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(54) Titre : METHODE DE PRODUCTION D'HYDROXYDE DE SODIUM A PARTIR D'UN EFFLUENT DE PRODUCTION DE PULPE FIBREUSE
(54) Title: METHOD OF PRODUCING SODIUM HYDROXIDE FROM AN EFFLUENT OF FIBRE PULP PRODUCTION

(57) **Abrégé/Abstract:**

The invention is directed to a method of producing sodium hydroxide from an effluent stream of a fibre pulp production process. The effluent stream comprises organic waste and sodium compounds which are bound to said organic waste. The method comprises concentrating the effluent stream, incorporating into the effluent stream borate or a compound which forms borate either before or after the concentration step, burning the concentrated effluent stream in oxidizing conditions in a two step process to produce a solid residue, and dissolving the residue in water. The two step burning process comprises subjecting the concentrated effluent stream to a temperature at or above 1000°C to cause an autocausticising reaction followed by a rapid cooling stage to a temperature at or below 600°C to desublimates the gaseous sodium reaction products directly into a solid phase.

ABSTRACT

The invention is directed to a method of producing sodium hydroxide from an effluent stream of a fibre pulp production process. The effluent stream comprises organic waste and sodium compounds which are bound to said organic waste. The method comprises concentrating the effluent stream, incorporating into the effluent stream borate or a compound which forms borate either before or after the concentration step, burning the concentrated effluent stream in oxidizing conditions in a two step process to produce a solid residue, and dissolving the residue in water. The two step burning process comprises subjecting the concentrated effluent stream to a temperature at or above 1000°C to cause an autocausticising reaction followed by a rapid cooling stage to a temperature at or below 600°C to desublimates the gaseous sodium reaction products directly into a solid phase.

METHOD OF PRODUCING SODIUM HYDROXIDE FROM AN EFFLUENT OF FIBRE PULP PRODUCTION

The present invention relates to a method of producing sodium hydroxide from an effluent or
5 waste stream of fibre pulp production.

According to such a method, an effluent comprising organic waste together with sodium
compounds is subjected to combustion at an elevated temperature, in order to break up the
dissolved organic material and to recover sodium. First, the effluent is concentrated, in particular
10 to a high concentration of more than 45 weight-% dry matter, and then the concentrated effluent
is burnt in oxidizing conditions. The combustion residue (ash) will yield sodium hydroxide when
dissolved or suspended in water.

A mill which produces chemi-mechanical pulp, such as BCTMP (i.e. bleached CTMP) generally
15 treats its effluents in separate waste water treatment plants, such as activated sludge plants, and
burns the generated sludges mixed with the bark in bark boilers. In most cases, the BCTMP mills
are independent mills, which produce dried baling pulp and which have their own biological
waste water purification units. Such mills have no recovery or recirculation of chemicals.

20 There are also alternative ways of treating waste water. Millar Western's Meadow Lake factory
in Canada was the first "effluent- free" BCTMP mill in the world. At this mill, the waste water to
be removed from the process is led into a series of internal evaporation units, where it is
evaporated to a high dry matter percentage, and the concentrate is burnt in an internal soda
recovery unit. After cooling, the melt from the soda recovery unit is pelletised and stored in
25 dumping areas. The melt comprises the alkaline chemicals used in the process, along with
inorganic salts which are dissolved from the wood. Consequently, in practice, the mill is waste
water free ("effluent-free"), but there is neither any recovery of chemicals nor recirculation.

The BCTMP mills built in the 2000s by M-real at Joutseno (2001) and Kaskinen (2005) are, for the purpose of treating concentrate and the recovery of chemicals, integrated with sulphate pulp mills.

5 The BCTMP mills evaporate their waste water in a cascade of evaporation units to a high dry matter percentage ($\geq 45\%$), and from evaporation unit section the concentrate is pumped to a mixing zone for mixing with black liquor received from a pulp mill located in the same mill area. After going through the evaporation unit of the pulp mill the mixture thus obtained is burnt in a soda recovery unit. In the soda recovery unit, combustion of the material generates carbon
10 dioxide and water ($\rightarrow \text{CO}_2 + \text{H}_2\text{O}$) and the inorganic ingredients form a melt on the bottom of the recovery unit. This melt is dissolved in water, which generates green liquor ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{S}$ / main products). Consequently, the sodium, which forms part of the alkaline chemicals used in the BCTMP mills, is recovered as a part of the process of dissolving the melt (green liquor) in the soda recovery unit. The cooking chemicals used in a sulphate pulp mill are sodium hydroxide
15 (NaOH) and sodium sulphide (Na_2S). The conditions of the burning in the soda recovery unit are reductive, thus sulphur is recovered directly in sulphide form. The main components of white liquor are sodium hydroxide (NaOH) and sodium sulphide (Na_2S).

A pulp mill uses a major part of the green liquor for manufacturing of white liquor, but part of
20 the green liquor is oxidised ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{S} \rightarrow \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$) and led to the BCTMP mill. Oxidising is a means of removing the sodium sulphide, which would otherwise cause problems at the BCTMP mill because it consumes hydrogen peroxide, which is used in bleaching of the pulp. Sodium sulphate (Na_2SO_4) is a neutral salt which passes as a “dead load” through the process of the CTMP mill and ends up, in the concentrate, back in the soda recovery unit, where
25 it is reduced back to sodium sulphide.

Sodium carbonate is not an effective chemical for removing lignin (i.e. for delignification) in the cooking of chemical pulp. Consequently, green liquor is unsuitable for use in impregnation or cooking in the production of chemical pulp. White liquor is produced from green liquor by

means of lime causticising. In this process, burnt lime (CaO) is added into green liquor, and as a result of causticising reactions, the carbonate is precipitated as calcium carbonate, while sodium forms sodium hydroxide. The lime is regenerated by burning ($\text{CaCO}_3 \rightarrow \text{CaO}$) in a lime sludge reburning kiln.

5

In the production of chemi-mechanical pulp, such as CTMP, lignin is not removed in the wood chip-impregnation stage by using alkaline treatment (impregnation), instead the lignin is softened and carbohydrates (hemicellulose) are treated in advance of the following refining stage (defibring of wood chips). The pH value of the impregnation solution or impregnation liquor is
10 lower (pH value 9–12) than in the production of chemical pulp (pH value 14). Consequently, it is possible also to use sodium carbonate for the impregnation of wood chips in the production of chemi-mechanical pulp.

In integrated BCTMP processes, oxidised green liquor from the pulp mill and lye (NaOH), which
15 is typically bought from external suppliers, are used in the impregnation of hardwood. The alkali used in the peroxide bleaching is lye. In impregnation of softwood, sodium sulphite is primarily used.

Besides using an integrated solution, it is also possible to carry out a separate recovery of sodium
20 chemicals at CTMP mills. According to one embodiment, namely the one known as the Alrec process (Alkali recovery process), the waste liquor which is concentrated to a dry matter percentage of approximately 65 % is burnt by using “drop burning” under oxidising conditions (oxygen excess) and at a temperature of 1000–1200 °C.

25 In the Alrec burning, in contrast to burning in a soda recovery unit, the conditions throughout the combustion chamber area are oxidative (excess oxygen). In Alrec burning, the percentage of oxygen in the combustion gas is 4–6 volume-%. In the burning in a soda recovery unit, the burning conditions are regulated, by introducing air, in phases, into different parts of the unit in such a way that the conditions for instance in the stack are reductive. Therefore

- COD (= dissolved organic material) is destroyed ($\rightarrow \text{CO}_2 + \text{H}_2\text{O}$), and
- sodium of the waste liquor is recovered as sodium carbonate (Na_2CO_3).

5 It is possible to recirculate the sodium carbonate which is to be used in impregnation of the wood chips and in bleaching of the CTMP pulp, where it also can be used, besides lye, as a source of alkali.

10 In the high-temperature process described above, the sodium in the waste water concentrate, which is bound to the organic material, is evaporated into its gaseous phase, where it is partly in the form of Na_2O and partly as elementary sodium (boiling point of sodium is 883°C). The lag or residence time in the Alrec process is only a few seconds at a burning temperature of $1000\text{--}1200^\circ\text{C}$, after which period the combustion gases from the combustion chamber are rapidly cooled to 600°C . In this case, the gaseous sodium compounds are desublimated directly as solid powdery sodium carbonate. This prevents the generation of sticky molten sodium carbonate and
15 thus any fouling of the walls.

The solid sodium carbonate (ash) generated in the process is dissolved in water, impurities are removed by filtering and the Na_2CO_3 solution is recirculated to the impregnation of wood chips and bleaching of pulp.

20

The process described above is reported in more detail in International Published Patent Application No. WO 2005/068711 (Rinheat Oy).

25 There are limitations associated with the known technology. In our experiments we have discovered that when lye (sodium hydroxide) is replaced during the impregnation stage by sodium carbonate, the pH value of the impregnation solution is lowered and impregnation and softening of hardwood chips are diminished, which tends to increase the specific energy consumption during refining. If the specific energy generated during refining increases, this limits the usability of the recovered alkali in the impregnation stage, i.e. the 100 % sodium

carbonate solution. Our test runs suggest that the effect of carbonate on the specific energy of refining depends at least on what quality of the CTMP to be produced (technical properties of paper) is desired and possibly on the proportions of wood species (birch/aspen).

- 5 The sulphite in sodium sulphite (Na_2SO_3), which is used in softwood-CTMP production, oxidises during the above-described, oxidative Alrec burning process to a neutral sulphate compound (Na_2SO_4). Sodium sulphate is a neutral salt and is not suitable as an alkaline chemical in impregnation or bleaching. Consequently, the Alrec process is not suitable for recovery and recirculation of sodium sulphite, without separate procedures for the regeneration of sulphite.

10

There are also limitations associated with the use of sodium carbonate as alkali in peroxide bleaching. Without the presence of lye, the pH value remains low which reduces the bleaching effect.

- 15 The purpose of the present invention is to achieve a completely new solution of recovering alkali in chemi-mechanical and mechanical pulp production. Another purpose of the present invention is, for instance, to extend the usability of alkaline chemicals which are recovered by using the Alrec process.

- 20 The present invention is based on the concept of producing sodium hydroxide from a waste stream or effluent of a fibre pulp production process. The stream used typically comprises organic waste and sodium and sodium compounds which are bound to the waste. Thus, to a waste stream or impregnation solution, borate or a corresponding boron-bearing material (in the following also called a “boron compound”) is added. The addition of the boron compound
25 renders it possible to generate sodium hydroxide, which is formed of sodium and sodium compounds, through a borate-autocausticising reaction and subsequent hydrolysis.

Autocausticising is a reaction which was described in literature already in the 1970s (see Jan Janson, “The Use of Unconventional Alkali in Cooking and Bleaching – Part 1. A New

Approach to Liquid Generation and Alkalinity”, *Paperi ja Puu* 59 (6-7), pp. 425-430 (1977), “The Use of Unconventional Alkali in Cooking and Bleaching – Part 2. Alkali cooking of wood with the use of borate”. *Paperi ja Puu* 59 (9), pp. 546-557 (1977) and US Patent No. 4,116,759.

5 According to Janson’s observations, a conventional separate causticising which uses burnt lime could even be avoided entirely during sulphate cooking by adding borate to the cooking liquor, which through the causticising reaction generates sodium hydroxide in association with the dissolving of the melt, i.e. production of green liquor. However, mill tests carried out by Enso Gutzeit in 1982 did not confirm initial expectations about the profitability of the process.

10

Approximately 20 years later, Honghi Tran examined borate autocausticising reactions anew and showed that the lye yield from borate was double that which Janson had described. According to the reaction formulas presented by Tran, one mole of tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) generates 8 moles of lye (NaOH), rather than 4 moles as Janson assumed. (Tran, H.; Mao, X.; Cameron, J.; Bair, C.M., *Pulp and Paper Canada* 1999, 100(8), 35-40). This discovery had a substantial effect on the profitability of borate autocausticising, because it demonstrated that only half the original borate dosage was required. Tran’s studies have resulted in borate autocausticising being partly applied at some sulphate pulp mills.

15

In an article titled "Borate autocausticizing: a cost effective technology" (*Pulp & Paper Canada* 20 103: 11 (2002), pp. 16-22, J. M. A. Hoddenbagh et al. describe two mill tests, which were carried out 15 years after the Enso tests and in which an autocausticising reaction was used both in recovery and in bleaching of chemicals. On the basis of the results, alkali which is produced by using the borate autocausticising process can possibly be used in the bleaching of CTMP and replace sodium hydroxide bought from external suppliers.

25

Incorporation of borates into a pulp production process, for instance in order to generate boron-bearing alkaline cooking liquors, has recently been described in the patent literature, as exemplified by International Published Patent Application No. WO 2004/025020. That document discloses a process, in which borate-carbonate cooking is integrated with the recovery of

chemicals in the production of chemical pulp of eucalyptus. This solution is at least partly based on autocausticising, during which part of the cooking chemicals, which are regenerated by using autocausticising, are used for cooking and/or oxygen delignification or during alkaline bleaching stages, such as peroxide bleaching without conventional causticising. Anthrachinon is used as the
5 delignification catalyst.

US Published Patent Application No. 2005/0155730 describes a high-yield process in which chemical softwood pulp is produced by using quinone catalyst in the stage of wood chips impregnation, in which the pH value is at least occasionally below 7, or in a cooking liquor
10 which has a low sulphidity level and which comprises mainly borate, sodium hydroxide and sodium carbonate. An alkaline cooking liquor is prepared without separate causticising by using calcium oxide or calcium compounds.

Two International Published Patent Applications Nos. WO99/63152 and WO99/63151 describe
15 how the efficiency of a calcination reaction is improved by using borate.

In the present invention, we have unexpectedly discovered that autocausticising reactions take place also during burning carried out under conditions of oxidization and high temperatures, such as the conditions prevailing during a burning process of the Alrec type.
20

The solution is implemented, according to the new technology presented, in such a way that the autocausticising reaction is carried out by burning an effluent in a combustion chamber under oxidising conditions and at a temperature which is high enough to vaporize at least part of the sodium (boiling point of sodium is 883 °C).
25

In particular, the operation is carried out at a temperature in which sodium is vaporized and primarily present in oxide (Na_2O) form. By subjecting the sodium and its compounds, which during the burning are released from organic material, to a reaction with borate mainly in gaseous phase, it is possible to produce sodium hydroxide when the ash which typically contains

sodium orthoborate is, during a dissolution step, dissolved or suspended in water. The effluent of this reaction can be used as an impregnation solution for instance in a BCTMP process or other chemi-mechanical defibring, and as a source of alkali in peroxide bleaching.

- 5 It is possible to use the present method for recovering alkaline sodium compounds, which are at least partly in the form of sodium hydroxide, and which compounds are suitable for the production process of fibre pulp.

More specifically, the method according to the present invention is a method of producing
10 sodium hydroxide from an effluent stream of a fibre pulp production process, which effluent stream comprises organic waste and sodium compounds which are bound to said organic waste, said method comprising the following steps:

- i) concentrating the effluent stream;
 - ii) incorporating into the effluent stream borate or a compound which
15 forms borate either before or after the concentration step;
 - iii) burning the concentrated effluent stream in oxidizing conditions to decompose the organic waste and the sodium compounds and to produce a combustion residue; and
 - iv) dissolving the residue in water to produce sodium hydroxide;
- 20 characterized in that the step of burning the concentrated effluent stream comprises subjecting the effluent stream to a two stage burning treatment, in which an autocausticising reaction occurs in the first stage at a temperature at or above 1000°C, after which the combustion gases which are generated in the first stage are rapidly cooled in a second stage to a temperature at or below 600°C to desublimates the sodium compounds from their gaseous phase directly to
25 their solid phase.

Considerable advantages are achieved with the present invention. Thus, the invention is generally suitable for use in burning processes in which, typically, waste liquor which is concentrated to a relatively high dry matter percentage, is burnt under oxidising conditions (i.e.

in excess oxygen). The temperature is preferably at least approximately 950 °C. In particular, at least a part of the sodium carbonate is converted to sodium hydroxide which improves the usability of alkali which is recovered for instance during the Alrec process. This, in turn, lowers the costs of chemicals and reduces energy consumption required in the defibering of wood chips, which is subsequent to impregnation. The usability of this alkali in peroxide bleaching is improved.

The present invention makes it possible to operate an independent (not-integrated) BCTMP mill and a mechanical pulp mill, which is waste water- free, and has the means of recovery of alkaline chemicals and cost-effective recirculation.

Thermal energy which is generated during the burning of organic waste is used as steam in the process.

In the following, the present invention will be examined in more detail with the help of a detailed explanation and the accompanying drawing. The process flowchart shown in the drawing represents one embodiment of the present technology.

In the present context, the terms "effluent" and "waste water" will be used largely synonymously to designate a stream containing organic residues and sodium compounds withdrawn from a process for producing fibrous pulp.

As described above, in the present technology, autocausticising and burning at a high temperature are combined to form a process in which sodium which is bound, typically chemically bound, to the organic material of an effluent (waste water), is subjected to, in gaseous phase and under oxidising conditions, a reaction with a boron compound. It would seem that at such conditions, sodium is reacted at least to some extent directly with borate, or another boron compound, probably instead of with carbon dioxide. As a result, a mixture of lye (NaOH) and sodium carbonate (Na₂CO₃) is generated during the dissolution of the ash, which is recovered in

the process. It should be pointed out that the present invention is not restricted to this explanatory model described here.

5 According to one embodiment of the present invention, metaborate or compounds that form metaborate are incorporated into the effluent, and the sodium and sodium compounds which are released during the processing, are reacted with the borate at a temperature which is high enough to vaporize sodium which then is present mainly in oxide form (Na_2O). There may be some elemental sodium present as well. It is possible to incorporate the borate compounds into the effluent by adding them directly into this stream or by adding them for instance into an
10 impregnation stream of chemi-mechanical or mechanical defibering, along with which they are carried through the process and form part of the effluent of the defibering (i.e. the waste stream).

Preferably, the effluent is first concentrated to a high dry matter concentration. According to one embodiment, the dry matter percentage of an effluent, which is subjected to
15 autocausticising, is at least 45 weight-%, preferably at least 55 weight-%, most suitably at least 60 weight-%, in particular at least 63 weight-%, or even at least 65 weight-% .

According to another embodiment, the waste water concentrate is dried to a powder, which is fed
20 into the burning as dry matter.

Preferably, an effluent which is concentrated to a high dry matter percentage of for instance at least approximately 60 weight-%, especially at least approximately 63 weight-% or at least 65 weight-%, is burnt in the presence of oxygen and borate or a compound that forms borate (a "boron compound"), at a temperature of at least 950 °C.

25 Typically, the dry matter of the waste comprises both an organic and an inorganic part. The weight ratio between these can vary within broad ranges, generally it is approximately 3:1...1 :1, although these are no absolute limits.

According to a preferred embodiment, autocausticising is carried out at a temperature of at least 1000°C, preferably 1000-1250 °C.

5 Here, “oxidising conditions” mean that during the entire or essentially entire burning process there is an excess of oxygen in order to prevent reductive conditions occurring in any part of the combustion chamber. The oxygen is in excess in respect of oxidizable compounds in the processed stream.

10 Most suitably, the quantity of borate or other boron compound added into the waste water or impregnation solution before burning is large enough to ensure that the Na:B molar ratio of the waste stream is at least 3:1. Preferably, the Na:B molar ratio is approximately 3:1...50:1, most suitably approximately 5:1...35:1.

15 When using borate, at least a major part of the inorganic borate is added as sodium metaborate or sodium tetraborate or as hydrates thereof. Other boron compounds are possible, too.

20 According to the present invention, the effluent stream to be treated is typically generated as waste water from fibre pulp production which takes place under alkaline conditions. In particular, the waste water stream comprises the effluent from an impregnation step, i.e. impregnating, of the raw material of chemi-mechanical or mechanical pulp production, or the waste stream of alkaline peroxide bleaching of fibre pulp, or a combination thereof. Thus, the waste stream can be sourced from the production of, for instance, groundwood pulp, pressure groundwood, refiner pulp or chemi-mechanical refiner pulp.

25 The waste stream which is subjected to burning comprises mainly organic compounds which are dissolved in pulp production, and sodium which is chemically bound to these compounds. Consequently, the sodium is sourced from sodium-bearing chemicals which are used in impregnation of raw materials or alkaline peroxide bleaching or both, such as sodium carbonate, sodium hydroxide and/or oxidised green liquor or oxidised white liquor which come from

chemical pulp production.

According to one embodiment, the burning treatment of an (organic) waste stream which comprises borate or to which borate is fed, is carried out in two stages, in which case the actual
5 burning takes place in the first stage under oxidising conditions and at a temperature of over 1000 °C, after which the combustion gases generated in the burning, containing sodium in oxide and elemental form, are rapidly cooled to a temperature below 600 °C, in order to desublimite the sodium compounds from their gaseous phase directly into solid phase (sodium carbonate and in particular borate compounds, such as Na_3BO_3).

10

The ash, which is generated from the burning of the waste stream, is recovered and dissolved in water in order to produce sodium hydroxide. At the same time, the metaborate (NaBO_2) is regenerated.

15 Typically, after the action described above, the ash contains a percentage of (calculated) sodium hydroxide which – depending on the organic material and the percentage of sodium in the waste water – is approximately 1–75 %, most suitably approximately 5–70 %, especially approximately 10–50 %, of the dry matter weight.

20 Autocausticising is carried out under conditions of excess oxygen, in which oxidising conditions prevail throughout the combustion chamber. Typically, the percentage of the oxygen in the exiting combustion gas is 4–6 volume-%.

Oxygen is conducted to the burning stage as a gas stream comprising oxygen, such as air or air
25 enriched with oxygen.

It is possible to carry out the burning as drop-burning, in which case the waste water concentrate which is subjected to autocausticising is dispersed to form droplets. The average drop size can be for instance approximately 0.1-5 mm, preferably < 1 mm and more preferably ≤ 0.1 mm.

It is possible to use the method described above generally for recovering alkaline sodium compounds, which are used in the fibre pulp production process, at least partly as sodium hydroxide.

5

In the production of chemi-mechanical pulps, such as BCTMP, ash, which is partly causticised in the production, is dissolved in water, the insoluble inorganic oxides (dregs) are removed by filtering or centrifuging, and the alkaline solution generated can be used directly, without further treatment with traditional lime causticising, as a source of alkali for impregnation and peroxide
10 bleaching.

The present invention can be implemented for instance in equipment arranged as shown in the drawing. The equipment comprises a combustion chamber 1 and a cooling chamber 2, which according to the drawing are arranged one below the other in such a way that it is possible to
15 lead the combustion gases, which are generated in the combustion chamber, to the cooling chamber, in which it is possible to cool them with the aid of cooling gas, such as cooling air or circulated combustion gas, which is led into the cooling chamber. The combustion chamber is equipped with a nozzle 3 for feeding the waste water concentrate to be burnt, through which nozzle it is possible to feed the concentrate for instance as a mist which comprises small droplets
20 which are dispersed by using steam.

The cooling gas can be conducted into the cooling chamber 2 through an inlet nozzle 4. The bottom of the cooling chamber is equipped with an outlet nozzle 5 for removing carbonate, and with an outlet nozzle 6 for removing cooling gases and cooled combustion gases.

25

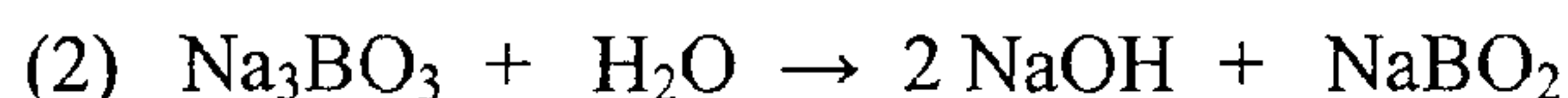
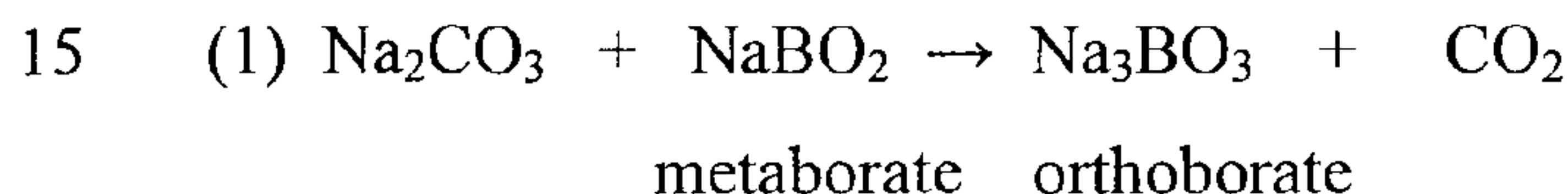
Effluent which is removed from a process and which comprises metaborate or boron compound that forms metaborate, is evaporated in an internal process evaporation unit preferably to achieve a dry matter percentage of at least 45 %. After that, it is conducted through feeding nozzle 3 into the combustion chamber 1, where it is burnt for instance at a temperature of over 1000 °C.

The burning process is described in more detail in the International Published Patent Application No. WO 2005/068711 (Rinheat Oy).

- 5 The residence time in the combustion chamber 1, at a high temperature, is only a few seconds and the combustion gas coming from the combustion chamber is rapidly cooled in the cooling chamber 2 to below 600 °C, in which case the sodium compounds are desublimated directly to solid material and can be removed as ash.

10

When the ash is dissolved in water, the sodium orthoborate (trisodiumborate) which is generated reacts with water, in which case it forms sodium hydroxide and, at the same time, the metaborate regenerates according to formulas (1) and (2).



- 20 Borates are completely water-soluble compounds and regenerated metaborate is transferred in the impregnating solution to the impregnation step and from there further on, in the effluent of the impregnation together with waste water, through the evaporation unit, back to oxidising burning. The percentage of borate in the waste water which goes to the evaporation unit is kept at a constant level, by adding make-up.

25

As pointed out before, the burning is carried out in the combustion chamber in excess oxygen, in order to ensure that the burning conditions in all parts of the chamber are those of oxidation.

It is also possible to carry out the dissolution of the ash in the cooling chamber 2. In that case, water is fed into the cooling chamber via inlet nozzle 4. The water thus fed can be either clean water or an aqueous solution, such as a solution generated from the recirculation. With the aid of water, a liquid film can be formed on the surface of the chamber, in which film it is possible to dissolve the alkali metal carbonate comprised in the cooled combustion gases.

Example

A concentrate from an evaporation unit, which concentrate has an organic material percentage of 52 % and an inorganic material percentage of 48 % of the dry matter, was burnt with excess air in laboratory conditions. The burning temperature was 1100 °C. Before burning, sodium metaborate was mixed into the concentrate.

Table

	Ash yield %	Na ₂ CO ₃ percentage of ash mg/g ash	pH value of aqueous solution of ash	Titrated NaOH percentage mg/g ash
Concentrate	43.1	719	11.8	40
Concentrate+NaBO ₂ Na/B mole/mole = 3:1	48.4	109	12.9	385

The Na₂CO₃ percentage of ash was determined by a TOC carbon analyser.

The percentage of lye in the aqueous solution of ash was determined by titration, which was based on the standard SCAN-N 30:85.

CLAIMS:

1. A method of producing sodium hydroxide from an effluent waste water stream from impregnation of a raw material in chemi-mechanical pulp production or mechanical pulp production, which effluent waste water stream comprises organic waste and sodium compounds which are bound to said organic waste, said method comprising the following steps:
 - i) concentrating the effluent waste water stream;
 - ii) incorporating into the effluent waste water stream borate or a compound which forms borate either before or after the concentration step wherein the molar ratio of Na to B is at least 3:1;
 - iii) burning the concentrated effluent waste water stream in oxidizing conditions to decompose the organic waste and the sodium compounds and to produce combustion products in a two-stage burning treatment in which an autocausticising reaction begins in the first stage at a temperature at or above 1000°C, the reaction generating combustion gases which are cooled in the second stage to a temperature at or below 600°C at a rate sufficient to desublimates the sodium compounds from their gaseous phase directly to their solid phase; and
 - iv) dissolving the desublimated solid phase in water to produce the sodium hydroxide and complete the autocausticising reaction.
2. The method according to Claim 1, characterized in that borate is incorporated into the effluent stream before the concentration step.
3. The method according to Claim 1, characterized in that borate is incorporated into the effluent stream by adding it into a chemical solution which is used in the impregnation of the raw material in the chemi-mechanical pulp production or the mechanical pulp production.

4. The method according to any one of Claims 1-3, characterized in that the molar ratio of Na to B in the effluent stream is between 3:1 and 50:1.
5. The method according to any one of Claims 1-3, characterized in that the molar ratio of Na to B in the effluent stream is between 5:1 and 35 :1.
6. The method according to Claim 2, characterized in that the borate added into the effluent stream comprises sodium metaborate, sodium tetraborate, or hydrates thereof.
7. The method according to Claim 3, characterized in that the borate incorporated into the chemical solution comprises sodium metaborate, sodium tetraborate, or hydrates thereof.
8. The method according to Claim 1, characterized in that the chemi-mechanical pulp production or the mechanical pulp production produces wood pulp, groundwood pulp, pressure groundwood, refiner pulp, or chemi-mechanical refiner pulp.
9. The method according to Claim 1, characterized in that the source of the sodium compounds are one or more sources selected from the group consisting of sodium carbonate, sodium hydroxide, oxidised green liquor, and oxidised white liquor.
10. The method according to any one of claims 1-9, characterized in that the autocausticising reaction is carried out at a temperature in the range of 1000°C-1250°C.
11. The method according to any one of Claims 1-10, characterized in that the effluent stream is subjected to the first stage in a combustion chamber for a residence time of 0.1-10 seconds.
12. The method of Claim 11, characterized in that the residence time is 0.5-5 seconds.

13. The method according to any one of Claims 1-12, characterized in that the oxidizing conditions are obtained and maintained by adding a gas stream comprising air or air enriched with oxygen.
14. The method according to any one of Claims 1-13, characterized in that the effluent stream comprises at least 45 wt% dry matter.
15. The method according to Claim 14, characterized in that the effluent stream comprises at least 55 wt% dry matter.
16. The method according to Claim 15, characterized in that the effluent stream comprises at least 60 wt% dry matter.
17. The method according to Claim 16, characterized in that the effluent stream comprises at least 65 wt% dry matter.
18. The method according to any one of Claims 1-17, characterized in that the effluent stream is introduced in the form of droplets to the first stage.
19. The method according to any one of Claims 1-18, characterized in that the effluent stream is concentrated to a dry powder which is subjected to the first stage.

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