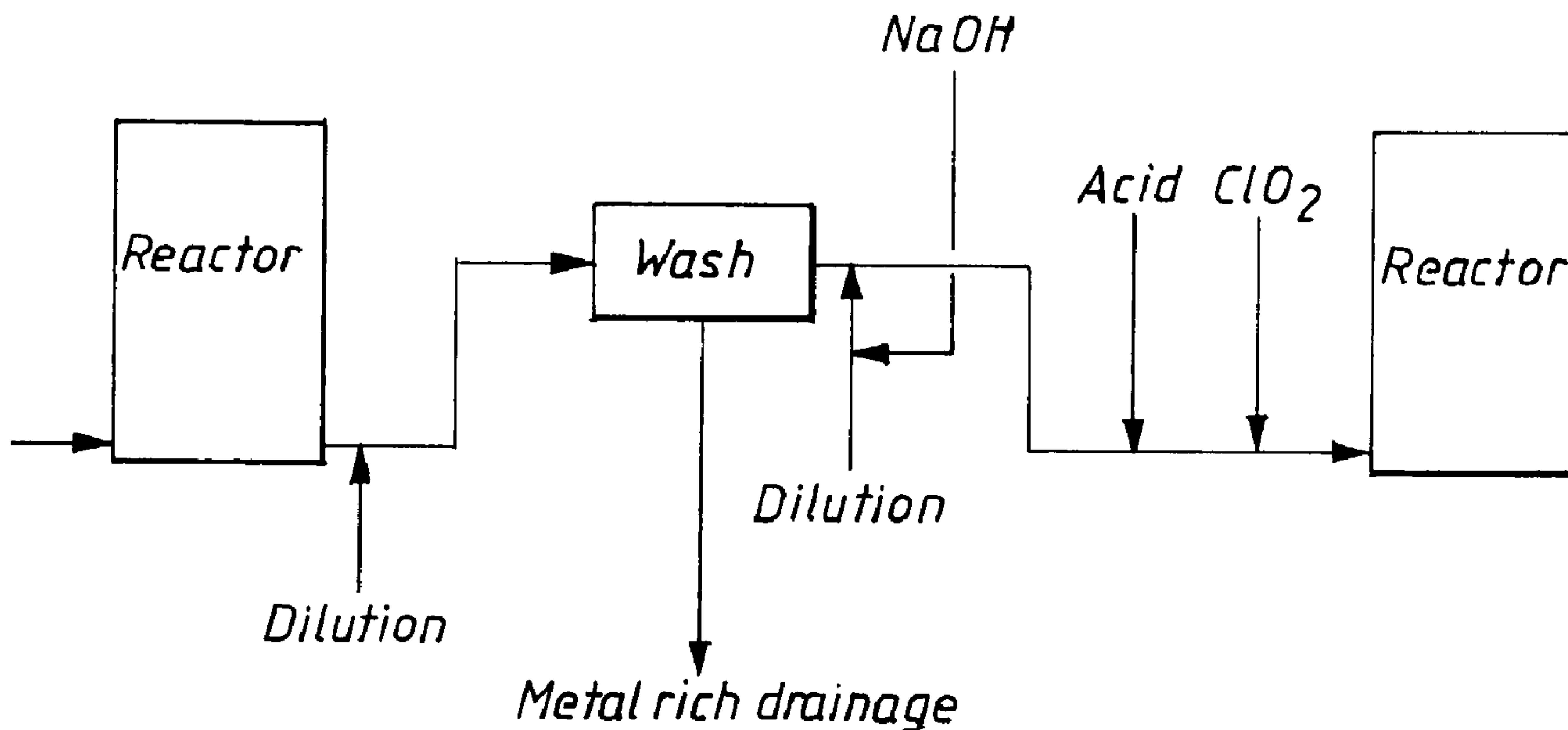




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(54) Titre : PROCÉDE DE BLANCHIMENT FINAL DE LA PÂTE À PAPIER À L'AIDE DE DIOXYDE DE CHLORE APRÈS UNE SÉQUENCE D'OPÉRATIONS DE BLANCHIMENT ALCALIN
 (54) Title: BLEACHING OF PULP WITH CHLORINE DIOXIDE AFTER ALKALINE BLEACHING



(57) **Abrégé/Abstract:**

The present invention relates to a method for end-bleaching of pulp containing metal ions after a sequence comprising alkaline bleaching stages only and optionally treatment with complex forming agent, wherein the end-bleaching comprises two chlorine dioxide stages at a pulp concentration of 8-20 % and pH 2.5-4.5 wherein the pulp after the first chlorine dioxide stage is washed and dewatered to a concentration of 12-50 % for removal of the out-dissolved metal ions and that alkali thereupon is added to the pulp for fast alkali extraction and increase of pH to 8-14, whereupon the pulp is provided with acid and chlorine dioxide and introduced into the second chlorine dioxide stage.

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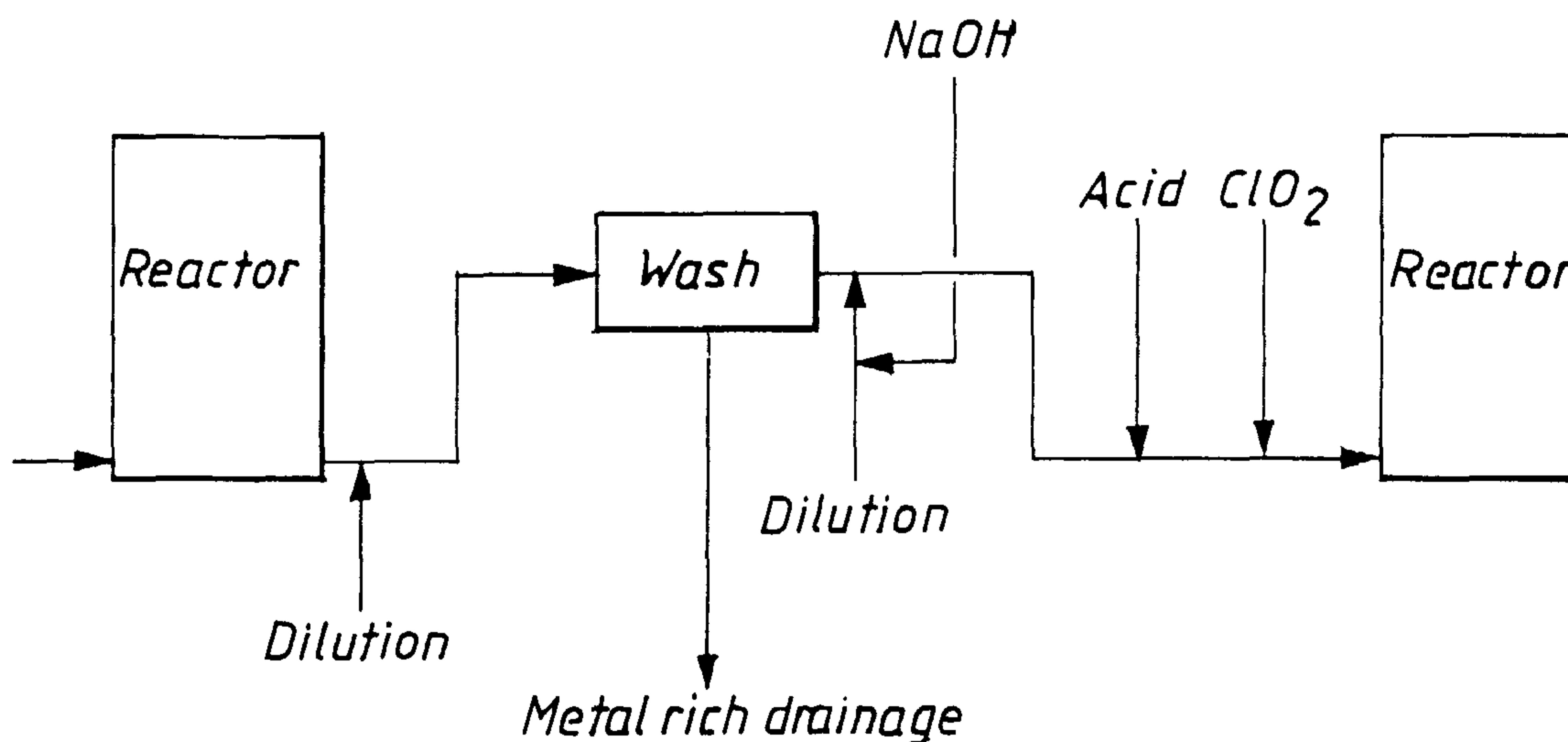
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(54) Title: BLEACHING OF PULP WITH CHLORINE DIOXIDE



(57) Abstract: The present invention relates to a method for end-bleaching of pulp containing metal ions after a sequence comprising alkaline bleaching stages only and optionally treatment with complex forming agent, wherein the end-bleaching comprises two chlorine dioxide stages at a pulp concentration of 8-20 % and pH 2.5-4.5 wherein the pulp after the first chlorine dioxide stage is washed and dewatered to a concentration of 12-50 % for removal of the out-dissolved metal ions and that alkali thereupon is added to the pulp for fast alkali extraction and increase of pH to 8-14, whereupon the pulp is provided with acid and chlorine dioxide and introduced into the second chlorine dioxide stage.

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BLEACHING OF PULP WITH CHLORINE DIOXIDE
AFTER ALKALINE BLEACHING

TECHNICAL FIELD

The present invention relates to a method for efficient
5 and economical end-bleaching with chlorine dioxide wherein the
method relates to a method for end bleaching of pulp
containing metal ions after a sequence comprising alkaline
bleaching stages only and optionally treatment with complex
forming agent, wherein the end-bleaching comprises two
10 chlorine dioxide steps with intermediate wash and alkali
extraction where the chlorine dioxide stages are performed at
a pulp concentration of 8-20% and pH 2.5-4.5 wherein the pulp
after the first chlorine dioxide steps is washed and dewatered
to a concentration of 12-50% for removal of out-dissolved
15 metal ions and that alkali thereupon is added to the pulp for
extraction and fast increase of pH to 8-14, whereupon the pulp
is provided with acid and chlorine dioxide and is introduced
into the second chlorine dioxide step.

20 BACKGROUND OF THE TECHNOLOGY

It is common that end bleaching of chemical pulp is
performed with chlorine dioxide, see for instance SE 466 062.
In most of the cases it is performed in two steps with an
extraction stage (E), that is an alkalisation of the pulp,
25 and/or with a wash between the stages. If there is no separate
extraction stage alkali may be added in order to raise the pH,
during the dilution at the end of the first chlorine dioxide
tower before the pulp is washed. A short
alkalisation/neutralisation step (n) results in that chlorine
30 dioxide bleaching in the following chlorine dioxide stage will
be more efficient (see for instance Papermaking Science and
Technology, Book 6A, Chemical Pulping, Editor J. Gullichsen
and H. Paulapuro, page A642). When alkali is added to the
chlorine dioxide bleached pulp lignin is out-dissolved which
35 would, if not out-washed before the following chlorine dioxide

stage, consume bleaching chemicals or result in a lower end-brightness. Therefore two-stage chlorine dioxide bleaching is presently performed with intermediate neutralisation stage according to the D_n-Wash-D.

5 Further, SE 98000797-4 describes a bleaching method for cooked and oxygen delignified pulp where you make use of a commencing acid bleaching stage which is followed by a washing stage at an even lower pH than in the bleaching stage from which washing stage a filtrate is taken out. The purpose here
10 is to bring metals, which forms difficultly dissolvable compounds, into solution so that they may be removed in the washing stage. Accordingly the degree of closing for the following bleaching may be increased.

15 PROBLEMS WITH THE PRESENT TECHNOLOGY

Concurrently with the bleach plants being closed even harder and pre-bleaching is preferably performed in alkaline stages (for instance O, OO, (OP), (PO), (EO), (EOP)) and complex forming agent stage (Q) the overcarry of metals with
20 the pulp to the end-bleaching increases, as they have not been washed out in any acid stage. This results in that the risk for precipitations increases if the pulp is taken into an acid stage for end bleaching which it does in a chlorine dioxide stage, D-stage. If the manufacture of pulp is performed in
25 alkaline bleaching stages and complex forming agent stage and the end-bleaching in D-stage the metals are out-dissolved in the surrounding liquid in the acid D-stage. When the pulp thereupon is alkalisied the conditions in the pulp suspension becomes favourable for precipitations, above all for calcium
30 compounds. An example of one such calcium compound is calcium oxalate, which may form a china-resembling precipitation, which may be very difficult to remove from process equipment. A change in pH in a pulp suspension where the pulp concentration is approximately 10-15% gives a gradual change
35 of pH, which may result in that the pH interval for

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precipitations (~ pH 4-9) is reached. If the pulp could have a high dry substance content, $ds > 25\%$ before the pH adjustment and dilution, a quick and stepwise change of pH from acid conditions to alkaline conditions could be performed and
5 critical conditions for precipitation would therewith be avoided.

SUMMARY OF THE INVENTION

The present invention solves the above problems through
10 providing a method which minimises the risk for precipitations during two-step chlorine dioxide bleaching with intermediate short alkali extraction, in which the alkalisation of the pulp suspension is performed after a dewatering step, including wash of the pulp, wherein the out-dissolved metals are
15 separated in the wash-/dewatering equipment. The wash/dewatering execution is preferably performed in a wash/dewatering press. That is the sequence will be after an alkaline pre-bleaching: D-dewatering (including wash)-nD. A further advantage with the invention is that a less amount of
20 alkali is consumed, as a smaller liquid amount is to be alkalised at high pulp concentration. Further pH gradients may be avoided as the dilution with alkaline filtrate is performed when the pulp essentially has a higher consistency, preferably high consistency.

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According to one aspect of the present invention, there is provided a method for end bleaching of pulp containing metal ions after a sequence of alkaline bleaching stages comprising: treating the pulp in a first chlorine dioxide stage; washing and dewatering said pulp to a consistency of 25-50% for removal
5 of out-dissolved metal ions; adding alkali to said pulp for extraction and an increase of pH to 8-14; providing said pulp with acid and chlorine dioxide; and treating the resulting pulp in a second chlorine dioxide stage.

The present invention relates to a method for end-bleaching of pulp containing metal ions after a sequence comprising alkaline bleaching stages only
10 and optionally treatment with complex forming agent, wherein the end-bleaching comprises two chlorine dioxide stages at a pulp concentration of 8-20% and pH 2.5-4.5, with intermediate wash and alkali extraction, wherein the pulp after the first chlorine dioxide stage is washed and dewatered to a concentration of 12-50% for removal of out-dissolved metal ions, and that alkali thereupon is added to the
15 pulp for extraction and fast increase of pH to 8-14, whereupon the pulp

is provided with acid and chlorine dioxide and introduced into the second chlorine dioxide stage.

DETAILED DESCRIPTION OF THE INVENTION

5 The expression "pulp" is intended to embrace in the present description preferably chemical pulp, which may be soft wood pulp or hard wood pulp or mixtures thereof. The chemical pulp is achieved through the fibre freeing being performed in a chemical way; for instance it may be bleached
10 pulp from both soft wood (softwood) and pulp from hard wood (hardwood).

 The expression "acid" is intended to embrace in the present description an acid which may be selected from the group consisting of sulphuric acid, hydrochloric acid, nitric
15 acid, sulphur dioxide, acetic acid or carbonic acid or a combination of these.

 Other chemicals which may be used in connection with chlorine dioxide bleaching is ozone, hydrogen peroxide, hypo
chlorite or alkali. If the pulp has high consistency ozone may
20 be preferred.

 According to a preferred embodiment of the present invention the pulp is de-watered after the first chlorine dioxide stage to a concentration of 25-50%, preferably 30-40%.

 According to a preferred embodiment of the present
25 invention the chlorine dioxide stages are performed at a pulp concentration of 8-15%, preferably 10-12%.

 Chlorine dioxide, which is used, is preferably in the form of a water solution. Further the bleaching is preferably performed in an acid environment, pH 2.5 to 4.5.

30 According to a preferred embodiment of the present invention the fast increase of pH in the method, during the alkali extraction, is performed to a pH 8-14, preferably 9-12, most preferred pH 9-11.

 According to a preferred embodiment of the present inven-
35 tion the in-going pulp has medium consistency (normally 8 to

20% pulp concentration; so called MC-pulp) and the de-watered pulp after the first end-bleaching stage with chlorine dioxide, high consistency (normally 25 to 50% pulp concentration; so called HC-pulp).

5 According to a preferred embodiment of the present invention the pulp is diluted and dewatered, including wash of the pulp, after the first chlorine dioxide stage wherein an acid outflow with high metal content is obtained from the pulp whereupon the pulp is diluted with alkalised filtrate so that
10 pH is increased to >8, preferably from pH 8 to 14, before the pulp is provided with chlorine dioxide and acid for the second chlorine dioxide stage.

 According to a preferred embodiment of the present invention the acid- and chlorine dioxide addition is performed
15 before the second chlorine dioxide stage 15 seconds to 5 minutes, preferably 30 seconds to 2 minutes after the alkali addition.

 According to a preferred embodiment of the present invention the treatment with complex forming agent has been
20 performed in a pH interval from 4.5 to 10, preferably from 4.5 to 7 before the end-bleaching.

 According to a preferred embodiment of the present invention the concentration of the pulp is performed in an apparatus for washing and dewatering in the method, for
25 instance by using a wash-press or a press, preferably a wash-press or a dewatering press. In order to convey (transport) the pulp between the reactors further a pump preferably is used or a corresponding apparatus.

 We will now in more details describe the present
30 invention by use of figures and example and these shall only be regarded as illuminating and not in any way limiting for the invention as it is set out in the appended set of claims.

DESCRIPTIONS OF FIGURE

Figure 1 shows a principal sketch where the method according to the invention is illuminated in the form of a system for end bleaching by using chlorine dioxide wherein said method
5 may be performed.

EXAMPLE

As can be seen in figure 1 the method for end bleaching according to the present invention may be performed through
10 the following:

Pulp which has been bleached in alkaline bleaching stages and which has been treated with complex forming agent is transported to a first chlorine dioxide (ClO_2) reactor whereupon the pulp is diluted and washed. (The initial pulp
15 may have a pH of 8-12). This washing may be performed by using a concentration apparatus as set out in the description before, preferably by using a wash-press or a dewatering-press. A metal rich drainage is removed during the washing of the pulp. At this moment the pulp has essentially a higher
20 consistency, preferably high consistency. The pulp is then quickly diluted to the earlier consistency with dilution liquid, which contains sodium hydroxide (NaOH), wherein a fast alkali extraction is achieved. Acid for regulation of pH and ClO_2 is added in connection with the introduction into the
25 second reactor, which is included in the end-bleaching phase for the pulp.

The invention is of course not limited to the showed embodiment but may be varied within the frame of the spirit of the invention.

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CLAIMS:

1. A method for end bleaching of pulp containing metal ions after a sequence of alkaline bleaching stages comprising:
- treating the pulp in a first chlorine dioxide stage;
- 5 • washing and dewatering said pulp to a consistency of 25-50% for removal of out-dissolved metal ions;
- adding alkali to said pulp for extraction and an increase of pH to 8-14;
 - providing said pulp with acid and chlorine dioxide; and
- 10 • treating the resulting pulp in a second chlorine dioxide stage.
2. The method according to claim 1, wherein said pulp is dewatered to a consistency of 30-40% after said first chlorine dioxide stage.
3. The method according to claim 1 or 2, wherein said increase of pH is performed to pH 9-12.
- 15 4. The method according to claim 1 or 2, wherein said increase of pH is performed to pH 9-11.
5. The method according to claim 1 or 2, wherein said pulp is chemical pulp.
6. The method according to any one of claims 1 to 5, wherein said acid and chlorine dioxide addition is performed from 15 seconds to 5 minutes after the alkali addition.
- 20 7. The method according to any one of claims 1 to 5, wherein said acid and chlorine dioxide addition is performed from 30 seconds to 2 minutes after the alkali addition.

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8. The method according to any one of claims 1 to 7, wherein said pulp is treated with complex forming agent prior to said first chlorine dioxide stage.

9. The method according to claim 8, wherein said treatment with
5 said complex forming agent is performed in a pH interval of from 4.5 to 10.

10. The method according to claim 8, wherein said treatment with said complex agent is performed in a pH interval of from 4.5 to 7.

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PATENT AGENTS

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Fig. 1

