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(54) Calcium removal in pulping

(57) A process for removal of calcium from wood chips prior to chemical pulping in a kraft pulping process in order to prevent scaling in an evaporation process in the recovery area **characterised** in that the wood chips are treated with an aqueous solution of uncausticised spent cooking liquor from an evaporation process having at least 30% total solids whereafter the liquid is recycled to an evaporation process at a location where the uncausticised spent cooking liquor has at least 40% total solids.

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Description

[0001] The present invention relates to a process for removal of metals such as calcium from wood chips prior to chemical pulping in a kraft pulping process in order to reduce scaling in the evaporation process where the wood ships are treated with an aqueous solution of uncausticised spent cooking having at least 30% total solids which is recycled to the evaporation process at a location where the uncausticized spent cooking liquor has at least 40% total solids.

[0002] Process equipment scaling in the fiberline and especially in the evaporation equipment subsequent the chemical pulping is a significant problem. Calcium can form inorganic and organic deposits that plug fiberline process equipment. Calcium carbonate and calcium oxalate are the two primary alkali-insoluble compounds of concern. Carbonate is formed in pulping reactions and enters as dead load with the white liquor. Oxalate is formed in pulping and bleaching reactions, particularly in oxidative bleaching stages such as oxygen and ozone. Futhermore, there is also a reduction of other trace metals such as Mn, Cu, Fe when treating wood ships according to the present invention.

[0003] US 5593544 discloses a process where wood chips are treated with spent liquor, i.e. weak black liquor, containing a complexing agent before the digestion. The object of this invention is to improve pulp properties already after the digestion process. There is no suggestion how to reduce scaling in the evaporation process in the recovery area.

[0004] The present invention provides a process according to the claims. More specifically, the present invention provides a process for removal of calcium from wood chips prior to chemical pulping in a kraft puling process in order to prevent scaling in the evaporation process where the wood chips are treated with an aqueous solution of uncausticized spent cooking liquor having at least 30% total solids which is recycled to the evaporation process at a location where the uncausticized spent cooking liquor has at least 40% total solids. Optionally, the treatment is done in the presence of a complexing agent.

[0005] In the kraft pulping process, uncausticized spent cooking liquor refers to spent liquor emerging from any location in the chemical recovery area between the digester and the causticizing unit. The chemical recovery area begins with the spent cooking liquor from the cooking process that is called weak black liquor (WBL) and that has a total solids content suitably between 10 - 25 %. The WBL is then evaporated in a multiple effect evaporation set that may include an integrated concentrator or a separate concentration unit or units. When the weak black liquor has been evaporated up to a total solids content of preferably between 30 - 60 % it is commonly referred to as strong black liquor (SBL). When the SBL has been further evaporated to a solids content of typically between 65 - 80 %, it is commonly referred to as fired black liquor or high solids black liquor (HBL). The HBL is combusted in the recovery boiler were the organics release heat that is used to make steam while the inorganics accumulate in a smelt bed that is formed on the floor of the boiler consisting primarily of $NaCO_3$ and Na_2S. The molten smelt from the recovery boiler flows to the smelt dissolving tank where it is mixed with water to form what is called green liquor (GL). The GL is subsequently fed to the causticizing unit for conversion of the NaCO3 to NaOH, thereby regenerating fresh cooking liquor referred to as white liquor (WL).

[0006] In the process according to the invention, calcium is removed from the wood ships prior to chemical pulping in a kraft pulping process by treating the wood ships with an aqueous solution of uncausticized spent cooking liquor suitably having at least 35% total solids more suitably at least 40% total solids. Moreover, the aqueous solution of uncausticized spent cooking liquor having a content of total solids of at least 30%, preferably a content of total solids of at least 35 and most preferably a content of total solids of at least 40% being used for the treatment of the wood ships is recycled to the evaporation process, subsequent the chemicals pulping, at a location where the uncausticized spent cooking liquor has a content of total solids of at least 40%, preferably a content of total solids of at least 45% and most preferably a content of total solids of at least 50%. The amount uncausticised spent cooking liquor added to the treatment is preferably from about 0.51/kg up to about 5.01/kg dry wood. Furthermore, the wood ships may be pre-steamed prior to the treatment. The removed calcium is preferably purged from the pulping processin the kraft chemical recovery process, e.g. green liquor dregs, slaker grits and lime purge.

[0007] According to another embodiment the aqueous solution of uncausticised spent cooking liquor is preferably fed counter-current to the wood ships.

[0008] In another process according to the invention calcium may be removed prior to chemical pulping by subjecting the wood chips to hot water with a temperature of preferably above 60 °C, more preferably above 70 °C and most preferably above 80 °C. The maximum temperature is set by process technical and economical reasons. Suitable maximum temperature is 150 °C.

In one embodiment a complexing agent may be present in the treatment. The complexing agent is suitably selected from the group of nitrogenous organic compounds, primarily nitrogenous polycarboxylic acids, nitrogenous polyphosphonic acids and nitrogenous polyalcohols. Preferred nitrogenous polycarboxylic acids are diethylenetriaminepentaacetic acid (DTPA), etylenediaminetetraacetic acid (EDTA) or nitriloacetic acid (NTA). DTPA and EDTA being especially preferred. Diethylenetriaminepentaphosphonic acid is the preferred nitrogenous polyphosphonic acid. Also other compounds can be used as complexing agents, such as polycarboxylic acids, suitably oxalic acid, citric acid or tartaric acid or phosphonic acids. The added amount of

complexing agent depends on the type and amount of transition metals of the incoming wood chips. Moreover, this amount depends on the type of agent used as well as the conditions in the pretreatment with the complexing agent, such as temperature, residence time and pH. However, the added complexing agent should preferably be in the range from about 0.1 up to about 10 kg/ton dry wood, calculated as 100% complexing agent. Suitably the amount lies in the range from about 0.5 up to about 5 kg/ton and preferably in the range of from about 1 up to about 2 kg/ton.

[0009] The pH in the treatment is preferably carried out from about 7,5 up to about 14 more preferably from about 9 up to about 12 and most preferably from about 10 up to about 11. A suitable pH range depends, among other things, on the type and amount of incoming wood chips.

[0010] The treatment is preferably carried out at a temperature at least above 35 °C for about 5 up to about 180 minutes. Suitable residence times for the treatment lies preferably from about 10 minutes up to about 90 minutes most preferably from about 15 minutes up to 45 minutes.

[0011] The wood ships may be dewatered from spent cooking liquor subsequent the pretreatment to preferably at least 30% solids content; more preferably the wood ships are dewatered from about 40% up to about 60% total solids.

[0012] According to yet another embodiment the uncausticised spent cooking liquor may be green liquir optionally added in presence of a complexing agent. Needless to say, the addition of spent cooking liquor such as SBL and/or GL as well as complexing agents may be accomplished anywhere upstream the digester in any mutual order.

Claims

1. A process for removal of calcium from wood chips prior to chemical pulping in a kraft puling process in order to prevent scaling in an evaporation process in the recovery area **characterised** in that the wood chips are treated with an aqueous solution of uncausticised spent cooking liquor from an evaporation process having at least 30% total solids whereafter the liquid is recycled to an evaporation process at a location where the uncausticised spent cooking liquor has at least 40% total solids.

2. A process according to claim 1 **characterised** in that the wood ships are treated with an aqueous solution of uncausticised spent cooking liquor having at least 35% total solids.

3. A process according to claims 1, 2 **characterised** in that the aqueous solution is recycled to the evaporation process at a location where the uncausticised spent cooking liquor has at least 45% total solids.

4. A process according to any of the preceding claims **characterised** in that the aqueous solution of uncausticised spent cooking liquor is feed countercurrent to the wood chips.

5. A process according to any of the preceding claims **characterised** in that a complexing agent is present in the treatment.

6. A process according to claim 5 **characterised** in that the complexing agents is diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA) or a mixture of those two agents.

7. A process according to claim 5 and 6 **characterised** in that the complexing agent is added in a range from about 0.1 g/kg up to about 10 g/kg based on dry wood.

8. A process according to any of the preceding claims **characterised** in that the uncausticized spent cooking liquor is added at an amount of from about 0.5 l/kg up to about 5.0 l/kg based on dry wood.

9. A process according to any of the preceding claims **characterised** in that the treatment is carried out at a pH from about 7,5 up to about 14.

10. A process according to any of the preceding claims, **characterised** in than the wood chips are dewatered subsequent the treatment to at least 30% solids content.

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EUROPEAN SEARCH REPORT

Application Number
EP 98 85 0200

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,X	US 5 593 544 A (FAHLGREN CHRISTER ET AL) 14 January 1997 * the whole document *	1,5-7	D21C1/06 D21C11/10
Y	* column 2, line 5 - line 65 *	1	
A		4,8-10	
X	US 4 578 149 A (FAGERLUND BERTIL K E) 25 March 1986 * the whole document, in particular column 8, paragraph 4 *	1	
A		8,9	
Y	J.P.CASEY: "Pulp and Paper; Chemistry and Chemical Technology, 3rd edition, vol. I, 1980, pages 377-396, 454-459" , JOHN WILEY & SONS , NEW YORK XP002101042 * page 389, paragraph 2 * * page 458, paragraph 2 *	1	
A	US 3 216 788 A (HOEFT JOHN E.) 9 November 1965 * the whole document *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	23 April 1999	Nestby, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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& : member of the same patent family, corresponding document

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 85 0200

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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