Abstract: The invention relates to a process for purifying recovery boiler electrostatic precipitator ash (via 19) from chlorides (Cl) and potassium (K), and recover useful pulping chemicals such sodium sulphate (Na₂SO₄). The inventive process uses two centrifugal separation stages (2a, 2b) in series with a leaching stage (1a and 1b) ahead of each centrifugal stage. The chlorides and potassium is bled out (26) with the first liquid fraction (LFI) from the first centrifugal separation stage and the final second dry matter substance (DM2) with enriched sodium sulphate content from the second centrifugal separation stage is sent (24) to the liquor recovery cycle, mixed into black liquor before the black liquor is being sent to the recovery process for reuse of the sodium sulphate in the pulping process. With the inventive process losses of sodium sulphate could be reduced significantly compared to a one stage leach-and-centrifuge process.
PROCESS FOR IMPROVED LEACHING OF ELECTROSTATIC PRECIPITATOR ASH FROM A RECOVERY BOILER

The invention relates to a process for leaching electrostatic precipitator ash from a recovery boiler in accordance with the preamble of Patent Claim 1.

STATE OF THE ART

In the present-day pulp mill, it is desired to minimize the discharges and consumption of chemicals. Several bleaching processes, in particular those which use chlorine dioxide, form chlorides which are either bound in the pulp or which leave together with used fabrication water. While preference is given to closing the process such that the fabrication water is returned, this leads to the contents of chloride in the process being gradually raised to undesirable levels.

Chlorides are also supplied to the pulp process by way of make-up chemicals and water. The wood also has a content of chloride, even if this content is normally low. Potassium is another non-process element which is principally supplied by way of the wood. Even low contents of the non-process elements such as potassium and chlorides in the flows entering the pulp process contribute to high contents in the pulp process since the process is becoming increasingly closed.

Potassium and chlorides contribute to major corrosion problems throughout the pulp mill, and especially to clogging of the recovery boiler and to corrosion of heating surfaces. High contents of potassium and chlorides in the dust which is separated off from the flue gases from the recovery boiler have a detrimental effect on the efficiency of electrostatic precipitators.

While the electrostatic precipitator ash which is separated off from the flue gases from the recovery boiler principally contains Na$_2$SO$_4$, it also contains, due to the process being closed, the highest concentrations of potassium and chlorides within the pulp mill.

One way of decreasing the content of potassium and chloride in the liquor stock in the pulp mill is to separate off part of the electrostatic precipitator ash from the chemical cycle in the mill. The separation can take place by the ash being dumped or by the ash being dissolved in water and then conducted to the water purification in the mill. These types of separation result in the heavy metals which are present in the electrostatic precipitator ash polluting the effluent.

The loss of sodium sulphate which occurs when electrostatic precipitator ash is separated off
from the chemical cycle must be compensated for by supplying make-up chemicals. Several different types of leaching process exist for recovering Na$_2$SO$_4$ from the electrostatic precipitator ash which has been separated off by freeing the latter from potassium and chlorides, in particular. The proposed solutions usually involve filters or constituent steps in which all the dissolved or leached electrostatic precipitator ash, or parts of this ash, is/are cooled. Other processes for recovering Na$_2$SO$_4$ also exist, in which processes the electrostatic precipitator ash is firstly dissolved completely and then crystallized by evaporation in a crystallizer, with subsequent separation of solid phase and liquid.

The filtration technique

SE, C, 504374 discloses a process in which the electrostatic precipitator ash is treated in a pressurized filter, in which process filtration and washing of the filter cake, and any possible leaching, take place in one and the same vessel. This process affords a good result as long as the filter can be kept free from clogging. Methods for cleaning the filter, with the cleaning taking place either during operation or in association with occasional interruptions in the filtration process, are required.

US, A, 3833462 discloses another process in which leaching takes place at pH 3-6 and 40-80 °C, followed by filtration in a filter.

In Tappi Proceedings, Chemical Recovery Conference 1992 in Seattle, pages 329-350,"Recycle of Bleach Plant Extraction Stage Effluent to the Kraft Liquor Cycle", B. Blackwell and A. Hitzroth present experiences from leaching processes which have been used. A leaching of the electrostatic precipitator ash in water at a dry substance concentration of around 15% by weight, and at pH 5, which low pH was pointed out to constitute a substantial corrosion problem, was performed in a Harmac system. The leached liquid was filtered in a filter (belt filter) and this filter exhibited substantial clogging problems due to small particles of organic material which clogged the filter mesh. A proposed remedial measure was that of using a larger filter; while such a filter should, per se, extend the period of operation, the filter would have to be cleaned sooner or later. It was stated that it was possible to leach out, from the electrostatic precipitator ash, a good 89% of the sodium chloride that was present in the ash.
The cooling technique

SE, A, 9504281 discloses another method which includes cooling. In this case, the leaching is to take place at a pH of less than 10 and at a temperature greater than 20 °C, typically at 30 °C, after which the total quantity of slurried material undergoes cooling down to a temperature of less than 20 °C. This process involves a need for cooling, with an attendant consumption of energy.

SE, A, 9603972 also discloses another method for leaching the electrostatic precipitator ash in which the latter firstly undergoes a leaching at least 32 °C, preferably in the vicinity of the boiling point of the aqueous solution, and in which a first substance which has crystallized out is returned, after separation, to the black liquor. The leachate which is obtained from the process then also undergoes cooling down to approximately 10-15 °C, after which a second substance which has crystallized out is likewise returned to the black liquor. While this system affords good leaching, it demands a high requirement of energy for the cooling even if the cooling is only required for the relatively small quantities constituted by the leachate.

The problem with the known solutions described above is that they suffer from one or more of the following disadvantages;

- are energy-intensive, resulting in high operational costs;
- require expensive and complicated apparatus/systems;
- involve filters which easily become clogged and render continuous operation more difficult;
- do not afford a sufficiently high degree of bleed-out of chlorides and potassium from the process liquid which is returned, or
- do not afford an equally high degree of recovery of Na₂SO₄ from the electrostatic precipitator ash.

The leaching and centrifugal technique

SE, C., 517587 (=WO03/01 6616) discloses another method patented by Metso Power AB which includes gentle leaching of the electrostatic precipitator ash, followed by a centrifugal stage. In this process the order of separation of chlorides and potassium has been reaching as high level as over 80-85% when maximizing the recovery efficiency of sodium sulphate. The losses are still high, amounting to losses in the order of 25-30% for sodium sulphate.
BRIEF DESCRIPTION OF THE INVENTION

The object of the invention is to obtain an improved process for recovering the useful chemicals, principally Na₂SO₄, in the electrostatic precipitator ash, which process does not suffer from the disadvantages of the prior art. While the improvement is first and foremost aimed at an increased recovery of useful chemicals in the pulping process, it is also aimed at an improved degree of recovery of these useful chemicals without these chemicals being accompanied by a high proportion of chlorides, in particular, but also potassium. This objective is met by a process wherein the ashes are leached in a first leaching tank and thereafter sent to centrifugal separation comprising at least two centrifugal separation stages in series, and where at least a part of the first liquid fraction from the first centrifugal separation stage containing chlorides and potassium is bled out from the process. The first dry matter substance obtained from the first centrifugal separation stage is further led to a second leaching tank where preferably similar conditions as in the first leaching tank is established as of pH and dry substance level. The total dwell time in this second leaching tank is not as important as of further crystallization of sodium sulphate, as most crystallization of sodium sulphate has already been made in first leaching tank. However, a dwell time in the second leaching tank could preferably be in the order of at least 40-80% of the dwell time in the first leaching tank, as further crystallization of sodium sulphate could take place at the larger particles of sodium sulphate already formed. The reslurried and leached first dry matter substance from the first centrifugal separation stage is thereafter fed to a second centrifugal separation stage from which a second liquid fraction is obtained that is led back to at least one preceding leaching tank, and a second dry matter substance which thereafter is mixed into black liquor before the black liquor is being sent to the recovery process. The difference between a one-stage leaching process and the two-stage leaching process according to the invention is the solubility equilibrium between the first and second leaching tanks. By leaching out chlorides and potassium after the first leaching step is crystallization of sodium sulphate favored in the second leach tank, reaching a higher sodium sulphate content of the final dry matter content, as well as high concentrations of chlorides and potassium in the first liquid phase bled out after first leaching stage.

Another object is to adapt and optimize the stages for the specific process function of the specific stage, such that the first centrifugal separation stage takes place in a high rotational speed centrifuge optimized for obtaining a clean first liquid fraction and a first dry matter substance, and that the second centrifugal separation stage takes place in a low rotational speed centrifuge optimized for obtaining a second dry matter substance at a dry matter concentration being at least 15% higher than that of the first dry matter substance.
The first centrifugal separation stage preferably takes place at a rotational speed above 3500 rpm, and the second centrifugal separation stage takes place at a rotational speed below 3500 rpm. While the difference in rotational speed between first and second centrifugal separation stages is at least 2000 rpm. The more aggressive separation in the first stage could thus obtain a cleaner filtrate, while not optimizing the dry matter concentration, as this dry matter concentration is subject to a following leaching stage and anyway needs dilution for that stage.

In a preferred embodiment of the invention the first centrifugal separation stage is taking place in a nozzle bowl separator centrifuge, which has proven its capability of obtaining clean filtrates from these kinds of slurries, but not necessarily as high concentration in the separated dry matter phase. The nozzle bowl separator is also less expensive than a decanter centrifuge for the same capacity, which latter decanter centrifuge is more than 2.5 times more expensive than a nozzle bowl separator.

In yet a preferred embodiment of the invention the second centrifugal separation stage is taking place in a decanter centrifuge, which has proven its capability of obtaining a high concentration in the separated dry matter phase (i.e. the sodium sulphate), with a clean filtrate in the separated liquid phase.

According to the invention is the leaching process in at least one leaching tank preferably established at a temperature in the interval 65-105 °C, and preferably below boiling temperature below 95 °C and most preferred at about 80 °C which provides a safe margin towards boiling. The slurried electrostatic precipitator ash having a dry substance level in the interval 15-40% by weight being obtained. The leaching process in at least one leaching tank is further preferably established such that the slurried electrostatic precipitator ash passing through, and being treated in, the leaching tank in at least two agitation zones, in which agitation zones the slurried electrostatic precipitator ash undergoes repeated gentle agitation in the leaching tank.

Other features and aspects and advantages of the invention are evident from the subsequent patent claims and from the detailed description of some embodiments of the invention which follows.

BRIEF DESCRIPTION OF THE FIGURE

Fig. 1 shows a prior art one-stage leaching and centrifugal process,
Fig. 2 shows the principal system set up and flow routing in a two-stage leaching and centrifugal process according to the invention,

Fig. 3 shows a nozzle bowl separator preferably used in the first centrifugal stage of the two-stage process shown in figure 2.

5

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT OF THE INVENTION

System set up according to prior art

Figure 1 show an apparatus set-up which is used in a prior art one-stage leaching and centrifugal process for leaching electrostatic precipitator ash. This system is also disclosed in SE,C,51 7587 (=WO 03/01661 6). In this system the electrostatic precipitator ash, from electrostatic precipitator 19, and liquids for leaching are supplied to a first leaching tank 1.

A part of the liquid for leaching (kond.) can expediently be fabrication water from the bleaching department or the pulp drying machine, evaporation condensate, scrubber condensate or tap-water. H₂SO₄ or other suitable acidic conditioner for establishment of correct pH can be supplied when the electrostatic precipitator ash contains high contents of Na₂CO₃.

The amount supplied is typically around 0.1 kg per 1.0 kg of electrostatic precipitator ash, i.e. in proportions of approx. 5-15% by weight.

20

The electrostatic precipitator ash can typically have a composition corresponding to the following;

<table>
<thead>
<tr>
<th>Component</th>
<th>% by weight (w %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>86</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>5</td>
</tr>
<tr>
<td>NaCl</td>
<td>2</td>
</tr>
<tr>
<td>KCl</td>
<td>7</td>
</tr>
</tbody>
</table>

The ash which is supplied to the leaching tank contains chloride ions and potassium ions. The chloride content in the slurry is typically 2.0-7.0 % by weight.

30

In order to achieve an optimal leaching process, a pH in the interval pH 8-13, preferably around pH 9, is established in the leaching tank. The mixture in the leaching tank should preferably not exceed 1600 kg/m³, which thus sets an upper limit to the leaching process. If the consistency becomes too high, something which
already begins to become apparent at 1570 kg/m³, the mixture then becomes increasingly
difficult to pump and agitate with the stirrers. In particular, the initial admixing with the
electrostatic precipitator ash using the first stirrer 11 is rendered more difficult at these
concentrations. A suitable lower concentration level corresponds to a mixture at 1450-1 550
kg/m³.

The temperature should preferably be kept within the interval 65-105 °C, with a relatively high
temperature within the interval 80-1 05 °C being most favorable for the leaching process. An
optimum temperature both from the point of view of the process and the point of view of the
apparatus is around 80°C.

If leaching takes place under these process conditions (pH, concentration and temperature)
for a relatively long time, within the interval 1-5 hours, preferably 2 hours, and while agitating
gently, favorable process conditions are created for crystal growth of, in particular, a solid
phase of Na₂SO₄. It has been found that the crystals which are formed are distributed
normally around a particle size of about 200 µm, which is a surprisingly good result which
should be compared with what can be obtained using the energy-intensive cooling technique,
where a crystal formation with particles normally distributed around 300 µm can be achieved
under optimum conditions. The leaching tank is shaped such that repeated gentle agitation is
obtained over the whole volume. An initial agitation preferably takes place using a first stirrer
11 in connection with the electrostatic precipitator ash being supplied. After that, the mixture
passes through at least one additional agitation zone and preferably two agitation zones.
This can be achieved by installing at least one double bottom 13 in the middle of the leaching
tank. An intermediate-stage stirrer 12a is arranged in an outlet from this double bottom 13,
and a final-stage stirrer 12b is arranged in connection with the outlet from the leaching tank.
The dwell time in the leaching tank, between agitations, when the mixture is not subjected to
direct agitation, should amount to at least 30% of the total dwell time in the leaching tank.
The intermediate-stage stirrer consequently acts on the slurried electrostatic precipitator ash
when the latter has had a dwell time in the region of 30-70% of the total dwell time in the
leaching tank, and the slurried electrostatic precipitator ash is subjected to a final-stage
stirrer in a lower part of the leaching tank in connection with the outlet from the leaching tank.
The agitation should preferably be gentle in order to ensure that particles which have already
crystallized out are not broken, and a mechanical blade-equipped stirrer of the propeller type
can expediently be used, in each respective position, for the intermediate-stage and final-
stage stirrers, with both the stirrers being driven by the same shaft, which latter is driven at a
moderate rotational speed in the region of 50-200 rpm, preferably around 80 rpm.

The slurry which is obtained in this way is pumped onwards, via the pump 4, to a
centrifugation stage, in this present case a decanter centrifuge 2, where particles which have been formed, i.e. solid phase containing Na$_2$SO$_4$, are separated out as a dry fraction. Using a decanter centrifuge affords a continuous process which does not require to be interrupted for regenerating the equipment (due to clogging, etc.). The decanter centrifuge comprises, in a known manner, a rotating screw body 20, on which a worm 21 has been formed. A casing 22, which also rotates, is arranged around the screw body 20. The screw body is imparted a rotation $R_1$ and the casing a parallel rotation $R_2$, with typical rotational speeds being in the range $R_1 = 1500-3400$ rpm and $R_2 = 1450-3350$ rpm; while $R_2$ is at least 50 rpm below $R_1$, consequently, a somewhat higher rotational speed is imparted to the screw, thereby contributing to the worm 21 of the rotational body slowly feeding the crystallized particles towards the outlet 24. The slurry is fed into the decanter centrifuge via the inlet 23 and, due to the rotation of the casing 22, the leached liquid is flung against the inside of the casing, where the heavier solid-particle fraction forms the outer layer 28, due to the centrifugal effect, and the liquid fraction forms the inner layer 29. The liquid fraction leaves the decanter centrifuge via the spillway 25, while the screw feeds the solid fraction out towards the outlet 24. Due to the spillway 25 for the liquid fraction being located at a shorter distance from the axis of rotation than the outlet 24, it will be mainly the solid fraction which is transported by the worm 21 towards the outlet 24 via the conformed outlet of the casing. The solid fraction which is obtained in this way, and which consists of enriched Na$_2$SO$_4$, is given, by the decanter centrifuge, a relatively high dry substance content, in the dry substance fraction, which is in the interval 58-97%, and is then fed to a slurrying vessel 3, where it is admixed with black liquor/BL, for example, for forwarding to recovery, either via evaporation (not shown) or directly to the recovery boiler 18.

The liquid fraction, with its content of chloride ions and potassium ions, can in part be returned to the leaching tank 1 or in part, 26, forwarded to the effluent for external purification or further working up.

In order to further leach out chlorides from the solid fraction, a washing zone can optionally be arranged in the decanter centrifuge. This is shown in the figure by means of a distribution ring 27 for washing liquid, which ring opens up radially inwards towards the layer 28 of the solid fraction which is passing by. The washing liquid, which is preferably pressurized, can expediently be the condensate (cond.) which is otherwise added to the top of the leaching tank in connection with the initial slurrying of the electrostatic precipitator ash. The washing liquid is advantageously added at a position in the decanter centrifuge at which a separating
effect is exerted on the liquid even after the position at which the washing liquid is added.

System set up according to the invention

In figure 2 is the system set up according to the invention shown. Here is the ash from the electrostatic precipitator 19 supplied to a first leaching tank 1a. The leaching tank and associated leaching process is preferably similar to the one described in figure 1, and similar components and flows have same reference numbers.

The slurry which is obtained in this way is pumped onwards, via a pump 4a, to a first centrifugation stage 2a. In this centrifugation stage is a first liquid fraction LF1 as well as a first dry matter substance DM1 obtained. The first liquid fraction LF1 contains high levels of chlorides and potassium and a part of this fraction is bled off from the process via 26. The remaining part of this first liquid fraction could be returned back to the first leaching tank 1a.

In order to establish the correct pH conditions for the leaching process could acidic liquids, such as Na$_2$SO$_4$ and/or H$_2$SO$_4$ be added in a dedicated supply conduit connected to the first leaching tank 1a as shown in figure 2. This pH correction is needed if the carbonate content of the ash is typically higher than 5 weight-%, and thus dependent on the specific overall mill process.

The first dry matter substance DM1 obtained contains high levels of sodium sulphate, and is sent to a second leaching tank 1b, where the crystallization of sodium sulphate is taken even further on the particles already formed. The crystallization process is improved as large parts of the chlorides and potassium has been bled off in the first centrifugal stage 2a.

The leaching process in the second leaching tank 1b is essentially at the similar conditions as in the first leaching tank as of pH and dry substance level, excluding the bled off part of the chlorides and potassium.

After the leaching process in the second leaching tank 1b the leached slurry which is obtained in this way is pumped onwards, via a pump 4b, to a second centrifugation stage 2b. In this centrifugation stage is a second liquid fraction LF2 as well as a second dry matter substance DM2 obtained. The second liquid fraction LF2 contains some residual levels of sodium sulphate and a part of this fraction is returned back to the first leaching tank 1a while the remaining part of this second liquid fraction could be returned back to the second leaching tank 1b.
The final dry matter substance DM2 is similarly to figure 1 led via outlet 2 to any appropriate mixing tank where this dry matter substance DM2 is mixed with black liquor before sending it further to the recovery process via the evaporation train of directly to the recovery boiler.

In a preferred embodiment of the invention is the first centrifugal separation stage 2a taking place in a high rotational speed centrifuge optimized for obtaining a clean first liquid fraction LF1 and a first dry matter substance DM1, and that the second centrifugal separation stage 2b takes place in a low rotational speed centrifuge optimized for obtaining a second dry matter substance DM2 with a dry matter concentration being at least 15% higher than that of the first dry matter substance. The first centrifugal separation stage takes preferably place at a rotational speed above 3500 rpm, and the second centrifugal separation stage takes place at a rotational speed below 3500 rpm, while the difference in rotational speed between first and second centrifugal separation stages is at least 2000 rpm.

The first centrifugal separation stage takes place in a nozzle bowl separator centrifuge which is shown in figure 3. The nozzle centrifuge consists basically of a stationary housing 50 and a bowl 51 rotating inside of the housing at high rotational speed. The slurry is fed from 1a via a feed inlet pipe into the inlet chamber 52 at the lower end of the rotating bowl 51, and passes thereafter around a lower edge of a conical wall to a disc stack 53 with conical discs where the main separation takes place. Separation takes place under the influence of high centrifugal force. The narrow conical discs establish interspaces which split the total liquid flow into several thin layers. In each layer the solid particles are flung and settle on the underside of the disc above and slide down into the outer separation chamber 54 for the denser solid particles. The separated solid particles (i.e. Na₂SO₄ crystals) are continuously discharged via nozzles 55 arranged in the radially outer part of the separation chamber 54.

The clarified liquid LF1 is conveyed to the centre of the bowl from where it is pumped by a centripetal pump 56 to the outlet 58.

This type of centrifuge could also preferably be equipped with a washing stage, where washing liquid (Kond.) may be added via a central pipe 60 to the lowermost part of the inlet chamber 52.

This type of centrifuge is impeding a strong centrifugal force on the separation, and the liquid fraction separated has a very low content of solid particles. The disadvantage is that the dry matter fraction has lower concentration as it must be kept at a fluent state as it flows off under gravity trough tight control nozzles in the separation chamber 54. However, this is an ideal separation process as a first separation stage, as the dry matter fraction still need reslurrying in front of the second leaching stage.
The second centrifugal separation stage 2b preferably takes place in a decanter centrifuge, also used in the prior art one-stage leaching and centrifugal process as shown in figure 1. This type of centrifuge is impeding somewhat less centrifugal force on the separation, and the dry matter fraction could be given a higher concentration as the out feed of this fraction is assisted by the screw conveyor. The disadvantage is that the liquid fraction can have higher content of particles as the separation effect from the centrifugal effect is lower. However, this is an ideal separation process as a second separation stage, as the liquid fraction is circulated back to at least one preceding leaching tank, where said solid particles (i.e. Na₂SO₄ crystals) is used as growth areas for further deposition of sodium sulphate.

The leaching process in at least one leaching tank 1a/1b, preferably both, is established at a temperature in the interval 65-105°C, preferably around 80°C with a slurried electrostatic precipitator ash having a dry substance level in the interval 15-40% by weight being obtained. The leaching process in at least one leaching tank 1a/1b is preferably also established such that the slurried electrostatic precipitator ash passing through, and being treated in, the leaching tank in at least two agitation zones, in which agitation zones the slurried electrostatic precipitator ash undergoes repeated gentle agitation in the leaching tank.

**Test example**

By means of the 2 stage process according to the invention, major improvements in recycling useful process chemicals Na and SO₄ to the pulping process while bleeding out chloride and potassium from the electrostatic precipitator ash. One case study was based on an electrostatic precipitator ash having the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>8.1</td>
</tr>
<tr>
<td>K</td>
<td>4.0</td>
</tr>
<tr>
<td>Na</td>
<td>30.4</td>
</tr>
<tr>
<td>SO₄</td>
<td>57.0</td>
</tr>
<tr>
<td>CO₃</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Success has been achieved in improving recovery of the Na and SO₄ content from 75-80% using the 1 stage process to over 90% using the two stage process. The losses of Na and SO₄ in this example have thus been reduced from 25-30% down to 5-10%.

The chlorides and potassium are bled out via the liquid fraction from the first centrifugal separation stage, with at least 0.5-2.0 ton of liquid fraction per ton of electrostatic precipitator ash being forwarded to effluent or further working-up.
By means of the 2-stage process, it was found possible to separate over 85% of its chloride and potassium content from the electrostatic precipitator ash.
PATENT CLAIMS

1. Process for purifying recovery boiler electrostatic precipitator ash from chlorides and potassium, in particular, by means of leaching and subsequently separating off a solid phase, which solid phase is returned to the pulp process, with the process comprising a first leaching stage, where the electrostatic precipitator ash is firstly slurried and agitated in a first leaching tank at a pH in the interval 8-13 at a dry substance level in the interval 15-40% and at a total dwell time in the first leaching tank in the interval 1-5 hours, after which the slurried electrostatic precipitator ash, which has thus been leached, is fed to a separation stage in which the leached electrostatic precipitator ash undergoes a separation of crystallized substance by means of a centrifugal separation characterized in that the centrifugal separation comprises at least two centrifugal separation stages in series, and where at least a part of the first liquid fraction from the first centrifugal separation stage containing chlorides and potassium is bled out from the process and the first dry matter substance obtained from the first centrifugal separation stage is led to a second leaching tank where similar conditions as in the first leaching tank is established as of pH and dry substance level, after which the reslurried and leached first dry matter substance from the first centrifugal separation stage is fed to a second centrifugal separation stage from which a second liquid fraction is obtained that is led back to at least one preceding leaching tank, and a second dry matter substance which thereafter is mixed into black liquor before the black liquor is being sent to the recovery process.

2. Process according to Claim 1, characterized in that the first centrifugal separation stage takes place in a high rotational speed centrifuge optimized for obtaining a clean first liquid fraction and a first dry matter substance, and that the second centrifugal separation stage takes place in a low rotational speed centrifuge optimized for obtaining a second dry matter substance at a dry matter concentration being at least 15% higher than that of the first dry matter substance.

3. Process according to Claim 2, characterized in that the first centrifugal separation stage takes place at a rotational speed above 3500 rpm, and the second centrifugal separation stage takes place at a rotational speed below 3500 rpm., while the difference in rotational speed between first and second centrifugal separation stages is at least 2000 rpm.

4. Process according to Claim 3, characterized in that the first centrifugal separation
stage takes place in a nozzle bowl separator centrifuge.

5. Process according to Claim 4, characterized in that the second centrifugal separation stage takes place in a decanter centrifuge.

6. Process according to Claim 1, characterized in that the leaching process in at least one leaching tank is established at a temperature in the interval 65-105°C, preferably around 80°C with a slurried electrostatic precipitator ash having a dry substance level in the interval 15-40% by weight being obtained.

7. Process according to Claim 6, characterized in that the leaching process in at least one leaching tank is established such that the slurried electrostatic precipitator ash passing through, and being treated in, the leaching tank in at least two agitation zones, in which agitation zones the slurried electrostatic precipitator ash undergoes repeated gentle agitation in the leaching tank.
AMENDED CLAIMS
received by the International Bureau on 24 March 2010 (24.03.2010).

1. Process for purifying recovery boiler electrostatic precipitator ash from chlorides and potassium, in particular, by means of leaching and subsequently separating off a solid phase, which solid phase is returned to the pulp process, with the process comprising a first leaching stage, where the electrostatic precipitator ash is firstly slurried and agitated in a first leaching tank at a pH in the interval 8-13 at a dry substance level in the interval 15-40% and at a total dwell time in the first leaching tank in the interval 1-5 hours, after which the slurried electrostatic precipitator ash, which has thus been leached, is fed to a separation stage in which the leached electrostatic precipitator ash undergoes a separation of crystallized substance by means of a centrifugal separation characterized in that the centrifugal separation comprises at least two centrifugal separation stages in series, and that the first centrifugal separation stage takes place in a high rotational speed centrifuge optimized for obtaining a clean first liquid fraction and a first dry matter substance, and that the second centrifugal separation stage takes place in a low rotational speed centrifuge optimized for obtaining a second dry matter substance at a dry matter concentration being at least 15% higher than that of the first dry matter substance, and where at least a part of the first liquid fraction from the first centrifugal separation stage containing chlorides and potassium is bled out from the process and the first dry matter substance obtained from the first centrifugal separation stage is fed to a second leaching tank where similar conditions as in the first leaching tank is established as of pH and dry substance level, after which the reslurried and leached first dry matter substance from the first centrifugal separation stage is fed to a second centrifugal separation stage from which a second liquid fraction is obtained that is led back to at least one preceding leaching tank, and a second dry matter substance which thereafter is mixed into black liquor before the black liquor is being sent to the recovery process.

2. Process according to Claim 1, characterized in that the first centrifugal separation stage takes place at a rotational speed above 3500 rpm, and the second centrifugal separation stage takes place at a rotational speed below 3500 rpm., while the difference in rotational speed between first and second centrifugal separation stages is at least 2000 rpm.

3. Process according to Claim 2, characterized in that the first centrifugal separation stage takes place in a nozzle bowl separator centrifuge.
4. Process according to Claim 3, characterized in that the second centrifugal separation stage takes place in a decanter centrifuge.

5. Process according to Claim 1, characterized in that the leaching process in at least one leaching tank is established at a temperature in the interval 65-105°C, preferably around 80°C with a slurried electrostatic precipitator ash having a dry substance level in the interval 15-40% by weight being obtained.

6. Process according to Claim 5, characterized in that the leaching process in at least one leaching tank is established such that the slurried electrostatic precipitator ash passing through, and being treated in, the leaching tank in at least two agitation zones, in which agitation zones the slurried electrostatic precipitator ash undergoes repeated gentle agitation in the leaching tank.
Fig. 3
### A. CLASSIFICATION OF SUBJECT MATTER

**IPC:** see extra sheet

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)

**IPC:** D21C, BOID

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

SE, DK, FI, NO classes as above

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

### EPO-INTERNAL, WPI DATA, PAJ

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 03016616 A1 (KVAERNER PULPING AB), 27 February 2003 (27.02.2003), page 9, line 22 - line 35, figure 1, claims 1-4, abstract</td>
<td>1-7</td>
</tr>
<tr>
<td>Y</td>
<td>figure 1, claims 1-3, abstract</td>
<td>1-7</td>
</tr>
<tr>
<td>Y</td>
<td>EP 1798297 A1 (CTU-CONZEPE TECHNIK UMWELT AG), 20 June 2007 (20.06.2007), figures 1,2, abstract, paragraphs [0014]-[0021]</td>
<td>1-7</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  - **A** document defining the general state of the art which is not considered to be of particular relevance
  - **E** earlier application or patent but published on or after the international filing date
  - **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - **O** document referring to an oral disclosure, use, exhibition or other means
  - **P** document published prior to the international filing date but later than the priority date claimed

**International application No.**

PCT/SE2009/050493

### Date of the actual completion of the international search

7 January 2010

### Date of mailing of the international search report

08-01-2010

**Name and mailing address of the ISA/Swedish Patent Office**

Box 5055, S-102 42 STOCKHOLM

**Facsimile No.** +46 8 666 02 86

**Authorized officer**

Linda Salomonsson/ELY

**Telephone No.** +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 2009)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>US 5840085 A (TOKUNAGA K ET AL), 24 November 1998 (24.11.1998), the whole document</td>
<td>1-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>WO 9612847 A1 (KVAERNER PULPING TECHNOLOGIES AB), 2 May 1996 (02.05.1996)</td>
<td>1-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>SE 526435 C2 (STFI SKOGSINDUSTRINS TEKNISKA FORSKNINGSINSTITUT AB), 13 Sept 2005 (13.09.2005), the whole document</td>
<td>1-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
International patent classification (IPC)

D21C 11/06 (2006.01)
B01D 43/00 (2006.01)
B01D 53/74 (2006.01)
B01D 53/80 (2006.01)

Download your patent documents at www.prv.se
The cited patent documents can be downloaded:
- From "Cited documents" found under our online services at www.prv.se (English version)
- From "Anförda dokument" found under "e-tjanster" at www.prv.se (Swedish version)

Use the application number as username. The password is FSPDLMIGCH.

Paper copies can be ordered at a cost of 50 SEK per copy from PRV InterPat (telephone number 08-782 28 85).

Cited literature, if any, will be enclosed in paper form.
<table>
<thead>
<tr>
<th>Application Number</th>
<th>Priority Date</th>
<th>Country</th>
<th>Application Number</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>517587 C</td>
<td>25/06/2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0102717 A,L</td>
<td>25/06/2002</td>
</tr>
<tr>
<td>EP 1798297 A1</td>
<td>20/06/2007</td>
<td>NONE</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>FI</td>
<td>111171 B</td>
<td>13/06/2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FI</td>
<td>955105 A</td>
<td>16/06/1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP</td>
<td>8170288 A</td>
<td>02/07/1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>515987 C</td>
<td>05/11/2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>9504281 A,L</td>
<td>16/06/1996</td>
</tr>
<tr>
<td>WO 9612847 A1</td>
<td>02/05/1996</td>
<td>AU</td>
<td>3818595 A</td>
<td>15/05/1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FI</td>
<td>971654 A</td>
<td>18/04/1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>504374 C</td>
<td>20/01/1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>9403598 A,L</td>
<td>21/04/1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US</td>
<td>5911854 A</td>
<td>15/06/1999</td>
</tr>
<tr>
<td>SE 526435 C2</td>
<td>13/09/2005</td>
<td>SE</td>
<td>0400395 A</td>
<td>20/02/2004</td>
</tr>
</tbody>
</table>