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(71) Applicant: **UPM-KYMMENE CORPORATION**
 [FI/FI]; Alvar Aallon katu 1, FI-00100 Helsinki (FI).

(72) Inventors: **RISTOLAINEN, Matti**; Upseeritie 14 B 9, FI-53900 Lappeenranta (FI). **SOLISMAA, Päivi**; Valto Käkelän katu 5 as. 6, FI-53130 Lappeenranta (FI). **VAR-TIA, Tuija**; Hauhianranta 30, FI-54915 Saimaanharju (FI).

(74) Agent: **TAMPEREEN PATENTTITOIMISTO OY**;
 Hermiankatu 1 B, FI-33720 Tampere (FI).

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(54) Title: METHOD OF TREATING PRIMARY EFFLUENT OF A PULP, PAPER OR PLYWOOD MILL BY INTRODUCING EXHAUST GAS COMPRISING CARBON DIOXIDE

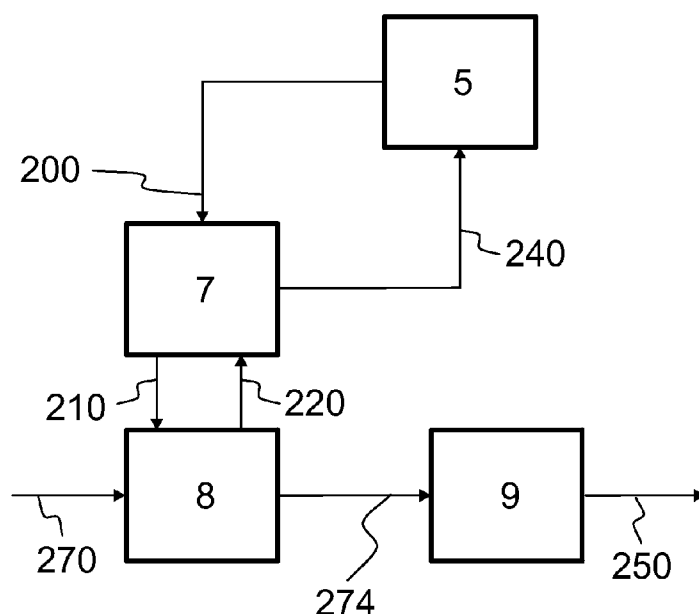


Fig. 2b

(57) Abstract: The invention relates to treating primary effluent of a pulp, paper or plywood mill at a waste water treatment plant by introducing exhaust gas comprising carbon dioxide (CO₂) into the primary effluent comprising calcium (Ca²⁺) and arranging the carbon dioxide (CO₂) to react with the calcium present in the primary effluent to form calcium carbonate (CaCO₃).

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— *with international search report (Art. 21(3))*

Field of the Invention

- 5 The invention relates to a method for treating an effluent of a pulp, paper or plywood mill at a water treatment plant.

Background

- 10 Effluents of pulp, paper or plywood mills are typically treated in waste water treatment plants in order to decrease the amount of the compounds that may be harmful for the environment. The effluents of chemical pulp mills may in addition comprise substances which may be valuable to the chemical pulp making process. Environmental trends and sustainable development are
15 driving factors to find new ways to enhance recyclability of these substances.

Summary

- 20 An object of the invention is to provide a method for treating primary effluent of a pulp, paper or plywood mill at a waste water plant. An object of the invention is to provide a method for introducing exhaust gas comprising carbon dioxide (CO_2) into primary effluent of a pulp, paper or plywood mill comprising calcium at a waste water plant to form calcium carbonate.
- 25 The primary effluent may be collected of pulp, paper and/or plywood mill effluents to a waste water treatment plant. Exhaust gas comprising carbon dioxide (CO_2) can be introduced into the primary effluent comprising calcium (Ca^{2+}). By arranging the carbon dioxide (CO_2) to react with the calcium (Ca^{2+}) present in the primary effluent, calcium carbonate (CaCO_3) and calcium free
30 effluent is formed. The formed calcium carbonate (CaCO_3) can be separated from the calcium free effluent, which can be purified to process water for further use at a pulp, paper and/or plywood mill process and/or a power plant process. The formed calcium carbonate can be reduced in a lime kiln into calcium oxide (CaO), which can be further used in the chemical pulp mill
35 chemical cycle. Embodiments of the invention may be used to obtain calcium carbonate with higher grade of purity.

Further, pulp, paper and/or plywood mill effluents can be purified at the waste water treatment plant and after purifying and carbonating the primary effluent turned into process water. The process water may be reused in a pulp, paper and/or plywood mill process and/or a power plant process.

The method provides a use of exhaust gas comprising carbon dioxide to form calcium carbonate (CaCO_3) from primary effluent comprising calcium of a pulp, paper or plywood mill. In particular, the primary effluent comprising calcium may be of a chemical pulp production process and the exhaust gas may be lime kiln exhaust gas.

Further, the method provides a use of process water obtained from the calcium free effluent in a pulp, paper and/or plywood mill process and/or a power plant process.

Description of the Drawings

Figure 1 presents the recovery process of the pulping chemicals at a chemical pulp mill.

Figure 2a presents the lime cycle used to complement the recycling of the spent cooking chemicals at a chemical pulp mill.

Figure 2b presents a method to use exhaust gas comprising carbon dioxide to recover calcium from primary effluent by precipitation.

Figure 3 describes a method for precipitating calcium carbonate with lime kiln exhaust gas from primary effluent.

Figure 4 describes a method for precipitating calcium carbonate with exhaust gas from primary effluent.

Figure 5 describes a method for precipitating calcium carbonate with exhaust gas from primary effluent.

Figure 6 describes a method for precipitating calcium carbonate with exhaust gas from primary effluent.

5 Figures 7a and 7b describe effluent terms used in a method for precipitating calcium carbonate with exhaust gas from primary effluent.

Detailed Description

10 In this application, reference is made to Figs. 1 to 7, in which the following reference numerals are used:

- 1 pulping
- 2 washing
- 3 evaporation
- 15 4 recovery boiler
- 5 causticizing
- 7 calcinating (lime kiln)
- 8 waste water treatment
- 9 pH adjustment
- 20 200 calcium carbonate (from causticizing)
- 210 exhaust gas comprising carbon dioxide
- 220 calcium carbonate (from primary effluent treatment)
- 240 calcium oxide
- 250 process water
- 25 260 calcium hydroxide (lime mud)
- 270 primary effluent
- 271 particle free effluent
- 272 calcium free effluent
- 274 purified effluent
- 30 280 flotation waste
- 290 solid waste

Reference numerals from 300 to 580 are used to describe process steps.

35 In this application, the term “effluent treatment plant” refers to a waste water treatment plant.

Figures 7a and 7b describe effluent terms used in a method for precipitating calcium carbonate with exhaust gas from primary effluent. The term “effluent” refers to waste water from a pulp, paper or a plywood mill. The term “primary effluent” 270 refers to effluent which is conveyed to the waste water treatment plant for a purifying process. The primary effluent 270 may comprise, for example, bleaching effluent and ash leaching purge. In addition, the primary effluent 270 may contain wood processing effluent. The primary effluent 270 may be integrated, which means that the primary effluent 270 is conveyed to the waste water treatment plant from pulp, paper and/or plywood mill processes and/or power plant processes which are in the vicinity of a pulp mill. The primary effluent 270 may be biologically treated.

The term “bleaching effluent” refers to effluent from the bleaching unit and the washing steps therein. Advantageously, the bleaching effluent contains bleaching filtrates. Most advantageously, the bleaching effluent consists of bleaching filtrates. The bleaching filtrates contain acidic and/or alkaline flows. Advantageously, the bleaching effluent does not contain fibers. Primary effluent 270 may comprise bleaching effluent.

The term “particle free effluent” 271 refers to primary effluent 270 treated by a filtration treatment or a flotation treatment. In other words, a treatment by filtration or flotation removes solid particles to at least some extent from the primary effluent 270, as shown in Figure 7a. The filtration treatment refers to removal of organic and/or inorganic matter to at least some extent. The filtration treatment may comprise, for example, ultrafiltration membranes, chemical precipitation, sedimentation, and/or filtration by sand and/or multimedia filter. The flotation treatment refers to use of a gaseous substance such as air to remove suspended organic and/or inorganic matter to at least some extent. In flotation, suspended organic and/or inorganic matter may be adhered to the gaseous substance and floated to the surface for skimming. The term “calcium free effluent” 272 refers to a primary effluent 270 or particle free effluent 271, from which calcium in ionic form (Ca^{2+}) has been separated to at least some extent by precipitating it as calcium carbonate (CaCO_3). The process for precipitation of calcium carbonate is referred to as carbonatation, denoting a chemical reaction in which calcium in alkaline aqueous conditions reacts with carbon dioxide and forms calcium carbonate. The carbonatation is accomplished by introducing flue gas comprising carbon

dioxide (CO_2) to the primary effluent 270. The order of carbonatation and removal of solid particles from the primary effluent 270 may be switched, as shown by comparing Figures 7a and 7b. In other words, the carbonatation of the primary effluent 270 may be performed either before or after solid particles have been removed to at least some extent from the primary effluent 270 by a filtration treatment or a flotation treatment. The term “purified effluent” 274 refers to primary effluent 270 which is purified in the waste water treatment plant by a filtration treatment or a flotation treatment to obtain particle free effluent 271 and from which calcium in ionic form (Ca^{2+}) has been removed to at least some extent by carbonatation with flue gas comprising carbon dioxide (CO_2), which precipitates the calcium as calcium carbonate (CaCO_3). In other words, purified effluent 274 is obtained from primary effluent 270 after removal of solid particles and calcium in ionic form (Ca^{2+}) as in Figure 7a or after removal of calcium in ionic form (Ca^{2+}) and solid particles as in Figure 7b.

The term “recyclable water” refers to process water and/or purified effluent 274 that are purified in a water treatment plant and are clean enough to be reused as process waters. When the pH of the purified effluent 274 is adjusted close to a neutral pH of 7, process water 250, which may be reused, is obtained.

The term “NPE” refers to non-process elements. NPEs are inorganic substances originating from process devices, some also from wood, raw water and chemicals, which are not wanted to process.

The term “calcium” refers to calcium as ions (Ca^{2+}) in a solution, unless otherwise stated. In general, calcium is present as calcium ions (Ca^{2+}) in a solution, unless precipitated out from the solution as a solid compound, such as calcium carbonate (CaCO_3), for example.

The term “exhaust gas” refers to a flue gas comprising carbon dioxide. Flue gas is combustion exhaust gas produced by a furnace or a power plant. An example of a flue gas is lime kiln exhaust gas.

The general purpose of cooking in bleached chemical pulp production is to recover fibers from chips that are fed to the digester by using chemicals and

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

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

The pulp mill has not only bleaching effluents but also process waters, such as cooling waters, sealing waters, reject flows, channel waters, washing waters of the plant, and rain waters, as well as wood processing water. Said process waters have typically not been in contact with the pulping process with the exception of wood processing water and some channel waters that originate from process overflows and are therefore in contact with the pulping process. Thus, the emissions accumulated therein are mainly leakages and overflows, occasional emissions caused by apparatus breakages, washing waters of devices, textiles (wires and felts) or containers originating from continuous or batch washings, and leakages from the reject system.

The pulp mill typically comprises a chemical recovery plant including an evaporation process typically with an in-series connected evaporation plant,

a recovery boiler, removal of chlorides from the process, and a chemical production plant for producing pulping chemicals.

Water quality requirements may vary at different stages of the chemical pulp production. Some production phases may require lower quality, where only light purification of the primary effluent 270 may be needed before the re-use as process water 250, and when water quality requirements are higher, strong purification of the primary effluent 270 may be needed before the re-use as process water 250. At least a portion of the primary effluent 270 may be recycled after the purification step(s) as a source of process water. Recyclable water may be reused, at least partly, as cooling water. Alternatively or in addition, the recyclable water may be reused, at least partly, for debarking. Alternatively or in addition, the recyclable water may be reused, at least partly, for log washing. Alternatively or in addition, the recyclable water may be reused, at least partly, as fire water. Alternatively or in addition, the recyclable water may be reused, at least partly, as boiler water. Alternatively or in addition, the recyclable water may be reused, at least partly, as shower waters of the pulp drying machine. Alternatively or in addition, the recyclable water may be reused, at least partly, for bleaching. Alternatively or in addition, the recyclable water may be reused, at least partly, for a recovery boiler. Alternatively or in addition, the recyclable water may be reused, at least partly, as sealing waters. Alternatively or in addition, the recyclable water may be reused, at least partly, as shower waters for a wire in a gravity table.

The waste water treatment plant may comprise a clarifier, from which the purified effluent is typically conveyed to a water system. At least a portion of the effluent purified in the waste water treatment plant may be reused as process water at the chemical pulp mill.

The large amount of chemicals used in a chemical pulp production requires recovery and re-use of these chemicals. Typically, the process for manufacturing bleached chemical pulp comprises pulping, washing, screening, bleaching, and cleaning stages. This requires chemicals which are used in a mixture denoted as white liquor. As a result of the pulping process, black liquor is formed which may be evaporated. The evaporation results into formation of concentrated black liquor. Concentrated black liquor may be

combusted in the recovery boiler. The recovery boiler may be used to reduce the cooking chemicals. The reduced cooking chemicals form a molten 'smelt' at the bottom of the recovery boiler. The smelt may be dissolved into a liquid. Thus formed liquid may be denoted as green liquor due to a characteristic green colour. Green liquor may be used to prepare white liquor for the pulping process. The recycling of these spent cooking chemicals is denoted as the liquor cycle or the chemical recovery process.

The liquor cycle is designed to recover the chemicals used in the pulping. In particular, the recovery boiler aims to recover sodium hydroxide (NaOH) and sodium sulfide (Na₂S), which may be re-used to make new white liquor for the pulping process. White liquor comprises also other sodium salts, such as sodium sulfate (Na₂SO₄) and sodium carbonate (Na₂CO₃) and small amounts of sulfites and chlorides.

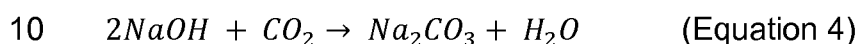
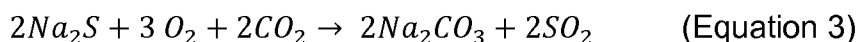
Figure 1 presents the recovery process of the pulping chemicals at the chemical pulp mill. In pulping 1 phase sodium sulfide (Na₂S) and sodium hydroxide (NaOH) from white liquor form hydrosulfide (HS⁻) and hydroxyl (OH⁻) groups in aqueous solution with water according to equations 1 and 2.



At least partly closed cycle systems for manufacturing bleached chemical pulp apply processes where at least part of the water and other chemicals is recycled and reused, which minimizes waste disposal. Said systems are particularly intended to minimize aqueous effluent and, hence, to protect the environment from the impact of disposal of effluents without significantly jeopardizing the processing cost or the value of saleable products. Chlorine, potassium, calcium, manganese, silicon, aluminum, phosphorous, iron, and barium are some elements of concern in a bleached chemical pulp mill.

The pulping 1 process consumes the sodium hydroxide (NaOH) and sodium sulfide (Na₂S) and produces black liquor. In addition to the spent cooking chemicals, the black liquor comprises other substances from the cooking, such as dissolved substances from the pulped wood and lignin, which

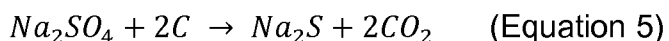
colours the liquor to a dark shade, hence the name 'black liquor'. The alkaline chemicals cause fragmentation of the lignin molecules into smaller segments, whose sodium salts are soluble in the black liquor. When heated, sodium sulfide (Na_2S) also oxidizes to sodium carbonate (Na_2CO_3) and sulfur dioxide (SO_2) according to equation 3. Sodium carbonate is also formed in an aqueous solution of sodium hydroxide according to equation 4.



After the pulping 1 process, the cooking liquor has turned into black liquor comprising water, organic dissolved residues and inorganic pulping chemicals, such as sodium sulphate (Na_2SO_4) and sodium carbonate (Na_2CO_3).

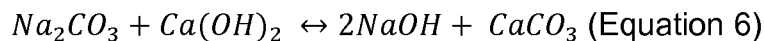
Typical organic compounds in black liquor are lignin, polysaccharides, carboxylic acids and extractives. Typical inorganic substances in black liquor are sodium hydroxide (NaOH), sodium hydrosulfide (NaHS), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), sodium sulphate (Na_2SO_4), sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium sulphite (Na_2SO_3), sodium chloride (NaCl) and non-process elements (NPE). Non-process elements may be, for example, Si, Ca, Fe, Mn and Mg.

Washing 2 may be used to separate the pulp and the black liquor. During washing 2 other fractions, such as soap, may be separated from the black liquor. Evaporation 3 may be used to concentrate the black liquor. The sodium sulphate may be reduced back into sodium sulfide (Na_2S) by using a recovery boiler 4 according to the equation 5. The recovery boiler combusts the organic portion of the concentrated black liquor. In addition to heat and vapor, exhaust gas comprising carbon dioxide is formed.



The main function of the recovery boiler 4 is to reduce oxidized sodium and sulfur compounds into useful cooking chemicals. For efficient reduction of inorganic sulfur to sodium sulfide a char bed is used. A molten inorganic flow

typically denoted as 'smelt' comprising sodium sulfide and sodium carbonate forms to the char bed. The molten smelt may be dissolved into weak white liquor to produce green liquor. The green liquor may be clarified or filtrated. The green liquor may be mixed with lime (CaO) in a slaker to form calcium hydroxide (Ca(OH)₂) and introduced into reaction tanks, where the calcium hydroxide (Ca(OH)₂) reacts with the sodium carbonate (Na₂CO₃) of the green liquor according to equation 6.



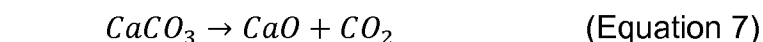
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As a result of this process denoted as causticizing 5, the sodium carbonate (Na₂CO₃) is transformed into sodium hydroxide (NaOH) and the calcium hydroxide (Ca(OH)₂) oxidized into calcium carbonate (CaCO₃). The filtrate comprising the sodium hydroxide (NaOH) and the sodium sulfide (Na₂S) may be clarified and further processed into white liquor.

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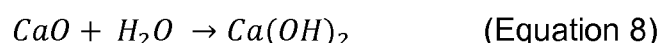
Figure 2a presents the 'lime cycle' which is a second cycle used to complement the recycling of the spent cooking chemicals. The lime cycle uses calcium carbonate (CaCO₃) 200 formed in caustizing 5. The formed calcium carbonate 200 is reduced in a calcinating process 7 into calcium oxide (CaO) 240 according to equation 7 below. Calcium hydroxide (Ca(OH)₂) may be produced from quicklime (CaO) by slaking the quicklime with green liquor. Quicklime reacts with water in the green liquor and forms calcium hydroxide (Ca(OH)₂). As the reactions proceed, the calcium hydroxide (Ca(OH)₂) reacts with the sodium carbonate (Na₂CO₃) present in the green liquor and forms sodium hydroxide (NaOH) and calcium carbonate (CaCO₃). Advantageously, the lime cycle uses a lime kiln to reduce the calcium carbonate (CaCO₃) 200 from the causticizing 5 process back into calcium oxide (CaO) 240.

20



In causticizing 5 the regenerated calcium oxide (CaO) 240 is mixed with green liquor, where it forms lime mud comprising calcium hydroxide (Ca(OH)₂) according to Equation 8.

25



30

35

The calcinating process 7 produces exhaust gas, also denoted as flue gas, which comprises significant amounts of carbon dioxide. The total emission of carbon dioxide may be around 1000 kg of CO₂ for every 1000 kg of calcium oxide. The heating of a lime kiln may involve the use of fossil fuels, which may increase the total emission of carbon dioxide to 1300 kg of CO₂ for every 1000 kg of calcium oxide.

Figure 2b presents a method to use the exhaust gas from a calcinating 7 process comprising carbon dioxide to recover calcium of a primary effluent 270 by precipitating calcium (Ca²⁺) ions from the primary effluent 270 as calcium carbonate 220. Calcium may be present in the primary effluent 270 conveyed to the waste water treatment plant 8 from various sources. In addition, the primary effluent 270 may comprise, for example, bleaching effluent and ash leaching purge, which may comprise calcium. Further, the primary effluent 270 may contain wood processing effluents which may comprise calcium. Wood ash may comprise calcium from 5% to 30% or calcium oxide from 2% to 37%. The calcium in the primary effluent 270 is dissolved as calcium (Ca²⁺) ions.

It is to be noted here, that the primary effluent 270 in this application refers to waste waters of pulp, paper or plywood mill processes and/or power plant processes conveyed to the waste water treatment plant 8 for purifying process. The primary effluent 270 may contain wood processing effluents. Calcium oxide or calcium hydroxide may be added to the primary effluent 270 for adjusting the pH of the primary effluent 270. Advantageously the calcium oxide may be obtained from the lime kiln or the calcium hydroxide may be obtained as a product of the lime kiln. However, the treatment of the primary effluent 270 does not comprise a lime-sludge treatment where the pH of the sludge would be adjusted. As an example, this application does not refer to sludge where the pH of the sludge obtained from the softening of raw waters is adjusted.

Calcium compounds are typically soluble in aqueous solutions, where the calcium may be present as a calcium ion (Ca²⁺). However, various calcium compounds have different solubility values. For example, calcium carbonate (CaCO₃) has a solubility of 14 mg/L to pure water. The solubility of calcium

carbonate (CaCO_3) is less than the solubility of calcium hydroxide (Ca(OH)_2), which enables the precipitation of calcium carbonate (CaCO_3) from calcium hydroxide (Ca(OH)_2). For example, at 30°C the solubility of Ca(OH)_2 to water is roughly 1,5 g/l, and at 100°C only 0,7 g/l.

5

- A pulp mill may produce exhaust gas 210 at various stages. Examples of these are the recovery boiler 4 and the calcinating 7 processes of a pulp mill, where furnaces are used. Of particular interest is the lime kiln, which requires energy for the combustion of the calcium carbonate (CaCO_3) 200, 220.
- 10 Combustion of the calcium carbonate (CaCO_3) 200 from the causticizing 5 stage produces calcium oxide (CaO) 240 and exhaust gas 210, which comprises carbon dioxide (CO_2). As a product of the combustion, the calcinating 7 step also produces heat. The reaction temperature where calcium carbonate (CaCO_3) 200, 220 is transformed into calcium oxide (CaO)
- 15 240 may be 900°C or more, preferably at least 950°C. The partial pressure of carbon dioxide in the lime kiln increases as a function of temperature, and at 900°C the partial pressure of carbon dioxide may be 1 atmosphere. At a temperature of 1000°C the partial pressure of carbon dioxide may be 3.8 atmospheres, which may accelerate the reaction. Therefore, higher
- 20 temperatures are beneficial to produce calcium oxide 240 more quickly. However, temperatures above 1200°C are rarely used, as the production of unreactive, "dead-burned" lime increases in proportion to the used reaction temperature.
- 25 Exhaust gas 210 comprising carbon dioxide may be produced also by power plants (e.g. waste heat boiler or a power boiler) in a pulp, paper or a plywood mill. A pulp, paper or a plywood mill requires considerable amounts of energy for operation.
- 30 The exhaust gas 210 may comprise other flue gas impurities, such as corrosive dust. Equipment may be installed to trap this dust. For example, the exhaust gas 210 may be directed through a filtration device to purify the gas. The dust may also contain elements such as alkali metals, halogens or sulfur in concentrations hazardous to the environment. Electrostatic precipitator
- 35 (ESP) is a filtration device that may remove fine particulate matter from the exhaust gas 210. The electrostatic precipitator may be suitable for removing particles such as dust and smoke from the exhaust gas 210.

Advantageously, an electrostatic precipitator allows a flow of gases 210 through the device with minimal effects on the air flow. An alternative method for trapping lime dust is wet scrubbers, which apply energy directly to the flowing fluid medium. An electrostatic precipitator applies energy only to the particulate matter being collected and therefore is efficient in its consumption of energy. Alternatively, or in addition, bag filters are used to purify the exhaust gas 210.

Table 1 presents determined mean value ranges in Finland for ESP purified lime kiln exhaust gas 210.

Table 1. Determined mean value ranges in Finland for ESP purified lime kiln exhaust gas.

15	Particles	between 20 and 40 mg/Nm ³ , dry gas (6 vol-% O ₂)
	CO	up to 60 mg/Nm ³ , dry gas (6 vol-% O ₂)
	NO _x (as NO ₂)	between 250 and 420 mg/Nm ³ , dry gas (6 vol-% O ₂)
	SO ₂	between 10 and 50 mg/Nm ³ , dry gas (6 vol-% O ₂)
	TRS (as S)	between 5 vol-% and 25 mg/Nm ³ , dry gas (6 vol-% O ₂)
20	CO ₂	between 18 vol-% and 20 vol-%, dry gas
	O ₂	between 3 vol-% and 5 vol-% dry gas
	H ₂ O	between 25 vol-% and 30 vol-%
	Temperature	between 250°C and 280°C

25 Lime kiln exhaust gas 210 may comprise ingredients in different ratios. The values of the various ingredients may vary. For example, the exhaust values may vary depending of the age, used fuel or capacity of the lime kiln in question. The small particle (CO, NO_x, SO₂, TRS) concentrations in Table 1 are presented as dry gas concentrations in milligrams (mg) per normal cubic meter (Nm³) in standard conditions (273.15K, 101.3 KPa), which is a typical way of expressing exhaust gas values for a lime kiln. The CO₂ and O₂ concentrations are presented as dry gas concentrations

35 The exhaust gas values may be presented alternatively as exhaust gas values comprising moisture, when the moisture content is known. The conversion between dry flue gas and flue gas comprising moisture may be calculated as shown in equation 9.

$$c_{dry} = \frac{c_m}{1 - \frac{c_w}{100}} \quad (\text{Equation 9})$$

, where

5 c_{dry} = dry exhaust gas concentration (mg/Nm³)

c_m = moisture concentration of a compound (mg/Nm³)

c_w = volumetric percentage of vapor (H₂O) in the exhaust gas (v-%)

10 In the method, the exhaust gas 210 is directed to a waste water treatment plant 8. In particular, lime kiln exhaust gas 210 may be used. At the waste water treatment plant 8 the exhaust gas 210 is arranged to react with the calcium (Ca²⁺) present in the primary effluent 270 to form calcium carbonate (CaCO₃) 220. Optionally, (as shown in Figures 7a and 7b,) solid particles may be removed from the primary effluent 270 before introducing the exhaust gas 210. In other words, the primary effluent 270 may be treated by filtration or flotation to obtain particle free effluent 271 before introducing the exhaust gas 210. Alternatively, the primary effluent 270 may be treated by filtration or flotation to obtain particle free effluent 271 after introducing the exhaust gas 210. Interestingly, the presence of carbon dioxide may have an effect on the solubility of calcium carbonate 220. The formation of calcium carbonate 220 from the exhaust gas 210 carbon dioxide and calcium present in the primary effluent 270 is an endothermic reaction and requires heat. Further, addition of an alkali to an excess of carbonic acid may be used to produce bicarbonate. With excess alkali, carbonic acid reacts to give carbonate salts. The reaction equilibrium may be shifted towards the precipitation of calcium carbonate 220 by controlling the amount of bicarbonate forming from the carbon dioxide and the reaction temperature tp3 (i.e. the temperature where the reaction takes place). Therefore, for the formation of calcium carbonate 220 it may be advantageous that the reaction between the carbon dioxide from the exhaust gas 210 and the calcium from the primary effluent 270 takes place in elevated temperatures. This reaction is denoted as carbonatation reaction.

35 The temperature tp3 of the carbonatation reaction may be controlled by the heat flow of the exhaust gas 210 and the temperature of the primary effluent 270. The temperature tp2 of the primary effluent 270 may vary. Typically the temperature tp2 of the primary effluent 270 is above 0°C for the primary

effluent 270 to have a liquid state. Advantageously the temperature tp2 of the primary effluent 270 may be at least 10°C. The waste water treatment plant 8 may be provided with a biological treatment unit. Biological processes in general take place in moderate temperatures. Therefore the temperature tp2 of the primary effluent 270 exiting a biological treatment may be above 0°C, advantageously at least 20°C, such as 21°C or above a room temperature of 25°C. Biological processes do not in general tolerate high temperatures, therefore advantageously the temperature tp2 of the primary effluent 270 may be below 60°C, preferably equal to or below 40°C, such as between 30°C and 35°C.

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 the primary effluent 270 coming from the bleaching plant. There are various wood-originating compounds, and part of the compounds may be chlorinated and part of them may be low-molecular compounds of carbon and hydrogen. As microbes act so that they use as nutrition only the organic portion of effluent, all inorganic substances, or at least inorganic elements remain in the primary effluent 270 and biosludge. Thus, biologically treated primary effluent 270, after separation of the solid and liquid fraction, e.g. by sedimentation, has an organic load that makes it clearly cleaner than primary effluent 270 treated in other ways, but due to the inorganic substances it typically has to be discharged from the process.

The production of calcium oxide 240 from calcium carbonate 200, 220 also produces exhaust gas 210 comprising carbon dioxide, which is a principal component of the exhaust gas 210. The exhaust gas 210 may be used to precipitate calcium as calcium carbonate 220 from the primary effluent 270. In particular, this is relevant to the recycling of calcium in the lime kiln. The precipitation of calcium as calcium carbonate 220 from the primary effluent 270 may be used to diminish the amount of chemicals introduced into the lime cycle. Furthermore, at least part of the carbon dioxide in the exhaust gas 210 may be used to form calcium carbonate 220. In addition, the method may be used to purify the primary effluent 270 to process water 250, which may be further reused. The exhaust gas 210 may, for example, be first

- purified by an electrostatic precipitator (ESP) such as described above. The temperature tp1 of the exhaust gas 210 may vary. Typically the exhaust gas 210 may have a temperature tp1 of at least 60°C, such as between 60°C and 400°C or between 60°C and 280°C. Advantageously the exhaust gas 210 may be lead to the waste water treatment plant 8 directly. Advantageously, the exhaust gas may have a temperature tp1 of at least 200°C, preferably at least 230°C. Alternatively, or in addition, the exhaust gas 210 may be cooled down.
- 10 In particular, the carbonatation reaction temperature tp3 may be controlled by introducing exhaust gas 210 at a temperature tp1 comprising carbon dioxide (CO₂) into the primary effluent 270 comprising calcium at a temperature tp2. Advantageously, the primary effluent 270 may be heated by introducing exhaust gas 210 to improve the precipitation of calcium carbonate (CaCO₃) 220 from the primary effluent 270. In other words, to improve the precipitation of calcium carbonate (CaCO₃) 220 from the primary effluent 270 the reaction temperature tp3 may be raised by controlling the lime kiln exhaust gas 210 temperature tp1. Alternatively, or in addition, to improve the precipitation of calcium carbonate (CaCO₃) 220 from the primary effluent 270 the carbonatation reaction temperature tp3 may be raised by controlling the temperature tp2 of the primary effluent 270. Reducing the temperature tp1 of the exhaust gas 210 may be a preferable way of controlling the carbonatation reaction temperature tp3, as this operation may be easier to implement at the carbonatation reaction site. The carbonatation reaction temperature tp3 may therefore be equal to or between the temperatures tp1 and tp2 of the exhaust gas 210 and the primary effluent 270, respectively. The carbonatation reaction temperature tp3 may preferably be at least 20°C, such as 21°C or above a room temperature of 25°C. The carbonatation reaction temperature tp3 may advantageously be below the boiling point of the primary effluent 270 or 100°C. Advantageously, the heat of the exhaust gas 210 may be used to warm the primary effluent 270 to a temperature tp3 of at least 20°C, for example between 20°C and 70°C or between 21°C and 70°C. Advantageously, the temperature tp3 is at least room temperature such as between 25°C and 70°C or between 30°C and 70°C. A temperature tp3 higher than 70°C may push the carbonatation reaction equilibrium even further towards the precipitation of precipitation of calcium carbonate (CaCO₃) 220 from the primary effluent 270. However, at temperatures above

70°C the evaporation of water may begin to accelerate in amounts detrimental to the process controllability, unless means for cooling down the primary effluent 270 during precipitation of calcium carbonate (CaCO_3) are provided. Cooling of the primary effluent 270 may be performed for example by a heat exchanger. The carbonatation reaction may be possible to perform under elevated pressure, which would shift the carbonatation reaction equilibrium towards increased precipitation of calcium carbonate (CaCO_3) 220. However, for economic reasons, increasing the pressure of the carbonatation reaction may not be feasible. In addition, when increasing the temperature further, the solubility of organic matter and other NPE's may also increase, which may be detrimental for the removal of these impurities.

Aeration devices may be used to introduce the exhaust gas 210 to the primary effluent 270 at the waste water treatment plant 8. An effective means to introduce the exhaust gas 210 into the primary effluent 270 may be by bubbling the exhaust gas 210 through the primary effluent 270. Alternatively, or in addition, the exhaust gas 210 comprising the carbon dioxide may be dissolved in the primary effluent 270 under pressure and then released at atmospheric pressure in a flotation tank or basin. The released exhaust gas 210 may thus form minute bubbles which float towards the surface of the primary effluent 270. The exhaust gas 210 stream may be broken into small bubbles also by mechanical elements, for example by using a microfilter. The pore size of the microfilter may advantageously be adjusted to have an extended residence time for the exhaust gas 210 in the primary effluent 270.

The method may preferably comprise a biological treatment stage prior to introducing the primary effluent 270 to the process. The carbonatation stage may be used to remove organic and inorganic substances in addition to precipitating calcium carbonate 220. The method may comprise a mechanical treatment stage, such as a coarse filtration, flotation or clarification to remove solid particles. When the primary effluent 270 comprising calcium (Ca^{2+}) is purified by a mechanical treatment such as flotation or filtration, thus obtained solution is referred to as a particle free effluent 271. The mechanical treatment stage may be implemented before or after precipitating calcium carbonate 220. Therefore, the calcium carbonate 220 may be separated from the primary effluent 270 or from particle free effluent 271. The process may comprise a stage for adjusting the pH of the

primary effluent 270. The process may comprise a stage for adjusting the pH of the purified effluent 274. Advantageously, the waste water treatment plant 8 comprises at least one, for example one, two or three of the above mentioned stages. The process may comprise a pH treatment 9 stage for
5 adjusting the pH of a calcium free effluent 272.

Biological treatments may typically be performed at neutral or near to neutral pH environments. The primary effluent 270 from a biological treatment may therefore have a pH value ranging between 6.5 and 7.8, preferably close to
10 or equal to a pH value of 7.4. The addition of carbon dioxide by introducing exhaust gas 210 into the primary effluent 270 drives the reaction equilibrium to bicarbonate ion formation, when an excess of alkali is present. Therefore, in order to drive the carbonatation reaction equilibrium to the side where precipitation of calcium carbonate 220 is favored, the pH of the primary
15 effluent 270 may be adjusted to be alkaline when introducing exhaust gas 210 into the effluent.

The pH of the primary effluent 270 may be adjusted to be alkaline by using a pH modifier. Advantageously the pH of the primary effluent 270 is adjusted
20 with calcium oxide (CaO) or with calcium hydroxide (Ca(OH)₂). In addition, sodium hydroxide (NaOH) may be used. Advantageously, calcium oxide (CaO) 240 from the lime kiln may be used. In an embodiment experiment, the pH of a primary effluent 270 having an initial pH value of 6.5 was adjusted by adding calcium hydroxide (Ca(OH)₂) to a final concentration of 0.02 w-%. The
25 pH of the primary effluent 270 was increased to a value of 11.8, respectively. Conversion of the amount of added calcium hydroxide to calcium oxide gave 151 mg/l of calcium. In contrast, the final primary effluent 270 concentration of 0.02 w-% equaled to 200 mg/l of calcium.

30 In particular, the use of exhaust gas 210 to precipitate calcium carbonate (CaCO₃) 220 of a primary effluent 270 comprising calcium (Ca²⁺) may increase the amount of calcium available for the lime cycle. Advantageously, the amount of calcium in the precipitated calcium carbonate 220 may exceed the amount of calcium added as lime (CaO) 240, which is used to increase
35 the pH of the primary effluent 270 prior to the introduction of the lime kiln exhaust gas 210 to the primary effluent 270.

The primary effluent 270 at the waste water treatment plant 8 before the precipitation of calcium carbonate 220 may comprise inorganic and/or organic impurities. Table 2 discloses primary effluent 270 values after a biological treatment and before the precipitation of calcium carbonate 220. In the example effluent of Table 2 the value of calcium (Ca^{2+}) was measured to be 110 mg/l. However, the calcium (Ca^{2+}) may be present in various amounts, such as at least 10 mg/l or at least 50 mg/l, depending of the primary effluent 270.

Table 2. Primary effluent 270, example

Description		Treated effluent
Aluminium, Al	mg/l	<0.005
Barium, Ba	mg/l	<0.05
Calcium, Ca	mg/l	110
Chromium, Cr	mg/l	<0.002
Copper, Cu	mg/l	<0.002
Iron, Fe	mg/l	0.1
Potassium, K	mg/l	80
Magnesium, Mg	mg/l	10
Manganese, Mn	mg/l	0.3
Sodium, Na	mg/l	860
Phosphorus, P	mg/l	0.4
Sulphur, S	mg/l	425
Silicon, Si	mg/l	10
Chloride	mg/l	240
Sulphate	mg/l	1250
Total oxalate	mg/l	0.4
Diss. oxalate	mg/l	0.0
Phosphate	mg/l	<0.3
Carbonate	%	0.1
Total organic carbon, TOC	mgC/l	100
Total inorganic carbon, TIC	mgC/l	120

Preferably, the primary effluent 270 pH is equal to or more than pH 9 prior to the introduction of the exhaust gas 210. Advantageously the pH value of the effluent 270 is at least 9 prior to the introduction of the exhaust gas 210 to the effluent 270. Addition of calcium hydroxide ($\text{Ca}(\text{OH})_2$) may advantageously
5 be used to increase the pH of the effluent 270. Further, higher pH values, such as pH 11 or 12 or even higher may be advantageous for the precipitation of calcium carbonate 220. In addition, or as an alternative to lime, other pH modifiers, such as soda ash (Na_2CO_3) or caustic soda (NaOH) may be used. However, due to the lime cycle and chemical recovery process,
10 lime is the preferred pH modifier. If solid particles have been removed, the primary effluent 270 described above may be denoted as particle free effluent 271.

The primary effluent 270 may comprise, among other things, bacteria,
15 chlorides, inorganic compounds, high molecular mass lignin residues and/or low molecular mass compounds. Thus, there may be at least one treatment step in order to decrease the amount of impurities before introducing the exhaust gas 210 to the primary effluent 270. The precipitation of calcium carbonate 220 from the primary effluent 270 may comprise a treatment to co-precipitate other substances, whereby inorganic and / or organic substances
20 may be removed from the primary effluent 270. Advantageously a filtration treatment may be applied to remove inorganic and / or organic substances from the primary effluent 270. The filtration treatment may comprise, for example, ultrafiltration membranes, chemical precipitation, sedimentation,
25 flotation, and/or filtration. An advantageous filtration treatment may be a method based on membrane technique or a technique using sand and/or multimedia filter. In addition, a flotation treatment may be used to remove inorganic and / or organic substances from the primary effluent 270. For example, dissolved air flotation (DAF) removes suspended matter from the
30 primary effluent 270. The removal may be achieved by dissolving air in the primary effluent 270 under pressure and consequently releasing the air at atmospheric pressure, for example in a flotation tank or basin. The released air forms tiny bubbles which may adhere to the suspended matter and cause the suspended matter to float to the surface of thus obtained particle free
35 effluent 271. The floating flocculants may then be removed, for example by skimming. In addition, sand and/or multimedia filter(s) may be used for primary effluent 270 filtration. The filter(s) should be washed at times in order

to maintain the efficiency of said filter(s). If the primary effluent 270 is dirty, the sand and/or multimedia filter(s) should be washed more often, which may increase the total cost of said treatment. However, these filtration treatments may serve to improve the yield or (purity) grade of the precipitated calcium carbonate 220. Furthermore, these filtration steps may purify the primary effluent 270 for further recycling. The filtering treatments may be done at various stages of the method. For example, the filtering treatment may be done prior to adjusting the pH of the primary effluent 270 with calcium oxide (CaO) 240 from the lime kiln. Alternatively, the filtering treatment may be done for example for the calcium free effluent 272 after precipitating the calcium carbonate 220.

After carbonation, the purified effluent 274 may have an alkaline pH value. Advantageously the pH of the purified effluent 274 may be adjusted to a neutral pH range for further use or recycling purposes. A suitable and neutral pH value for the purified effluent 274 may be close to or equal to 7, for example between pH 6.5 and 7.4. The pH of the purified effluent 274 may be decreased by using a pH modifier. A suitable acidic pH modifier for the pH adjustment of the purified effluent 274 may be, for example carbon dioxide (CO₂). Advantageously, exhaust gas 210 comprising carbon dioxide (CO₂) from the lime kiln may be used. Alternatively, other acidic pH modifiers such as sulphuric acid (H₂SO₄) may be used. By adjusting the pH of the calcium free effluent 272 after calcium carbonate 220 has been precipitated, process water 250 may be obtained. Process water 250 having a pH value close to 7 may be used further, for example in recycling purposes.

The method may be used to decrease the total amount of inorganic and/or organic impurities present in the primary effluent 270. This can be measured by using, for example, generally known methods to measure COD, TOC, BOD, AOX and/or percentage of solids. A chemical substance or a compound may be used to precipitate organic compound and/or inorganic compound from the primary effluent 270. The term "flocculation of organic compound" refers to decreasing COD and/or color of the primary effluent 270 using chemical precipitation method(s). COD can be high due to, for example, lignin fragments.

Flocculants may comprise, for example, long chain organic polymeric compounds with or without electrical charges (cationic, anionic or non-ionic polymers or their salts).

- 5 Preferably, the flocculant may comprise polyamine. Alternatively or in addition, the flocculant may comprise poly(diallyldimethylammonium-chloride) (i.e. poly-DADMAC). Alternatively or in addition, the flocculant may comprise poly(amidoamine) (i.e. PAA). Alternatively or in addition, the flocculant may comprise poly(vinylformamide) (i.e. PVAm). Alternatively or in addition, the
10 flocculant may comprise poly(ethyleneimine) (i.e. PEI). Alternatively or in addition, the flocculant may consist of homopolymerized form and/or may carry branched structures in which the functionality of the polymer is based on quaternary ammonium groups, such as in starch based derivatives. Alternatively or in addition to the flocculants, other compounds such as
15 coagulants and/or adsorbents may be used. The adsorbents may comprise, for example, clay, bentonite and/or talc.

- The coagulants may comprise aluminium compounds. The aluminium compounds may comprise alum and polymeric forms of alumn, such as
20 polyaluminiumnitrate (PAN), polyaluminiumchloride (PAC), and/or polyaluminiumsulfate (PAS). In particular, for certain suspended solids which sometimes may be present in the primary effluent 270, alumn may be an effective flocculant. The addition of alumn may therefore be used for removing said suspended solids from the primary effluent 270. The use of a
25 coagulant such as alumn in the process of precipitating calcium carbonate 220 is not mandatory. A coagulant may be used as an option to improve the removal of organic and/or inorganic matter from the effluent 270 purified effluent 274 when flocculation technique is used.

- 30 Alternatively or in addition, the coagulants may comprise ferrous compounds, such as FeCl_2 , and/or FeSO_4 . Alternatively or in addition, the coagulants may comprise ferric compounds, such as FeCl_3 , and/or $\text{Fe}_2(\text{SO}_4)_3$.

- The treatment used for precipitating calcium carbonate 220 from the primary
35 effluent 270 may comprise at least one flocculation stage. The flocculation process may be used to clean the sand and/or multimedia filter of the water treatment plant 8. For example, possible organic impurities in the primary

effluent 270 may lead to decreased efficiency of the sand and/or multimedia filter unless they are repeatedly cleaned. Chemicals used in the flocculation stage can vary due to differences in the primary effluent 270 to be cleaned.

- 5 The primary effluent 270 may comprise calcium in various amounts. Calcium in a solution is in general present as calcium ions (Ca^{2+}), unless precipitated from the solution as a solid compound, such as calcium carbonate (CaCO_3), for example. The primary effluent 270 may comprise waste water from the bleaching unit and the washing steps therein, and the concentration of
- 10 calcium (Ca^{2+}) may be at least 10 mg/l or at least 20 mg/l or higher, such as at least 50 mg/l. When calcium hydroxide is added to the primary effluent 270, the concentration of calcium (Ca^{2+}) may be above 100 mg/l, such as at least 150 mg/l or at least 200 mg/l. The upper limit of calcium ion concentration in a solution, when calcium hydroxide (Ca(OH)_2) is added to
- 15 the effluent 270, may be derived from the solubility of calcium hydroxide (Ca(OH)_2) to water. The solubility of calcium hydroxide is temperature dependent. For example, at 30°C the solubility of calcium hydroxide (Ca(OH)_2) to water is roughly 1500 mg/l, and at 100°C only 700 mg/l.
- 20 The temperature tp3 may be controlled by selecting the temperature tp1 or tp2 to improve the precipitation of calcium carbonate (CaCO_3) 220 from the primary effluent 270. In other words, the primary effluent 270 may be heated by introducing lime kiln exhaust gas 210 to improve the formation of calcium carbonate (CaCO_3) from the primary effluent 270.
- 25 A method for precipitating calcium carbonate 220 with lime kiln exhaust gas 210 from the primary effluent 270 is described in Figure 3. The method comprises multiple operations, which may be denoted as process steps. The method may comprise a step 310, where the pH of the primary effluent 270 may be adjusted. The pH of the primary effluent 270 may have a value close to 7, such as pH 7.4. Preferably, the primary effluent 270 pH may be adjusted with calcium oxide (CaO) 240 to have a pH value of at least 9. The method may comprise a step 320, where exhaust gas 210 may be introduced into the primary effluent 270. The step 320 may comprise introducing the exhaust gas
- 30 210 into the primary effluent 270 by bubbling the exhaust gas 210 through the primary effluent 270. The method may comprise a step 330, where calcium carbonate 220 may be formed. The calcium carbonate 220 may be
- 35

separated from the calcium free effluent 272. Forming the calcium carbonate (CaCO_3) may be accomplished, for example, by precipitation. The calcium carbonate (CaCO_3) may therefore be in a precipitated form, and separated from the calcium free effluent 272. The calcium free effluent 272 may be further processed to process water 250, for example by a pH adjustment step 370, and the process water 250 may be further reused. The process water 250 may be used for example in pulp, paper and/or plywood mill processes and/or power plant processes. Preferably the step 320 may be executed after step 310 such that the pH value of the primary effluent 270 may be at least 9. Preferably the step 330 may be performed after step 320, as lime kiln exhaust gas 210 may be needed to provide carbon dioxide for the precipitation of calcium carbonate 220.

Some of the steps in the method may be optional. The order of the process steps may be changed. Different embodiments may be used for precipitating calcium carbonate 220 with exhaust gas 210 from the primary effluent 270. It may be useful, for example, to determine the timing for the process step 330, where the calcium carbonate 220 may be precipitated out from primary effluent 270. For example, the process step 330 may be selected to be near the end of the process, which may result to precipitated calcium carbonate 220 (PCC) comprising higher grade. The higher the grade of the precipitated calcium carbonate 220 (PCC), the better it may be re-used in various applications. For example, the precipitation step 330 may produce a co-precipitation of calcium carbonate 220 and organic and/or inorganic matter. Further, a filtration step may be used for the removal of organic and/or inorganic matter from the primary effluent 270. The method may comprise a step wherein the filtering is done prior to adjusting the pH of the primary effluent with calcium oxide (CaO) 240 from the lime kiln. In addition, the method may comprise a step, wherein the filtering is done to the calcium free effluent 272 after precipitating the calcium carbonate (CaCO_3) 220. Removing at least part of the organic matter from the effluent 270 by a biological treatment may precede the step 310. For example, the removal of solid waste comprising organic and/or inorganic matter may have an effect on the grade of the purified effluent 274. The method and/or timing of the filtration step may have an effect on the reuse of process water 250. The filtration step may further be selected such that solid waste may be collected in different forms. Alternatively, the filtration step may be replaced by a

flotation step, which may produce particle free effluent 271 and flotation waste. The filtration step may optionally be preceded by a pH adjustment step, where the pH may be adjusted to a value between 5 and 6. The pH adjustment may be achieved for example by addition of the exhaust gas 210 comprising carbon dioxide into the primary effluent 270, which may provide the primary effluent 270 with carbonate and/or bicarbonate ions acting as an acidic pH modifiers. The filtration step may be followed by a pH adjustment step 370, where the particle free effluent 271 may be adjusted close to a neutral pH value 7 to obtain process water 250. Neutral pH value may improve the reuse of the process water 250 in further processes.

Therefore, a method for treating primary effluent 270 of a pulp, paper or plywood mill may comprise:

- introducing exhaust gas 210 comprising carbon dioxide (CO_2) into the primary effluent 270 comprising calcium (Ca^{2+}); and
- arranging the carbon dioxide (CO_2) to react with the calcium (Ca^{2+}) present in the primary effluent 270 to form calcium carbonate (CaCO_3) and calcium free effluent 272 at a temperature tp_3 .

As an alternative, the exhaust gas 210 comprising carbon dioxide (CO_2) may be introduced into a particle free effluent 271 obtained from a primary effluent 270.

The primary effluent 270 may be of a chemical pulp production process. The exhaust gas 210 may be lime kiln exhaust gas. In particular, before introducing the exhaust gas 210 the temperature tp_3 may be at least 20°C and below 70°C .

Further, the method may comprise:

- collecting the primary effluent 270 of pulp, paper and/or plywood mill effluents to a waste water treatment plant 8;
- separating the formed calcium carbonate (CaCO_3) 220 from the primary effluent 270;
- processing the calcium free effluent 272 to process water 250 for further use at the pulp, paper and/or plywood mill process and/or a power plant process;

- reducing the formed calcium carbonate (CaCO_3) 220 in a lime kiln into calcium oxide (CaO) 240;
- controlling the temperature tp3 by selecting a temperature tp1 of the exhaust gas 210 and/or a temperature tp2 of the primary effluent 270 to improve the precipitation of calcium carbonate (CaCO_3) 220 from the primary effluent 270;
- treating the primary effluent 270 to remove organic or inorganic matter; and
- removing at least part of the organic matter of the primary effluent 270 by a biological treatment.

In particular, the temperature tp1 may be between 60°C and 280°C, advantageously at least 200°C and below 280°C. The temperature tp2 may be above 0°C, advantageously above 10°C and below 40°C.

15

Further, before introducing the exhaust gas 210, the primary effluent 270 may

- comprise calcium at least 10 mg/l such as at least 20 mg/l or advantageously at least 50 mg/l; and
- have a pH value of at least 9.

20

Further, separating the formed calcium carbonate (CaCO_3) from the calcium free effluent 272 may be done by precipitation.

Further, the pH of the primary effluent 270 may be adjusted with calcium oxide (CaO), calcium hydroxide (Ca(OH)_2) or NaOH. Alternatively, or in addition, the pH of the primary effluent 270 may be adjusted with exhaust gas 210 comprising carbon dioxide (CO_2). In addition, pH of the purified effluent 274 may be adjusted with exhaust gas 210 comprising carbon dioxide (CO_2).

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Further, a sand and/or a multimedia filter may be used for treating the primary effluent 270 to remove organic or inorganic matter. Alternatively, or in addition, flotation may be used for the treating. Alternatively, or in addition, a chemical compound may be used to remove inorganic or organic matter. The treating may be done before adjusting the pH with calcium oxide (CaO), calcium hydroxide (Ca(OH)_2) or NaOH. Alternatively, the treating may be done after separating the formed calcium carbonate (CaCO_3) 220.

35

Precipitated calcium carbonate 220 may be obtained according to the method.

- 5 The method provides a use of exhaust gas 210 comprising carbon dioxide to form calcium carbonate (CaCO_3) 220 from a primary effluent 270 comprising calcium of a pulp, paper or plywood mill. In particular, the primary effluent 270 comprising calcium may be of a chemical pulp production process and the exhaust gas 210 may be lime kiln exhaust gas.
- 10 Further, the method provides a use of process water obtained from the calcium free effluent 272 in a pulp, paper and/or plywood mill process and/or a power plant process.
- 15 Figure 4 presents an embodiment of a method for precipitating calcium carbonate 220 with exhaust gas 210 from the primary effluent 270. The primary effluent 270 having a pH value close to 7.4 may be treated with an alkaline pH modifier to increase the pH of the primary effluent 270. Advantageously the pH of the primary effluent 270 is adjusted in step 310
- 20 with calcium oxide (CaO) 240. Preferably, the primary effluent 270 pH is be adjusted with calcium oxide (CaO) 240 to have a pH value of at least 9. Calcium oxide 240 is a product of the calcinating 7 step in the lime kiln and reacts readily with water to form alkaline calcium hydroxide ($\text{Ca}(\text{OH})_2$). In the next step 320, flue gas 210 is introduced into the primary effluent 270.
- 25 Advantageously, lime kiln exhaust gas 210 available from a chemical pulp production process is used to precipitate calcium carbonate (CaCO_3) 220. The lime kiln exhaust gas 210 may be purified by means of an electrostatic precipitation (ESP) before introducing the exhaust gas 210 into the primary effluent 270. As shown in step 330, calcium carbonate (CaCO_3) 220 is
- 30 formed from the primary effluent 270. By raising the carbonatation reaction temperature tp_3 , the reaction kinetics may be altered and the yield of precipitated calcium carbonate (CaCO_3) 220 may be improved. The reaction temperature tp_3 may be controlled by selecting the exhaust gas 210 temperature tp_1 and/or the primary effluent 270 temperature tp_2 . The
- 35 precipitation step 330 may comprise a co-precipitation, where other organic and/or inorganic matter precipitates from the primary effluent 270. The precipitated calcium carbonate (CaCO_3) 220 may be separated, collected

and processed further. For example, the precipitated calcium carbonate (CaCO_3) 220 may be recycled back into the lime kiln, where the co-precipitated organic matter may be removed from the calcium carbonate (CaCO_3) 220 by combustion. Inorganic matter may be separated from calcium carbonate (CaCO_3) 220 before the lime kiln. However, minor amounts of inorganic matter may be recycled with the calcium carbonate (CaCO_3) 220 into the lime kiln to be further used in the causticizing process without detrimental effects on the process controllability. The calcium free effluent 272, from the precipitation step 330 may be further purified by an optional pH adjustment as illustrated by step 340. The pH of the calcium free effluent 272 may be decreased to have a value between 5 and 6 by introducing exhaust gas 210 comprising carbon dioxide (CO_2) into the calcium free effluent 272. A chemical treatment may be used in conjunction with the pH adjustment to further remove organic and/or inorganic matter from the calcium free effluent 272. In particular, the calcium free effluent 272 may be purified by using a filtration treatment, as presented in step 350. The filtration may use, for example a sand and/or multimedia filter. The filtration step 350 removes solid waste 290 from the calcium free effluent 272. The purified effluent 274 from the filtration step 350 may have a pH value deviating from neutral pH range. The purified effluent 274 at this stage no longer comprises calcium (Ca^{2+}) ions which have been removed by precipitation in step 330. Advantageously a pH adjustment 370 may be performed on the purified effluent 274. The pH of the purified effluent 274 may be adjusted to obtain a neutral pH value and may then be further used as process water 250. A neutral pH value close to or equal to 7, for example between pH 6.5 and 7.4, may be obtained by using either an acidic or an alkaline pH modifier, depending on whether the pH of the purified effluent 274 is above or below a neutral pH range, respectively. The process water 250 may be used, for example in pulp, paper and/or plywood mill processes and/or power plant processes.

Figure 5 presents an advantageous embodiment of a method for precipitating calcium carbonate 220 with exhaust gas 210 from the primary effluent 270, where precipitated calcium carbonate 220 (PCC) comprising higher grade of purity may be obtained. By improving the purity of the precipitated calcium carbonate 220 (PCC), the product may be better suitable for an increased number of applications. The primary effluent 270 having a pH value close to

7.4 is treated with an acidic pH modifier to decrease the pH of the primary effluent 270. The pH of the primary effluent 270 may be decreased to have a value between 5 and 6, for example by introducing exhaust gas 210 comprising carbon dioxide (CO_2) into the effluent 270. Without an excess of an alkali the carbonatation reaction may not be favoured and the calcium (Ca^{2+}) ions may remain in the primary effluent 270. A chemical treatment may be used in conjunction with the pH adjustment to remove organic and/or inorganic matter from the primary effluent 270. In particular, the primary effluent 270 may be purified by using a filtration treatment, as presented in step 350. The filtration may use, for example a sand and/or multimedia filter. Alternatively, or in addition, a treatment using flotation, such as dissolved air flotation (DAF), may be used. The filtration step 350 removes solid particles 290 from the primary effluent 270. The particle free effluent 271 may then be treated in step 310 with an alkaline pH modifier to increase the pH of the particle free effluent 271. Advantageously the pH of the particle free effluent 271 is adjusted with calcium oxide (CaO). Advantageously the calcium oxide (CaO) 240 is obtained from the lime kiln. Preferably, the pH of the particle free effluent 271 is adjusted with calcium oxide (CaO) 240 to have a pH value of at least 9. Calcium oxide 240, a product of the calcinating 7 step of the lime kiln reacts readily with water to form alkaline calcium hydroxide ($\text{Ca}(\text{OH})_2$). In the next step 320, flue gas 210 may be introduced into the particle free effluent 271. Advantageously, lime kiln exhaust gas 210 available from a chemical pulp production process is used to precipitate calcium carbonate (CaCO_3) 220. The lime kiln exhaust gas 210 may be purified by means of an electrostatic precipitation (ESP) before introducing the exhaust gas 210 into the particle free effluent 271. As shown in step 330, calcium carbonate (CaCO_3) 220 may be formed from the particle free effluent 271. By raising the carbonatation reaction temperature tp_3 , the reaction kinetics may be altered and the yield of precipitated calcium carbonate (CaCO_3) 220 may be improved. The reaction temperature tp_3 may be controlled by selecting the exhaust gas 210 temperature tp_1 and/or the particle free effluent 271 temperature tp_2 . The precipitation step 330 may comprise a co-precipitation, where other organic and/or inorganic matter precipitates from the particle free effluent 271. The precipitated calcium carbonate (CaCO_3) 220 may be separated, collected and processed further. Advantageously, in the method the precipitation step 330 may be selected to be near the end of the process. By filtering other organic and/or inorganic

matter from the particle free effluent 271 before the precipitation step 330, purity of the precipitated calcium carbonate 220 (PCC) may be improved. The precipitated calcium carbonate (CaCO_3) 220 may be recycled back into the lime kiln, where co-precipitated organic matter may be removed from the calcium carbonate (CaCO_3) 220 by combustion. Inorganic matter may be separated from calcium carbonate (CaCO_3) 220 before the lime kiln. The precipitated calcium carbonate (PCC) 220 may also be used in a paper manufacturing process, e.g. as paper filler or as a coating chemical. However, minor amounts of inorganic matter may be recycled with the calcium carbonate (CaCO_3) 220 into the lime kiln to be further used in the causticizing process without detrimental effects on the process controllability. The purified effluent 274 from the precipitation step 330 may have a pH value deviating from neutral pH range. Advantageously in step 370, the pH of the purified effluent 274 may be adjusted to a neutral pH range for further use as process water 250. A neutral pH value close to or equal to 7, for example between pH 6.5 and 7.4, may be obtained by using an acidic pH modifier, such as exhaust gas 210 comprising carbon dioxide (CO_2). The process water 250 may be used, for example in pulp, paper and/or plywood mill processes and/or power plant processes.

Figure 6 presents an embodiment of a method for precipitating calcium carbonate 220 with exhaust gas 210 from the primary effluent 270. The primary effluent 270 having a pH value close to 7.4 may be treated with an alkaline pH modifier to increase the pH of the primary effluent 270. Advantageously the pH of the primary effluent 270 is adjusted in step 310 with calcium oxide (CaO). Preferably, the primary effluent 270 pH may be adjusted with calcium oxide (CaO) 240 to have a pH value of at least 9. Calcium oxide 240, a product of the calcinating 7 step in the lime kiln, reacts readily with water to form alkaline calcium hydroxide ($\text{Ca}(\text{OH})_2$), which may increase the pH of the primary effluent 270. In the next step 320, flue gas 210 may be introduced into the primary effluent 270. Advantageously, lime kiln exhaust gas 210 available from a chemical pulp production process may be used to precipitate calcium carbonate (CaCO_3) 220. The lime kiln exhaust gas 210 may be purified by means of an electrostatic precipitation (ESP) before introducing the exhaust gas 210 into the primary effluent 270. The primary effluent 270 may then be treated by a flotation treatment, as presented in step 351. The flotation may be, for example a technique using

dissolved air flotation (DAF). By dissolving air into the primary effluent 270, inorganic and / or organic suspended matter from the primary effluent 270 floats to the surface of the primary effluent 270 as flotation waste 280. Flocculants may be used to improve the rising and adhering of flotation waste 280 to the surface of the particle free effluent 271. The flotation waste 280 may then be removed, for example by skimming. The flotation may be followed by step 330, where precipitation of the calcium carbonate (CaCO_3) 220 may occur from the particle free effluent 271. By raising the carbonation reaction temperature t_{p3} , the reaction kinetics may be altered and the yield of precipitated calcium carbonate (CaCO_3) 220 may be improved. The precipitation step 330 may comprise a co-precipitation, where other organic and/or inorganic matter precipitates from the particle free effluent 271. The precipitated calcium carbonate (CaCO_3) 220 may be collected and processed further. The precipitated calcium carbonate (CaCO_3) 220 may be recycled back into the lime kiln, where co-precipitated organic matter may be removed from the calcium carbonate (CaCO_3) 220 by combustion. Inorganic matter may be separated from calcium carbonate (CaCO_3) 220 before causticizing the calcium carbonate (CaCO_3) 220 in the lime kiln. However, minor amounts of inorganic matter may be recycled with the calcium carbonate (CaCO_3) 220 into the lime kiln without detrimental effects on the process controllability. The purified effluent 274 from the precipitation step 330 may have a pH value deviating from neutral pH range. Advantageously the pH of the purified effluent 274 may be adjusted to a neutral pH range in step 370 for further use as process water 250. A neutral pH value close to or equal to 7, for example between pH 6.5 and 7.4, may be obtained by using an acidic pH modifier, such as lime kiln exhaust gas 210 comprising carbon dioxide (CO_2). Thus obtained process water 250 may be used, for example in pulp, paper and/or plywood mill processes and/or power plant processes.

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

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Claims:

1. A method for treating primary effluent of a pulp, paper or plywood mill, said
5 method comprising:
- introducing exhaust gas comprising carbon dioxide (CO_2) into the primary effluent comprising calcium (Ca^{2+}); and
 - arranging the carbon dioxide (CO_2) to react with the calcium (Ca^{2+}) present in the primary effluent to form calcium carbonate (CaCO_3) and
10 calcium free effluent at a temperature t_p3 .
2. The method according to claim 1, wherein the primary effluent is a particle free effluent.
- 15 3. The method according to claim 1, wherein the exhaust gas comprising carbon dioxide (CO_2) is lime kiln exhaust gas.
4. The method according to claim 1, wherein the exhaust gas comprising carbon dioxide (CO_2) is introduced into a particle free effluent obtained from
20 the primary effluent.
5. The method according to claim 1, further comprising:
- collecting the primary effluent of pulp, paper and/or plywood mill effluents to a waste water treatment plant.
25
6. The method according to claim 1, wherein the primary effluent is an effluent of a chemical pulp production process.
7. The method according to claim 1, further comprising:
- 30 - separating the formed calcium carbonate (CaCO_3) from the primary effluent.
8. The method according to claim 1, further comprising:
- processing the calcium free effluent to process water for further use at the
35 pulp, paper and/or plywood mill.

9. The method according to claim 1, wherein before introducing the exhaust gas, the effluent comprises calcium (Ca^{2+}) at least 20 mg/l.
10. The method according to claim 1, wherein before introducing the exhaust gas, the effluent has a pH value of at least 9; and the temperature tp3 is at least 20°C and below 70°C.
11. The method according to claim 7, wherein separating the formed calcium carbonate (CaCO_3) from the primary effluent is done by precipitation.
12. The method according to claim 1, further comprising:
- reducing the formed calcium carbonate (CaCO_3) in a lime kiln into calcium oxide (CaO).
13. The method according to claim 1, further comprising:
- controlling the temperature tp3 by selecting a temperature tp1 of the exhaust gas and/or a temperature tp2 of the primary effluent to improve the precipitation of calcium carbonate (CaCO_3) from the primary effluent, wherein the temperature tp1 is between 60°C and 280°C and the temperature tp2 is above 0°C.
14. The method according to claim 1, wherein the pH of the primary effluent is adjusted with calcium oxide (CaO), calcium hydroxide ($\text{Ca}(\text{OH})_2$) or NaOH.
15. The method according to claim 1, wherein the pH of the primary effluent is adjusted with exhaust gas comprising carbon dioxide (CO_2).
16. The method according to claim 1, further comprising:
- treating the primary effluent to remove organic or inorganic matter.
17. The method according to claim 16, wherein a sand and/or a multimedia filter is used for the treating.
18. The method according to claim 16, wherein flotation is used for the treating.

19. The method according to claim 16, wherein a chemical compound is used to remove inorganic or organic matter.
- 5 20. The method according to claim 16, wherein the treating is done before adjusting the pH with calcium oxide (CaO), calcium hydroxide (Ca(OH)₂) or NaOH.
- 10 21. The method according to claim 16, wherein the treating is done after separating the formed calcium carbonate (CaCO₃).
22. The method according to claim 1, wherein the exhaust gas is introduced into the primary effluent by bubbling the exhaust gas through the primary effluent.
- 15 23. The method according to claim 1, further comprising
- removing at least part of the organic matter of the primary effluent by a biological treatment.
- 20 24. Precipitated calcium carbonate obtained according to any of the claims 1 to 23.
- 25 25. Use of exhaust gas comprising carbon dioxide to form calcium carbonate (CaCO₃) from primary effluent comprising calcium of a pulp, paper or plywood mill.
26. The use of exhaust gas according to claim 25, where the primary effluent comprising calcium is of a chemical pulp production process and the exhaust gas is lime kiln exhaust gas.
- 30 27. Use of a process water obtained from a calcium free effluent in a pulp, paper and/or plywood mill process and/or a power plant process.

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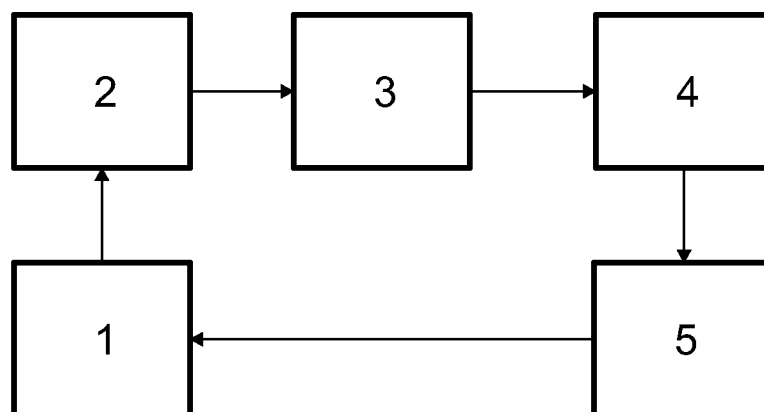


Fig.1

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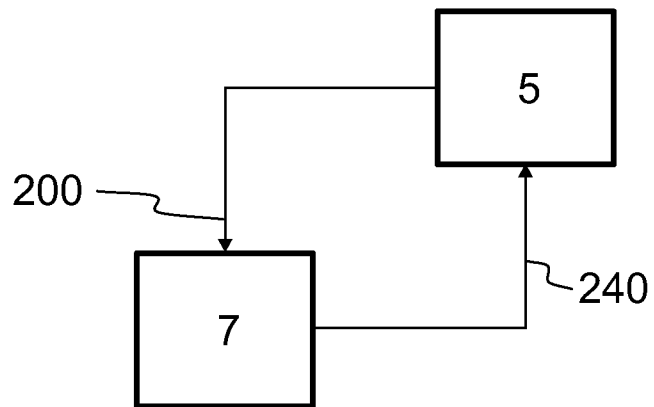


Fig 2a.

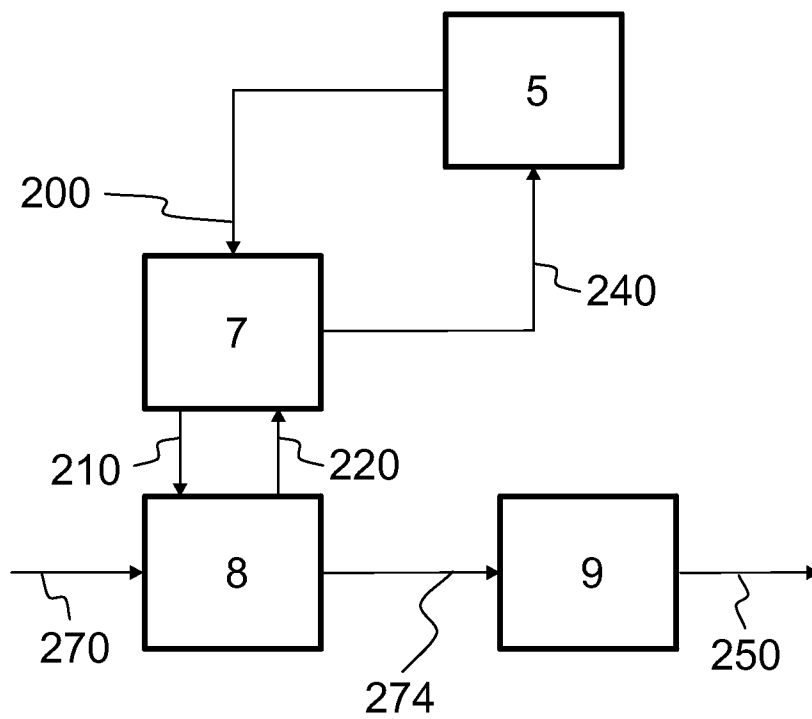


Fig. 2b

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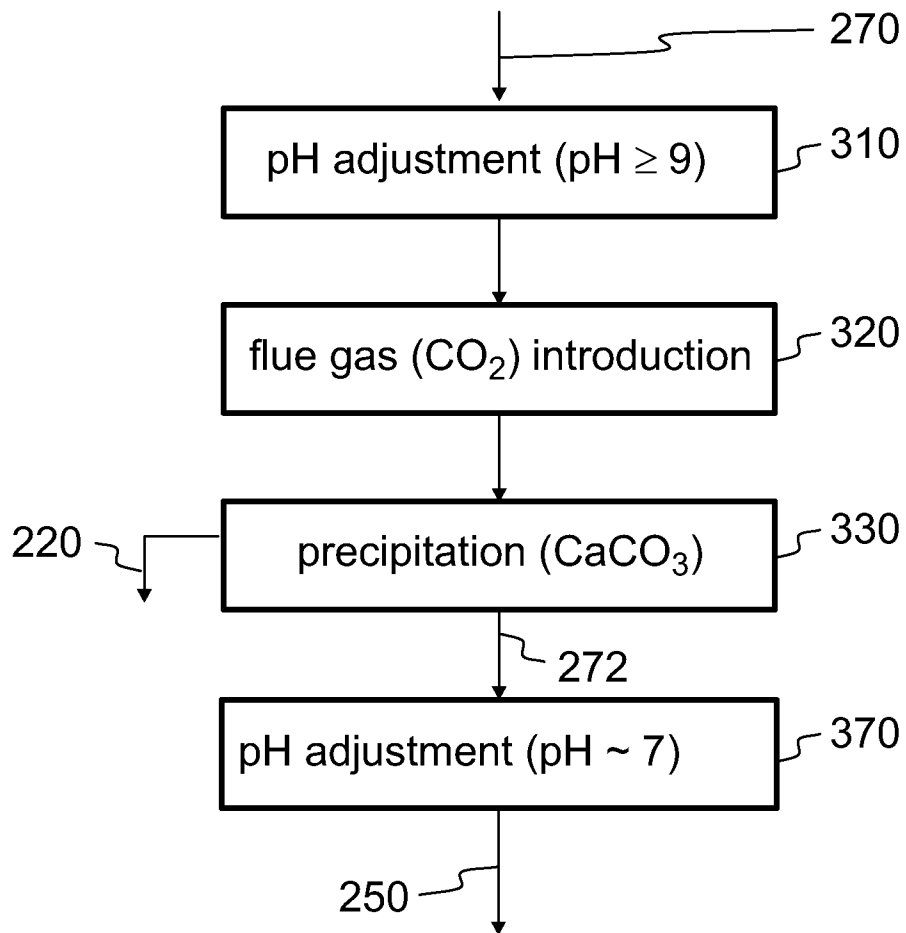


Fig.3

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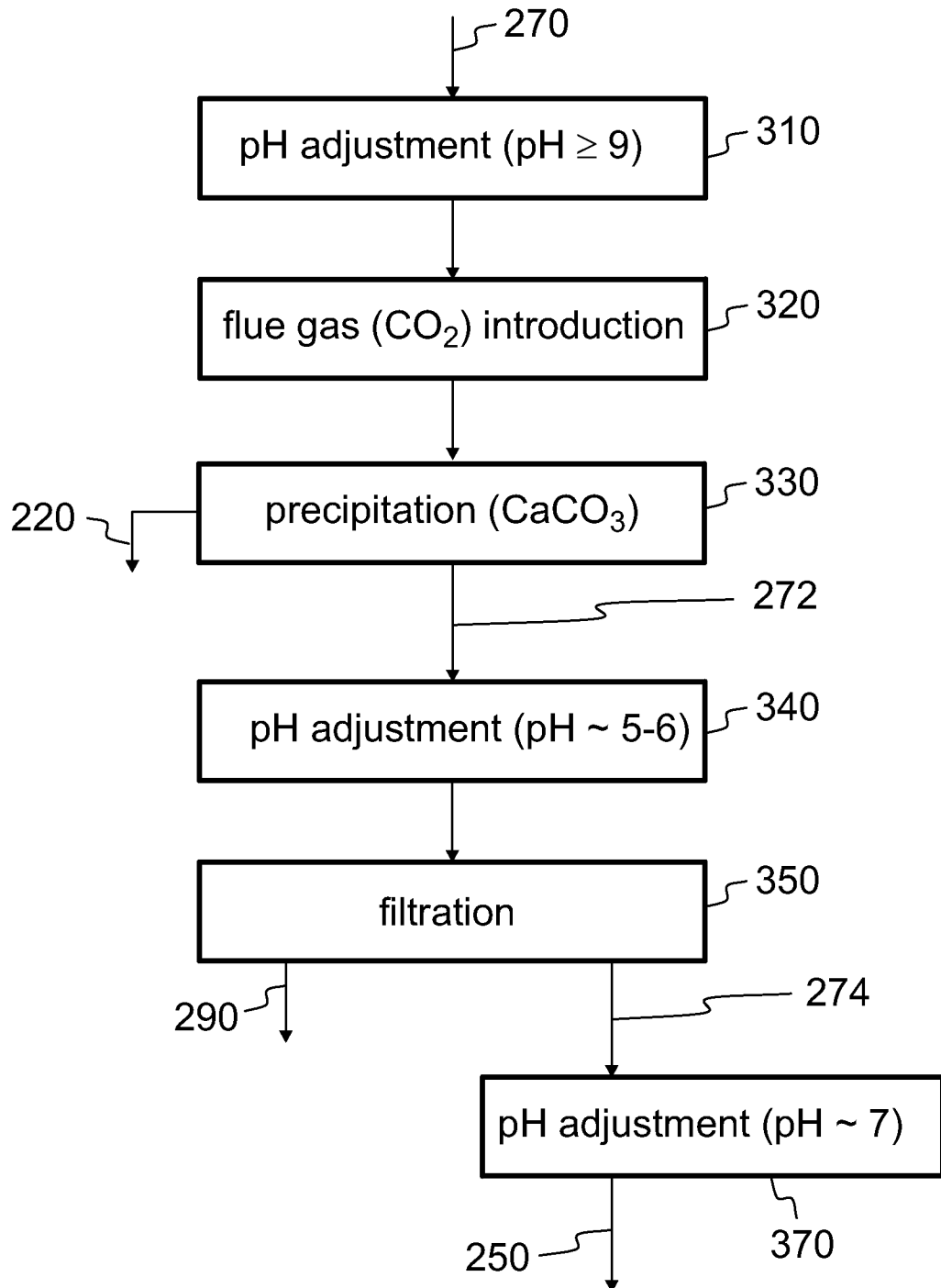


Fig. 4

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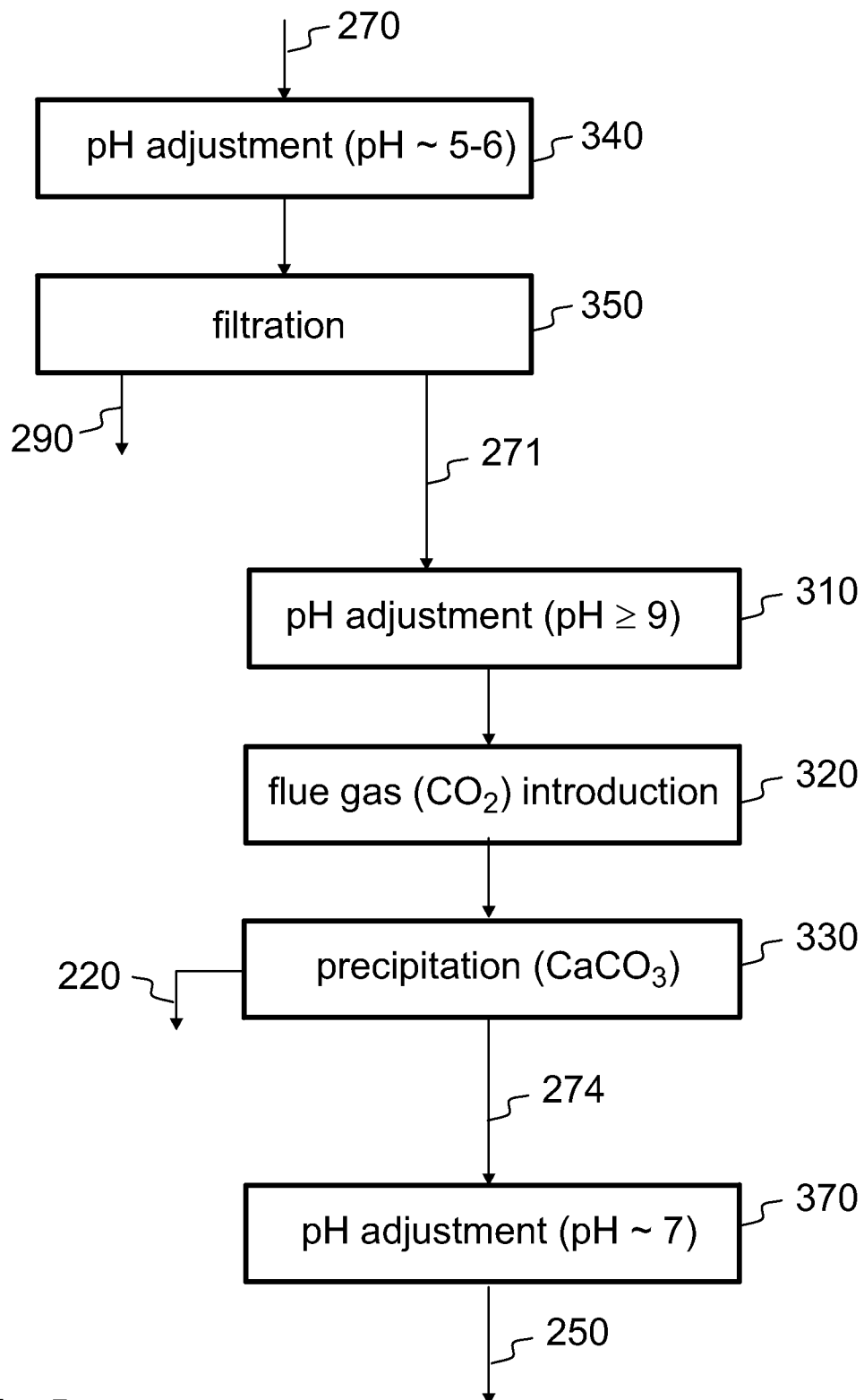


Fig. 5

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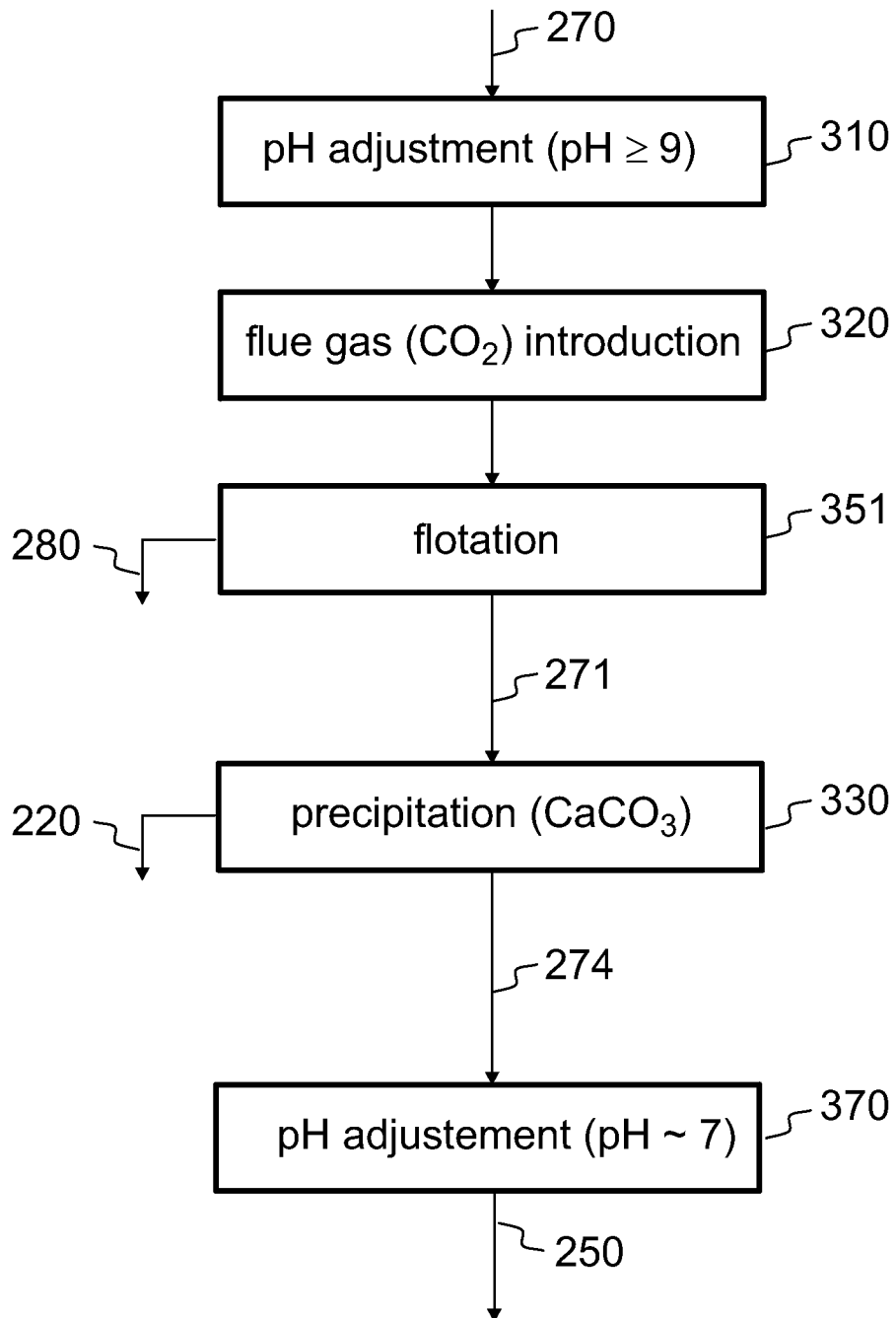


Fig. 6

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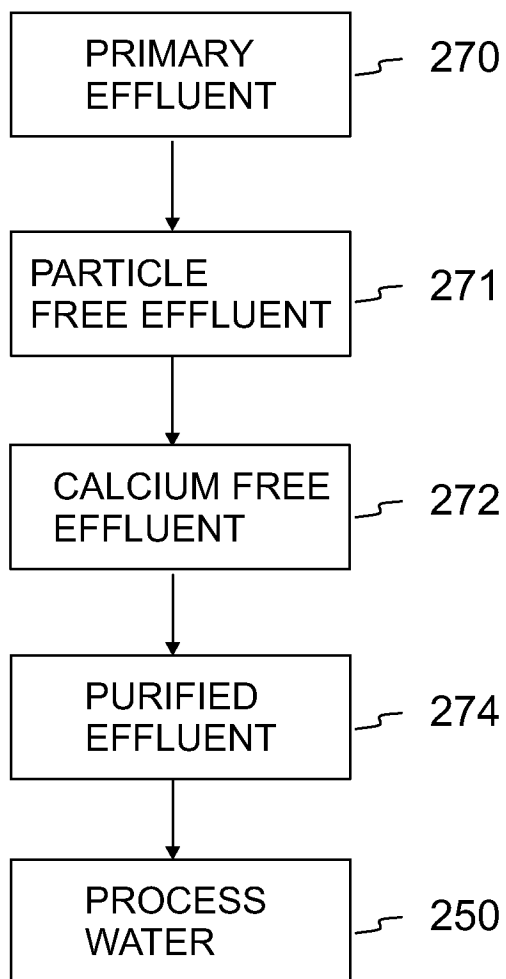


Fig. 7a

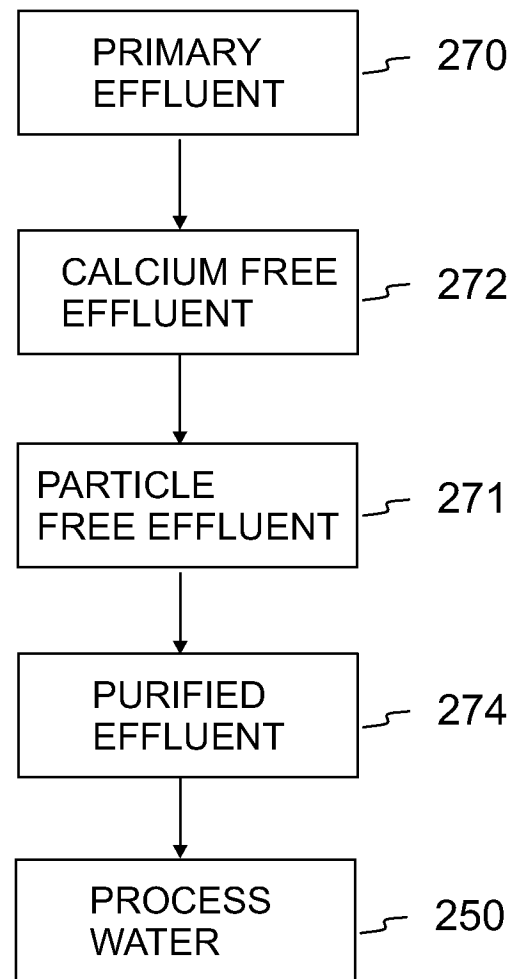


Fig. 7b

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2013/051150

A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F1/52 C02F1/66 D21H17/00 D21C11/00
ADD. C02F103/28

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C02F D21H D21C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 3 833 463 A (CROOM H) 3 September 1974 (1974-09-03) figure 1 column 4, line 31 - line 34 column 5, line 1 - line 3 -----	1-27
X	WO 02/097189 A1 (LINDE AG [DE]; UPM KYMME NE OYJ [FI]; LE NY CORINNE [FR]; LEINO HANNU [] 5 December 2002 (2002-12-05) example 1 ----- -/--	1-27



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

10 February 2014

Date of mailing of the international search report

18/02/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Janssens, Christophe

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2013/051150

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 96/28517 A1 (MINERALS TECH INC [US]) 19 September 1996 (1996-09-19) page 5, line 5 - page 8, line 11 -----	1-27

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Information on patent family members

International application No

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