important factor in mill operation of a causticizing system.

During the stirring operation it was observed that less foam formed above the solution containing the recovered caustic extraction liquor indicating that this liquor would decrease rather than increase the foaming problem when it is used in a causticizing system.

The clear liquor was decanted from the settled sludge, and the latter was filtered. The rate of filtration was approximately the same in both cases, indicating that the caustic extraction liquor does not adversely affect filtration of the "mud."

When the filtrate was analyzed using TAPPI Standard Method No. T624*m*–60, it was found that essentially the same proportions of sodium carbonate were converted to sodium hydroxide in both cases, 81.4 percent with distilled water and 81.6 percent with the caustic extraction effluent liquor, indicating that the solids in the caustic extraction liquor do not adversely affect the causticizing operation.

EXAMPLE 2

This example further illustrates the present invention compared to normal mill operation. A sample of normal green liquor from pulp mill was compared with a green liquor made by dissolving smelt in a liquor in which 70 percent by volume of the water normally used for dissolving the smelt had been replaced by caustic extraction effluent liquor taken from the same mill. Both solutions contained the same concentrations of chemicals, e.g., NaOH, Na_2S and Na_2CO_3, in the range of 180 to 190 grams per liter. White liquor was prepared from both green liquor samples by causticizing for one hour at a temperature of 200–215 degrees Fahrenheit with continuous stirring with lime taken from the mill kiln using an amount of 6 percent excess over the stoichiometric requirement, which approximated as closely as possible the amount of excess lime normally used in the mill system. The following observations were made:

(a) The white liquor obtained from the green liquor containing caustic extraction effluent settled a little faster than the normally prepared white liquor;

(b) The causticizing efficiency, i.e., percentage conversion of sodium salts to sodium hydroxide, was 1–4 percent higher using green liquor made with caustic extraction effluent; and

(c) The filtered sludge from the liquor containing caustic extraction effluent allowed the wash water to drain therethrough at a faster rate, indicating easier filtering as well as faster settling.

Thus, unexpected improvements in the processing of these liquors are obtained by the process of this invention.

Reburning the comparative lime muds in a furnace at 1700 degrees Fahrenheit showed slightly more loss on ignition of the reburned lime originating from the caustic extraction liquor. This is as would be expected since the caustic extraction liquor contains some organic matter. Both lime muds showed very little caking, indicating that no additional difficulties occur in burning lime mud produced in the process of this invetnion.

An important difference between the procedure of Example 1 and Example 2 was that when only the stoichiometric amount of lime was added to the green liquor prepared from caustic extraction effluent as in Example 1, the sludge was light tan in color and the filtered liquor was dark brown. Analysis showed that only sodium carbonate had been converted into sodium hydroxide and the colored salts of organic acids remained with the filtrate.

When an excess of lime was used as in Example 2, the

sludge was dark brown in color and the filtered liquor was a very much lighter brownish-orange color, indicating that the colored sodium salts of organic acids were also converted into sodium hydroxide and the colored calcium salt remained with the sludge. This was confirmed by analysis.

The latter observations show the great flexibility of the process of this invention in that the sodium salts of organic acids may either be precipitated with the lime sludge and burnt in the lime kiln or may be left in solution to go with the white liquor to the digester and the evaporators and chemical recovery system. This option can be very important in the operation of the pulp mill.

EXAMPLE 3

The process of the present invention is operated as an integrated part of a pulping and bleaching mill in accordance with the drawing. Wood chips are digested in a white liquor comprising an aqueous solution of sodium hydroxide and sodium sulfide. After digestion, the wood chips now a fibrous pulp, are separated from the black liquor. The black liquor is passed to an evaporator wherein it is concentrated. Replenishing amounts of sodium sulfate are added to the liquor which is subsequently fired to produce the smelt. The produced cellulosic pulp is washed with water and then passed to a chlorinator wherein an aqueous mixture of chlorine dioxide and chlorine is used to partially bleach the pulp. The pulp is separated from the chlorinating liquors and again washed with water. The washed pulp is then mixed with steam and a portion of recycled white liquor from the white liquor clarifier. Sufficient steam is used to heat the pulp and white liquor to about 180 degrees Fahrenheit before passing the mixture to a caustic extraction tank in which additional amounts of aqueous NoOH are added, if desired, to the pulp mixture to further dissolve the impurities therein. The caustic extraction liquor is drained from the pulp and the pulp washed with water. The extraction liquors and wash water are passed to a seal tank from which portions thereof are drawn for use as wash water for (1) the chlorinated pulp, (2) the dregs from the green liquor clarifier, (3) the mud washer and (4) the mud thickener. The wash water passing through the dregs washer, the mud washer and the mud thickener is ultimately passed to the smelt dissolver wherein it is used as a quench and dissolving liquor for the hot smelt. This caustic extraction liquor, after being used as a wash, results in about 70 to 80 percent of the total solution used to quench and dissolve the smelt.

The dissolved smelt is a green liquor having a composition of about 29 grams Na_2S. 22.7 grams NaOH, 160 grams Na_2CO_3 and some minor amounts of undissolved solids per liter of solution. The green liquor is clarified by filtering to remove the dregs and the clarified liquor is then causticized by reacting the carbonates therein with a slight stoichiometric excess, about 6 percent, of lime based on the calculated sodium carbonate present. The causticization is effected by stirring and heating the mixture of lime and green liquor at a temperature of about 200 degrees Fahrenheit for about two hours. Under these conditions, about 81 to 82 percent of the sodium carbonate previously present in the green liquor is converted to sodium hydroxide. The calcium carbonate precipitates are removed in the mud washer and the resulting white liquor is recycled to the process as previously described. The mud, or calcium carbonate, is subsequently fired in a lime kiln to convert the carbonate to lime for reuse in the process.

In addition to the method of Example 3, the caustic extraction liquor can be used directly as the smelt dissolving liquor without first using it as a wash liquor. Further, greater and lesser amounts of the caustic extraction liquor can be used to dissolve the smelt so that the caustic extraction liquor can comprise about 10 to 100 percent of the total aqueous medium used in making the green liquor. Under such conditions, correspondingly good results are obtained.

What is claimed is:

1. A cellulosic pulping and bleaching process, comprising the steps of:

(a) digesting fibrous cellulosic material;

(b) separating the fibrous pulp and the waste liquor produced by said digestion step;

(c) evaporating and burning said waste liquor, thereby forming a smelt;

(d) partially bleaching said fibrous pulp which has been separated from said waste liquor;

(e) extracting said partially bleached pulp with an alkali metal hydroxide solution; and

(f) using effluent liquor from said alkali metal hydroxide extraction of said partially bleached pulp as an aqueous medium for dissolving said smelt.

2. The process of claim **1**, wherein:

(a) said fibrous cellulosic material is fibrous cellulosic pulp;

(b) said fibrous cellulosic pulp is digested in an aqueous medium containing a compound selected from the group consisting of alkali metal hydroxide, alkali metal sulfide, and mixtures thereof; and

(c) at least part of said dissolved smelt is used to digest said fibrous cellulosic pulp.

3. The process of claim **2** wherein said alkali metal hydroxide and alkali metal sulfide are sodium hydroxide and sodium sulfide, respectively.

4. The process of claim **2** wherein said bleaching is effected using a bleaching agent selected from the group consisting of chlorine, chlorine dioxide and mixtures of the same.

5. The process of claim **2** wherein the fibrous pulp is subjected to at least one further bleaching stage subsequent to the alkali metal hydroxide extraction.

6. The process of claim **2** wherein the dissolved smelt is causticized with lime prior to reuse in the digestion stage.

7. The process of claim **6** wherein the precipitates formed in causticizing the dissolved smelt are washed with the caustic extraction liquor prior to using said extraction liquor for quenching and dissolving the smelt.

8. The process of claim **2** wherein said caustic extraction liquor is used completely as the aqueous solution for quenching and dissolving said smelt.

9. The process of claim **8** wherein the caustic extraction liquor is used as 10 to 100 percent of the aqueous solution for quenching and dissolving said smelt.

10. The process of claim **2** wherein the dissolved smelt solution is used as an extraction liquor for said partially bleached fibrous pulp.

11. The process of claim **2** wherein the dissolved smelt is causticized with lime and subsequently used partially as an extraction liquor for said partially bleached fibrous pulp.

12. The process of claim **2** wherein the process is continuous.

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