A METHOD AND A SYSTEM FOR TREATING LIQUID FLOWS AT A CHEMICAL PULP MILL

Fig. 3

Brown stock from Oxygen treatment of the Oxygen delignification unit

To washing

Unbleached pulp to bleaching

26a

26b

27

27a

Filtrate to washing

Acidification chemical

Acidification chemical

25X washing step

Acidified pulp

Filtrate containing phosphorus compounds

27

Pulp flow

Water/ filtrate

Acid

To recovery island 40

(57) Abstract: This invention relates to a method for treating liquid flows at a chemical pulp mill. The method comprises producing unbleached pulp in a brown stock preparation unit (20), dosing first acidification chemical to the unbleached pulp flow in an acidification stage (26) in order to dissolve at least part of the phosphorus compounds in the unbleached pulp flow, forming a phosphorus compounds containing filtrate, removing at least a portion of said phosphorus compounds containing filtrate from the unbleached pulp flow in a phosphorus removal step (27), and bleaching the unbleached pulp in a bleaching unit (30). In addition, the invention relates to a system for treating liquid flows at a chemical pulp mill.
A METHOD AND A SYSTEM FOR TREATING LIQUID FLOWS AT A CHEMICAL PULP MILL

Field of the Invention

The invention relates to a method and a system for treating liquid flows at a chemical pulp mill.

Background of the Invention

Nowadays, chemical pulp mills are often being built in areas and surroundings with very strict environmental regulations. In many areas, a cleaner environment is desired in such a way that the mills produce substances that are less detrimental to the environment. Therefore, nowadays, it is important to look for new solutions for pulp mills.

Summary of the Invention

The present invention discloses a method and a system for treating liquid flows at a chemical pulp mill. Aspects of the invention are characterized by what is stated in the independent claims 1 and 11. Various embodiments of the invention are disclosed in the dependent claims.

The system according to the present invention preferably comprises

- a brown stock preparation unit comprising a cooking unit, a brown stock washing unit, and an oxygen delignification unit, and
- a bleaching unit comprising bleaching stages to bleach the produced pulp.

Preferably, the system further comprises:

- a wood handling unit, and
- a recovery island.

In addition, the system preferably comprises a pulp drying machine to dry the produced pulp.
The cooking and the brown stock washing steps are preferably followed by the oxygen delignification stage. After the oxygen delignification stage, the pulp is preferably conveyed to the bleaching unit. Therefore, the oxygen delignification is typically a process stage between the brown stock washing and a first stage of the bleaching.

The oxygen delignification unit is typically used to remove lignin from unbleached pulp. In the oxygen delignification stage, the pulp is treated with oxygen. The oxygen delignification stage comprises an oxygen treatment step, after which is typically a post-washing step of the oxygen treatment stage. Oxygen delignification tower(s) are preferably used for the oxygen treatment step. A washing unit is preferably used for the post-washing step of the oxygen treatment stage. The washing unit may comprise, for example, a DD washer and/or a wash-press device.

Advantageously, the oxygen delignification is used because it may give, in addition to the additional delignification after the cooking, reduced consumption of bleaching chemicals and reduced emissions from the bleaching unit.

Wood material that is used for pulp making, comprises phosphorous compounds. A part of these compounds end up in the effluents and waste waters of a pulp mill and are an element of concern in a chemical pulp mill. The phosphorous compounds may comprise, for example, phosphates and organic phosphorous compounds. Part of these compounds are acid dissolving compounds, i.e. by acidification they can be dissolved to the liquid effluent. Advantageously, the solution according to the present invention is particularly intended to minimize the amount of phosphorus compounds, including phosphorus compounds that are conveyed to the waste water treatment plant. Most preferably, the amount of phosphorus is reduced from the pulp flow before the bleaching unit, i.e. during the brown stock preparation stages.

The method according to the present invention preferably comprises
removing at least a portion of phosphorus compounds by removing phosphorous containing filtrate during the brown stock preparation stages, and

conveying said phosphorus containing filtrate to a recovery process, i.e. to a recovery island of the chemical pulp mill, to remove the phosphorus from the pulp mill in a controlled manner.

Advantageously, acid soluble phosphorus is dissolved from unbleached pulp flow into filtrate in an acidification stage and removed from said unbleached pulp flow in a phosphorus removal step; hence, the amount of phosphorous compounds in the unbleached pulp flow is decreased due to the acidification stage and the phosphorus removal step. Preferably said steps are placed between the post-washing step of the oxygen delignification unit and the first bleaching stage of the bleaching unit.

The acidification stage preferably comprises one, two or three acidification steps. Preferably, only one acidification chemical is dosed in one acidification step. Therefore, if the acidification stage comprises two acidification steps, first acidification chemical is preferably added in the first acidification step, and second acidification chemical is preferably added in the second acidification step of the acidification stage.

The phosphorus containing filtrate is preferably conveyed from the phosphorus removal step, at least partly, to the recovery island of the pulp mill, and preferably discharged from the system. Therefore, the system according to the present invention preferably comprises a conveying apparatus for conveying at least a portion of the phosphorus containing filtrate from the brown stock preparation unit to the recovery island. The conveying apparatus(es) preferably comprise(s) at least pipe(s) and pump(s).

Therefore, thanks to the present invention, it is possible to significantly decrease the amount of the phosphorus in the waste waters conveyed to the waste water treatment plant and thus decrease the phosphorous load of the whole pulp mill.
Advantageously, the method for treating liquid flows at a chemical pulp mill comprises
- producing unbleached pulp in a brown stock preparation unit comprising a cooking unit, a brown stock washing unit and an oxygen delignification unit,
- dosing first acidification chemical to the unbleached pulp flow in an acidification stage situated before a first bleaching step of the bleaching unit in order to dissolve at least part of phosphorus compounds in the unbleached pulp flow and to form a phosphorus compounds containing filtrate,
- removing at least a portion of said phosphorus compounds containing filtrate from the unbleached pulp flow in a phosphorus removal step, and
- bleaching the unbleached pulp in a bleaching unit comprising at least one bleaching stage.

The acidification stage is preferably situated after an oxygen treatment of the oxygen delignification unit. The phosphorus removal step is preferably situated after the acidification stage and before the first bleaching step of the bleaching unit.

Advantageously, the method further comprises conveying at least a portion of said phosphorous compounds containing filtrate to a recovery island.

Advantageously, the oxygen delignification unit comprises a post-washing unit, and the method comprises
- dosing the first acidification chemical after the pulp is washed in the post-washing unit of the oxygen delignification unit.

In an example embodiment, the pH of the acidified pulp flow is between 2 and 8 in the phosphorus removal step. In addition, the pH of the phosphorus containing filtrate is preferably between 3 and 9 in the phosphorus removal step.

The method may further comprise:
dosing second acidification chemical to the unbleached pulp flow in the second acidification step of the acidification stage, the second acidification step being situated after the first acidification step and before the first bleaching step of the bleaching unit, most preferably before the phosphorus removal step.

The method may further comprise:
- dosing third acidification chemical to the unbleached pulp flow in the third acidification step of the acidification stage, the third acidification step being situated after the second acidification step and before the first bleaching step of the bleaching unit, most preferably before the phosphorus removal step.

The first and/or second and/or third acidification chemical preferably comprises
- sulfuric acid,
- acetic acid,
- carbon dioxide, and/or
- sulfur dioxide.

Advantageously, at least 40% of the acid soluble phosphorus compounds is dissolved from the unbleached pulp flow into the phosphorus compounds containing filtrate due to the acidification stage.

Advantageously, a system for treating liquid flows at a chemical pulp mill comprises:
- a brown stock preparation unit comprising a cooking unit, a brown stock washing unit, and an oxygen delignification unit,
- a bleaching unit, and
- a recovery island,
wherein the system further comprises
- a first apparatus adapted to dose first acidification chemical to the system before a first bleaching step of the bleaching unit to dissolve at least part of the phosphorus compounds in the unbleached pulp flow, and
a second apparatus for forming a phosphorous containing filtrate and removing at least a portion of said phosphorous containing filtrate comprising dissolved phosphorus compounds from the unbleached pulp flow.

The first apparatus that is used to dose first acidification chemical preferably comprises a pipe and a pump. The second apparatus for forming and removing the phosphorous containing filtrate preferably comprises a washing unit, such as a DD washer, or a wash press-device.

The first apparatus adapted to dose the acidification chemical and the second apparatus adapted to form and remove at least a portion of the phosphorous containing filtrate are preferably situated after the oxygen delignification unit and before a first bleaching stage of the bleaching unit.

The amount of phosphorus in the waste water treatment plant may be a problem in some cases at the pulp mill. Therefore, the total amount of phosphorous compounds in the waste water treatment plant is preferably decreased. It is very common to remove phosphorous compounds in the waste water treatment plant for example by precipitation by using calcium, aluminium or iron. Typically, this has been quite difficult, for example, due to problems caused by additional slurry comprising precipitated phosphorous compounds. Thanks to the present invention, it is possible to remove the phosphorous compounds, or at least part of the phosphorus compounds already before the waste water treatment plant. Therefore, thanks to the present invention, a system able to decrease the amount of phosphorus before the waste water treatment plant and, hence, to decrease the amount of phosphorous compounds at the waste water treatment plant may be provided.

The present invention can be implemented, for example, at a chemical pulp mill having a digestion process, at least one bleaching stage, chemical recovery and various reactors, vessels, pumps, mixers, filters etc. known per se.
Description of the Drawings

In the following, the invention will be described in more detail with reference to the appended drawings, in which

Figs 1 to 3 show example embodiments in a reduced schematic chart.

Detailed Description of the Invention

In this application, reference is made to Figs 1 to 3, in which the following reference numerals are used:

20 brown stock preparation, comprising a digester for cooking, brown stock washing, and oxygen delignification stages,
21 cooking,
22 brown stock washing,
25 oxygen delignification stage comprising, among other things, an oxygen treatment stage,
20 25X post-washing stage of the oxygen delignification stage, located after the oxygen treatment stage,
26 acidification stage,
26a first acidification step of the acidification stage comprising a dosage of the first acidification chemical,
25 26b second acidification step of the acidification stage comprising a dosage of the second acidification chemical,
27 phosphorus removal step comprising an apparatus to separate at least a portion of the phosphorus compounds containing filtrate from the unbleached pulp flow,
30 bleaching, comprising bleaching stages and washing therein,
40 recovery island,
50 waste water treatment plant, and
80 drying machine for drying pulp.

The term "raw water treatment plant" refers to a fresh water treatment plant.
The term "effluent treatment plant" refers to a waste water treatment plant.

The term "ECF" refers to elemental chlorine free.

The term "TCF" refers to totally chlorine free.

The term "NPE" refers to non-process elements. NPEs are inorganic substances originated from the process devices, some also from wood, raw water and chemicals, which are not wanted to be processed.

The term "Adt" refers to air dry metric ton of 90% dry chemical pulp.

The term "phosphorus" refers to compounds containing phosphorus, such as organic phosphorus compounds and phosphates.

The term "effluent" refers to waste waters including filtrates. Effluents are conveyed to the waste water treatment plant for purifying process. Effluents may comprise, for example, bleaching effluents and ash leaching purge. In addition, the effluents may contain wood handling effluents.

The term "bleaching effluents" refers to water streams from bleaching unit conveyed to waste water treatment plant. Thus, bleaching effluents comprise effluents from the bleaching unit and washing steps therein. Advantageously bleaching effluents contain bleaching filtrates. Most advantageously bleaching effluents consist of bleaching filtrates. The bleaching filtrates contain acidic and/or alkaline flows. Advantageously, bleaching effluents do not contain substantial amounts of fibers.

The term "EOP" refers to the alkaline extraction stage of the bleaching unit using oxygen and peroxide as additional chemicals.

The term "A-stage" refers to an acid stage of the bleaching unit.

The term "P-stage" refers to an alkaline hydrogen peroxide (chlorine peroxide) stage of the bleaching unit.
The term "D-stage" refers to a chlorine dioxide stage of the bleaching unit.

Advantageously, the system according to the invention comprises
- a brown stock preparation unit 20 to produce brown stock,
- a bleaching unit 30 to bleach the brown stock, and
- a recovery island.

Advantageously, the brown stock preparation unit 20 comprises
- a cooking stage 21,
- a brown stock washing stage 22,
- a screening step, and
- an oxygen delignification stage 25 comprising
  - oxygen treatment, and
  - at least one post-washing step 25X after the oxygen treatment.

In addition, the brown stock preparation unit 20 preferably comprises an acidification stage 26 comprising at least one acidification step 26a, 26b, and a phosphorus removal step 27 after said acidification stage 26.

In an embodiment, at least one post-washing step 25X of the oxygen delignification stage 25 is implemented by a washing unit comprising a DD-washer and/or a wash press-device.

The bleaching unit 30 can comprise, for example,
- an Acid-stage (A-stage),
- an EOP-stage,
- an alkaline extraction stage, such as an extraction with sodium hydroxide (E-stage),
- a chlorine stage (C-stage),
- a sodium hypochlorite stage (H-stage)
- an oxygen stage (O-stage),
- an ozone stage (Z-stage),
- a peracids (peroxy acids) stage (Paa-stage),
- a sodium dithionite (sodium hydrosulfite) stage (Y-stage),
- a chelation stage to remove metals (Q-stage),
- an enzyme stage, such as a xylanase stage (X-stage),
- a chlorine dioxide stage (D-stage) and/or
- an alkaline hydrogen peroxide stage, such as a chlorine peroxide stage (P-stage).

The general purpose of cooking in bleached chemical pulp production is to recover fibers from wood chips that are fed to the digester by using chemicals and heat to remove fiber binding lignin and, in addition, to remove wood extractives which can later cause foaming and precipitants in the process. Therefore, chemicals that dissolve as much lignin and as little cellulose as possible are preferably used in the pulping process. Typically, the process for manufacturing bleached chemical pulp comprises pulping, washing, screening, bleaching, and cleaning stages. Advantageously, sulfate cooking, also called as kraft cooking or pulping, which uses a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na₂S), is the used pulp production method in this invention. The cooking process may be based on batch cooking or continuous cooking comprising a digester or several digesters.

Brown stock treatments after the cooking process 21 preferably include a brown stock washing process 22, a screening process, and an oxygen delignification process 25 comprising the oxygen treatment and the post-washing unit. Advantageously, the brown stock treatments further include an acidification stage 26, and a phosphorus removal step 27.

When the phosphorus compounds containing filtrate 27a is recovered from the phosphorus removal step 27, it may be forwarded, at least partly,
- to a washing unit of the oxygen delignification stage 25,
- directly to an evaporation plant of the recovery island 40, and/or
- to be used in digester plant processes for dilution and displacement, after which it ends up in the black liquor flow.

The screening process may be located after digester blowing, in the middle of or after the brown stock washing process, and/or after the oxygen delignification.
Typically, brown stock treatments are followed by a bleaching process, preferably based on an ECF technique, which comprises a pulp bleaching plant with one or more bleaching stages based on the use of chlorine dioxide in addition to other possible stages using other known bleaching chemicals. Advantageously, the bleaching sequence comprises at least one alkaline extraction stage, wherein preferably at least oxygen and/or peroxide are/is used. Ozone stage(s), acid stage(s), and/or chelation stage(s) for removing heavy metals can also be used.

Typically, the last washing apparatus in the oxygen delignification stage receives the purest washing liquid for facilitating the bleaching of the pulp, and the filtrate obtained from this last washing apparatus is used in accordance with counter-current washing principles as washing liquid and in dilutions.

Advantageously, after the post-washing stage 25X of the oxygen delignification stage, the acidification stage 26, and the phosphorus removal step 27, the pulp is diluted and then conveyed to the bleaching unit 30. Before the pulp is conveyed to the bleaching unit 30, at least a portion of phosphorus compounds containing filtrate is preferably removed from the unbleached pulp flow in the phosphorus removal step 27.

Advantageously, the unbleached pulp flow is at least partly acidified 26 between - the oxygen treatment in the oxygen delignification unit 25, and - the first stage of the bleaching unit 30 in order to dissolve the acid soluble phosphorus from the unbleached pulp flow into the phosphorus compounds containing filtrate 27a.

Advantageously, due to the acidification stage 26, the pH of the unbleached pulp flow is decreased to a level less than 8, more preferably less than 7 to dissolve at least part of the acid soluble phosphorous compounds into the filtrate and hence to form phosphorus compounds containing filtrate. Therefore, the pH of the acidified pulp flow is preferably less than 8, more preferably less than 7. However, advantageously the pH of the acidified pulp
flow is at least 3, more preferably at least 4 or at least 5, and most preferably at least 6.

Bleaching steps in the bleaching unit 30 are typically used to improve the brightness, cleanliness, and brightness stability of pulp. Residual lignin is a major contributing factor in color, so it usually is removed or brightened. Generally, the aim of bleaching pulp is to continue delignification and, by using bleaching chemicals, to remove lignin, known as residual lignin, that remains in the pulp after the cooking and oxygen stages, and which could not be broken down and dissolved in the cooking and oxygen stages without sacrificing pulp yield or fiber properties. Also, in bleaching, chromophorous compounds are typically removed and oxidized to colorless compounds. Typically, an important part of bleaching is washing dissolved lignin out of the pulp on the washer following the bleaching stage.

For bleaching purpose, for example,
- chlorine (Cl₂), ozone (O₃) and/or peroxide acid (Paa and Caa) can be used to react with aromatic lignin units, and/or
- chlorine dioxide (ClO₂) and/or oxygen (O₂) can be used to react in general with lignin structures that have free phenolic hydroxyl groups, and/or
- hypochlorite (H) and/or hydrogen peroxide (H₂O₂) can be used to react with some functional groups.

Usually, the chemical pulp industry desires to maintain a technique in which pulp is bleached in at least one stage with chlorine-containing chemicals in such a way that chlorine dioxide is the main chemical of the bleaching process of the mill. Thus, advantageously at least chlorine dioxide (ClO₂) stage (D-stage) is used for the bleaching purpose.

Bleaching effluent is typically a significant source of both biological and chemical oxygen consumption. For example, phosphorous compounds, chlorine-containing inorganic compounds and/or organic chlorine compounds from the reactions of chlorine dioxide and/or chlorine may remain in the process. Bleaching separates various compounds of lignin from the fibers, which compounds remain in the effluent in the form of organic molecules.
Additionally, sulfuric acid may be used in bleaching stage(s) for pH regulation and as main chemical in the hydrolysis of hexenuronic acids. Sodium hydroxide may also be used for pH regulation and lignin extraction in alkaline stages. In addition to these, depending on the bleaching sequence, oxygen and/or peroxide may be used in bleaching. However, in elementary analysis, they are such substances that their contribution in, for example, purification processes is not noticed.

In an example, sulfuric acid is used for pH regulation, and/or sulfur dioxide and/or other reductants are used for elimination of chemical residuals from the bleaching, i.e. for elimination of unreacted bleaching chemicals.

Advantageously, ECF bleaching is used at the pulp mill according to the present invention, wherein said bleaching preferably comprises both acid and alkaline stages. ECF bleaching covers all such bleaching sequences, which comprise at least one chlorine dioxide stage and which do not use elemental chlorine in any bleaching stage. Modern ECF bleaching used for bleaching pulp typically consists of at least two, more advantageously of at least three bleaching stages comprising preferably at least three washing apparatuses. Advantageously, the number of the bleaching stages in the bleaching unit is 1, 2, 3, 4, 5, 6 or 7, more preferably between 2 and 6, and most preferably between 3 and 5.

If chlorine dioxide is used in the bleaching stage, most typically the doses are between 5 and 15 kg chlorine dioxide /adt pulp. The chlorine dioxide doses for softwood are preferably between 25 and 35 kg act. Cl/adt and for hardwood between 20 and 30 kg act. Cl/adt pulp. If a mill is to further decrease the amount of organic chlorine compounds, the aim of the mills is typically to treat them within the mill rather than to decrease the use of chlorine dioxide.

The pulp mill preferably comprises a chemical recovery plant including an evaporation process, for example, with an in-series connected evaporation plant, a chemical recovery boiler, removal of chlorides from the process, and a chemical production plant for producing cooking chemicals.
At least partly closed cycle systems for manufacturing bleached chemical pulp apply to processes where at least part of the water and other chemicals is recycled and reused, which minimizes waste disposal. Advantageously, said systems are used to minimize aqueous effluent and, hence, to protect the environment from the impact of disposal of effluents without significantly jeopardizing the processing cost or the value of saleable products. In addition to the phosphorus, chlorine, potassium, calcium, manganese, silicon, aluminum, iron, and barium are often some elements of concern in a bleached chemical pulp mill.

Advantageously, at least one effluent treatment line of the waste water treatment plant is provided with biological treatment. Biological treatment is efficient specifically when the proportion of detrimental organic substances is decreased, which mainly comprise lignin compounds separated in bleaching, hemicelluloses and components originating from extractives, which constitute a significant portion of effluent coming from the bleaching plant. There are various wood-originating compounds, and part of the compounds may be chlorinated and part of them may be low-molecular compounds of carbon and hydrogen. As microbes act so that they use as nutrition only the organic portion of effluent, all inorganic substances, at least inorganic elements, remain in the effluent. Thus, biologically treated water, after separation of the solid and liquid fraction, e.g. by sedimentation, has an organic load that makes it clearly cleaner than effluent treated in other ways, but due to the inorganic substances it typically has to be discharged from the process.

In addition to or instead of the biological treatment, the purification stage may be e.g. chemical, whereby the purpose is to remove, for example, metals by precipitating, whereby also part of the organic substances are removed. Alternatively or in addition to the above mentioned stages, a filtration technique can be applied, such as ultrafiltration and/or a method based on membrane technique and/or osmosis. In other words, in addition to or instead of the biological treatment, for example ultrafiltration membranes, ion exchange, chemical precipitation, sedimentation, flotation, and/or filtration may be used for treating effluents.
The pulp mill has also process waters, such as cooling waters, white water from the drying machine, sealing waters, reject flows, channel waters, washing waters of the plant, and rain waters, as well as wood processing water. These waters, or at least part of them, may be circulated at the pulp mill without a purifying step in the waste water treatment plant.

Figure 1 shows an example of a pulp mill.

Typically at the pulp mill, chips and white liquor are supplied to a digester for the cooking of the pulp. After the cooking the cooked pulp, so called brown stock, is fed to the washing and oxygen stages. Typically, hot water is used for said washing stage(s). Weak black liquor coming from the cooking is conveyed from the cooking to a recovery island 40. The recovery island 40 comprises all the equipment for chemical recirculation. The recovery island preferably comprises
- an evaporation plant,
- a recovery boiler
- a recausticizing plant, and
- a lime kiln.

Advantageously, the phosphorus containing filtrate 27a is first conveyed from the phosphorus removal step 27 to an evaporator plant of the recovery island 40.

The weak black liquor from the cooking is typically conveyed to an evaporation stage, in which some water is removed from the weak black liquor and, therefore, strong black liquor is generated. The water removed from the weak black liquor, i.e. condensates from the evaporation, is preferably conveyed to the washing stages or the brown stock.

The strong black liquor generated in the evaporation stage is treated in order to obtain green liquor. The green liquor is further treated in order to obtain white liquor that can be reused for the cooking. From the washing and oxygen stages of the brown stock, the pulp is conveyed to the bleaching unit.

The bleaching unit typically comprises several bleaching stages for bleaching the pulp. The bleaching unit typically generates acid and alkaline effluents
while bleaching the pulp, which effluents are typically conveyed to the waste water treatment plant. The bleached pulp is preferably conveyed to the pulp drying machine 80.

Figures 2 to 3 show some example process steps in a reduced schematic chart. These can be implemented, for example, at the pulp mill according to Figure 1.

The present invention preferably comprises

- a brown stock preparation unit 20 comprising at least an alkaline cooking unit 21, a brown stock washing unit 22 and an oxygen delignification unit 25 for producing pulp,
- a bleaching unit 30 that preferably uses ECF bleaching in which chloride-containing effluents are formed, or alternatively uses TCF bleaching instead of the ECF bleaching, and
- an effluent purification plant (waste water treatment plant 50) for treating bleaching plant effluents and/or other effluents generated at the pulp mill.

The oxygen delignification unit preferably comprises an oxygen treatment stage, after which is a post-washing unit 25X of the oxygen delignification unit. The post-washing unit may comprise, for example, a DD washer, a wash press, and/or a press for washing the pulp after the oxygen treatment.

In addition to the above mentioned, the present invention preferably comprises an apparatus, such as pipe(s) and pump(s), for an acidification stage 26, in which phosphorus compounds containing filtrate is formed, and another apparatus, for example a washing unit, such as a DD, a wash press, and/or a press, for phosphorus removal step 27, in which said phosphorus compounds containing filtrate is at least partly removed from the unbleached pulp flow. Said apparatuses are preferably placed before the first bleaching stage of the bleaching unit, most preferably after the post-washing 25X apparatus of the oxygen delignification unit. In addition, the invention preferably comprises a recovery island 40 where the phosphorus compounds containing filtrate 27a is preferably conveyed.
The phosphorus removal step 27 and the post-washing unit 25X of the oxygen delignification stage may be implemented by similar washing units.

During the oxygen delignification stage 25, a part of the residual lignin left in pulp after the cooking 21 and the brown stock washing 22 is removed using oxygen and alkali. Thus, the oxygen delignification stage 25 is used to remove much of lignin from unbleached pulp. Delignification with oxygen is typically a more gentle way of reducing the kappa number, than extended cooking. It may also lower the amount of bleach plant effluents, and may reduce the need for environmentally unfriendly chlorine-based bleaching agents in the bleaching.

During the oxygen delignification stage 25 that is implemented in the oxygen delignification unit, alkali, oxygen and steam are preferably added to the pulp coming from the brown stock washing unit 22. During the oxygen treatment, oxygen gas is preferably brought into contact with the fiber material under alkaline conditions. The fiber material preferably has enough OH-ions to neutralize and dissolve the organic acids, which are generated in oxygen-lignin reactions. After a predetermined retention time the substances formed in the reactions and residual chemicals are washed out in washing and dilution step(s).

The oxygen delignification stage 25 typically comprises the oxygen step followed by washing unit(s). After the post-washing unit 25X of the oxygen delignification step, the system preferably comprises the acidification step 26, after which is the phosphorus removal step 27. Preferably the phosphorus removal step is implemented by a washing unit.

The amount of phosphorus compounds in the pulp flow is preferably decreased during the brown stock preparation stages. Preferably, the amount of phosphorus compounds is decreased after the oxygen treatment step of the oxygen delignification unit, most preferably after the post-washing step of the oxygen delignification unit, but before the first stage of the bleaching unit. Advantageously, the oxygen delignification washing steps comprise post oxygen delignification (PO) washing device, after which the unbleached pulp is acidified at least partly. Therefore, most preferably the unbleached pulp is
acidified in an acidification stage 26 to dissolve the acid soluble phosphorus at least partly from the unbleached pulp flow into the filtrate to form the phosphorus containing filtrate.

After the acidification stage 26, is preferably a phosphorus removal step 27 to remove at least part of said phosphorus containing filtrate from the acidified pulp flow. In the phosphorus removal step, the pH of the acidified pulp flow is preferably less than 9, less than 8, or less than 7.5, more preferably less than 7. In addition, the pH of the acidified pulp flow is preferably at least 2 or at least 3, more preferably at least 4 or at least 5 and most preferably at least 5.5 or at least 6 in the phosphorus removal step 27.

The pH of the phosphorus containing filtrate 27a is preferably less than 9, less than 8, or less than 7.5, more preferably less than 7, in the phosphorus removal step 27. In addition, the pH of the phosphorus containing filtrate 27a is preferably at least 2 or at least 3, more preferably at least 4 or at least 5 and most preferably at least 5.5 or at least 6 in the phosphorus removal step 27.

During the acidification stage 26, the acid soluble phosphorus is typically at least partly dissolved from the pulp into the filtrate, after which at least part of the phosphorus compounds containing filtrate 27a is conveyed to the recovery island 40. Therefore, the amount of phosphorus in the unbleached pulp flow is preferably decreased after the post-washing step of the oxygen delignification unit, and before the first bleaching stage of the bleaching unit 30.

The total phosphorus content in the brown stock flow depends, among other things, on the phosphorus content of the wood that is used as raw material. Advantageously, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, or at least 95% of the acid soluble phosphorus is dissolved from the pulp into the filtrate due to the acidification stage 26.

Advantageously,
- sulfuric acid,
- acetic acid,
If at least two different chemicals are used for the acidification stage 26, every acid has preferably a separate dosage point. Therefore, the acidification stage 26 preferably comprises at least as many acidification steps 26a, 26b as it has acidification chemicals.

In an example embodiment, the total amount of the acidification chemical(s) needed for the acidification stage 26 may be calculated when:

- the pH level before the acidification stage 26, and
- the pH level that is wanted in the phosphorus removal step 27 are known.

The retention of the acidification chemical(s) used in the acidification stage 26 preferably happens very fast, and preferably does not take more than few seconds, for example less than 5 seconds.

Preferably, sulfuric acid (H₂SO₄) is used for the acidification stage 26. Advantageously, the amount of sulfuric acid calculated from the all kinds of acid(s) dosed in the acidification stage is at least 30%, or at least 40%, more preferably at least 50%, at least 60% or at least 70%.

Advantageously, the acidification chemical(s) used for the acidification stage 26 is/are added to the unbleached pulp flow during the acidification stage 26 in at least one dosage point, preferably in one, two, three, four, or five dosage points. Advantageously there are 1 or 2 dosage points for the acidification chemical(s) in the acidification stage 26, most preferably exactly 1 dosage point for the acidification chemical(s) in the acidification stage 26.

In an embodiment, a portion of chemical(s) to be used in the first bleaching stage is used for the acidification stage. Therefore, the acid dosage of the first bleaching stage is preferably divided into two doses, they being added to different points of the process: first dose for the acidification stage 26, and the second dose for the bleaching stage. In this case, the system preferably
has only one dosage point for the acidification chemical dose, i.e. the dose of the acidification stage 26. In another example, the system has two or three dosage point for the chemical dose of the acidification stage 26.

The phosphorus compounds containing filtrate 27a is preferably at least partly removed from the unbleached pulp flow in the phosphorus removal step 27. Different technologies may be used to remove either partially or totally the phosphorus compounds containing filtrate 27a from the unbleached pulp flow in the phosphorus removal step 27. Advantageously, the phosphorus removal step 27 comprises a washing stage that comprises a washing unit. In this case, the removed phosphorus compounds containing filtrate 27a coming from the washing unit is preferably conveyed to the recovery island 40. In addition, a portion of the phosphorus compounds containing filtrate 27a may be conveyed to the post-washing unit 25X of the oxygen delignification stage located before the acidification step.

Advantageously, at least 20%, or at least 40%, more preferably at least 60% or at least 80%, and most preferably at least 90%, at least 95%, or exactly 100% of the phosphorus compounds containing filtrate 27a that is removed in the phosphorus removal step 27 is conveyed to the recovery island 40.

The phosphorus removal step 27 preferably comprises or consists of at least one washing unit and/or at least one filtration unit.

In an example embodiment, the phosphorus compounds containing filtrate 27a is at least partly separated from the acidified pulp flow by using filtration technologies during the phosphorus removal step 27.

In an example embodiment, a nanofiltration technique is used in the phosphorus removal step 27.

However, advantageously the phosphorus containing filtrate is at least partly separated from the acidified pulp flow by using a washing device and/or a thickening device during the phosphorus removal step 27, for example by using a wash press, a drum displacement washer and/or a press.
Membranes can be used to remove dissolved phosphorus from the phosphorus compounds containing filtrate. In an embodiment, a method based on membrane technique is used, such as an ultrafiltration membrane, to remove at least a portion of the phosphorus from the phosphorus containing filtrate 27a.

The amount of phosphorous compounds that is preferably removed from the unbleached pulp flow depends, among other things, on the amount of phosphorus in the unbleached pulp flow and the impact of the acid filtrate on Na/S and NPE balance of the mill.

Removing this phosphorus compounds containing filtrate from the main stream, i.e. from the unbleached pulp flow, will reduce phosphorus content of the pulp to be treated in the bleaching unit. Therefore, the total phosphorus load in the waste water treatment plant is also reduced and, as a consequence, the total amount of phosphorus discharged from the waste water treatment plant into the water streams will be reduced.

Most advantageously, the phosphorus compounds containing filtrate 27a removed from the unbleached pulp flow is conveyed (totally or at least partly) to the recovery island. Therefore, the amount of the phosphorous compounds at the waste water treatment plant decreases.

Thanks to the present invention, operational costs and overall efficiency of control of phosphorus discharges may be improved.

**Example 1**

One kind of process for phosphorus reduction according to the present invention is disclosed in this example.

Tests were done at a pulp mill. Acid was added for the acidification stage 26 between the last washing stage of the oxygen delignification unit and the first bleaching stage of the bleaching unit. In addition, another acid dosage was used for a first bleaching stage of the bleaching unit. Thus, the acid was added in two dosage points, but only the first one was for the acidification
stage and the second one was for the first bleaching stage of the bleaching unit. Test results are shown in Table 1.

Before the acidification step, the pH of the unbleached pulp was 10.0, the amount of phosphorus in the pulp was 33.1 mg/kg and the amount of phosphorus in the filtrate was 2.3 mg/L. After the first dosage point of the acid, i.e. the only dosage point of the acidification step, the pH of the pulp was 6.9, the amount of phosphorus in the pulp was 19.3, and the amount of phosphorus in the filtrate was 6.2 mg/L. After the second dosage point, i.e. the dosage point of the bleaching unit, the pH of the pulp was 3.3, amount of phosphorus in the pulp was 11.3 mg/kg and amount of phosphorus in the filtrate was 6.3 mg/L. Therefore, a large amount of phosphorous found in pulp after oxygen treatment dissolved already in the acidification stage at pH between 6 and 7.

Table 1. Test results of the first acidification trial

<table>
<thead>
<tr>
<th>Description</th>
<th>pH</th>
<th>Filtrate (mg/L)</th>
<th>P</th>
<th>Dry pulp (mg/kg) P</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample 1: Post oxygen washed pulp</td>
<td>10.0</td>
<td>2.3</td>
<td>33.1</td>
<td></td>
</tr>
<tr>
<td>sample 2: acidified pulp</td>
<td>6.9</td>
<td>6.2</td>
<td>19.3</td>
<td></td>
</tr>
<tr>
<td>sample 3: after the second dosage</td>
<td>3.3</td>
<td>6.3</td>
<td>11.3</td>
<td></td>
</tr>
</tbody>
</table>

Example 2

Another example for phosphorus reduction according to the present invention is disclosed in this example.

Tests were done at a pulp mill. Acid was added to the system between the last washing stage of the oxygen delignification unit and the first bleaching stage of the bleaching unit. The effect of the acid was tested using 10 sample points having different amount of the acid. The acid used was sulphuric acid.
Before the acid was dosed, the pH of filtrate was 10, and the total amount of phosphorus in the filtrate was 3.4 mg/L. When the amount of the sulphuric acid was 1 kg/adt, the pH of the filtrate was 8.8, and the phosphorus content of the filtrate was 4.7. When the amount of sulphuric acid was 3 kg/adt, the pH of the filtrate was 6.6, and the phosphorus content of the filtrate was 5.9. When the amount of sulphuric acid was 5 kg/adt, the pH of the filtrate was 4.9, and the phosphorus content of the filtrate was 7.0. After this, the amount of phosphorus in the filtrate increased only slightly when the amount of sulphuric acid was increased. The test results are shown in Table 2.

As can be seen from the test results, the acidification of the pulp flow from a pH level of 10 to the pH level between 6 and 7 was already able to increase the amount of phosphorus compounds in the phosphorus containing filtrate from 3.4 mg/L to approximately 6 mg/L.

Table 2. Effect of the acid on the amount of phosphorus

<table>
<thead>
<tr>
<th>Test number</th>
<th>H₂SO₄ dose (Kg/ADT)</th>
<th>Filtrate pH</th>
<th>total P (mg/L)</th>
</tr>
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<tr>
<td>1</td>
<td>0</td>
<td>10,0</td>
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<td>2</td>
<td>1</td>
<td>8,8</td>
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<tr>
<td>3</td>
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</tr>
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<tr>
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<tr>
<td>9</td>
<td>10</td>
<td>3,4</td>
<td>7,6</td>
</tr>
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</table>

One skilled in the art understands readily that the different embodiments of the invention may have applications in environments where optimization at the pulp mill is desired. Therefore, it is obvious that the present invention is not limited solely to the above-presented embodiments, but it can be modified within the scope of the appended claims.
Claims

1. A method for treating liquid flows at a chemical pulp mill, the method comprising
   - producing unbleached pulp in a brown stock preparation unit (20) comprising a cooking unit (21), a brown stock washing unit (22) and an oxygen delignification unit (25),
   - dosing first acidification chemical to the unbleached pulp flow in an acidification stage (26) situated before a first bleaching step of the bleaching unit (30) in order to dissolve at least part of the phosphorus compounds in the unbleached pulp flow,
   - forming a phosphorus compounds containing filtrate,
   - removing at least a portion of said phosphorus containing filtrate from the unbleached pulp flow in a phosphorus removal step (27), and
   - bleaching the unbleached pulp in a bleaching unit (30) comprising at least one bleaching stage.

2. The method according to claim 1, wherein the acidification stage is situated after an oxygen treatment of the oxygen delignification unit.

3. The method according to claim 1 or 2, wherein the phosphorus removal step is situated after the acidification stage and before the first bleaching step of the bleaching unit.

4. The method according to claim 1, 2 or 3, wherein the method further comprises
   - conveying at least a portion of said phosphorous compounds containing filtrate to a recovery island (40).

5. The method according to any of the preceding claims, wherein the oxygen delignification unit comprises a post-washing unit, and the method comprises:
   - dosing the first acidification chemical after washing the pulp in the post-washing unit of the oxygen delignification unit.
6. The method according to any of the preceding claims, wherein the pH of the pulp flow is between 2 and 8 in the phosphorus removal step (27).

7. The method according to any of the preceding claims, wherein the pH of the phosphorus compounds containing filtrate is between 3 and 9 in the phosphorus removal step (27).

8. The method according to any of the preceding claims, wherein the first acidification chemical comprises:
   - sulfuric acid,
   - acetic acid,
   - carbon dioxide, or
   - sulfur dioxide.

9. The method according to any of the preceding claims, wherein the method comprises:
   - dosing second acidification chemical to the unbleached pulp flow after the first acidification chemical dose and before the phosphorus removal step (27),
   - the second acidification chemical comprising:
     - sulfuric acid,
     - acetic acid,
     - carbon dioxide, or
     - sulfur dioxide.

10. The method according to any of the preceding claims, wherein at least 40% of the acid soluble phosphorus is dissolved from the pulp into the phosphorus compounds containing filtrate due to the acidification stage 26.

11. A system for treating liquid flows at a chemical pulp mill, the system comprising:
   - a brown stock preparation unit (20) comprising a cooking unit (21), a brown stock washing unit (22), and an oxygen delignification unit (25),
   - a bleaching unit (30), and
   - a recovery island (40),
   wherein the system further comprises
a first apparatus adapted to dose first acidification chemical to the system before a first bleaching step of the bleaching unit to dissolve at least part of phosphorus compounds in the unbleached pulp flow, and
- a second apparatus for forming a phosphorous containing filtrate and removing at least a portion of said phosphorous containing filtrate comprising dissolved phosphorus compounds from the unbleached pulp flow.

The system according to claim 11, wherein the first apparatus and the second apparatus are situated after the oxygen delignification unit (25) and before a first bleaching stage of the bleaching unit (30).
Fig. 1
Fig. 2

Bleached Pulp

Wood material

Acidified pulp flow

20

21

22

25

26

27

30
Brown stock from Oxygen treatment of the Oxygen delignification unit

Filtrate to washing

25X washing step → 26a → 26b → 27

Acidification chemical

To washing

Unbleached pulp to bleaching 30

Filtrate

27a

Acidified pulp

Filtrate comprising phosphorus compounds

To recovery island 40

Pulp flow

Water/filtrate

Acid

Fig. 3
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. D21C3/04 D21C9/02 D21C9/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Relevant to claim No.</th>
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<td>US 5 938 892 A (MAPLES GERALD E [US] ET AL) 17 August 1999 (1999-08-17) claim 1 column 10, line 18 - line 23 figure 2</td>
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Date of the actual completion of the international search 16 January 2014

Date of mailing of the international search report 28/01/2014

Name and mailing address of the ISA/European Patent Office, P.B. 5818 Patentlaan 2 NL - 2380 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer Ponsaud, Philippe

Further documents are listed in the continuation of Box C. See patent family annex.

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