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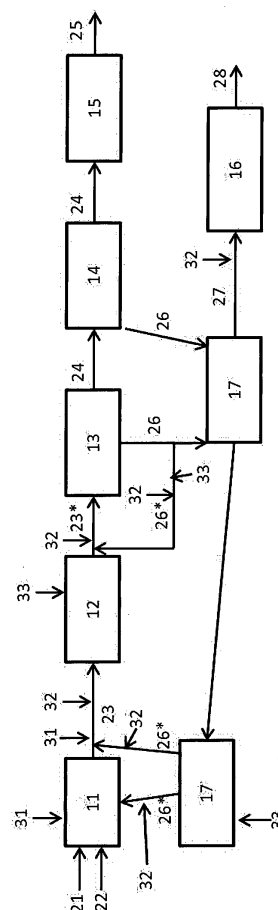
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(54) **PROCESS FOR REDUCTION OF PAPERMAKING WATER HARDNESS AND COD**

(57) The present inventions relates to a process for manufacturing paper or board comprising the steps of providing a pulp suspension, wherein the pulp suspension comprises CaCO_3 , filtrating the pulp suspension, wherein at least a fraction of the added water is separated from the pulp suspension, and optionally pressing and/or drying the filtrated pulp suspension yielding paper or board. According to the invention an alkaline agent comprising or consisting of CaO and/or Ca(OH)_2 is added to the pulp suspension before filtrating until the pH of the pulp suspension is above 8, particularly above 9, more particular above 10, even more particular above 11, yet more particular between 8 and 12, and CO_2 is added to the pulp suspension after adding the alkaline agent and before filtrating to adjust the pH to a value between 6,5 and 8, particularly to a value between 7 and 7.5.



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Description

[0001] The invention relates to a process for paper making.

[0002] Such a process comprises the steps of providing a pulp suspension, comprising pulp, water and a calcium salt of the carbonic acid, particularly CaCO_3 , filtrating the pulp suspension, wherein at least a fraction of the added water is separated from the pulp suspension, and particularly pressing and/or drying the filtrated pulp suspension yielding paper or board.

[0003] The packaging paper and board production is experiencing the fastest growth of all paper grades in the world. The utilisation of recycled fibres is more and more important, and many of the packing mills are using up to 100 % recycled material. Mills in developed countries mostly have high restrictions on fresh water usage, and they use less and less fresh water per kg paper produced. This causes accumulation of disturbing substances in the process water, both of inorganic and organic nature. Furthermore, the pH in these processes is normally relatively low due to a high load of acid producing bacteria, the increasing concentration of VFA (volatile fatty acid) in the process, mainly acetic acid. The low process pH caused by the activity of these bacteria induces the dissolution of solid CaCO_3 , which enters the process with the recycled raw material. This results in a high process water hardness caused by dissolved calcium ions, which further increases with increasing closure of the water circuit.

[0004] Particularly, as organic acids, VFA cause partial dissolution of CaCO_3 , but they also are able to form complexes with calcium ions (e.g., $\text{Ca}^{2+} + \text{CH}_3\text{COO}^- \leftrightarrow \text{Ca}(\text{CH}_3\text{COO})^+$), so that CaCO_3 dissolution is further enhanced (compared with noncomplexing acid at the same pH).

[0005] The dissolved calcium ions and the dissolved organic compounds that are contributing to the COD (chemical oxygen demand) have negative impacts on the paper/board making process. The dissolved calcium ions also have negative effects on the waste water treatment plant. In developed countries a wastewater treatment plant of this kind of paper/board mill commonly comprises a combination of anaerobic and aerobic treatment. If the waste water is characterized by a high hardness, the dissolved calcium ions can precipitate in the anaerobic reactor, particularly on the pellets, blocking their pores, so that the microbes have less access to the waste water. This reduces the efficiency of the anaerobic treatment. The treated water exiting the anaerobic reactor contains a substantial amount of carbon dioxide that was formed in the reactor. The formed carbon dioxide keeps a high concentration of calcium ions in solution due to the low pH of the water. In the subsequent aeration carbon dioxide is stripped from the water causing the pH to rise and the CaCO_3 to precipitate. This reduces the available water volume of the aerobic treatment, reducing its efficiency. Furthermore, CaCO_3 precipitates on cooling

towers, heat exchangers and in pipes resulting particularly in false flow measurements and blocking of pipes.

[0006] For preventing problems caused by dissolved calcium ions in the wastewater treatment plant of paper/board mills several technical solutions have been proposed:

In the so called lime trap method, NaOH is added to the wastewater, which is then led to a dissolved air flotation unit, wherein CaCO_3 is floated and separated from the water.

A drawback of the method is that rather often CaCO_3 precipitates in the pipes and pumps after the flotation unit.

[0007] In the aerobic cyclic softening (as described in EP 1120380 A2), wastewater leaving the anaerobic treatment step is fed into a reactor. Then, NaOH is fed into the reaction and some already precipitated CaCO_3 is recycled into the reactor to act as seeds. There is a circular movement in the reactor for increasing the speed of precipitation and stripping some of the carbon dioxide from the water.

[0008] According to another method known in the art, calcium hydroxide and NaCO_3 is fed to the waste water, which then is fed into a high rate clarifier. After this the water is acidified with HCl.

[0009] The above described solutions are technically difficult and/or expensive. Furthermore, the suggested solutions only solve the problem in the wastewater treatment, not in the production process, unless some of the treated water is taken back into the production process.

[0010] Another possibility is the addition of biocide to the process to reduce the bacterial count and to increase the redox potential. This significantly reduces the formation of acetic acid and therefore significantly the hardness. However, it may have a negative impact on the yield of biogas in the anaerobic reactor. Additionally, many mills want to avoid the use of biocides because of environmental reasons.

[0011] Therefore, the problem underlying the present invention is to provide a simple and cost efficient method that reduces the afore-mentioned disadvantages in an environment-friendly manner.

[0012] This problem is solved by adding an alkaline agent consisting of or comprising CaO and/or $\text{Ca}(\text{OH})_2$ to the pulp suspension before filtrating the latter until the pH of said pulp suspension is above 8, particularly above 9, more particular above 10, even more particular above 11, yet more particular between 8 and 12, and adding CO_2 to the pulp suspension after adding the alkaline agent and before filtrating to adjust the pH to a value between 6.5 and 8, more particular between 7.0 and 7.5.

[0013] Particularly, by raising the pH as described above the chemical equilibrium between bicarbonate and carbonate is shifted towards carbonate, which then rapidly forms insoluble salt with bivalent calcium ions resulting in precipitation of CaCO_3 . On the other hand present

solid CaCO_3 is kept in its insoluble form.

[0014] Particularly, after adding of the alkaline agent the pulp suspension is kept at the above mentioned pH at least close to the point when the equilibrium between the calcium salts is reached or as far as possible within reasonable time limits, and particularly until the maximal possible concentration of insoluble CaCO_3 has been formed, before CO_2 is added to the pulp suspension.

[0015] By adding carbon dioxide to the pulp suspension, CO_2 is converted to carbonic acid, which rapidly dissociates into hydronium ions and bicarbonate and carbonate anions leading to acidification of the pulp suspension to the above mentioned pH value. Advantageously, the pH is shifted to a value that is suitable for the following paper making process, but at which already precipitated CaCO_3 at least mainly is kept in its insoluble form. Moreover, bicarbonate and carbonate ions serve as a buffer system keeping the pulp suspension at the pH value suitable for the paper making process. Additionally, further carbonate is provided for precipitating remaining bivalent calcium ions, to prevent dissolution of CaCO_3 and/or to precipitate (at least part of) the remaining Ca ions.

[0016] The precipitated CaCO_3 is kept in the pulp suspension until it is incorporated into the paper or board product of the process of the invention. Beside the precipitation of CaCO_3 , some of the dissolved organic matter that may be present in the pulp suspension is precipitated as well.

[0017] Particularly, the pulp suspension is prepared by adding water to pulp in a pulper or to recycled papers when the fibers originate from recovered papers. In some embodiments, the pulp comprises a calcium salt of the carbonic acid, particularly CaCO_3 .

[0018] In some alternative embodiments, a calcium salt of the carbonic acid, particularly CaCO_3 , is added to the pulp suspension on the paper machine/board machine, to e.g. the mixing chest or in the short circulation.

[0019] In some embodiments, the alkaline agent is added concomitantly or immediately subsequently after adding the water to the pulp. Advantageously, CaCO_3 is precipitated during formation of the pulp suspension.

[0020] In some embodiments, the pulp suspension is homogenized, particularly by stirring, until the pulp suspension exhibits an essentially uniform and constant consistency (concentration of fibres in water).

[0021] In some embodiments, CO_2 is added to the pulp suspension, after the formation of the pulp suspension is completed, particularly after the pulp suspension exhibits an essentially uniform and constant consistency (concentration of fibres in water).

[0022] In some embodiments, a fraction of the added water is separated during pressing from the pulp suspension.

[0023] In some embodiments, CO_2 is added to the fraction of the added water that is separated during filtration or pressing. During filtration and/or pressing, the pulp suspension is typically exposed to the ambient environment, to which some of the added CO_2 emits. The lost

amount of CO_2 is replenished to maintain the pH and to provide carbonate to the separated fraction.

[0024] In some embodiments, at least a part of the fraction of the added water that is separated during filtration is recycled into said pulp suspension, particularly before filtration.

[0025] In some embodiments, the fraction of the water that is separated during filtration and/or pressing is used to provide another pulp suspension or added to a new pulp batch for papermaking. The recycling of process water into the papermaking process lowers the need of fresh water.

[0026] In some embodiments, the alkaline agent comprises or consists of a combination of $\text{Ca}(\text{OH})_2$ and/or CaO and NaOH . Advantageously, with such a combination an excess of calcium ions can be avoided. Preferably, NaOH is added first and then CO_2 is added resulting in an in situ formation of NaCO_3 .

[0027] In some embodiments, NaOH is comprised within the alkaline agent in a mole fraction below 0.5 with respect to $\text{Ca}(\text{OH})_2$, CaO or $\text{Ca}(\text{OH})_2$ and CaO .

[0028] In some embodiments, a biocide is added to the pulp suspension. In some embodiments, the biocide is added before filtrating. In some embodiments, a biocide is added to the fraction of the added water that is separated during filtration or pressing. Advantageously, the biocide inhibits the growth of microorganisms in the pulp suspension and the separated process water. The pulp suspension and the process water comprise nutrients for microorganisms such as bacteria or fungi. Those microorganisms can produce considerable amounts of organic matter, e.g., acetic acid, which can lower the pH of the pulp suspension or the process water.

[0029] In some embodiments, at least another fraction of the added water is separated during filtration and/or pressing of the pulp suspension before or after wastewater treatment of the fraction. Particularly, the wastewater treatment is performed in a clarifier.

[0030] Particularly, the term "wastewater treatment" refers to a process, wherein at least one contaminant (such as e.g. organic matter or suspended solids) is removed from the process water, before it can be released into the environment.

[0031] Further advantages, features and examples of the present invention shall be described in the following with reference to the Figure, wherein

Fig. 1 shows a scheme of an embodiment of the invention.

Examples:

[0032] The present invention relates to the reduction of the process water hardness and dissolved or colloidal substances that have an impact on COD. The method of the invention takes places in the paper and board making process and thus improves not only the waste water treatment but also the paper and board making process.

[0033] According to the invention, CaO and/or Ca(OH)₂ 31 is added to a pulper 11, increasing the pH to > 8, preferable to > 9, more preferably to > 10, even more preferably to > 11, most preferable to a value between 8 and 12. Hereby CaCO₃ is precipitated and some of the organic matter that contributes to the COD is coprecipitated with CaCO₃. The result is a reduced process water hardness as well as a reduced water COD level. The precipitated CaCO₃/COD remains within the pulp or pulp suspension 23, respectively, and leaves the mill as paper 25 of the produced paper/board. A part of the precipitated organic matter (COD) appears to be recalcitrant organic matter (COD). Thus the coprecipitation of the organic matter (COD) reduces the COD levels of the effluent water 27 leaving the water treatment plant 16. For optimum COD removal more CaO (or Ca(OH)₂) 31 needs to be added than required for precipitation of calcium and carbonate ions. This consumes (almost) all carbonate species in the water phase.

[0034] Preferably, CO₂ 32 is added to the pulper 11 to control the pH avoiding a too high pH and pH swings, and to precipitate excess calcium (from CaO or Ca(OH)₂ addition). Furthermore, the addition of CO₂ 32 advantageously increases the buffer capacity of the process water or the pulp suspension 23, respectively. Furthermore, CO₂ is added to make sure that all added CaO or Ca(OH)₂ is reacted and to reduce pH to such a level that further precipitation is avoided or at least reduced.

[0035] A second CO₂ 32 addition point is advantageous in the short circulation of the paper machine, wherein at least a part 26* of the separated fraction 26 of the process water is recycled back into the pulp suspension 23*, since some CO₂ is stripped from the water phase, when the fibre/water mixture 23* is entering the wire section 12 due to a high contact area between the suspension 23 and the surrounding air. If this is not compensated for it may lead to precipitation on the paper machine.

[0036] Advantageously, a combination of Ca(OH)₂ and/or CaO and NaOH 31 is added to the pulper 11. The amount of added NaOH 31 is limited not to cause a high increase in ash content. Production of packing papers does not benefit from high ash content as this weakens the paper and packaging papers need to be strong.

[0037] Alternatively, the necessary CO₂ 32 is added to the pulper or the pulp suspension in form of process water saturated with CO₂ 32 after the alkaline compounds 31 as described above have been added and have had some time to react.

[0038] One alternative is to combine the invention with the use of biocides 33 so that only a fraction of biocide is needed to be added to the pulp suspension or the process water in order to reduce the bacterial count without having an adverse effect on the biogas formation (in the anaerobic waste water treatment step).

[0039] Advantageously, the reduction in process water hardness leads to improved paper chemistry, savings in starch consumption, and less breaks. The reduction is

achieved without getting an unfavourable ratio between Ca and Na in the process water, which could have a negative impact on the sludge setting properties and COD of the effluent of wastewater treatment plant.

[0040] Fig 1 shows a preferred embodiment of the method of the present invention. Waste paper is placed in a pulper with the purpose of disintegrating the fibers to obtain a recycled paper pulp 21. Water 22 is added. The pulp is suspended in the water 22 such that a pulp suspension 23 forms. To the pulp suspension 23 CaO, Ca(OH)₂ 31 or a mixture thereof is added until the pH value of the pulp suspension is above 8, particularly above 9, more particular above 10, even more particular above 11, yet more particularly between 8 and 12. As a consequence, bicarbonate ions in the pulp suspension 23 are transformed to a certain extent into carbonate ions, which then rapidly form an insoluble salt with bivalent calcium ions present in the suspension. Before entering the machine chest of the paper machine 12, CO₂ is added to the pulp suspension 23. By adding CO₂ the pH of the pulp suspension is adjusted to a value between 6.5 and 8, particularly between 7 and 7.5, and bicarbonate and carbonate are resupplied to the pulp suspension 23, which may then bind residual bivalent calcium ions under formation of CaCO₃.

[0041] The pulp suspension 23 is then transferred to the machine chest 12. After the machine chest 12 the pulp suspension 23 is diluted with paper machine white water and led to the paper machines headbox, from which it is distributed across the width of the wire section, wherein a fraction 26 of the white water is separated from the pulp suspension. Typically, the pulp suspension 23* is sieved, whereby the fraction 26 of the process water is drawn off the suspension 23* by mechanical pressure resulting in a wet web of fibres 24 representing a precursor of the paper/product 25 of the process.

[0042] The wet web of fibres 24 is then transferred to the pressing section 14, wherein remaining process water 26 is pressed out of the web of fibres 24 by mechanical forces, typically applied by rolls, and afterwards dried in a dry section 14, wherein residual water is removed or heat yielding in dry paper or board 25.

[0043] A part 26* of the process water 26 that was separated in the wire section and/or the pressing section is recycled to the pulp suspension 23* entering the wire section, after CO₂ has been added to the part 23*. Additionally or alternatively the part 26* of the process water 26 is recycled into the pulper 11 or to the pulp suspension 23 exiting the pulper 11 via one or several process water tanks 17, wherein CO₂ is added before entering the pulper 11 or the pulp suspension 23. Because the majority of all calcium ions are present in form of insoluble CaCO₃ they remain in the wet web of fibres 24, whereas the amount of calcium ions is reduced by 30% to 50% or even more in the separated fraction 26, which is then characterized by a reduced hardness. Since the pulp suspension 23, 23* is exposed to the ambient air, a part of the added CO₂ emits from the pulp suspension 23, 23*.

This loss is compensated by addition of CO₂ 32 to the separated fraction 26 as described above.

[0044] The residual fraction 27 of separated process water 26 that is not recycled described above is subjected to a wastewater treatment 16, wherein contaminants are removed from the process water before releasing it into the environment.

Reference signs

11	pulper
12	machine chest
13	wire section
14	pressing section
15	drying section
16	clarifier
17	process water tank
21	pulp
22	process water
23	pulp suspension
23*	pulp suspension jet
24	filtrated pulp suspension/wet web of fibres
25	paper/board
26	separated process water
26*	separated process water for recycling
27	separated process water for disposal
28	treated water for disposal
31	CaO+Ca(OH) ₂ /CaO +Ca(OH) ₂ + NaOH
32	CO ₂
33	biocide

Claims

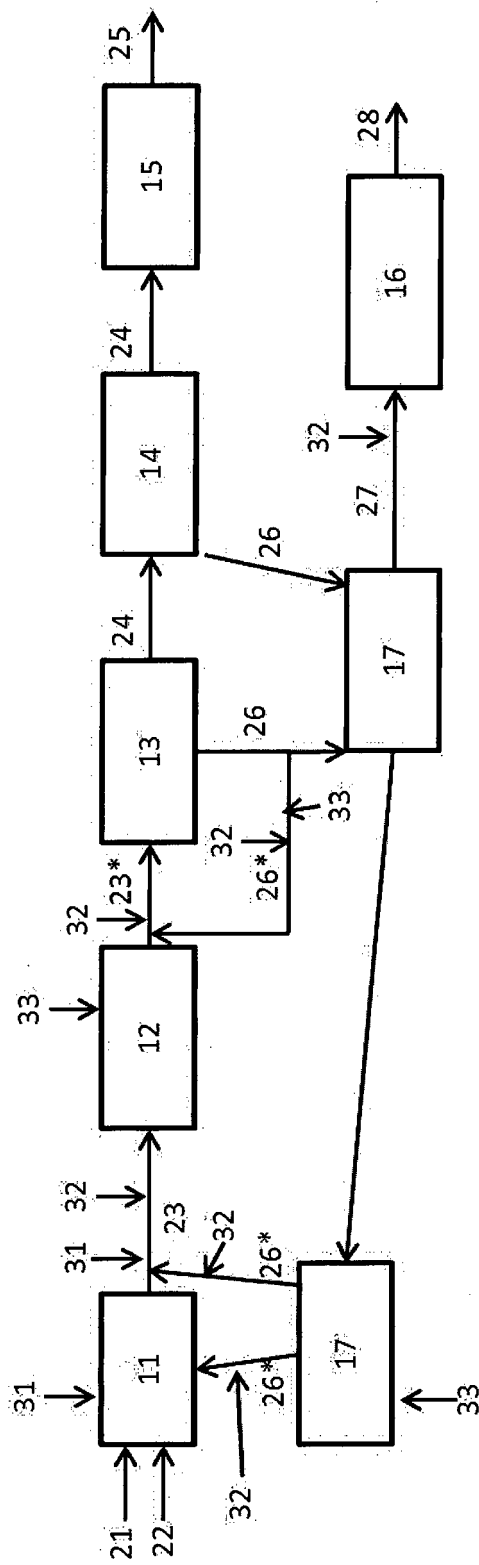
1. Process for manufacturing paper or board comprising the steps of:

- providing a pulp suspension (23, 23*), comprising pulp, water and CaCO₃,
- filtrating (12) said pulp suspension (23, 23*), wherein at least a fraction (26) of said water (22) is separated from said pulp suspension (23, 23*),
- and optionally pressing (14) and/or drying (15) said filtrated pulp suspension (24) yielding paper (25) or board (25),

characterized in that

- an alkaline agent consisting of or comprising CaO and/or Ca(OH)₂ (31) is added to said pulp suspension (23) before filtrating (13) until the pH of said pulp suspension (23) is above 8, particularly above 9, more particular above 10, even more particular above 11, yet more particular between 8 and 12, and
- CO₂ (32) is added to said pulp suspension (23) after adding said alkaline agent (31) and before filtrating (12) to adjust the pH to a value between 6.5 and 8, particularly to a value between 7 and 7.5.

2. The process according to claim 1, wherein said pulp suspension (23) is provided by adding water (22) to a pulp (21) or to waste paper or to paper products, wherein said pulp (21) comprises CaCO₃, and wherein preferably said pulp is obtained from waste paper.
3. The process according to claim 1 or 2, **characterized in that** CO₂ (33) is added to said fraction (26) of said water (22).
4. The process according to any one of the preceding claims, **characterized in that** said alkaline agent consists of or comprises a combination of Ca(OH)₂ and/or CaO and NaOH (31).
5. The process according to any one of the preceding claims, **characterized in that** at least a part (26*) of said fraction (26) of said water (22) is recycled into said pulp suspension (23, 23*).
6. The process according to any one of the preceding claims, **characterized in that** at least another part (26*) of said fraction (26) of said water (22) is used to provide another pulp suspension.
7. The process according to any one of the preceding claims, **characterized in that** a biocide (33) is added to said pulp suspension (23), particularly before filtrating (12), or to said fraction (26) of said water (22).
8. The process according to any one of the preceding claims for reducing the COD level of said fraction (26) of said water (22) which is separated from said pulp suspension (23, 23*).
9. The process according to any one of the preceding claims for reducing the hardness of said fraction (26) of said water (22) which is separated from said pulp suspension (23, 23*).





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Place of search Munich		Date of completion of the search 5 September 2016	Examiner Karlsson, Lennart
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REFERENCES CITED IN THE DESCRIPTION

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