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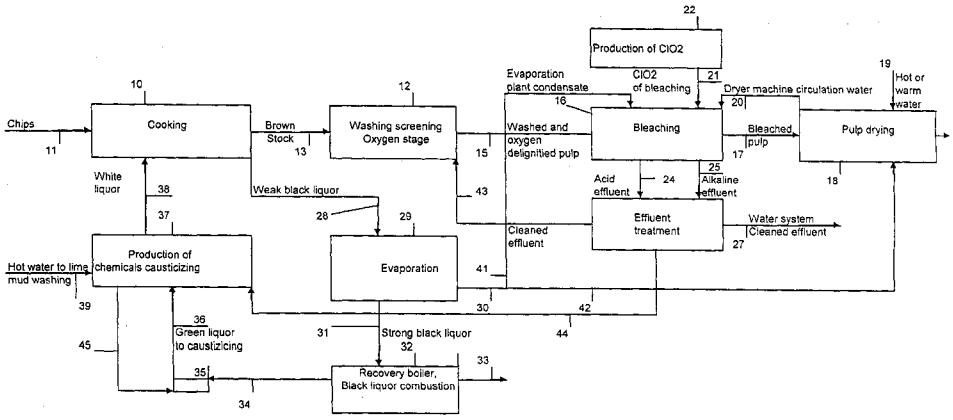
(54) **Title:** METHOD FOR TREATING LIQUID FLOWS AT A CHEMICAL PULP MILL



(57) **Abstract:** The invention relates to a method of treating liquid flows at a chemical pulp mill comprising at least an alkaline cooking process utilizing cooking liquor for producing pulp, brown stock treatment with essentially closed liquid cycles, a pulp bleaching plant using ECF-bleaching wherein chloride- containing effluents are generated, a chemical recovery plant comprising a causticizing plant and chemical recovery boiler plant, and effluent purification. A characteristic feature of the method is that chloride-containing effluents of the bleaching plant are introduced to the effluent purification where they are treated for decreasing the organic matter content thereof, at least 20 % of the purified effluent is led back to a pulp mill process, purified effluent is used in at least one stage of causticizing as raw water source so that the chloride-containing liquid formed in the process stage is a weak white liquor fraction that is led to the recovery boiler plant as a smelt dissolving liquid component and therefrom further via regeneration of cooking liquor, pulp cooking and pulp washing as a waste liquor component to evaporation, wherefrom the concentrated waste liquor is led for treatment into a recovery boiler process, wherein a separation process for chlorides is arranged in order to control the chloride-level of the liquor cycle.

WO 2008/152189 A2

METHOD FOR TREATING LIQUID FLOWS AT A CHEMICAL PULP MILL

The present invention relates to a method for treating liquid flows at a chemical pulp mill comprising at least an alkaline cooking process utilizing cooking liquor for producing pulp, brown stock treatment with essentially closed liquid cycles, a pulp bleaching plant using ECF-bleaching, in which chloride-containing effluents are formed, a chemical recovery plant comprising a causticizing plant and a chemical recovery boiler plant, and effluent purification.

The size of pulp mills has grown intensively during the last years, as today a pulp mill producing 1 million ton/a is of normal size and it does not seem that the growth of the size of pulp mills would be ceasing. At the same time that the size of the pulp mills is growing, the mills are being built in areas and surroundings with very strict environmental regulations. For example, the amount of water used by a mill is strongly restricted. Because the size of the mill grows, minor decreases in the water amounts used by the mill per one ton of pulp do not absolutely decrease the amount of water used by the mill, but the amount is compensated back to the same level as the production size increases. This development is difficult especially in countries where the mill simply does not have enough water available or the water resources should be saved for the needs of people and cultivation. In this kind of situation it is simply impossible to build a mill at a place where other demands of production are easily fulfilled, but due to water resources it is not possible to build a mill. Additionally, 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, it is essential to look for solutions for finding an increasingly closed process.

Chlorine-containing chemicals have been used throughout the production of chemical pulp in several different forms, of which elemental chlorine Cl_2, chlorine dioxide ClO_2 and hypochlorite NaOCl or CaOCl are the best known. Chlorine-containing chemicals have been used also e.g. in the form of hypochlorous acid in bleaching, but no permanent applications remained in use. On the other hand, the chemical pulp industry has desired to tightly maintain a technique in which pulp is bleached with chlorine-containing chemicals so that chlorine dioxide is the main chemical of the bleaching process of the mill. Years-long pressure to reduce the amount of organic chlorine compounds in bleaching effluents has led to the point that first the use of chlorine and hypochlorite was abandoned and further the kappa number of the pulp after digestion was decreased from level 30 to level 10-15 for soft wood and from level 16-20 to level

10-13 for hard wood using an oxygen stage. In 1990s, the aim was to abandon the use of chlorine dioxide as well and many mills switched to the use of total chlorine free (TCF) bleaching technique, wherein the use of chlorine dioxide, too, was replaced by totally chlorine-free bleaching chemicals, such as ozone and peroxide. With this technique, the mills got rid of all chlorine-containing chemicals, but on the other hand many paper producers were unsatisfied with the properties of pulp produced without chlorine chemicals. Therefore, the marginal term for all solutions relating to the closing of the mill is that chlorine dioxide is still used as bleaching chemical.

Thus the dominating position of chlorine dioxide as bleaching chemical has even gained more power during the last years, and not even the latest researches or industrial experiences have managed to destabilize its position, but as a rule the whole pulp industry, with only a few exceptions, has approved the use of chlorine dioxide as the key chemical in bleaching. Thus, if a mill is to further decrease the amount of organic chlorine compounds, the aim of the mills will be, first and foremost, to eliminate them and to treat them inside the mill, rather than to decrease the use of chlorine dioxide.

Chlorine dioxide is a chemical compound having one chlorine atom and two oxygen atoms. So, the atomic weight of the compound is about 67.5 g/l, wherefrom the portion of chlorine is 52.5%. As one chlorine dioxide as oxidation potential corresponds 2.63-fold to the oxidation potential of chlorine, it can be calculated that the use of one kilogram of chlorine dioxide in bleaching corresponds to a chlorine dose of 2.63 kg, and because 52.5% of the chlorine dioxide is in the form of chlorine atom, the bleaching stage receives only 19.9% of the amount of chlorine that would be dosed into the pulp for example in the chlorination stage. For this reason, chlorine dioxide is a compromise in view of bleaching efficiency and environmental effects, combining both a good bleaching efficiency and reasonable emissions to the surroundings.

Modern ECF-bleaching used for bleaching pulp, is typically formed of at least three bleaching stages and three washing apparatuses. In a special case there may be only two washing apparatuses, but such applications are rare. ECF-bleaching covers all such bleaching sequences, which have at least one chlorine dioxide stage and which do not use elemental chlorine in any bleaching stage. Because the use of hypochlorite is due to pulp quality reasons restricted to the production of only a few special pulps, such as dissolving pulps, also hypochlorite is not regarded to be used in the production of ECF-pulp, but it is not totally ruled out. Additionally, the bleaching sequence comprises one alkaline stage, wherein the additional chemicals used are today typically ei-

ther oxygen, peroxide or both. Further, modern bleachings may use ozone, various types of acid stages and a chelate stage for removing heavy metals. In literature, the bleaching stages are described with letters:

O= oxygen delignification
D= chlorine dioxide stage
H=hypochlorite stage
C=chlorination stage
E=alkaline extraction stage
EO=alkaline extraction stage using oxygen as additional chemical
EP=alkaline extraction stage using peroxide as additional chemical
EOP(PO)=alkaline extraction stage using oxygen and peroxide as additional chemical
P=alkaline peroxide stage
A=acid hydrolysis stage, stage of removal of hexenuronic acids
a=pulp acidation stage
Z=ozone stage
PAA=peracetic acid stage, acid peroxide stage

In this patent application the chemical amounts and other amounts are given per one ton of air dry pulp (adt pulp, i.e. air dry metric ton of 90% dry chemical pulp).

When bleaching is called ECF-bleaching, the amount of chlorine dioxide used in the bleaching sequence is more than 5 kg act.Cl/adt pulp. If chlorine dioxide is used in one bleaching stage, most typically the doses are between 5-15 kg act. Cl/adt. The doses refer to active chlorine, whereby when converting to chlorine dioxide the dose has to be divided by a ratio of 2.63.

If the use of peroxide in bleaching is restricted to doses smaller than 6 kg and if chlorine dioxide is the main bleaching chemical, so then the chlorine dioxide dose in the bleaching increases from a level of 25 kg/adt depending on the bleaching properties of the pulp and on how much the kappa number of the pulp has been decreased before starting the bleaching using chlorine-containing chemicals. Thus, the bleaching technique may in view of the process be fairly freely adjusted to various levels of chlorine dioxide consumption so that the amount of chlorine-containing chemicals exiting the bleaching corresponds to the capacity of the chemical cycle to receive chlorides.

In connection with the present invention it is in view of practice most preferable to choose as reference sequence for hard wood a bleaching sequence A/D-EOP-D-P ef-

fected with four bleaching stages and leave ozone out. The corresponding sequence for soft wood is D-EOP-D-P. Then the quality of the pulp can be regarded to correspond to the qualities required from ECF-pulp and the pulp yield remains reasonable. Then the chlorine dioxide doses for soft wood are typically between 25-35 kg/adt and for hard wood 20-30 kg/adt. These values can be regarded as design values, and there is no need to invent any new specific techniques for bleaching. The theory of bleaching and various connection alternatives render a possibility for countless different bleaching sequences starting from the connection of two washing apparatuses up to six-stage bleaching sequences. At the same time, the number of chlorine dioxide stages may vary from one up to four and therebetween are alkaline stages as appropriate.

When the amount of active chlorine is calculated as described above in form of the chloride amount, it is noted that even with soft wood, for obtaining a good bleaching result, the bleaching line produces about 10 kg of chlorides per one ton of pulp and a hard wood bleaching line even less. If the plant is closed such that less and less of fresh water is led into bleaching, there may be a need to prepare for chlorine dioxide doses of even 50% greater, and on the other hand the amount of chlorides in bleaching effluents increases up to a level of approximately 15 kg, meaning that in practice the greatest doses of active chlorine are 60-70 kg/adt. Values higher than this cannot be considered economically reasonable, but the basic bleaching solution complies with these starting points.

One suggested technique for decreasing the environmental effects of chlorine-containing chemicals is the closing of the liquids cycles of bleaching plants, and modern bleaching plants have reached to an effluent level of 10-15 m^3/adt without a decrease in pulp quality. Nevertheless, even when decreasing the amount of bleaching effluent from a level of 15 m^3/adt to a level of 10 m^3/adt an increase in chemical consumption is seen, which thus leads to an ever increasing amount of organic chlorine compounds out of bleaching. Thus, a conclusion may be drawn that the closing of the water cycles of bleaching as such does not have a direct influence in the amount of organic chlorine compounds, but on the other hand a smaller amount and a greater concentration of effluents allow for easier and more economical cleaning thereof.

Chloride-containing chemicals are used in bleaching so that the total chloride dose into the chemical cycle is 5-10 kg of chlorides per one ton of chemical pulp. Because this amount has to be made to pass so that the amount of liquid to be evaporated in the process remains reasonable, the challenge is to find such a process arrangement,

where a chloride-containing liquid replaces some other liquid used in a process at the mill. Thus there is no need for separate treatment stages, new non-productive sub-processes at the mill, but the treatment can be carried out by means of existing process stages.

In order to be able to optimize the treatment of a chloride-containing liquid and in practice the treatment of bleaching effluent, it is inevitable to first know the properties of the effluent. In the bleaching, inorganic chlorine-containing compounds and organic chlorine compounds from the reactions of chlorine dioxide or chlorine remain in the process. Bleaching separates from the fibers various compounds of lignin, which remain in the effluent in form of organic molecules. Additionally, sulfuric acid is used in bleaching for pH regulation and as main chemical in the hydrolysis of hexenuronic acids. Sodium hydroxide is also used for pH regulation and lignin extraction in alkaline stages. In addition to these, depending on the bleaching sequence, oxygen and peroxide are used in bleaching, which, however, are in elementary analysis such substances that their contribution in for example purification processes is not noticed. In some special cases, also hydrochloric acid may be used in pH regulation and sulfur dioxide or other reductants in elimination of chemical residuals from the bleaching, i.e. in elimination of unreacted bleaching chemicals.

Closing of the bleaching is based on recycle of filtrates of washing apparatuses from later bleaching stages to preceding stages. The bleaching is planned only for circulating filtrates between bleaching stages and pulp from one stage to another to react with different bleaching chemicals. Thus, closing the whole bleaching is as an idea based on the fact that all substances separated in bleaching end up in filtrates. Optimizing the closing of bleaching is in a great part based on the way how reaction products of bleaching disturb the process of bleaching. Although in many various connections it has been stated that different degrees of closing are possible, practical experience has shown that such washing water arrangements of bleaching where the filtrates are connected so that the amount of effluent is less than 12-13 m^3/adt increase the consumption of bleaching chemicals. Naturally, the quality of the pulp and the construction of the bleaching plant dictate the amount of additional chemicals used in the bleaching as the effluent amount of the plant decreases below the above presented level.

Often a research dealing with the closing of bleaching ends in a conclusion that the closing of bleaching succeeds, but the bleaching should be provided with a sink or a kidney in which detrimental inorganic substances could be separated from the proc-

ess. This kind of kidney is often described as a process operating with either membrane technique or ultrafiltration, which again would be a kind of new and separate by-process at the mill. In addition to that, the processes are fairly new and their continuous technical performance has been questioned. As the above-stated is combined with remarkable operational costs, the technology development has not become general.

Thus, partial closing of bleaching and external purification of the generating filtrates (with a volume of 10–15 m^3/adt) using e.g. filtration, various known forms of biological treatment, different techniques of chemical treatment and clarification has been regarded as the so-called best available technology for bleaching effluents. After this, the treated water is led back to the water way to the same channel wherefrom the liquid was taken to the mill process or to a different channel. This is in use at both TCF- and ECF- mills. 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 is an ample amount of various wood-originating compounds, and part of the compounds are chlorinated and part of them are low-molecular compounds of carbon and hydrogen. As microbes act so that they use as nutrition only the organic portion of effluent, all in-organic substances, at least in-organic elements remain in the effluent. Thus, biologically treated effluent has an organic load that makes it clearly cleaner than effluent treated in other ways, but due to the in-organic substances the only choice has been to discharge it from the process.

The present invention eliminates above-mentioned problems and provides a pulp production process using chlorine dioxide and a chemical recovery process, in which the effluent emission is minimized such that the chloride does not accumulate in the process. Thus, when combined with an efficient chloride-removal from the process at the recovery boiler, chloride compounds led in the chemical cycle will not be a problem, but the only criterion for water being circulated at the pulp mill will be the amount of organic compounds and their adverse effect in the process. So, modern recovery boiler technique is key to a closed pulp mill and the present invention determines the principles according to which the whole chemical cycle of a chemical pulp mill is to be finally arranged so that it utilizes to the maximum the possibilities provided by the new technique.

A public research was carried out at the University of Oulu, Finland, on the washing process of pulp bleaching and the operational efficiency of process stages between the washing processes compared to the efficiency of a preceding washing stage (Viirimaa, M., Dahl, O., Niinimäki, J., Ala-Kaila, K. and Perämäki, P. Identification of the wash loss compounds affecting the ECF bleaching of softwood kraft pulp. Appita Journal 55(2002)6, 484-488). The decrease in the bleaching stage efficiency is observed either as decreased brightness development or as a higher kappa number after a bleaching stage or bleaching stages. According to an essential result of the research, the most important individual component in the filtrate hindering the bleaching is lignin. Based on said research, two conclusions can be drawn: The amount of inorganic substances in a bleaching stage is not essential in view of the bleaching result and by specifically removing the lignin or remarkably decreasing the amount of lignin the bleaching result could be clearly improved and finally reach a bleaching result which is at the same level as in a bleaching plant, the filtrate cycles of which are not closed. This result renders a possibility of significantly optimizing the bleaching process. As the effect of inorganic compounds on chemical consumption is basically not significantly essential, for pulp washing can be accepted a washing water having significant amounts of inorganic compounds. These issues are utilized in the process according to the invention.

A causticizing plant of a chemical pulp mill typically comprises green liquor filtration, mixing of unslaked lime and green liquor, and causticizing vessels for carrying out a causticizing reaction. In the reaction, sodium carbonate reacts with calcium oxide such that sodium hydroxide and calcium carbonate are obtained. The generated white liquor is filtered by means of filters dedicated thereto and calcium carbonate i.e. lime mud is washed by means of a lime mud filter so that it can be transferred to a lime kiln. In the lime kiln, the calcium carbonate under the effect of heat reacts to calcium oxide. Additionally, causticizing produces different precipitates from e.g. metal and organic substances, which are collected from the causticizing slaker and causticizing vessels and filters thereafter, and these are removed from the dregs filter. Thus, also the causticizing plant has liquid cycles that need to be closed and connected to other processes of the pulp mill in a preferable way.

US patent 4039372 (FI-patent 63794) discloses that a portion of the acid bleaching filtrate after neutralization is used in white liquor production.

The present invention relates to a method of treating liquid flows at a chemical pulp mill provided with an alkaline cooking process and a closed chemical cycle based on liquor,

which comprises at least an alkaline cooking process utilizing cooking liquor for production of pulp, and brown stock treatment with essentially closed liquid cycles, a pulp bleaching plant using ECF-bleaching, in which chloride-containing effluents are formed, a chemical recovery plant comprising a causticizing plant and a chemical recovery boiler plant, and effluent purification. A characteristic feature of the invention is that chloride-containing effluents of the bleaching plant are introduced to effluent purification where they are treated for decreasing the organic matter content thereof, at least 20 % of the purified effluent is led back to a chemical pulp mill process, at least a portion of the purified effluent is used in at least one stage of causticizing as raw water source so that the chloride-containing liquid formed in the process stage is a weak white liquor fraction that is led to a recovery boiler plant as a smelt dissolving liquid component and therefrom further via regeneration of cooking liquor, pulp cooking and pulp washing as a waste liquor component to evaporation, wherefrom the concentrated waste liquor is led for treatment into a recovery boiler process, wherein a separation process for chlorides is arranged in order to control the chloride-level of the liquor cycle.

Purified effluent is typically used at the causticizing plant as dilution and/or washing liquid. Preferably purified effluent is used at some process filter of causticizing as dilution liquid, and weak liquor formed therein is taken into a recovery boiler dissolver. Preferably, purified effluent is used for lime mud washing, and the weak liquor formed therein is taken into a recovery boiler dissolver.

Preferably, evaporation plant condensates and hot water are additionally used as dilution and/or washing liquid at some process filter of causticizing.

According to an embodiment, untreated effluent is additionally used in lime mud dilution and/or washing in a lime mud washing device, and the formed weak liquor is taken into a recovery boiler dissolver.

According to a preferred embodiment of the invention, purified effluent is also used in a last washing stage included in brown stock treatment, and in brown stock treatment the liquid flow is passed counter-currently to evaporation, wherefrom it is led for treatment to a recovery boiler process, wherein a separation process for chlorides is arranged for controlling the chloride level of the liquor cycle.

An alkaline cooking process, such as a kraft process or a sulfate process or a soda process, is based on batch cooking or continuous cooking comprising a digester or several digesters. Brown stock treatment comprises a washing process, and typically oxygen delignification, typically a screening process and washing after oxygen delignification, which washing can comprise one or several washing devices. The screening may be located after digester blowing, in the middle of or after the washing process or after oxygen delignification. These process stages are followed by a bleaching process based on ECF-technique, which comprises a pulp bleaching plant with one or more bleaching stages based on the use of chlorine dioxide in addition to stages using other known bleaching chemicals. The arrangement of the mill also comprises a chemical recovery plant comprising a black liquor evaporation process typically with an in-series connected evaporation plant, a chemical recovery boiler, removal of chlorides from the process, a chemical production plant for producing cooking chemicals.

According to a preferred embodiment of the invention the effluent being returned is heated by means of heat obtained from the effluent being led to purification and heated effluent is used at the chemical pulp mill. Preferably the connection comprises a heat exchanger system, in which the effluent being returned from purification is heated by means of heat obtained from the effluent being led to purification. Heated, purified effluent is used in the caustizicing plant and e.g. in the last washing stage included in brown stock treatment.

In accordance with the invention, at least 20 % of the purified effluent is recycled to the chemical pulp mill, preferably at least 40 %, most preferably at least 60 %. In addition to the causticizing, a portion of the returned purified effluent, at least 40 %, preferably more than 60 %, is typically used for brown stock washing, adding it most preferably to the last washing apparatus of the washing following the oxygen stage.

Because the technique presented herein is based on solutions affecting the arrangements of the mill and the balance of the mill, it is not possible here to define in great detail all the processes which are influenced by the new arrangement. Nevertheless, e.g. literature describes known processes of the whole mill, and the apparatuses and pulp production methods included in this patent application are essentially known per se. Further, the application of the present invention is based on apparatuses known per se. Thus, developing new technical innovations sometime in the future is not necessary for implementing the present invention. The present invention can be implemented at a chemical pulp mill having a digestion process, bleaching, other

treatment of pulp, chemical recovery and chemical production comprising various reactors, vessels, pumps, mixers, filters etc. known per se. For instance, the invention is not limited to certain washing devices, but the pulp washing appparatus using purified effluent can be a Drum Displacer™(DD) -washer, a washing press, a drum washer, suction washer, pressure washer, disc filter or corresponding device for washing pulp.

When the effluent coming from the bleaching plant has been purified in a biological effluent treatment plant representing the newest technologies, the chemical oxygen demand, COD, thereof has decreased by more than 70 % and the organic chlorine compounds content by AOX-measuring has decreased by more than 50 %. If an anaerobic treatment stage is added to the system, so also the color of the water being treated has decreased remarkably. Thus, this biologically treated water is clearly cleaner than conventionally recycled filtrates in the D_0 stage and the first alkaline stage of the bleaching plant. The effluent can also be subjected to chemical purification methods that are based on precipitation or oxidation of oxidizable compounds. The availability of this treated filtrate at a last washing apparatus of the oxygen stage, wherefrom it is passed in remarkable amounts entrained in the pulp to the first stage of bleaching, is much better in view of the organic matter than the use of filtrates from said bleaching stages, for instance from the D_0 -stage, in bleaching or even in brown stock washing. For instance the technology definition of the European Union dealing with the technology of the forest industry, Bat, i.e. Best Available Technology, defines the object of application of the filtrate from the first alkaline stage to be the washing following the oxygen stage. On the other hand, chemical pulp producers utilizing pressing technology have already during many years diluted pulp only with a filtrate from the D_0 stage prior to the D_0-stage. Due to this connection, chemical consumption of the bleaching as a whole has increased, but nevertheless it has remained at a level that has in many cases been acceptable.

If the last apparatus before bleaching is a press or a washing press, then the water consumption thereof is divided such that the washing uses liquid in the amount of 3-6 m^3/adt and the pulp is discharged from the apparatus at a consistency of higher than 20 %, typically at 25–35 %. Because after this the situation is such that the pulp is to be diluted prior to bleaching to a pumping consistency of 8–16 %, for which purpose the consumption of dilution liquid is 3–6 m^3/adt. Now, if both liquids are purified effluent from the purification plant, chlorides are passed into the chemical cycle. If only the dilution liquid is replaced with purified effluent from the purification plant, lignin removal provides remarkable advantages in chemical consumption compared to unpurified fil-

trates from the bleaching, but then the chemical cycle remains unchanged and chlorides are not passed to the recovery boiler. This can be a recommendable connection when the recovery boiler is not provided with devices by means of which chloride levels can be controlled. If, however, a press-type of washing apparatus is used, purified effluent from the purification plant can be used for washing, and fresh water, filtrate from the bleaching or a mixture of them can be used for dilution.

US patent application 12/107877 and corresponding patent application PCT/FI2008/000053 describe possible techniques for treating bleaching effluents so that they are finally passed into the recovery boiler for combustion and separation. An essential feature of this application is that the treatment of chloride-containing liquids in the recovery boiler process does not lead to stronger corrosion and that the recovery boiler process is excellent for separating chloride-containing compounds from the process in order to prevent the accumulation of chlorine. There the chlorine content of flue gases is maximized by increasing the temperature of the combustion zone, where the chloride-containing liquor is combusted. Preferable combustion conditions are determined for the recovery boiler, under which chlorides will start to volatilize into flue gases, and a process location, where the chloride can be removed from the process. More than 30 %, preferably more than 40 % of the chlorine content of liquor being combusted is volatilized into flue gases, which are treated for removing chloride-containing compounds. Chloride and potassium are enriched in the flue gas ash, wherefrom Cl and K can be removed e.g. by means of know methods, which are most typically based on leaching, evaporation-crystallization or cooling crystallization. Thus, the novel process allows making the recovery boiler a chloride sink of the mill and the whole problem caused by chloride is eliminated there, where it was previously supposed to be most harmful. If the chloride-content would grow excessively high in this solution in view of the desired temperature of steam or temperatures of steams, the final superheating or final superheatings of the steam can be carried out in a way describe in US patent applications 2005/0252458 and 2006/0236696, utilizing in a front chamber fuels that do not cause corrosion.

This process arrangement results in a technique that allows leading the filtrates or purified effluent from the bleaching at a mill utilizing ECF-bleaching to the chemical cycle so that between the introduction point of the chloride-containing liquid and the combustion process in the recovery boiler there are no process stages for decreasing the chloride-content prior to the recovery boiler process. Thus, the novel techniques presented herein are based on a mill unity where the recovery boiler process is capable of treat-

ing the chloride contained in the normal known ECF-process without a separate separation technique prior to the recovery boiler. Known partial processes connected to the recovery boiler process include e.g. methods based on dissolving or dissolving and recrystallizing the flue ash of the recovery boiler. In sulfur-free cookings, chlorine removal can be made also from a dissolver or generally from green liquor. A special feature of the present invention is to provide a clearly more closed system compared to previous pulp mill solutions and to present how to utilize the possibilities provided by the recovery boiler technology. The goal of all the presented solutions is:

1. Decreasing the environmental load of the chemical pulp mill
2. Keeping the use of the pulp mill's chemicals and commodities at least at the present level
3. Maintaining the pulp quality at the chemical pulp mill at essentially the same level as in the existing processes
4. Decreasing the amount of water used by the chemical pulp mill.

Of these goals points 1 and 4 could be accomplished with the same techniques, but in that case goals 2 and 3 will be very laborious and difficult to reach with the same methods. Therefore, the technique presented herein makes all the four goals reachable simultaneously.

ECF-bleaching comprises both acid and alkaline stages. In a typical ECF-bleaching arrangement, a filtrate is discharged as effluent from the first D-stage and from the first alkaline stage. Closing of the bleaching has been studied from many starting points in several publications and the general conclusion has been a level, wherein the connection of the bleaching has been arranged so that a modern ECF-pulp mill produces bleaching effluent in the amount of 6-20 m^3/ adt, most typically 7-16 m^3/adt. When the amount of generated effluent is less than 10 m^3/adt, it has been shown that due to the low effluent amount also the use of bleaching chemicals at the mill starts to grow. Thus, it is essential that the bleaching plant receives an adequate amount of such clean or purified water fractions, which do not increase the bleaching chemical consumption.

Now that the bleaching is part of a closed water process, it is preferable to use oxidized white liquor as an alkaline source for alkaline stages or in neutralizing of effluent instead of clean technical sodium hydroxide. Further, the lime used in effluent neutralization can be replaced with oxidized white liquor. This because of the fact that in the pre-

sent invention the alkaline liquor is returned into the chemical cycle with the purified effluent.

A bleaching sequence, several of which are determined by the relevant literature in the field starting from either two-stage sequences up to historical seven-stage sequences so that after a first acid combination stage or first acid combination stages follows an alkaline stage and after that at present an acid plus acid stage or an acid plus alkaline stage. Acid stages comprise chlorine dioxide stages, ozone stages, a hexenuronic acid removal stage or some stage based on acid peroxide treatment. An alkaline stage is typically a treatment, wherein the pH is increased to exceed 7 by means of some hydroxide compound, most typically sodium hydroxide, and wherein hydrogen peroxide, oxygen, hypochlorite or some other oxidizing chemical is used as additional chemical. In this kind of arrangement, circulation water originating from a pulp drying process after the bleaching plant is introduced to the last washing apparatus located after all bleaching stages, but it can also be used in earlier stages. As this water originates from the water removal process of the drying machine, it belongs to the internal circulation of the chemical pulp mill and thus does not increase the amount of consumed water.

Brown stock treatment after the cooking process includes a washing process, and typically an oxygen stage, screening and an oxygen stage followed by washing. It is known that this process complex is arranged such that the last washing apparatus in the oxygen stage receives the cleanest 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. When the filtrate is recovered from the first brown stock washing apparatus, it is forwarded either directly to a black liquor evaporation plant or it is used in digester plant processes for dilution and displacement, after which it ends up in the black liquor flow.

In the novel solution, the water consumption of the mill has been modernized. Per one ton of air-dry pulp, a conventional arrangement had to use:

3-5 m^3 of condensate or hot water in white liquor production.
4-10 m^3 of condensate or hot water in brown stock washing. Hot water from the digester plant.
1-3 m^3 of liquid originating from the bleaching chemicals, mainly from chlorine dioxide.

1-5 m^3 of hot water for bleaching washes for washing either the drum or rolls and e.g. to EOP-washer as washing water.

2-4 m^3 of fresh water to the pulp drying machine for washing of felts.

1-3 m^3 of purified or raw water to be used as sealing water and for coolings. Of this water approximately 60–80 % can be circulated inside the mill.

Additionally the digester plant uses 0-6 m^3 of fresh water for cooling, and this water is the main source of hot water. Because the digester plant has conventionally been considered as the main source of hot water, the aim has been to produce hot water a certain amount, for instance 2-5 m^3.

As a result of this kind of water consumption, the flows exiting the mill can be determined:

8-11 m^3 together with black liquor to evaporation. Thus the condensate forms an internal circulation.

The solid matter of black liquor is formed of many kinds of compounds which originate from organic, mainly lignin and carbohydrate based compounds.

Condensates are formed from various stages of the evaporation plant in the amount of 7-10 m^3.

8-10 m^3 of effluent from the bleaching to the purification plant containing the chemicals of bleaching,

1-5 m^3 of effluent from the drying plant from felt washing and sealing waters as well as coolings.

The sealing and cooling water flows generate 1-3 m^3, but these fractions can under certain preconditions be circulated with rain waters to channels. Thus, the total amount of generated effluents is

15-25 m^3 per a pulp ton and added thereto the effluent from wood handling. Further, also in wood handling either a filtrate from bleaching or purified filtrate from bleaching can be used without process problems, but as the conventional devices in wood handling are made of carbon steel, the use of a chloride-containing liquid would require revision of the material specifications.

In the novel arrangement, the water consumption per an air-dry pulp ton is mainly divided in the following way:

3-5 m^3 of purified effluent and filtrate from bleaching and/or hot water in white liquor production at the causticizing plant.

4-10 m^3 of purified effluent from the effluent treatment plant in brown stock washing.

1-3 m³ of liquid originating from bleaching chemicals, mainly from chlorine dioxide. Now this can be replaced with e.g. condensate from the evaporation plant or filtrate from the effluent treatment plant.

1-5 m³ of condensate from the evaporation plant for washes in the bleaching for washing of drums or rolls and to the EOP-washer as washing water.

2-4 m³ of condensate water to the drying machine for washing of felts.

1-3 m³ of condensate from the evaporation plant or raw water to be used as sealing water and for coolings. Of this water approximately 60–80 % can be circulated inside the mill.

Additionally the digester plant uses 0-6 m³ of fresh water for cooling, and this water is the main source of hot water. Because the digester plant has conventionally been considered as the main source of hot water, the aim has been to produce hot water a certain amount, for instance 2-5 m³. However, in the novel arrangement the digester plant can heat effluent from the effluent treatment plant or the hot water is to be cooled without utilizing the heat.

As a result of this kind of water consumption, the flows exiting the mill can be determined:

9-11 m³ together with black liquor to evaporation. Thus the condensate forms an internal circulation.

Condensates are formed from various stages of the evaporation plant in the amount of 6-9 m³. These condensates are used at various locations in the process, as presented in the above.

10-15 m³ of effluent from the bleaching to the effluent treatment plant and through the effluent treatment plant to brown stock washing and the causticizing plant, including the chemicals from bleaching.

2-5 m³ of effluent from the drying plant from felt washing and sealing waters as well as coolings.

The sealing and cooling water flows generate 1-3 m³, but these fractions can under certain conditions be circulated with rain waters to channels.

Thus, the total amount of generated effluents is 0-10 m³ per a ton of pulp, more preferably 0-7 m³, most preferably 0-4 m³. Added thereto is the effluent from wood handling. A remarkable portion of these flows consists of sealing waters, collection waters from the channels or other sources that are secondary in view of the process.

So it can be seen that a real technological improvement is obtainable, where the goal can be set as high as to a level of 0 m^3 /adt effluent from the process in a steady running situation.

The amount of effluent is now dependent on the efficiency of utilization of condensate in the mill processes. Additionally, the digester plant always produces a certain amount of hot water, which is either circulated to the process or, if the process does not have opportunities to utilize the water, the water is to be cooled.

Further, also in wood handling either a filtrate from bleaching or purified filtrate from bleaching can be used without process problems, but as the conventional devices in wood handling are made of carbon steel, the use of a chloride-containing liquid would require revision of the material specifications. In a normal mill process the effluents from wood handling are introduced into a common purification process, wherefrom they are returned in form of clean water to the processes of the mill.

In addition to said main streams, there are so-called secondary streams in a chemical pulp mill depending on the locations of the mill, the chosen processes and required final cleanliness levels, which streams have to be subjected to separate treatment stages when closing the mill process. This kind of streams include vent vapors containing mainly water, such a dissolver vent vapor, vent vapor from the gas scrubber of bleaching, vapor originating from flue gases, vent vapor from pulp drying or in case of an integrate even vent vapor from the paper machine drying sector, vent vapor of continuous outblow, ventings of white liquor oxidation, gassings originating from the digester plant, gaseous emissions and water vapor from the oxygen stage, water vapor concentrated from HCLV and LCHV gases and other corresponding secondary streams. Also, the combustion of hydrogen-containing organic substances produces water, which in the total balance of the mill converts to one liquid stream of the mill. All these have their own specific chemical features, and if the aim is a more and more closed pulp mill, e.g. microfiltration, membrane technology, ion change technique, developed evaporation techniques and other developed purification techniques may be needed in addition to the present so-called conventional purification methods. Also these streams can be utilized, either directly or after applicable treatment stages, as process waters of the pulp mill. Thus, these secondary streams are comparable to the condensates of the evaporation plant or to purified bleaching effluent.

The streams presented herein are only examples of some possible solutions. Because there are hundreds of chemical pulp mills having processes with various connections and technologies, it is impossible to define such water usage areas that would apply for all mills. Thus, the areas and amounts presented herein are directive and set frames to the use of water at modern chemical pulp mills, and describe the possibilities that the technique presented herein will improve.

Condensates originate from the black liquor evaporation plant, which condensates are mainly equated with distilled water and comprise several organic small molecule substances of evaporation, which are known from literature and the best known of which is methanol, as well as inorganic compounds of sodium and sulfur. Because condensates from the evaporation plant have already during several years been used in the brown stock washing process to economize on fresh water, cleaning methods for cleaning condensates have been developed inside the evaporator itself, such as condensate segregation systems and external cleaning methods, for instance condensate stripping. Actually it is the object of application of the condensate that dictates the amount worth investing by the mill in the cleaning of condensates. Additionally, an object of study has been the oxidation of organic substances in the condensates with e.g. ozone. The condensates will be very clean and applicable in several objects in the bleaching plant and the fiber line. Now in the novel arrangement it is preferable to use condensate in the fiber line and other departments to new objects, because real economy and advantage in view of chemicals and pulp quality are not reached simultaneously if condensate is not utilized to full extent.

In the system presented herein condensate is used not only and mainly in brown stock washing, but the objects of application of condensate are in pulp bleaching and pulp drying machine process. Thus, the novel arrangement will require adequate cleaning of condensates, so that these can be used in new objects, which finally provide the advantage obtainable from the novel arrangement. As brown stock washing in accordance with an embodiment of the invention is carried out using purified effluent, the bleaching plant has to receive an adequate amount of liquid, so that via a purification process a sufficient amount of washing liquid is obtained for brown stock washing and for a lime mud washing process. For that reason, a preferred water connection for bleaching is a connection, in which a sufficient amount of condensate is introduced to the washing apparatuses of bleaching, whereby 11-15 m^3 of effluent can be delivered to the bleaching effluent purification process.

Further, in view of the operation of the plant, it can be considered preferable, if not all effluent is returned to the process after the treatment, but 0.5-5 m^3/adt of effluent is led in purified form back to the water way. In view of the operation of the mill it can decrease the number of malfunction in the purification process and in mill processes connected to the use of purified effluent, although nothing prevents from using all the purified effluent at the mill.

In addition to bleaching, clean water is needed in the pulp drying plant for cleaning felts and dryer machine textiles. When the condensate is cleaned to an adequate extent, e.g. to a very low content of COD and malodorous compounds, it can be used also in dryer machine processes, such as cleaning water for felts. Further, the condensate is applicable to high-pressure washing of wires used in web formation in a drying process, but typically a precondition for this is that a significant amount of malodorous compounds has been removed from the condensate. As the objects of application of condensate this way increase remarkably, new cleaning methods in addition to conventional condensate cleaning may be needed, such as e.g. ozonization for decreasing the amount of malodorous compounds in the condensate.

The concentrate, i.e. strong black liuquor formed from evaporation is combusted in the recovery boiler process, most preferably as described in the above-mentioned US patent application 12/107877. In that process, the liquor is combusted into energy, but also chlorine-containing inorganic and organic compounds are removed. Thus, in the arrangement according to the invention, the recovery boiler plant preferably forms a so-called sink, wherein the chloride compounds are delivered for removal. In many discussions, a sink or a kidney has been searched for bleaching effluents prior to the recovery boiler process and typically in the fiber line, now this sink is located in the actual recovery boiler.

The chemicals to be regenerated exit the recovery boiler in form of smelt. Smelt is mainly sodium carbonate, sodium sulfide in form of cooking chemicals as well as compounds of mainly sulfur, sodium, carbon and oxygen known from literature. The smelt is dissolved below the recovery boiler in a so-called smelt dissolver, into which filtrate e.g. from lime mud washing is introduced as dissolving liquid.

In a causticizing process, sodium carbonate of chemical smelt is converted to sodium hydroxide. Because sodium sulfide, which is important in view of the total pulp mill process, is generated in the reducing combustion process of the recovery boiler, the

main task of the causticizing process is to convert the sodium carbonate of the dissolved recovery boiler smelt into sodium hydroxide. This is done by mixing calcium oxide and sodium carbonate, whereby the reaction results in the formation of sodium hydroxide and calcium carbonate. Of these, sodium hydroxide is a liquid, but calcium carbonate forms a solid precipitate that can be clarified or filtered for separation.

Prior to the causticizing process, sodium carbonate is in the form of smelt in the recovery boiler, from where it is led from the boiler process into a smelt dissolver. In the dissolver the smelt is dissolved in water, whereby sodium carbonate and sodium sulfide are dissolved in the dissolving liquid. Simultaneously soot and other impurities are passed from the recovery boiler into the dissolver, due to which the color of the liquid i.e. green liquor discharged from the dissolver is turbid and the liquid contains plenty of impurity particles. This green liquor is filtered by means of a green liquor filter and the precipitate is led from the filter to a dregs filter. Because the precipitate of the green liquor filter contains plenty of inorganic components of green liquor, the precipitate is dissolved and diluted after the separation and finally thickened at a dregs filter for recovery of sodium components. From the dregs filter the separated liquid is introduced into weak white liquor in order to be used at the smelt dissolver.

The filtered green liquor is led into a lime slaker, wherein calcium oxide in solid form is mixed into it in. In the mixing reaction the calcium oxide converts to calcium hydroxide and thereafter reacts with sodium carbonate forming calcium carbonate and sodium hydroxide. Impurities in liquid form from the chemical circulation are accumulated at the bottom of the lime slaker, which impurities under alkaline conditions convert to solid form and deposit at the bottom of the slaker. From there they are typically collected out by means of an inclined screw.

After the slaker the mixture of green liquor and calcium hydroxide is led into causticizing vessels, wherein the reaction which has started already in the slaker is allowed to continue long enough in order to obtain a good causticizing level. The causticizing vessels are in series connected containers provided with an intermediate floor so that several compartments are arranged in the containers for maximixing the retention time and each compartment is provided with mixing for ensuring most effective reaction.

After the causticizing vessel the green liquor has converted to white liquor and in the next process stage calcium carbonate i.e. lime mud is separated from the white liquor by means of either clarification or filtration. The filtered white liquor is ready to be used

in cooking as a cooking chemical and the generated lime mud is washed and dried at a lime mud filter. Thus, this process requires clean liquid, which can be condensate, hot water, but in accordance with the invention the liquid is preferably purified effluent originating from effluent purification. Filtrates originating from these lime mud washes and filter dilutions are alkaline and form a portion of the weak white liquor that can be used at the smelt dissolver.

The dry-solids content of purified and dried lime mud is typically over 75 %. It is led into the lime kiln for combustion, whereby the calcium carbonate reacts under the effect of thermal energy and again calcium oxide is formed to be used in the causticizing.

It can be noticed about this process comprising the main features of a causticizing process that causticizing comprises several filtration and washing stages and plenty of liquids are generated in them, which in the case of a closed cycle end up at a smelt dissolver to the beginning of a white liquor production process. Thus, when at least a portion of these liquids is replaced with purified effluent and possibly additionally with unpurified bleaching plant filtrate, it is possible to feed abundantly of chlorides into the chemical cycle and therethrough make them abundantly transfer through the whole chemical cycle into the recovery boiler process.

The water cycle in causticizing is connected so that the so-called clean fractions, such as condensate, hot water or in this case purified effluent from the purification plant or bleaching filtrate are first introduced to said washing devices as dilution water or washing water or to another process location of causticizing so that it is passed to the main flows and finally into weak liquor.

The weak liquor is led to the recovery boiler so that the smelt coming from the recocery boiler is dissolved in it, after which the dry-solids content increases and it is taken into said green liquor filter. In connection with smelt dissolving, liquid is evaporated from the dissolved together with dissolver vent vapor. Thus, a portion of the weak liquor is treated via the vent vapor system of the recovery boiler.

After the smelt dissolver, the weak liquor has converted to green liquor, from which the final cooking liquor is produced in the causticizing process. Filtration, the lime slaker process, causticizing vessels and white liquor filtration for separation of lime mud are connected to this process. However, it is essential that small amounts of foreign substances do not usually affect the properties of cooking liquor, so that e.g. chlorides that

are fed into the cooking liquor are inert in the actual cooking, which is the main object of use of white liquor.

Because the chloride-contents of the liquids of causticizing now change, also the material specifications of causticizing are to be revised to conform to the new situation.

As is known, a causticizing plant uses approximately 2.5-5 m^3/adt of fresh water, most typically 3-4m^3/adt, depending on the sort of wood and the alkali requirement. This is divided such that approximately 1-2 m^3 of it is clean washing liquid for minimizing TRS-emissions and the rest 2-4 m^3 is condensate originating from the evaporation plant. These liquids used for washes and dilutions originate from e.g. the lime mud filter, where the lime mud is washed prior to the lime kiln and which thus has received a portion of the alkali. Because new objects of application are desired for bleaching effluents, either purified or unpurified and because in accordance with the invention the aim is to obtain chloride-containing liquids as much as possible via chemical circulation to the recovery boiler, in accordance with the invention, unpurified bleaching effluent can additionally directly be used for lime mud washing. As the effluent may contain compounds that are not suitable for lime mud washing, a liquid passed through a purification process is more preferably used for the same purpose. Thus, the system can be provided with chloride-containing liquid, which can to an adequate extent be removed in the recovery boiler process.

Further, fibers and solid matter has been removed in clarification from an effluent passed through a purification plant process, so that these substances do not cause trouble in the filters in the causticizing.

However, the chemical production plant has been developed such that the water used therein is as clean as possible and above all the amount of volatile sulfur compounds is to be low. At the chemical plant liquids are needed in all the filters of the plant, such as in a green liquor filter, dregs filter or lime mud filter for dilutions and in some cases for washing. As the unpurified bleaching filtrate contains mainly non-volatile substances of lignin and cellulose, and chlorides, sodium and sulfur in form of sulfate, the emissions therefrom, e.g. TRS-effluents, do not cause a major risk. TRS-emissions are generated when substances used in lime mud washing are passed into the lime kiln and released in form of malodorous or other detrimental compounds. In the presented solution, preferably a remarkable portion of the water from a white liquor plant is introduced after biological treatment, whereby the organic load has decreased remarkably. It is possible

to wash the lime mud additionally with clean water even though in filter dilution the presented solution is used, in which a portion of the liquid is replaced with liquid fractions originating from bleaching.

As the use of liquid fraction originating from bleaching has been solved in a new way and provides clear economy either in water usage or effluent amount, it provides a possibility to contemplate installing additional devices or cleaning systems in the lime kiln. In the lime kiln, a large amount of substances regulated by environmental licenses are released, the amount of which is determined for the mill with official decision. Thus, if the mill with the novel arrangement is capable of dramatically decreasing the amount of effluent from the mill, a situation will finally be reached where the cost of the filtering and cleaning devices installed in the lime kiln is as a whole reasonable in view of the whole mill.

Because in the novel arrangement purified effluent is delivered to various objects of application in the process, different fractions of the effluent may be exposed to various types of quality requirements. Thus, the effluent treatment process can be carried out so that e.g. fractions containing more lignin are divided into one purification line and fractions containing less lignin but more color compounds are purified in another line. Also various effluent fractions such as foul filtrate of an acid filtrate, clean fraction of an acid filtrate and alkaline filtrate can be purified in a process following the bleaching as separate fractions so that their properties in the object of reuse will be optimal.

Effluent purification processes typically comprise pre-treatment, neutralization, biological treatment by an aerobic or anaerobic method and possible chemical treatment. It is possible that effluent treatment is solved using a so-called aerated lagoon, whereby the purification efficiency is lower than that of a biological effluent purification process. Finally, clarification is performed, where sludge generated from bacterial activity is removed. This sludge can be delivered further into the recovery boiler for combustion together with black liquor, which is already the practice at many mills. Chemical methods allow precipitating of detrimental substances from the effluent so that the quality of the effluent is improved. Additionally, effluent can be oxidized with e.g. ozone or oxygen. With these methods, a solution for a purification plant can be found, by means of which the effluent is made adequately clean for the presented objects of application.

The neutralization of effluent being purified changes the solubility of inorganic matter in the effluent and simultaneously boosts the precipitation of some non-process elements

(NPE) during the purification process. The precipitated fractions are removed in the clarification together with sludge. Thus, the purification process improves the control of NPE.

Various methods have also been studied which are based on microfiltration and membrane technique and osmosis, of which not many industrial applications have yet been reported. However, their use is not excluded from the scope of the present invention.

There are several effluent treatment plant producers around the world who have their own connections for purification processes. Thus, the processes can not be determined universally, but they are characterized by the above-mentioned issues. Additionally, retentions etc. properties vary, so that the invention is not limited to a single known purification plant specification.

In all purification methods it has been stated that chloride-containing inorganic substances are passed out of the mill entrained in liquid, but remarkable amounts of the organic substances are either converted or decomposed as a result of purification. As the aim is to remove significant amounts of compounds that are detrimental to bleaching, it can be stated that especially biological effluent treatment reaches this goal very well. Because biological effluent treatment removes significant amounts of lignin, the water thus treated is most suitable for the purpose of being used in a brown stock washing process.

For effluent treatment, the effluent has to be cooled first so that the bacteria can act properly. Because the treated water is returned to the process most preferably at process temperature, the system is arranged by means of usual heat exchangers so that one part of an effluent cooler is reserved for the effluent to be cooled and treated effluent acts as a cooling liquid. In such a case the untreated effluent reaches the temperature that is required for effluent treatment, typically below 40 °C, and the recycled liquid is heated to a temperature of 65-80 °C so that when the liquid returns to the fiber line, the heating thereof consumes reasonable amounts of steam. When an adequate number of heat exchangers is added to the system, in a most preferable situation e.g. cooling towers can be omitted, which have been used in great numbers for effluent cooling at chemical pulp mills.

Another possibility for heating the treated effluent are the digester plant circulations. The digester plant requires for the coolings a liquid at a temperature of approximately

20-60 °C and warm water or some unheated water fraction of the mill is commonly used for that purpose. If a proper material is selected for the heat exchanger, the cooling can be carried out by means of treated effluent. It is true that treated effluent contains chlorides, but because the pH is neutral or can be adjusted to be even slightly alkaline, the material does not cause an unreasonable cost.

The recycled treated effluent can, due to the presence of bacteria, be assumed to contain remarkable micro-organism activity, which may cause dirt or odor problems. Nevertheless, if the conditions of ECF-bleaching are analyzed in more detail, it can be stated that chlorine dioxide is a strong oxidant and bacterial activity is insignificant in the conditions of chlorine dioxide bleaching. Further, temperatures over 80 °C and change of pH between the bleaching stages from acid to alkaline so that also peroxide is typically present in the stage result in a situation that all remarkable organism activity is almost impossible when the treated effluent reaches the bleaching stage.

Effluents can be introduced to one purification plant from several sources. If there is other wood processing industry in the same industrial area or nearby, typically paper machines, mechanical pulp mills or sawmills, these effluents can still be treated in one and the same purification plant. Additionally, the purification plant can treat municipal waste waters from nearby cities and in some cases also waters from other production plants. In case the purification plant also treats other effluents in addition to the chemical pulp mill effluents, the quality of elements originating elsewhere than from the pulp mill is to be studied before water from this kind of purification plant is used at the chemical pulp mill. It may e.g. be difficult to use calcium-containing purified effluent in the fiber line due to precipitates, but the use thereof may well be possible in causticizing.

As the invention presented herein has an effect on all liquid flows of the plant as a whole, when outlining the entirety the basic issues are to be understood, to which the invention provides a solution.

Now the treated effluent with a certain residual chemical oxygen consumption level and a level of organic halogens (AOX) is passed into the chemical cycle where it is in practice concentrated in evaporation to the form where it is combusted in the recovery boiler. If 90 % of the effluent is returned to the chemical cycle after purification, the amount of AOX-level being passed to the water way is also reduced by approximately 90 %. Thus, if the AOX amount being passed to the water way after purification would

be 0.2 kg/adt, so with the novel arrangement, in which 90 % of the purified effluent is recycled to the mill, a level of 0.02 kg/adt is reached. The same reduction can be noted also with chemical oxygen demand. Due to these reasons, the use of purified effluent is a real step towards a closed chemical pulp mill process and allows for an almost pollutant-free process. Nevertheless, it has to be accepted that there are some exceptional situations when effluent can not be recycled from the purification but it has to be temporarily delivered to the water way.

When a sink for the chlorides has been arranged, the process is to be arranged such that significant amounts of chloride-containing liquid flows can be fed into the sink so that the sink will remove chlorides to an adequate extent and the chlorides will not be accumulated in any circulation of the mill. In accordance with the present invention, two liquid flows are found, via which significant amounts of chlorides can be fed into the liquid flow being passed into the recovery boiler:

1. Brown stock washing and the chloride passed therefrom to the chemical cycle; and
2. White liquor production and lime mud washing.

Of these, lime mud washing may be successfully carried out also partly or completely without bleaching effluent purification, but in order to carry out the bleaching economically without major chemical additions, it is preferable that the liquid delivered to the bleaching is treated off the substances that cause quality or brightness losses in the bleaching. Thus, bleaching effluent with the dissolved lignins is purified in an external treatment with either mechanical, chemical, biological or oxidizing methods or by means of some combination of methods, where the COD of the effluent is decreased without dilution by at least 30 %, preferably more than 40 %, most preferably more than 60 %, and/or the lignin-content of the effluent is decreased without dilution by at least 30 %, preferably more than 40 %, most preferably more than 60 %.

A resulting effect of this is that it is worth while to use in the fiber line condensate coming from the evaporation plant in significant amounts, i.e. 1-5 m^3/adt, in order to maintain adequate cleanliness of the pulp and to obtain an adequate amount of liquid into the mill's liquid circulation for preventing accumulation of inorganic substances. In the novel arrangement there is a real need for this, because a conventional object of use of condensate does not exist any more. Thus, new objects of use of the mill condensates will be clean water flows of the drying machine, for instance such that the washing of felts and wires will in the future be carried out using condensates from the evaporation plant. In that case the condensates are to be cleaned so that detrimental or malodor-

ous compounds are not released via the dryer machine or dryer room into the atmosphere.

Also, condensates can be used as sealing water. As an object at pulp mills that clearly requires clean water is sealing water in rotating apparatuses and pumps, an object for evaporation plant condensates is their use as sealing water. At present, mainly cleaned raw water of the mill is used as sealing water. In many mill the sealing water is a remarkable object of water consumption and thus causes a significant cost. As the evaporation plant condensate does not contain minerals, humus and mixed solid particles, the condensate is as such suitable to be used in mechanical apparatuses.

In rotary apparatuses the sealings are at present typically mechanical sealings, whereby the sealing is either single-acting or double-acting. In a single-acting sealing the sealing water is led into the process and the water is thus not recovered. In double-acting sealings the water comes out and can be recovered for reuse or is led into effluent treatment. Mechanical sealings are used in pumps, discharging devices, mixers, screens and scraper devices. In addition, packed sealing solutions are used in objects of application with shafts having a large diameter.

Sealing water is needed in some other devices as well, such as in washing devices. In them, also, in view of water quality it is essential that no humus or particles enter the sealing with water, but small amounts of organic compounds do not prevent the use of the condensate as sealing water. Of the known washing devices, sealing water in some form is used in e.g. the DrumDisplacer™ (DD) washer, suction drum filters, disc filters, pressure diffusers and diffusers. Additionally, sealing water is used in certain presses and washing presses. The digester plant, the evaporation plant, the drying plant, the recovery boiler and all other mill-related departments have rotary or other devices, which require sealing water, to which purpose condensate is suitable.

If the sealings are so-called double-acting sealings, the sealing water exits the device in approximately as clean a form as it was before entering the device. Therefore the sealing water can further be recovered and circulated either for sealing water without purification treatment or so that before reuse in a sealing the water is purified by means of some filtering method or another method.

It is to be ensured that organic substances in the condensates do not cause premature wearing, corrosion, dissolution or other kind of damaging of the sealings. This espe-

cially when the materials comprise e.g. plastic, rubber or other volcanic or polymer-based compounds.

When the sealing water is condensate, it can be used also elsewhere in the process to replace clean water, such as washing water, dilutions, cleaning water for devices and in all such objects where usually in pulp mill conditions the use of clean water is desired.

The solutions presented herein also allow using condensates or effluent in e.g. the production of chlorine dioxide water. As the chlorine dioxide water is typically made in raw water of the mill, the raw water can at some stage be replaced even with purified effluent or condensate. An essential issue is that the liquid in these flows is sufficiently cold. Cooling the condensate to a temperature below 20 °C consumes a lot of energy, but on the other hand it is possible under cold conditions. Economical issues and energy requirement in cooling are decisive in determining whether this kind of water usage is recommendable or not.

Because these arrangements as such create a particular number of process conditions to be redefined, at least the following of those can be regarded as solved:

The use of liquor so that oxidized white liquor acts in neutralization within the whole bleaching and the neutralization of effluent. This oxidized white liquor can be subjected to very strict quality requirements. Because tiosulfate is known to cause reduction of oxidizing chemicals, the following are to be set as quality requirements for oxidized white liquor: residual sulfide below 2 g/l, preferably below 1 g/l, and of the tiosulfate at least 50 %, preferably more than 80 % is oxidized in relation to its starting level. This goes as well for neutralization of effluent, because therethrough a remarkable portion of the effluent is returned to brown stock washing and therefrom to bleaching.

Heat exchanger arrangements, by means of which the effluent is cooled and the treated effluent is heated by cross-connected heat exchangers or the treated effluent is heated in digester circulations.

An effluent treatment process shall in the future produce such liquid which is well suitable for use mainly in two objects, white liquor production and brown stock washing. Their quality requirements may differ to such an extent that at the treatment plant they are preferably treated even as separate fractions.

When a pulp mill is arranged as presented in the above, it can be stated that in view of effluents, an almost closed pulp mill process has been invented without adding any new departments in addition to the existing ones.

The chemical pulp mill can continue to use chlorine dioxide for guaranteeing the quality of the pulp also in a closed process.

Bleaching chemical consumption remains at essentially the same level as in the best present mill solutions and all targeted brightness levels of the pulp are reached.

A primary object of the present invention is to ensure chemical pulping essentially without environmentally detrimental liquid effluents and with very low gaseous and solid emissions. The invention is described in more detail with reference to the accompanying figures, of which

Figure 1 is a schematic illustration of the connections of the sub-processes of a prior art pulp mill, and

Figure 2 is a schematic illustration of a preferred embodiment according to the present invention for carrying out the method of the invention.

In the prior art system illustrated in Figure 1, a conventional digester is illustrated with reference numeral 10, which is e.g. a continuous digester, which receives hard- or softwood chips 11 or other comminuted cellulosic material. In the digester 10, the wood chips are treated with cooking chemicals under conventional temperature and pressure conditions for producing chemical pulp, e.g. kraft pulp, after which the thus generated brown stock 13 is preferably delignified with oxygen in stage 12. After the oxygen stage the pulp is washed with hot water 14, e.g. condensate. The oxygen stage typically comprises also screening. The washing solution 9 is led countercurrently in relation to the pulp.

After oxygen delignification the washed and oxygen treated pulp 15 is led to an ECF-bleaching plant 16, where it is treated in various bleaching stages, but at least one of them uses chlorine dioxide. The other bleaching stages that are used can vary, and they are also dependent on the quality of the pulp being treated. After the bleaching stages the pulp 17 can be dried in a pulp drying machine 18 and conveyed further to a paper

mill. Hot or warm water 19 is introduced to the drying and the circulation water 20 of the drying machine is led to bleaching 16 to be used as clean washing water.

The bleaching sequence is e.g. A/D-EOP-D-P or D-EOP-D-P. Dioxide 21 is introduced to the bleaching as one bleaching chemical e.g. from a chlorine dioxide plant 22. Between the stages the pulp is washed, whereby the drying machine circulation water and/or fresh water 23 can be used as washing water. The washing filtrates are circulated countercurrently, but finally both acid 24 and alkaline 25 bleaching filtrates are formed, which are removed from the process to effluent treatment 26. The purified effluent 27 has typically been discharged to a water way near the mill.

According to common practice, the weak black liquor 28 is discharged from the digester 10 (or from a brown stock washer communicating with it) and it is led to evaporators 29. Condensate 30 generated in the evaporation plant is used in brown stock treatment 12 as washing liquid.

From the evaporation plant the strong black liquor 31 is finally led into a recovery boiler 32, and flue gas 33 generated therein is led into further treatment to be cleaned.

Smelt 34 obtained from the recovery boiler 19 is taken into a smelt dissolver 35 for production of green liquor. Green liquor 36 is used at a caustisizing plant for white liquor production, to which figure 1 refers by reference numeral 37. Insoluble precipitate material is removed from the green liquor e.g. by filtration, and the separated precipitate is further treated by means of a so-called dregs filter (not shown). The green liquor thus clarified is treated with lime for carrying out a caustisizing reaction and for production of white liquor and lime mud. The lime mud is separated from white liquor by filtration and washed. The thickened lime mud is burned in a lime kiln.

White liquor is led via a conduit 38 into the digester 10. Hot water 39 is typically introduced to the washing of lime mud separated from white liquor, whereby weak white liquor is formed, which is used in the dissolver 35.

Figure 2 illustrates a preferred embodiment according to the present invention. It uses the same reference numerals as figure 1 where applicable.

In the process according to the invention, effluents obtained from ECF-bleaching, typically acid effluent 24 and alkaline effluent 25 are taken to an effluent treatment plant for

decreasing the organic matter content thereof. When the effluent coming from the bleaching plant has been purified in a biological effluent treatment plant, the chemical oxygen demand, COD, thereof has decreased by more than 70 % and the organic compounds content by AOX-measuring has decreased by more than 50 %. If an anaerobic treatment stage is added to the system, so also the color of the water being treated has decreased remarkably. The effluent can also be subjected to chemical treatment methods which are based on precipitation or oxidation of oxidizable compounds. Chloride-containing effluent 43 purified off organic matter is in accordance with an embodiment of the invention led into washing following the oxygen stage. If the number of washing devices is two or more, the purified effluent 43 is introduced to the last of them in the pulp flow direction. From this washing device the filtrate is led by a method known per se in brown stock treatment countercurrently in relation to the pulp flow, whereby the filtrate is recovered from the first brown stock washing device in the pulp flow direction. The chloride-containing filtrate is delivered either directly to the evaporation plant 29 or it is used in digester plant processes for dilution and displacement, after which it ends up in weak black liquor flow 28. Although the chloride-content of this filtrate increases in the system according to the invention, its high alkali content in a sulfate or soda process converts chloride-containing compounds into salt and does not cause significant corrosion or process risk in brown stock treatment. As chlorides are added in the system to different locations than before, the whole material specification of the mill is to be checked as to both apparatuses, pipings, valves and other surfaces which are in contact with the process substances. This goes for all departments of the chemical cycle, departments of the fiber line and those sub-departments where clean water is now replaced with a chloride-containing liquid in accordance with the invention.

Condensates 30 of the evaporation plant are used in the process according to the invention in Figure 2 as washing water at the bleaching plant 16, whereto condensate is introduced via line 41. Condensate can be used instead of fresh water also in pulp drying, whereto condensate is led via line 42.

In accordance with the invention, purified chloride-containing effluent from the bleaching plant is used for producing cooking chemicals. The purified effluent in line 44 is used at filters of the caustisizing plant 37, such as green liquor filters, dregs filters and/or lime mud filters, as washing liquid. The filtrates separated by means of the filters or a portion of the filtrates are then introduced via line 45 into a smelt dissolver 35. This way, chlo-

ride-containing liquid to the system is obtained via this way, which can be removed to a sufficient extent in the recovery boiler process.

If so required by the liquid balance of the process, purified effluent can be discharged from the process if needed via line 27.

Strong black liquor generated at the evaporation plant is combusted in a recovery boiler or if needed, the filtrate obtained from brown stock washing is evaporated separately and taken alone or together with the black liquor into the recovery boiler 32. US patent application 12/107877 discloses a preferred method of treating chloride-containing liquor in a recovery boiler. Thus, the treatment of chloride-containing liquids in the recovery boiler process does not lead to stronger corrosion and the recovery boiler process is excellent for separating chloride-containing compounds from the process in order to prevent the accumulation of chlorine. There the chlorine content of the flue gases 33 is maximized by increasing the temperature of the combustion zone, where the chloride-containing liquor is combusted. Preferable combustion conditions are determined for the recovery boiler, under which chlorides will start to volatilize into flue gases, and a process location, where the chloride can be removed from the process. The passing of chloride into the flue gas can be preferably enhanced by using oxygen or oxygen-enriched air. Thus, in the novel process the recovery boiler can be made the chloride sink of the mill. The chloride compounds enrich into the ash of the flue gas 33 mainly as sodium chloride and potassium chloride, wherefrom chlorine can be separated and removed from the process, as is presented e.g. in said US patent application, or in some other way. Chloride and potassium are enriched into the flue gas ash, wherefrom Cl and K can be removed e.g. by methods know per se, which are based most typically on leaching, evaporation-crystallization and cooling crystallization. Thus the recovery boiler process comprises e.g. reducing combustion, smelt dissolving, steam production for producing energy and heat and flue gas treatment as well as several sub-processes, and chloride-removal is regarded as a sub-process included in the recovery boiler process.

As can be noticed from the above, the method and apparatus according to the present invention allow decreasing the emissions of a chemical pulp mill to absolute minimum. Although the above description relates to an embodiment that is in the light of present knowledge considered the most preferable, it is clear to a person skilled in the art that the invention can be modified in many different ways within the broadest possible scope defined by the appended claims alone.

Claims:

1. Method of treating liquid flows at a chemical pulp mill comprising at least an alkaline cooking process utilizing cooking liquor for producing pulp, brown stock treatment with essentially closed liquid cycles, a pulp bleaching plant using ECF-bleaching, in which chloride-containing effluents are formed, a chemical recovery plant comprising a causticizing plant and a chemical recovery boiler plant, and an effluent purification plant, characterized in that chloride-containing bleaching plant effluents are led to the effluent purification, where they are treated in order to decrease the organic matter content thereof, at least 20 % of the purified effluent is led back to a pulp mill process, purified effluent is used in at least one process stage of causticizing as a raw water source so that the chloride-containing liquid formed in the process stage is one fraction of weak white liquor, which is led to the recovery boiler plant to be used as a dissolving liquid component for smelt and therefrom further via cooking liquor regeneration, pulp cooking and pulp washing to evaporation as a component of waste liquor, from which evaporation the concentrated waste liquor is led for treatment to a recovery boiler process, where a separation process for chlorides is arranged for controlling the chloride level of the liquor cycle.

2. Method according to claim 1, characterized in that purified effluent is used at some process filter of caustisizing as dilution liquid, and the weak liquor formed therein is introduced into a recovery boiler dissolver.

3. Method according to claim 1 or 2, characterized in that the effluent is purified in order to decrease the lignin-content thereof.

4. Method according to claim 1, 2 or 3, characterized in that the effluent is purified biologically.

5. Method according to claim 3 or 4, characterized in that the effluent purification further comprises a chemical treatment.

6. Method according to any one of the preceding claims, characterized in that purified effluent is used for lime mud washing, and the weak liquor formed therein is introduced into a recovery boiler dissolver.

7. Method according to any one of the preceding claims, characterized in that condensate is further used as dilution and/or washing liquid at some process filter of caustisizing , and the weak liquor formed therein is introduced into a recovery boiler dissolver.

8. Method according to any one of the preceding claims, characterized in that evaporation plant condensates and hot water are further used as dilution and/or washing liquid at some process filter of caustisizing, and the weak liquor formed therein is introduced into a recovery boiler dissolver.

9. Method according to any one of the preceding claims, characterized in that untreated effluent is further used in lime mud dilution in a lime mud washing device, and the weak liquor formed therein is introduced into a recovery boiler dissolver.

10. Method according to any one of the preceding claims, characterized in that untreated effluent is further used in lime mud washing, and the weak liquor formed therein is introduced into a recovery boiler dissolver.

11. Method according to any one of the preceding claims, characterized in that a portion of the purified effluent is used in a last washing stage included in the brown stock treatment, and in the brown stock treatment the liquid flow is passed countercurrently to black liquor evaporation, wherefrom it is led for treatment into a recovery boiler process, wherein a separation process for chlorides is arranged for controlling the chloride level of the liquor cycle.

12. Method according to claim 11, characterized in that the last washing stage included in the brown stock treatment is washing of oxygen-delignified pulp.

13. Method according to any one of the preceding claims, characterized in that condensate originating from the evaporation plant is used in bleaching as a main source of fresh water.

14. Method according to any one of the preceding claims, characterized in that purified condensate from the evaporation plant is further used at the pulp drying machine.

15. Method according to any one of the preceding claims, characterized in that evaporation plant condensate is further used as sealing water in rotary devices of the mill.

16. Method according to any one of the preceding claims, characterized in that the effluent is purified in separate flows so that various fractions are formed in such a way that their properties in an object of reuse are optimal.

17. Method according to any one of the preceding claims, characterized in that oxidized white liquor is used as a main alkali source in bleaching and effluent neutralization.

18. Method according to any one of the preceding claims, characterized in that of the effluent preferably at least 40 %, most preferably at least 60 % is returned to the chemical pulp mill.

19. Method according to any one of the preceding claims, characterized in that of the returned purified effluent at least 40 %, preferably more than 60 %, is used for brown stock washing.

20. Method according to any one of the preceding claims, characterized in that condensate originating from the evaporation plant is used at the drying department for felt washing.

21. Method according to any one of the preceding claims, characterized in that the effluent being returned is heated by means of heat obtained from the effluent being led to purification and the heated effluent is used at the chemical pulp mill.

22. Method according to claim 21, characterized in that the temperature of the effluent being led to purification and returned therefrom is regulated in a cross-flow heat exchanger.

23. Method according to any one of claims 1–20 , characterized in that the purified effluent is heated by means of heat obtained from the digester plant liquid cycles.

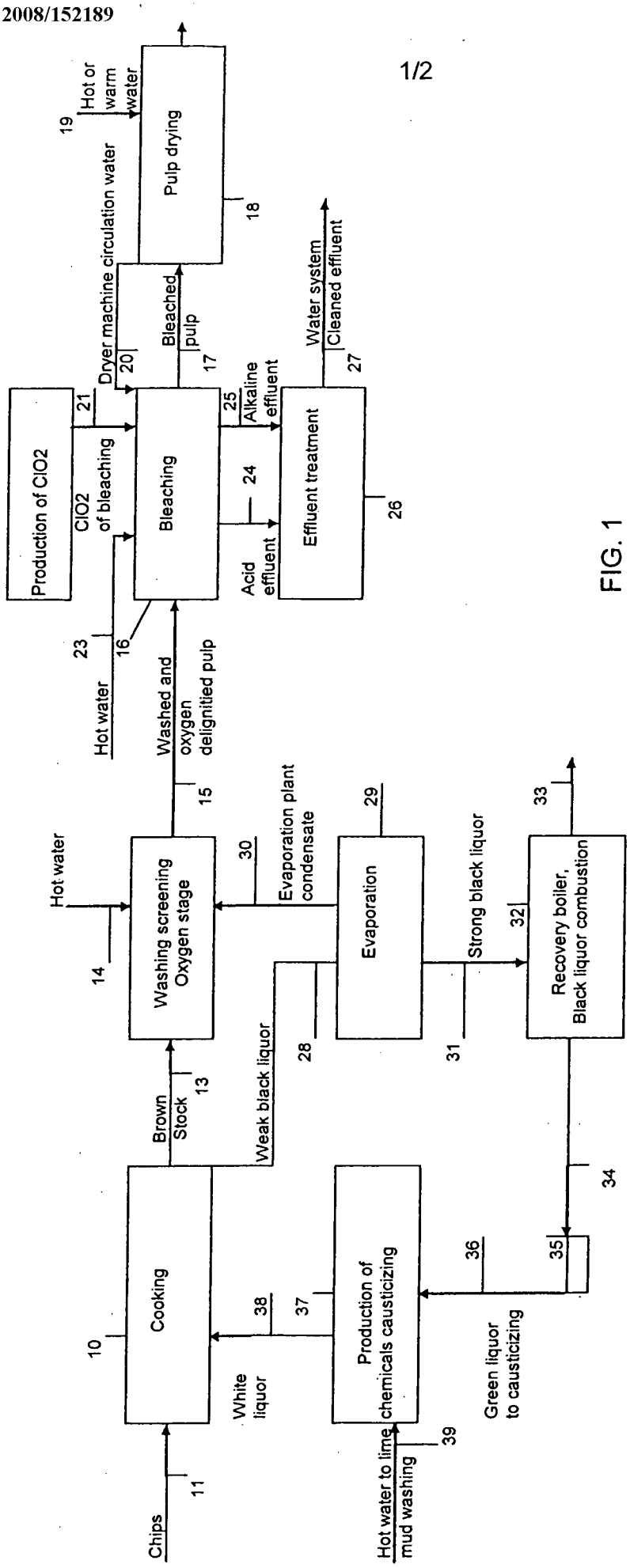

Chips
11
Cooking
10
Brown Stock
13
Hot water
14
Washing screening Oxygen stage
Hot water
23
16
Washed and oxygen delignified pulp
15
Evaporation plant condensate
30
Weak black liquor
28
Evaporation
29
Strong black liquor
31
Recovery boiler, Black liquor combustion
32
33
34
35
36
Green liquor to causticizing
Hot water to lime mud washing
39
Production of chemicals causticizing
37
38
White liquor
Production of ClO2
ClO2 of bleaching
21
Dyer machine circulation water
20
Bleaching
Bleached pulp
17
Pulp drying
18
Hot or warm water
19
25
Alkaline effluent
24
Acid effluent
Effluent treatment
26
Water system
Cleaned effluent
27

FIG. 1

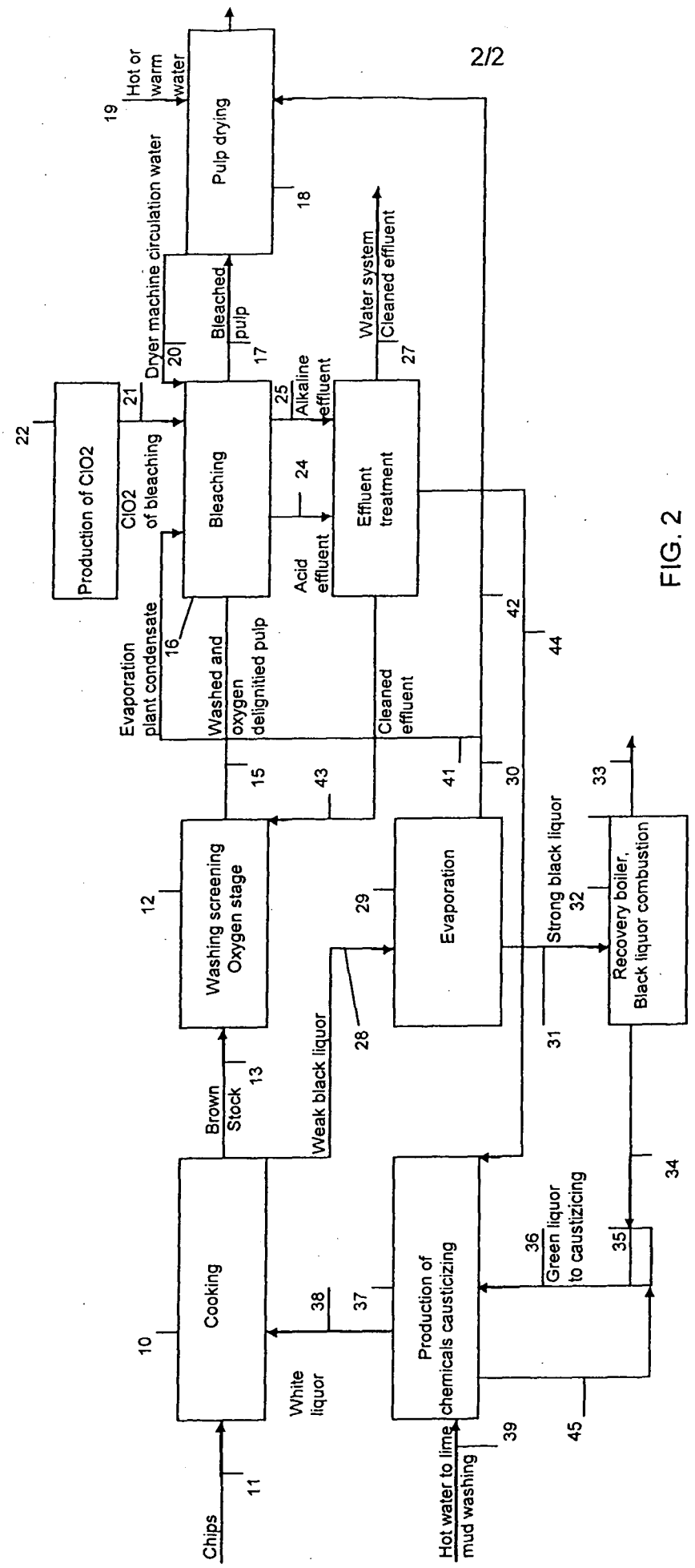

Hot or warm water
19
Pulp drying
18
Dryer machine circulation water
20
Bleached pulp
17
Water system
Cleaned effluent
27
Production of ClO2
22
21
ClO2
Bleaching
25
Alkaline effluent
24
Effluent treatment
of bleaching
Acid effluent
Evaporation plant condensate
16
Washed and oxygen delignified pulp
15
Cleaned effluent
43
41
42
44
30
Washing screening Oxygen stage
12
29
Evaporation
Strong black liquor
32
33
Recovery boiler, Black liquor combustion
Brown Stock
13
Weak black liquor
28
31
Cooking
10
38
37
Production of chemicals causticizing
36
Green liquor to caustizicing
35
34
White liquor
Chips
11
Hot water to lime mud washing
39
45

FIG. 2