A method of treating lignocellulosic pulp in which an aqueous pulp mixture is treated with a bleaching agent and then subjected to an alkaline extraction at a reduced pH with a combination of alkaline agents comprising caustic soda and soda ash and using caustic soda for pH control.
PULP BLEACHING AND ALKALINE EXTRACTION METHOD

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention
[0002] The present invention relates to the bleaching and alkaline extraction of lignocellulosic pulp and more particularly to the use of a combination of alkaline agents in the alkaline extraction of bleached pulp.
[0003] 2. Description of the Related Art
[0004] The production of bleached lignocellulosic pulp is a major worldwide industry, with such bleached pulp being used primarily for the manufacture of white paper.
[0005] Pulp processing facilities typically include multiple unit operations, in which pulp feedstock is converted to a digested pulp that is subsequently treated in multiple stages involving bleaching, alkaline extraction and washing, to yield a bleached pulp suitable for papermaking.
[0006] The term pulp, as used in this specification, refers to lignocellulosic pulp and typically is processed as a suspension or slurry of cellulose fibers in water (also called an aqueous pulp mixture). Lignocellulosic pulp consists of cellulose fiber (the chief structural element and major cell wall component of trees and other plants; this is the primary component of paper made from processed pulp), lignin (a complex constituent of lignocellulose that binds the cellulose fibers together) and hemicellulose (which is solubilized along with lignin in pulp processing).
[0007] Lignin is further characterized by being brown in color and thus responsible for the non-white or off-white coloration of unbleached pulp. Most lignin is normally removed via delignification, during the chemical digestion (pulping stage) in pulp processing, where about 85%-95%+ of the lignin may be removed.
[0008] Additional lignin is typically removed during subsequent bleaching and extraction steps, which are employed to remove residual lignin bound within the cellulose fibers. The degree of pulp delignification is normally measured via the well-known permanganate test and is defined by the kappa or “K” number. A kappa number of less than about 5 is normally required for pulp used in the production of white paper.
[0009] In chemical pulp processing, the wood pulp feedstock, or other plant-source pulp feedstock, is treated with chemicals in a reactor vessel, also called a digester, to separate lignin from the cellulose. The most commonly-utilized chemical digestion or pulping processes used for delignification of pulp are the kraft process (the dominant pulping process, which uses sodium sulfide and caustic soda as the active reagents), the sulfite process (which uses acidic bisulfite) and the soda process (which uses caustic soda). The kraft pulping process and its many variants are the most commonly utilized pulping process primarily since its cellulose fiber (and resulting paper) is stronger than that obtained in competing pulping processes.
[0010] The resulting digested pulp still contains residual lignin closely associated with or bound to the cellulose fibers and that contribute to an off-white coloration of the pulp. Such residual lignin cannot be removed via further chemical digestion without adverse degradation of fiber strength.
[0011] Pulp bleaching treatments, typically effected in multistage operations, are used to remove residual lignin and other color-causing bodies from the chemically-digested pulp to yield a white-colored pulp having the desired brightness.

[0012] Pulp bleaching is most commonly carried out using chlorine dioxide (ClO2) as the bleaching agent; chlorine dioxide has largely replaced chlorine for environmental reasons. Chlorine dioxide is believed to function primarily as a true oxidizing agent, rather than as a chlorinator (as is the case with chlorine).

[0013] Other bleaching agents are also used in some instances for pulp bleaching, often in separate bleaching stages in addition to a chlorine dioxide bleaching stage, e.g., including ozone, oxygen, hydrogen peroxide and the like.

[0014] Following a bleaching stage, using chlorine dioxide or other bleaching agent, the bleached pulp is conventionally subjected to an alkaline extraction operation or washing steps or both. Alkaline extraction procedures serve to separate and solubilize residual lignin from the bleached cellulose pulp and most commonly employ caustic soda as the alkaline extraction agent in an aqueous medium.

[0015] Such alkaline extraction procedures are described in the prior art patent literature that describe pulp processing, and, in addition to the widely-used caustic soda, other alkaline extraction agents are also mentioned as alkaline extraction agents.

[0016] U.S. Pat. No. 2,203,212 of Casciani relates to the bleaching of pulp and discloses its preference for caustic soda in the alkaline extraction of partially bleached pulp but mentions that other alkalis or bases, for example soda ash or hydrated lime, can be employed (page 3, col. 1, lines 38-41).

[0017] U.S. Pat. No. 3,874,992 of Liebergott concerns a single stage alkaline extraction procedure for treating bleached pulp. The ’992 patent utilized sodium hydroxide in its Examples as the alkaline extraction agent and states that its alkaline extraction is also possible with calcium hydroxide or sodium bicarbonate as the alkali agent. The ’992 patent also mentions in its Description of the Prior Art about alkaline extraction that “[c]auostic soda is a preferred agent, but other alkalis (e.g., ammonia, sodium carbonate, calcium hydroxide, etc.) have been suggested and used” (col. 1, lines 47-49).

[0018] U.S. Pat. No. 4,222,819 of Fossum et al. relates to bleaching of pulp with a peroxide bleaching agent and mentions that extraction of the bleached pulp may be carried out with “alkali metal and alkaline earth metal hydroxides and carbonates, for example, sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, ammonia, sodium bicarbonate, potassium bicarbonate, and oxidized white liquor solids” (col. 5, lines 61-66).

[0019] U.S. Pat. No. 4,568,420 of Nonini describes a multistage pulp delignification and bleaching process in which the first alkaline extraction stage utilizes caustic in the presence of oxygen and either a hypochlorite or a peroxide. The ’420 patent states that the preferred alkaline extraction agent is sodium hydroxide but that “other suitable alkaline extractants such as potassium hydroxide or sodium carbonate” could be used (col. 3, lines 36-39).

[0020] U.S. Pat. No. 5,248,389 of Heimberger et al. describes a process for the bleaching of pulp using peroxide in an alkaline medium containing sodium carbonate and sodium silicate, the latter two components replacing sodium hydroxide and sodium silicate used in prior peroxide bleaching operations. The ’389 patent contains no disclosures concerning alkaline extraction of the peroxide-bleached pulp.

[0021] U.S. Pat. No. 5,770,010 of Jelks describes a pulping process in which its fiber slurry is delignified with nascent oxygen. The ’010 patent describes subjecting the delignified pulp to an extraction stage, using an alkaline material that
may be "caustic soda, soda ash, aqueous ammonia, lime, and combinations thereof." (col. 10, lines 61-64).

[0022] The present invention is directed to a method for the alkaline extraction of bleached pulp using a combination of alkaline agents that provides unexpected benefits and advantages, as compared with the use of caustic soda alone, as described in more detail below.

SUMMARY OF THE INVENTION

[0023] In accordance with the present invention, a pulp bleaching alkaline extraction method comprises contacting an aqueous lignocellulosic pulp mixture previously treated with a bleaching agent with an alkaline extraction medium comprising caustic soda and soda ash, wherein the soda ash comprises about 10% to about 80% of the total alkali (measured as Na₂O) of the alkaline extraction medium and, further, wherein the pH of the aqueous pulp mixture during the alkaline extraction is controlled at a target pH via addition of caustic soda.

[0024] In another aspect of the invention, a pulp bleaching alkaline extraction method comprises contacting an aqueous pulp mixture previously treated with a bleaching agent with an alkaline extraction medium comprising caustic soda and soda ash, wherein the pH of the aqueous pulp mixture during the alkaline extraction is maintained at a pH from about 9 to about 10.5 through addition of caustic soda and wherein the soda ash comprises about 10% to about 80% of the total alkali (measured as Na₂O) of the alkaline extraction medium.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The present invention provides a method of treating lignocellulosic pulp in which an aqueous pulp mixture is treated with a bleaching agent and then subjected to an alkaline extraction with a combination of alkaline agents comprising caustic soda and soda ash. The present invention is applicable to many conventional pulp processing operations, as well as to many pulp sources. The method of the present invention is well-suited to implementation in existing pulp processing facilities that use caustic soda as the alkaline extraction agent, particularly facilities that also use chlorine dioxide as a bleaching agent.

Advantages and Benefits of the Invention

[0026] The present invention provides several unexpected benefits and advantages, as compared with prior art alkaline extraction operations treating bleached pulp.

[0027] The present invention essentially results in the substitution or replacement, with a second alkaline agent, of a portion of caustic soda that is used as the alkaline agent in prior art alkaline extraction operations. This combination of alkaline extraction agents provides extraction performance that is essentially equivalent to use of caustic soda alone in most instances, yet reduces the disadvantages of using caustic soda alone as the alkaline extraction agent.

[0028] An essential element of the invention is the control and maintenance of the desired pH set point during the alkaline extraction via addition of caustic soda. In addition, total alkali content is preferably adjusted and maintained in the alkaline extraction operation via control of soda ash addition.

[0029] The use of soda ash in present invention in conjunction with caustic soda reduces the amount of caustic soda that would otherwise be required for alkaline extraction. Caustic soda in recent years has become increasingly more costly, and the use of less expensive soda ash in the method of this invention provides a significant operational cost benefit in pulp processing. Another benefit to the use of soda ash is that a portion of the caustic soda is replaced with a safer and more easily handled alkaline agent, soda ash.

[0030] Another advantage to the use of soda ash in alkaline extraction, to reduce the amount of caustic soda required, is that the pH of the alkaline extraction is less alkaline than if caustic soda alone were used as the alkaline extraction agent. Soda ash is less aggressive in its detrimental or adverse activity against the pulp being treated, which can result in improvement in pulp quality when the method of this invention is implemented.

[0031] Another unexpected benefit to the method of the present invention is that overall bleaching performance of the treated pulp is largely unchanged, despite the use of an alkaline extraction agent (a combination of soda ash and caustic soda) that would normally be expected to be less effective in its bleaching activity with the treated pulp.

Context of Pulp Bleaching and Alkaline Extraction

[0032] As mentioned earlier, the present invention is applicable to a wide range of different pulp processing techniques, as well as to many lignocellulosic pulp sources. The pulp may be chemical pulp (obtained from the chemical digestion of wood or other plant pulp source), mechanical pulp (obtained by mechanical grinding wood and primarily used for pulp used for lower grade papers like newsprint), semi-chemical pulp (typically obtained by chemical treatment followed by mechanical treatment) or recycled fiber pulp (obtained from recovered or recycled paper).

[0033] The pulp source may be any of the traditional pulp sources, including lignocellulosic pulps obtained from wood (e.g., hardwood/deciduous trees, softwood/coniferous trees) or non-wood plant pulp sources like bamboo, bagasse, jute, kenaf, hemp, cotton or straw. The pulp source may also be recovered or recycled paper or cotton rags or the like.

Pulp Bleaching and Alkaline Extraction

[0034] The present invention involves two unit operations in pulp processing, a bleaching treatment and a subsequent alkaline extraction procedure. The bleaching treatment and alkaline extraction of this invention may be an initial bleaching-extraction operation or one or more intermediate (downstream) bleaching-extraction operations in a pulp processing that has multiple bleaching-extraction stages, or a final bleaching-extraction operation, or combinations of these. The bleaching operation will now be discussed first, in more detail, followed by a discussion of the alkaline extraction procedure, which is unique to this invention.

Pulp Bleaching Treatment

[0035] The bleaching treatment of the present invention is a chemical operation that employs one or more bleaching agents. The method of this invention is suitable for use with bleaching agents commonly employed in pulp processing and pulp bleaching operations.

[0036] The bleaching treatment in the method of this invention employs bleaching agents conventionally used in pulp processing and may be carried out using bleaching stage parameters that are well known to those skilled in the pulp processing art. Bleaching treatment of lignocellulosic pulps
results in decreased color of the pulp, providing an increase in the brightness of the bleached pulp and of the resultant paper made from such pulp.

[0037] The bleaching treatment in the method of this invention is particularly suited for an initial bleaching (and alkaline extraction) operation in a conventional pulp processing facility but is likewise also adapted for use in subsequent bleaching and extraction operations in pulp processing facilities utilizing multiple bleaching and alkaline extraction stages.

[0038] The bleaching agent employed in the bleaching treatment of this invention may be any oxidizing or whitening agent conventionally used for bleaching pulp. Suitable pulp bleaching agents include chlorine dioxide, chlorine, peroxides like hydrogen peroxide and sodium peroxide, peracids like peroxyacetic acid, ozone, oxygen, sodium hypochlorite, and the like.

[0039] Chlorine dioxide (ClO₂) is a particularly preferred bleaching agent for use in the method of this invention. Chlorine dioxide is currently widely used as a bleaching agent in pulp processing facilities and is readily generated in a pulp processing facility using reactant chemicals from chemical suppliers to the pulp processing industry. Chlorine dioxide is normally prepared on site via the reaction of sodium chlorate (NaClO₃) in a strong acid solution using a reducing agent, e.g., methanol, sulfur dioxide or hydrochloric acid.

[0040] Combinations of bleaching agents, such as chlorine dioxide and chlorine, may also be used. In situations where the method of this invention is adapted to a pulp processing facility having multiple bleaching stages, the bleaching agent may be the same or different in the various bleaching stages. When chlorine dioxide is used as a bleaching agent in a pulp processing operation having multiple bleaching stages, the ClO₂ bleaching treatment is preferably the initial bleaching stage.

[0041] The bleaching treatment serves to delignify previously-digested pulp further and break down the lignin into smaller molecules that can contain oxygen. These delignification products are typically soluble in water and remain with the aqueous pulp mixture after bleaching operation is completed. The delignification products are desirably removed since they can result in discoloration of the pulp as well as increase the bleaching agent load in any subsequent bleaching stages. The aqueous extraction procedure of this invention serves to remove these delignification products.

[0042] The bleaching treatment typically involves contacting the aqueous pulp mixture, having a consistency (discussed below) between about 1% and 40%, with the bleaching agent for a period of time and at a temperature sufficient to provide the desired degree of bleaching and/or delignifying activity. The bleaching agent may be added directly to the aqueous pulp slurry, in suitable equipment, e.g., as is typically the case using chlorine dioxide, or may be introduced as an aqueous solution into contact with the aqueous pulp mixture, e.g., as is typically the case using aqueous hydrogen peroxide as the bleaching agent.

[0043] The bleaching treatment of this invention is preferably carried out under operating parameters conventionally used in pulp bleaching treatments. Such bleaching operating parameters, which include pulp consistency, bleaching temperature and exposure time of the pulp to the specific bleaching agent employed, are well known to those skilled in pulp processing and pulp bleaching. By way of illustration, use of chlorine dioxide as the bleaching agent in an initial bleaching stage of a pulp processing facility may be carried out on a kraft pulp at a temperature of about 30°C. to about 75°C. for an exposure (residence) time of about 1 minute to 1 hour, with a pulp consistency (defined below) of about 1% to about 15%.

Bleaching Step—Brightness

[0044] The bleaching step of the present invention is a chemical operation that serves to purify the treated pulp and also to brighten the pulp (sometimes described as whitening or decolorizing). The bleaching operation purifies the pulp via delignification, via removal of at least a portion of the lignin component still associated with the pulp cellulose. Such lignin is brown in color and is responsible for the coloration or discoloration of pulp and of paper made from such pulp. In addition, pulp bleaching and delignification normally serves to improve the strength and durability of paper made from such bleached pulp.

[0045] Pulp brightness is a well-understood term in pulp and paper processing and normally refers to the reflectance or brilliance of pulp or paper, expressed as a percentage, when measured under a standardized light source (TAPPI Brightness Standard T 452 or its European counterpart ISO 2470-2:2008). Brightness is a recognized pulp and paper standard, but whiteness, sometimes used synonymous with brightness, is not a recognized pulp bleaching standard. Bleaching operations in pulp processing are often described as whitening or decolorizing the pulp, but brightness is the standard actually employed to measure the effectiveness or degree of bleaching achieved.

Alkaline Extraction—Soda Ash and Caustic Soda

[0046] The alkaline extraction of this invention is characterized by the use of two alkaline agents in combination, rather than a single alkali like caustic soda alone as is conventionally used in prior art pulp alkaline extraction procedures. The method of this invention replaces a portion of the caustic soda (sodium hydroxide) with soda ash (sodium carbonate) in the alkaline extraction procedure but maintains pH control during the alkaline extraction via addition of caustic soda to maintain the aqueous extraction mixture at the desired target pH value.

[0047] In the alkaline extraction of this invention, the pulp subjected to a bleaching treatment is subsequently contacted with caustic soda and soda ash in an alkaline extraction procedure. The soda ash moiety of the soda ash and caustic soda alkaline agent employed in this invention should be at least about 10% of the total alkali, up to about 80% of the total alkali. Total alkali of the two alkaline agents is measured as the Na₂O equivalents, by weight, of caustic soda (NaOH=½Na₂O+½ H₂O) and soda ash (Na₂CO₃=Na₂O+ CO₂).

[0048] The soda ash preferably comprises about 20% to about 60% of the total alkali of soda ash and caustic soda employed in the alkaline extraction procedure of this invention. More preferably, the soda ash comprises about 30% to about 50% of the total alkali of soda ash and caustic soda employed in the alkaline extraction procedure. The soda ash most preferably comprises about 35% to about 45% of the total alkali of soda ash and caustic soda employed in the alkaline extraction procedure.

[0049] The more preferred range of about 30% to about 50% soda ash and most preferred range of about 35% to about 45% soda ash, both based on total alkali, are particularly suited for pulp bleaching treatments and alkaline washing procedures where
high pulp brightness is sought, e.g., over 85% brightness and particularly at least 90% brightness (TAPPI Brightness Standard T 452).

[0050] In situations where high pulp brightness is not essential, the soda ash component of the soda ash and caustic soda alkaline agents used in the alkaline extraction procedure of this invention may be in excess of 50%, based on total alkali as Na₂O equivalents.

[0051] In the present specification, the terms total alkali and effective alkali are used in reference to the alkali content measured as Na₂O (i.e., equivalent Na₂O) of the alkaline agent comprising soda ash and caustic soda. The total alkali may be determined or measured via titration of an aqueous solution containing dissolved soda ash and dissolved caustic soda, with the soda ash alkali component being measured by the carbonate (including bicarbonate as equivalent carbonate) content. The total alkali content is preferably measured with reference to Na₂O equivalents, but it should be apparent to those skilled in the art that other alkali equivalents units could also be used in lieu of Na₂O equivalents, e.g., Na₂CO₃ or CaCO₃, as long such alternative alkali equivalent units are used consistently.

Total Alkalinity in Alkaline Extraction

[0052] Just as the caustic soda is used for pH adjustment of the alkaline extraction in this invention, the total alkalinity of the aqueous phase of the pulp mixture being subjected to alkaline extraction is desirably controlled via addition of soda ash (aqueous sodium carbonate solution). The total alkali in the present invention is preferably controlled and maintained at a level that is essentially similar to that which would be employed in an alkaline pulp extraction operation using caustic soda alone.

[0053] Since alkaline pulp extraction total alkali content in any given pulp processing operation will vary according to the bleaching agent previously employed, extraction temperature, pulp consistency and like parameters, the total alkali value employed in the alkaline extraction of this invention is best determined by reference to the analogous extraction conducted with caustic soda alone as the alkaline agent, as is conventionally done.

[0054] Control of the total alkali level in the alkaline extraction operation is most effectively maintained through adjustments in the addition of aqueous sodium carbonate alone, since the addition of soda ash (as compared with caustic soda) has a relatively small effect on the pH of the aqueous phase of the alkaline extraction pulp mixture (which pH is maintained and controlled via caustic soda addition). The total alkali content of the aqueous phase of the alkaline extraction operation in this invention is preferably maintained at a value that is substantially equivalent to or slightly higher than the total alkali value of an alkaline extraction procedure utilizing caustic soda alone as the alkaline agent.

Introduction of Alkaline Agent

[0055] The soda ash and caustic soda alkaline agents used in the alkaline extraction procedure are preferably introduced into the alkaline extraction as aqueous solutions of sodium carbonate and sodium hydroxide, respectively. The soda ash solution (aqueous sodium carbonate) and caustic soda solution (aqueous sodium hydroxide) are preferably introduced as separate solution streams, with the relative amounts of each stream being adjusted to maintain the desired ratio, i.e., relative amounts, of soda ash and caustic soda in the aqueous extraction medium. The two solution streams may be introduced concurrently, or the two streams may be introduced alternately, e.g., with caustic soda being introduced for pH control and soda ash being introduced for adjustment of total alkali content and/or for control of the desired relative amounts of caustic soda and caustic soda in the aqueous extraction operation.

[0056] The soda ash solution and caustic soda solution may alternatively be introduced as a combined single solution stream. However, several factors make use of separate streams of sodium hydroxide and sodium carbonate the preferred mode of operation in the present invention. One disadvantage to the use of combined streams is that the maximum solubility of sodium carbonate in such a combined stream is less than solution stream containing only sodium carbonate. In addition, a separate sodium hydroxide stream is preferably linked to the pH controller used for pH control and pH maintenance in the alkaline extraction. Likewise, a separate sodium carbonate stream is desirably used for making adjustments to the total alkali content of the alkaline extraction. Such separate streams can readily be controlled to provide relative flow rates that yield the desired ratio (relative amounts) of soda ash and caustic soda employed in this invention.

Caustic Soda

[0058] Caustic soda, also called sodium hydroxide (NaOH), is a well-known alkali that has long been employed in pulp processing, including its use as an alkaline extraction agent in the alkaline extraction of bleached pulp. Caustic soda is readily available from commercial chemical suppliers to the pulp processing industry.

[0059] Caustic soda, as used in the method of the present invention, is employed in grades, solution concentrations, and the like, analogous to its use in prior art alkaline extraction procedures, well known to those skilled in the pulp processing art. Caustic soda is typically available from chemical suppliers as a 50 wt % NaOH aqueous solution and is normally diluted with water at the pulp processing facility for use in various unit operations at the pulp processing facility, e.g., pulp delignification/digestion or alkaline extraction or pH adjustment. Caustic soda employed as the caustic soda source in the aqueous extraction of this invention preferably has a concentration of about 5 wt % to about 30 wt % NaOH, more preferably about 8 wt % to about 15 wt % NaOH.

Soda Ash

[0060] The soda ash employed in the present invention is not critical, insofar as its grade, and most commercial grades of soda ash (also called sodium carbonate) may be used with satisfactory results in the method of this invention. The soda ash may be shipped to the pulp processing site as a granular or
powdered product to save transportation costs, and a concentrated sodium carbonate solution prepared on site. Alternatively, the concentrated sodium carbonate solution may be supplied via truck or railcar delivery from a vendor who prepares such concentrated solutions at a distribution center convenient to the pulp processing facility, in order to avoid capital investment and increased operating costs.

[S061] Soda ash (sodium carbonate) is readily available from several commercial suppliers, e.g., FMC Corporation (Philadelphia, Pa.), Solvay Chemicals (Houston, Tex.), General Chemical Industrial Products (East Hanover, N.J.), and OCI Chemical Corp. (Marietta, Ga.). Concentrated sodium carbonate solutions, particularly for use in pulp processing, are available from Savage Safe Handling (Auburn, Me.).

[S062] The soda ash may be any of several commercial grades of soda ash or sodium carbonate (that are typically recrystallized from Na₂CO₃-containing mineral ores), with light density grades and dense soda ash grades being suitable. The purity of most commercial grades of soda ash is sufficiently high that this factor is normally not critical. Impure soda ash grades high in impurities should be avoided if such impurities may adversely affect the brightness of the treated pulp.

[S063] The soda ash used in this invention may also be a Na₂CO₃-containing product such as sodium sesquicarbonate (Na₂CO₃·NaHCO₃·2H₂O), including recrystallized and mechanically-purified grades of sodium sesquicarbonate.

[S064] The soda ash employed in the method of this invention is normally dissolved in water or other aqueous solution, e.g., aqueous sodium hydroxide, to provide a relatively concentrated sodium carbonate solution, e.g., at least about 10 wt % Na₂CO₃. Aqueous sodium carbonate solutions preferably contain at least about 15 wt % Na₂CO₃, more preferably at least about 20 wt % Na₂CO₃, and most preferably at least about 25 wt % Na₂CO₃. A saturated sodium carbonate solution contains about 32 wt % Na₂CO₃.

Other Optional Additives

[S065] The soda ash and caustic soda alkaline agents used in the alkaline extraction procedure may also contain other optional chemical additives to enhance the efficiency of the extraction procedure. Oxidative additives can be used along with the soda ash and caustic soda alkaline agents to achieve oxidative reinforcement of the extraction procedure, to reduce the bleaching agent (e.g., ClO₂) requirements in subsequent bleaching stages or to enhance the overall brightness of the bleached and extracted pulp or both. Such oxidative additives, also called oxidative reinforcement agents, may be oxygen or hydrogen peroxide or both.

[S066] Conventional extraction procedures using caustic soda alone for treating bleached pulp have benefited from oxidative reinforcement with oxygen or hydrogen peroxide or both. Such oxidative reinforcement is well known to those skilled in pulp processing and has applicability to the extraction procedure of this invention.

Alkaline Extraction pH

[S067] The extraction step of the present invention is carried out under alkaline pH conditions. The pH of the alkaline extraction procedure in the method of this invention is noteworthy in that it is less alkaline than the pH typically employed during a conventional alkaline extraction using caustic soda alone. The pH for the alkaline extraction of this invention is normally less than pH 11. Preferably, the pH of the pulp mixture during the alkaline extraction is about pH 9 to about pH 10.5 and, more preferably, about pH 10 to about pH 10.

[S068] The above-noted pH ranges are applicable to most existing alkaline extraction operations that are modified, to implement the present invention, by employing a combination of soda ash and caustic soda in lieu of the previous caustic soda alone. The target pH employed in the method of this invention, using the more preferred amounts of about 30 to about 50% soda ash, is typically about 0.5 to about 1 pH units less than the target pH value conventionally employed with caustic soda alone.

[S069] It should be noted that some conventional alkaline extraction operations may currently be operated under extremely alkaline pH conditions, e.g., above pH 12, and modification of such highly alkaline extraction operations to implement the method of this invention will result in a significant decrease in operating pH value but one that may still be above the preferred pH range noted above and possibly above pH 11.

[S070] The present invention can provide several advantages based on its use of a lower pH value during the alkaline extraction procedure, as compared with a conventional alkaline extraction using caustic soda alone. First, the lowered pH value can result in better quality pulp, since the combination of alkaline agents employed, soda ash and caustic soda, are less aggressive in its action against the pulp during the extraction procedure.

[S071] Despite the reduced aggressiveness of the two component alkaline agent of this invention, resulting pulp brightness is still very good, particularly when using the preferred amounts of soda ash and caustic soda, e.g., 30% to 50% soda ash (based on total alkali). In some pulp processing operations, an offset to the lowered pH and less aggressive activity of the two component alkaline extraction agent is that subsequent bleaching steps may require a slight increase in bleaching agent where high levels of pulp brightness are desired.

Control of pH via Caustic Soda Addition

[S072] The inventors have unexpectedly discovered that the target pH value in the alkaline extraction operation should be controlled in the method of the present invention via the controlled addition of caustic soda as the pH-adjusting agent, rather than via soda ash addition. It has been discovered that use of soda ash as the alkaline agent component for adjusting and controlling pH of the alkaline extraction operation can result in excess alkaline agent being introduced into the alkaline extraction operation, leading to an undesirable increase of total alkali or unwanted swings in the total alkali value of the aqueous phase of the alkaline extraction mixture, in an effort to reach the desired pH target value.

[S073] Proper process control and maintenance of the desired pH target point in the alkaline extraction operation therefore requires that caustic soda be the primary alkaline agent for pH control. The caustic soda may be introduced in several different ways, to achieve pH control and maintenance of the desired target pH value in the aqueous alkaline extraction mixture containing the pulp. The caustic soda for pH control may be introduced as a concentrated sodium hydroxide solution, e.g., 20-50 wt % NaOH, or as a more dilute solution, e.g., 5-20 wt % NaOH. The caustic soda
solution added for pH adjustment or control is preferably introduced as aqueous sodium hydroxide solution (containing no soda ash).

[0074] Addition of the caustic soda employed for pH adjustment is preferably achieved automatically, via a pH controller that effects addition of aqueous sodium hydroxide into the aqueous alkaline extraction mixture as needed, to adjust and maintain the pH value of the alkaline extraction operation at the desired target value.

Caustic Soda and Soda Ash Maintenance

[0075] Maintenance of the desired relative amounts of soda ash and caustic soda in the aqueous alkaline extraction may be achieved through periodic measurements of the alkali content of the aqueous alkaline extraction mixture containing the pulp. This is typically accomplished via titration of a sample of the aqueous alkaline extraction mixture, to determine the relative amounts of soda ash and caustic soda present in solution, and also the total alkali content of the aqueous extraction mixture. Such periodic titrations may be carried out on samples obtained, e.g., hourly during start-ups, or at longer intervals, e.g., 4–6 times per day, once steady state operation and good control of the soda ash and caustic soda relative amounts have been achieved. Such measurements can confirm the amounts of soda ash and caustic soda being employed and can quantify the amount of total alkali present in solution the aqueous alkaline mixture.

[0076] Periodic adjustments may then be made, e.g., adding soda ash or withholding further soda ash addition, to maintain the desired relative amounts of soda ash and caustic soda in the aqueous alkaline extraction mixture, as well as to maintain the desired total alkali content. Such soda ash addition, if needed, has been discovered to have relatively low impact on the pH value being maintained in the aqueous alkaline extraction mixture, such that the caustic soda component of the soda ash-caustic soda alkaline agent is still the primary agent for providing pH control in the alkaline extraction mixture.

Extraction Temperature

[0077] The temperature employed for the extraction step of the present invention may vary over a wide range and is not critical. Extraction temperature may be as low as ambient temperatures, e.g., about 20–25°C, or as high as about 130°C. The extraction temperature is preferably in the range of about 45°C to about 95°C. A more preferred extraction temperature range is about 60°C to about 95°C. The most preferred alkaline extraction temperature is about 70°C to about 75°C.

[0078] Higher extraction temperatures than 95°C are feasible but typically require special operating conditions, e.g., super-atmospheric operating pressures, to prevent the water in the aqueous pulp mixture from boiling. Low extraction temperatures, e.g., less than 45°C, are likewise feasible but may require longer contact times during the extraction to compensate for reduced extraction efficiencies.

[0079] References to the extraction temperature are intended to describe the temperature of the alkaline extraction mixture containing the pulp being subjected to extraction. The temperature of the alkaline solutions of caustic soda and soda ash (that are introduced into the aqueous pulp mixture being subjected to alkaline extraction) may be the same as the alkaline extraction temperature or may be higher or lower.

Extraction Contact Time

[0080] The alkaline extraction of this invention employs contact times and equipment similar to those used in conventional extraction procedures using caustic soda alone as the alkaline extraction agent. Longer extraction contact times are generally not required for the alkaline agent combination (soda ash and caustic soda) employed in the method of this invention, despite such alkaline agent combination being less detrimental to pulp quality.

[0081] Alkaline extraction contact time, also called residence time, is understood to be the time the bleached pulp mixture is in contact with or admixed with the alkaline extraction agent. Contact times for the alkaline extraction of this invention may range from a little as a few minutes up to several hours, but preferred alkaline extraction contact times are within the range of about five minutes to about five hours, more preferably about thirty minutes to about three hours.

Extraction—Pulp Consistency

[0082] The pulp consistency of the pulp subjected to the alkaline extraction of this invention is preferably a medium-to-high consistency. Consistency is a well-understood term in pulp processing and refers to the solids content of an aqueous pulp mixture, measured as the bone dry solids, by weight, in an aqueous pulp mixture. Pulp consistency may be categorized as low (less than 5%), medium (5% to 20%) or high (greater than 20%) consistency. Pulp consistency may be measured by TAPPI Standard T 240, “Consistency (Concentration) of Pulp Suspensions.”

[0083] The pulp consistency of pulp subjected to the bleaching treatment and alkaline extraction of this invention may vary widely, ranging from about 1% to about 50% consistency. The pulp consistency during the alkaline extraction is preferably about 5% to about 40% consistency and is more preferably about 10 to about 20% consistency.

[0084] The consistency of the pulp mixture in the bleaching treatment may be different from the pulp consistency in the alkaline extraction procedure and is most typically lower than the consistency of the bleached pulp subjected to alkaline extraction. Preferably, the consistency of the pulp mixture from the bleaching step is increased or concentrated by dewatering the bleached pulp mixture. Such dewatering may be carried out in conjunction with an optional washing step between the bleaching procedure and alkaline extraction.

Extraction—Optional Washing Step

[0085] The bleached pulp subjected to the alkaline extraction of this invention may optionally be subjected to an intermediate washing step, e.g., with a water wash, to remove at least a portion of the bleaching agent used to treat the pulp, before the washed pulp is subjected to the alkaline extraction of this invention.

Process Equipment—Pulp Bleaching and Alkaline Extraction

[0086] An advantage of the method of the present invention is that conventional process equipment may be used for both the bleaching treatment and the alkaline extraction procedure. The method of this invention may therefore be implemented in and existing pulp processing plant with relatively small
additional capital investment, the only new equipment typically required being a vessel or tank for the soda ash solution and, if the solution is prepared on site, solids storage and mixing apparatus for the solid soda ash used to prepare the soda ash solution. Conventional process equipment may be used for both the bleaching treatment and the alkaline extraction procedure in practicing the method of the present invention, and such equipment and process control means, e.g., pH control, are well known to those skilled in the design, engineering and construction of a pulp processing facility.

[0087] The following non-limiting Example illustrates a preferred embodiment of the present invention.

EXAMPLE

[0088] This Example describes a bleaching treatment and alkaline extraction operation, in one embodiment of this invention, to produce a high quality bleached pulp.

[0089] The bleaching treatment and alkaline extraction in this Example is a D$_{2}$E$_{OP}$D$_{3}$ three stage procedure in which pulp feedstock is bleached in a first bleaching stage (D$_{1}$), the D$_{1}$-bleached (D$_{1b}$) pulp is subjected to an alkaline extraction in an oxygen- and peroxide-reinforced extraction treatment using 40% Na$_{2}$CO$_{3}$ and 60% NaOH (in lieu of a conventional 100% NaOH alkaline extraction agent), and the pulp from the extraction stage is subjected to a second bleaching stage (D$_{2}$). The D$_{2}$ and D$_{1}$ bleaching stage treatments each utilize chlorine dioxide as the bleaching agent.

[0090] The pulp feedstock of this Example is unbleached brownstock pulp obtained via digestion of softwood wood chips in a Kraft process.

[0091] The pulp feedstock is first introduced to the D$_{1}$ bleaching stage, at a low pulp consistency, about 4%, is contacted with chlorine dioxide as the bleaching agent at a temperature of about 55°C. The resultant D$_{1b}$-bleached pulp is next introduced to the E$_{OP}$ alkaline extraction stage.

[0092] In the this alkaline extraction, the D$_{1b}$-bleached pulp is subjected to alkaline extraction in an oxygen- and peroxide-reinforced extraction treatment using 40% Na$_{2}$CO$_{3}$ and 60% NaOH, based on Na$_{2}$O content, as the alkaline extraction agent. The alkaline extraction agent is introduced as separate solution streams of aqueous sodium hydroxide (25 wt%) and aqueous sodium carbonate (25 wt%), into the bleached aqueous pulp mixture that is the feed stream to the aqueous extraction unit operation. The respective flow rates of the two alkali solution streams are adjusted to provide the desired 40% Na$_{2}$CO$_{3}$ and 60% NaOH ratio in the alkaline extraction operation.

[0093] The pulp mixture in the aqueous extraction has a medium consistency, about 12%, and temperature during the alkaline extraction is about 75°C. The residence time of the pulp in the alkaline extraction is about one hour.

[0094] The pH of the alkaline extraction is maintained at about pH 9.8 via the controlled addition of aqueous 25 wt% NaOH. This target pH range is 0.5-1.0 pH units less than if caustic soda alone was to be used in the E$_{OP}$ alkaline extraction procedure.

[0095] The 40% Na$_{2}$CO$_{3}$-60% NaOH ratio and the total alkali content of the aqueous solution in the aqueous pulp mixture in the alkaline extraction operation are monitored via periodic measurements of carbonate and alkali content in samples taken every four hours. The total alkali content of the aqueous phase in the alkaline extraction is monitored and maintained, via appropriate adjustments in the soda ash introduced, at a value equivalent to the total alkali content that would normally be used in an alkaline extraction of the same pulp mixture with caustic soda alone as the alkaline extraction agent.

[0096] The extracted pulp is next passed to as second bleaching treatment, D$_{2}$, where the extracted pulp is again treated with chlorine dioxide as the bleaching agent, under operating conditions essentially the same as those used in the initial bleaching (D$_{1}$) stage.

[0097] The resultant pulp obtained form the second bleaching stage in the procedure of this Example is generally of a quality similar to that of pulp obtained with use of caustic soda (NaOH) alone, instead of the soda ash-caustic soda alkaline extraction agent of this Example, in the E$_{OP}$ alkaline extraction procedure.

[0098] Pulp brightness using the soda ash-caustic soda alkaline extraction agent in this Example is very good for a three stage bleaching operation, about 87 (TAPPI Brightness Standard T 452), but is slightly less, e.g., about 2 units less, than if caustic soda alone were the alkaline extraction agent in the E$_{OP}$ extraction procedure.

[0099] This brightness result is also consistent with a slight increase in kappa number expected for the extracted pulp using the soda ash-caustic soda alkaline extraction agent in the E$_{OP}$ extraction procedure of this Example, as compared with use of caustic soda alone as the alkaline extraction agent. Usage of chlorine dioxide in the post-extraction D$_{2}$ bleaching stage is also expected to be slightly higher as a result of the increased lignin content of the soda ash-caustic soda extracted pulp.

[0100] It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed but is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

What is claimed is:

1. A pulp bleaching alkaline extraction method comprising contacting an aqueous lignocellulosic pulp mixture previously treated with a bleaching agent with an alkaline extraction medium comprising caustic soda and soda ash, wherein the soda ash comprises about 10% to about 50% of the total alkali (measured as Na$_{2}$O) of the alkaline extraction medium and, further, wherein the pH of the aqueous pulp mixture during the alkaline extraction is controlled at a target pH via addition of caustic soda.

2. The method of claim 1 wherein the bleaching agent is selected from the group consisting of chlorine dioxide, chlorine, hydrogen peroxide, sodium peroxide, peracetic acid, ozone, oxygen, sodium hypochlorite and chlorine/chlorine dioxide.

3. The method of claim 1 wherein the bleaching agent is chlorine dioxide.

4. The method of claim 1 wherein the soda ash in the alkaline extraction medium comprises about 20% to about 60% of the total alkali (measured as Na$_{2}$O) of the alkaline extraction medium.

5. The method of claim 1 wherein the soda ash in the alkaline extraction medium comprises about 40% to about 50% of the total alkali (measured as Na$_{2}$O) of the alkaline extraction medium.

6. The method of claim 1 wherein the target pH of the aqueous pulp mixture during the alkaline extraction is less than about 11.
7. The method of claim 1 wherein the target pH of the aqueous pulp mixture during the alkaline extraction is from about 9 to about 10.5.

8. The method of claim 1 wherein the target pH of the aqueous pulp mixture during the alkaline extraction is maintained at a pH from about 9 to about 10.

9. The method of claim 1 wherein the caustic soda and soda ash are introduced into the alkaline extraction as a separate aqueous solutions of caustic soda and soda ash.

10. The method of claim 1 wherein the desired relative amounts of soda ash and caustic soda employed in the alkaline extraction are maintained through the adjustment of the amount of soda ash introduced.

11. The method of claim 1 wherein the total alkali content employed in the alkaline extraction is adjusted and maintained through addition of soda ash.

12. The method of claim 1 wherein the temperature of the aqueous pulp mixture during the alkaline extraction is about 45°C to about 95°C.

13. The method of claim 1 wherein the alkaline extraction medium further comprises an oxidative reinforcement agent selected from the group consisting of oxygen, hydrogen peroxide and combinations of oxygen and hydrogen peroxide.

14. A pulp bleaching alkaline extraction method comprising contacting an aqueous pulp mixture previously treated with a bleaching agent with an alkaline extraction medium comprising caustic soda and soda ash, wherein the pH of the aqueous pulp mixture during the alkaline extraction is maintained at a pH from about 9 to about 10.5 through addition of caustic soda and wherein the soda ash comprises about 10% to about 80% of the total alkali (measured as Na₂O) of the alkaline extraction medium.

15. The method of claim 14 wherein the bleaching agent is selected from the group consisting of chlorine dioxide, chlorine, hydrogen peroxide, sodium peroxide, peracetic acid, ozone, oxygen, sodium hypochlorite and chlorine/chlorine dioxide.

16. The method of claim 14 wherein the bleaching agent is chlorine dioxide.

17. The method of claim 14 wherein the soda ash in the alkaline extraction medium comprises about 20% to about 60% of the total alkali (measured as Na₂O) of the alkaline extraction medium.

18. The method of claim 14 wherein the soda ash in the alkaline extraction medium comprises about 40% to about 50% of the total alkali (measured as Na₂O) of the alkaline extraction medium.

19. The method of claim 14 wherein the pH of the aqueous pulp mixture during the alkaline extraction is maintained at a pH of about 9 to about 10.

20. The method of claim 14 wherein the caustic soda and soda ash are introduced into the aqueous pulp mixture during alkaline extraction as separate aqueous solutions of caustic soda and soda ash.

21. The method of claim 14 wherein the desired relative amounts of soda ash and caustic soda employed in the alkaline extraction are maintained through the adjustment of the amount of soda ash introduced.

22. The method of claim 14 wherein the total alkali content employed in the alkaline extraction is adjusted and maintained through addition of soda ash.

23. The method of claim 14 wherein the temperature of the aqueous pulp mixture during the alkaline extraction is about 45°C to about 95°C.

24. The method of claim 14 wherein the alkaline extraction medium further comprises an oxidative reinforcement agent selected from the group consisting of oxygen, hydrogen peroxide and combinations of oxygen and hydrogen peroxide.