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(54) Title: METHOD OF TREATING INDUSTRIAL WATER

(57) Abstract: The invention relates to a method and apparatus of removing sulphate and soluble metals such as calcium from water. The invention relates also to a method of controlling the method. The method comprises steps of a) precipitating a first part of sulphate of the water by contacting the water with a first calcium compound and adjusting pH of the water to 10.5 or higher so as to form a first sludge containing gypsum and metal hydroxides, b) subjecting the first sludge containing gypsum to electrocoagulation for precipitating a second part of sulphate as ettringite, and for precipitating calcium-aluminium/iron-sulphate hydroxides, c) conducting the sludge formed in steps a) and b) to solid-liquid separation for separating precipitated solids from the water, d) neutralizing the water received from step c) to provide water decreased in sulphate and soluble metal such as calcium content.



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METHOD OF TREATING INDUSTRIAL WATER

FIELD OF THE INVENTION

The present invention relates to treating and cleaning of industrial waters. The invention is method and apparatus for treating process and industrial waters, especially industrial waste waters. Particularly the invention provides a method of removing sulphate and metals, especially calcium and other soluble metals from water.

BACKGROUND OF THE INVENTION

Sulphate is a common compound in metallurgical process streams and causes problematic gypsum precipitation with calcium. Gypsum blocks process piping and causes scaling of coating and surface of process equipment. Current methods of removing dissolved sulphate in waters include controlled gypsum precipitation, biological sulphate reduction and membrane separation. All of the methods have technical and economical limitations. Sulphate is not a toxic compound per se, thus the problems caused by sulphate are increased salinity and malfunctioning process equipment caused by gypsum precipitation. Even though sulphate has no direct toxic effects in the environment, the sulphate load in a receiving water increases salinity and causes secondary toxic effects, when sulphate is biologically reduced to toxic H_2S .

Sulphate removal by electrocoagulation (EC) has been studied e.g. for tannery effluent, acid mine drainage and various metal containing waste waters. However, the method of sulphate removal and the formed solids are not specified in the studies. Even more importantly, the decrease in sulphate concentrations is seldom presented or the tested concentrations are low (< 200 mg/l), the reason being that studies concentrate on removing of metals and chemical oxygen demand (COD) from different waters and the sulphate removal is reported as additional benefit of the treatment. Publicly reported studies discussing sulphate removal using EC with aluminium electrodes are scarce, and most of the studies report only removal of sulphate when original sulphate concentration was lower than 200 mg/l.

Orescanin et al. have published in "A combined CaO/electrochemical treatment of the acid mine drainage from the "Robule" Lake". Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering. Volume 47, Issue 8, Pages 1186-1191, a study wherein electrocoagulation was used with combination of iron

and aluminium electrodes for treatment of acid mine drainage (AMD) containing up to 12 g/l sulphate. The AMD was pre-treated by adjusting pH to 7.4 with CaO. The reported sulphate removal by pH adjustment only was 71 %: the sulphate concentration decreased from 12 g/l to 5 g/l after pH adjustment. The following electrocoagulation with Al-Fe anode combination resulted in final sulphate concentration of 3.5 g/l. After EC treatment the water pH was 6.7, which condition is not favourable for ettringite formation. The invention in the present application results in lower final sulphate concentrations in the treated water.

Muraganathan et al. reported in "Separation of pollutants from tannery effluents by electro flotation", Separation and Purification Technology 40 (2004) 69–75, a 22-23 % sulphate removal from 1850-2400 mg/l original concentration for electroflotation treatment of tannery waste water with both Al and Fe anodes. For these tests the pH was only 8.5, thus ettringite formation is not expected due to low pH value.

Basha et al. reported in "Removal of arsenic and sulphate from the copper smelting industrial effluent", Chemical Engineering Journal. Volume 141, Issues 1–3, pages 89–98, sulphate removal during arsenic treatment with electrocoagulation, but the tested sulphate concentrations were below 50 mg/l. Similar results were reported by Murugananthan et al. in "Removal of sulfide, sulfate and sulfite ions by electro coagulation", Journal of Hazardous materials. Volume 109, Issues 1–3, pages 37–44, for treatment of tannery waste water, but also the tested sulphate concentration was 54 mg/l.

Electrocoagulation apparatuses are known in the art. For example WO 99/43617 discloses an apparatus for electrocoagulation treatment of liquids.

BRIEF DESCRIPTION OF THE INVENTION

An object of the present invention is to provide a method and an apparatus for implementing the method so as to alleviate the disadvantages of the state of the art. The objects of the invention are achieved by a method and an arrangement, which are characterized by what is stated in the independent claims. The preferred embodiments of the invention are disclosed in the dependent claims.

Conventional gypsum precipitation methods cannot decrease the sulphate concentration much below 1400 mg/l. This invention is based on the finding that sulphate precipitation as ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$)

after gypsum precipitation enables the decrease of the sulphate concentration even close to zero. By ettringite precipitation even the sulphate associated to the highly soluble sodium and potassium sulphates can be completely or partially removed.

5 Further the present invention is based on the idea of precipitating sulphate by electrocoagulation by selecting the working anodes and precipitation conditions such that ettringite, aluminium sulphate hydroxides and/or iron-aluminium sulphate hydroxides are precipitated thereby removing the sulphate from water. Electrocoagulation with aluminium or iron-aluminium anodes produces aluminium ions or aluminium and iron ions into the water to be treated
10 when electric current is applied.

 An advantage of the present invention is that clean water is provided from which sulphate, calcium and other soluble metals have been removed. Another advantageous feature of the method and arrangement of the invention
15 is that the use of expensive aluminium compounds traditionally used in the ettringite precipitation can be replaced by relatively cheap aluminium anodes. Even more importantly, the required aluminium is provided in the electrocoagulation to the process without undesired dissolving counter ions, such as chloride from aluminium chlorides or sodium from sodium aluminate, which is typical for the use of typical technical grade aluminium chemicals. In electrocoagulation aluminium is dissolved from the anodes as aluminium ions and hydrated
20 in the water without the disturbing counter ions. This ensures that the total ion concentration of the treated effluent is remarkably lower and therefore enables the water to be of required quality for recycling back to the industrial process.
25 The process conditions in the present invention are selected so that the precipitation of ettringite and/or aluminium/iron sulphate hydroxides is facilitated. This is done by ensuring the presence of soluble calcium, soluble aluminium and hydroxide ions and sufficiently high pH.

 The water suitable for treating in accordance with the method and
30 apparatus of the present invention may be any water from which it is desired to re-move sulphate, calcium and/or other soluble metals. Typically the water is process water or effluent, more typically the water is sulphate-containing water, such as mine water, recycle water from concentrator or discharge water from concentrator.

35 The method of the present invention is especially suitable for treating the waste waters from concentrators, where sulphate is a problem in recy-

cle or discharge streams. The specific problem in concentrator's plant waters is the simultaneous high sulphate and calcium load, making the configuration of the present invention feasible. Concentrators may also use sulphidic chemicals in flotation process and these may in addition produce thiosalts, such as thio-
5 sulphate, polythionates and other sulphur compounds, during milling and flotation stages. The sulphur compounds convert over time to sulphate.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following the invention is described in more detail by means of preferred embodiments with reference to the attached drawings, in which
10 Figure 1 is a flow diagram of an example embodiment of the invention;
Figure 2 is a flow diagram of an example embodiment of the invention;
Figure 3 is a flow diagram of an example embodiment of the invention;
15 Figure 4 is a flow diagram of an example embodiment of the invention;
Figure 5 is a flow diagram of an example embodiment of the invention;
20 Figure 6 is diagram showing sulphate removal in tests 1 to 4;
Figure 7 is a block diagram of a pH adjustment equipment preceding the electrocoagulation according to an exemplary embodiment; and
Figure 8 is a flow diagram of a control of a pH adjustment equipment preceding the electrocoagulation according to an exemplary embodiment;
25 Figure 9 is a block diagram of exemplary pH adjustment in a separate balancing equipment;
Figure 10 is an exemplary flow diagram of a pH adjustment in the exemplary equipment of Figure 9;
30 Figure 11 is a block diagram of exemplary arrangement for adjusting the feed of electric power in the electrocoagulation step.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a method and an apparatus for removing sulphate, calcium and/or other soluble metals from water. The selection of the
35 steps of the method of removing of sulphate and soluble metals such as calci-

um is done based on the initial chemical composition of the water to be treated by the method. The mentioned chemical composition of the water comprises sulphate concentration, concentration of Na, K and Ca ions and the amount of gypsum which is precipitateable. The chemical composition of the water is related to the desired stoichiometric amount of ettringite precipitated. The amount of sulphate which can be precipitated as gypsum depends on the concentration of Na, K and Ca in the water to be treated. The invention relates also to controlling of the method.

According to the invention the method of removing sulphate and soluble metals such as calcium from water comprises

a) precipitating a first part of sulphate of the water by contacting the water with a first calcium compound and adjusting pH of the water to 10.5 or higher in the first pH adjustment step so as to form a first sludge containing gypsum and metal hydroxides,

b) subjecting the first sludge containing gypsum to electrocoagulation in the presence of at least one set of aluminium anodes or in the presence of at least one set of iron anode and aluminium anode for precipitating a second part of sulphate as ettringite,

c) conducting the sludge formed in steps a) and b) to solid-liquid separation for separating precipitated solids from the water,

d) neutralizing the water received from step c) to provide water decreased in sulphate and soluble metal such as calcium content.

According to a preferred embodiment of the invention the method of removing sulphate, calcium and/or other soluble metals from water further comprises a balancing step of contacting the sludge formed in the electrocoagulation step b) with a second calcium compound for completing the sulphate precipitation and for providing required retention time for the precipitation.

In the first pH adjustment step dissolved metal ions with oxidation stage between +1 to +3 are precipitated as hydroxides.

The method of the invention comprises a first pH adjustment step, where the first part of sulphate and metal hydroxides are precipitated, and wherein the water to be treated is contacted with a first calcium compound for producing a first sludge containing gypsum and metal hydroxides and adjusting the pH of the first sludge to be 10.5 or higher. According to an embodiment of the invention the first calcium compound in the first pH adjustment step is se-

lected from the group consisting of calcium hydroxide, calcium oxide, calcium carbonate and a mixture thereof.

Typically the first calcium compound in the first pH adjustment step (a) is calcium hydroxide, which enables the precipitation of soluble sulphates depending on the pH-dependent solubilities of the counter-cations, especially K, Na and Ca, of the soluble sulphate species. Sulphate and metal impurities from the solution will typically precipitate according to the following equation:



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Typical metal impurities are divalent or trivalent metals. Typically in the first pH adjustment step most of the metal impurities, including magnesium sulphate, are precipitated as hydroxides at pH from 10.5 to 13, more typically from 11 to 12. The solubility of gypsum in the specific process conditions, such as in the presence of potassium and sodium, defines the final dissolved sulphate concentration in the solution (water). Sulphate concentration in gypsum saturated solution is typically about 1200 to 1600 mg/l. However, the presence of high concentration of sodium and potassium sulphate can cause the final sulphate level to be higher as these sulphates are highly soluble even at very high pH.

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According to one embodiment of the invention the pH of the first sludge in the first pH adjustment step is adjusted to be 10.5 or higher. Preferably the pH is adjusted to be in the range from 10.5 to 13. More preferably the pH is in the range of 11 to 12. The pH is adjusted by adding a suitable amount of the selected first calcium compound into the first process liquor. Typically the dosing of the calcium compound is adjusted and controlled through measuring and monitoring the pH of the process liquor, alternatively it can be done on the basis of the existing calcium concentration.

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The method of the invention comprises at least one electrocoagulation step performed after the first pH adjustment step, when in the electrocoagulation step the first sludge containing gypsum is subjected to electrocoagulation in the presence of a set of aluminium anodes or in the presence of a set of iron anode and aluminium anode for producing a second sludge containing ettringite and/or calcium-aluminium/iron-sulphate hydroxides and gypsum. The set of anodes comprises at least two anodes. Typically the number of anodes used in the method depends on the amount of water to be treated

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and/or size of the apparatus. The purpose of the electrocoagulation is to produce ions in the process liquor for precipitating sulphate as ettringite. The method of the invention may also comprise more than one electrocoagulation steps. A second or further electrocoagulation step is performed when more treatment time or efficiency is needed or more capacity for treatment of a large amount of water is needed. Alternatively more than two electrodes may be used in the electrocoagulation step(s). A further alternative is to increase the amount of current used in the electrocoagulation step(s). The second or further electrocoagulation step may be performed in the same way as the first electrocoagulation step.

According to another embodiment of the invention the electrocoagulation step after the first pH adjustment step involves a balancing step. Typically this is realised with arranging balancing section in the electrocoagulation cell for example in different sections of an electrocoagulation tank.

According to one embodiment of the invention the electrocoagulation step is followed by a balancing step as an additional process step. In such a case the electrocoagulation step typically comprises an electrocoagulation cell and a separate balancing tank in connection with the electrocoagulation cell. In both embodiments the second sludge is contacted with a second calcium compound for adjusting the pH, for providing calcium ions and for producing longer retention time for the precipitation of ettringite. This enables suitable conditions for ettringite precipitation. In the balancing step the precipitation reaction of ettringite is forced to complete by adjusting the conditions and giving retention time

In the context of the present invention electrocoagulation means an electrocoagulation (EC) process, wherein the coagulant is generated in situ by electrolytic oxidation of an appropriate anode material. Consumable metal plates, such as iron or aluminium, are usually used as sacrificial electrodes to continuously produce ions in the water. As in the case of chemical coagulation with metal salts, aluminium or iron cations and hydroxides anions are the reagents in EC. The released ions remove undesirable contaminants either by chemical reaction and precipitation, or by causing the colloidal materials to coalesce.

EC systems are typically constructed of a set of electrodes (usually in form of plates), through which water flows between the spaces of the electrodes. Typically, direct current (DC) has been used in EC systems.

According to one preferred embodiment of the invention the method comprises two or more electrocoagulation steps connected in series. In an embodiment of the invention there is one common balancing step after the two or more electrocoagulation steps connected in series. According to another
5 embodiment the invention comprises more than one electrocoagulation steps each involving a balancing step. According to a further embodiment of the invention the first, second and further electrocoagulation steps are each followed by a separate balancing step.

According to an embodiment of the invention the method comprises
10 two or more electrocoagulation steps connected in parallel. In such cases the method comprises typically also a second or further balancing step between the first and the second and/or subsequent electrocoagulation steps. In an embodiment of the invention there is one common balancing step after the two or more electrocoagulation steps connected in parallel. According to one more
15 embodiment of the invention the first, second and further electrocoagulation steps in parallel each involve a balancing step. According to a further embodiment of the invention the first, second and further electrocoagulation steps are each followed by a separate balancing step.

Typically, when the electrocoagulation step does not involve a balancing step, then the electrocoagulation step is followed by a balancing step
20 as a separate, additional step.

In the balancing step(s) the pH of the process liquid is adjusted by a suitable compound to be in the range of 10.5 to 13, more typically from 11 to 12. Typically the pH is adjusted by using a second calcium compound selected
25 from the group consisting of calcium hydroxide, calcium oxide, calcium carbonate and a mixture thereof. Typically the balancing is performed in the same manner as the first pH adjustment step. The purpose of the addition of the second calcium compound in the balancing is to ensure that the pH is in the range suitable for ettringite precipitation and that appropriate concentration of
30 calcium ions is present for ettringite precipitation. This enables the completion of ettringite precipitation and enables efficient sulphate removal resulting in a very low concentration of sulphate in the water solution. The retention time in the actual electrocoagulation phase is typically short, so it is also desired that the ettringite precipitation takes place or continues in the balancing step(s) and
35 hence, another purpose of the balancing is to provide longer retention time for the process and for the reactions to complete.

According to an embodiment of the invention the electrocoagulation step comprises a set of aluminium anodes or a set of aluminium anode and a set of iron anode. According to another embodiment of the invention the electrocoagulation step comprises more than one set of aluminium anodes or more than one set of aluminium anode and iron anode.

According to an embodiment of the invention the anodes are made of aluminium, which contain recycled aluminium or virgin aluminium. According to another embodiment the anodes are made of iron or steel, which may contain recycled or virgin material. Typically the anodes can be made of any suitable aluminium or iron ion source.

The retention time in the electrocoagulation step including the balancing step(s) is preferably between 5 to 60 minutes, more preferably from 15 to 30 minutes. The retention time used depends on the implementation of the electrocoagulation step.

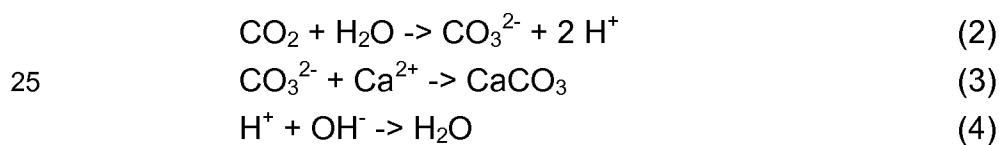
The second calcium compound to be fed to the balancing step(s) is selected independently from the group consisting of calcium hydroxide, calcium oxide, calcium carbonate and a mixture thereof.

After the electrocoagulation step the method comprises a separation step, wherein a solid-liquid separation is performed for the second sludge containing precipitated ettringite and/or calcium-aluminium/iron sulphate hydroxides and gypsum for separating solids from the liquid. The solid-liquid separation is typically performed by any suitable equipment for separating solids from liquid, such as a settling device, a filter, a clarifier, a lamella clarifier, hydrocyclone or decanter. One or more of these equipments may be used in any combination if necessary. Typically the solid-liquid separation step comprises a clarifier, such as a conventional round clarifier with an optimized feed well design followed by a filtration unit to further dewater the produced clarifier underflow.

According to an embodiment of the invention a part of the water from the solid-liquid separation step is recycled back to the electrocoagulation step in order to dilute and thus affect the ionic strength of the feed to the electrocoagulation unit.

After the solid-liquid separation the liquid obtained is routed to a neutralisation step wherein the liquid obtained from the first separation step is neutralised thereby producing a waste water with reduced sulphate, calcium, and/or other soluble metals content.

According to an embodiment of the invention the neutralisation is performed by contacting the liquid obtained from the separation step with a neutralising agent for neutralising the liquid and precipitating calcium contained in the liquid as calcium compound. According to an embodiment of the invention the neutralisation may be performed by contacting the solution with a carbonating agent for neutralising the solution and precipitating calcium contained in the first solution as calcium carbonate. The carbonating agent may be any suitable carbonating agent, such as CO₂, sodium carbonate or sodium bicarbonate. Preferably the carbonating agent is CO₂. If sodium carbonate is used, also acid can be fed to the neutralisation step. The neutralisation step is preferably performed by decreasing the pH and precipitating calcium as calcium carbonate (CaCO₃) by adding CO₂ to the first solution. If the calcium concentration (Ca-hardness) needs to be lowered further a sodium hydroxide (NaOH), or other alkaline, stream may be added to the process step thereby allowing further removal of Ca as CaCO₃ by adding alkalinity and avoiding the pH to decrease to the unfavourable area for CaCO₃ precipitation, below pH 8 to 9. According to an embodiment of the invention in the neutralisation step the first solution is contacted with an alkaline, such as sodium hydroxide, for increasing the precipitation of calcium as calcium carbonate. The carbon dioxide is used for both neutralising the solution and for removing the calcium hardness from the solution. The neutralisation and calcium precipitation reactions for CO₂ neutralisation may be summarized by the following equations:



According to an embodiment of the invention the neutralization is performed by using hydrochloric acid or an organic acid.

According to an embodiment of the invention the neutralisation is performed by diluting the liquid obtained from the first separation step with water. The water may be any available water with sufficient quality and pureness.

The gypsum and ettringite are separated before the neutralisation step, as the lowering of the pH increases the solubility of the precipitated ettringite. It is possible to recycle the calcium carbonate solids to the beginning of the process to be used as neutralising agent to acidic waste waters to be

processed. Calcium carbonate may also be used for producing alkaline buffering capacity for the gypsum and ettringite residues.

According to an embodiment of the invention the method comprises an optional second separation step a') between steps a) and b) wherein the
5 gypsum contained in the first sludge is separated from the first sludge by solid liquid separation before the first sludge is routed to electrocoagulation step b). In the second separation step a'), which may also be called a gypsum removal step, a solid-liquid separation is performed for removing precipitated gypsum from the first sludge. The presence of the optional solid-liquid separation step
10 (or the presence of the separation unit if apparatus is in question) may be selected on the basis of the amount of gypsum solids formed in the first pH adjustment step. The optional solid-liquid separation is typically performed so that the gypsum formed in step a) is separated from the first sludge, typically by a clarifier.

According to an embodiment of the invention the electrocoagulation
15 step may be performed in the sludge containing gypsum, i.e. without the optional second solid-liquid separation step. Thus, according to an embodiment of the invention the method does not contain a solid-liquid separation step between the pH adjustment step a) and the electrocoagulation step b). According
20 to an embodiment of the invention the method comprises an optional second balancing step b') between steps b) and c), According to an embodiment of the invention the method comprises a second electrocoagulation step b'') between steps b) and c). According to a further embodiment of the invention the method comprises a second electrocoagulation step b'') between steps b') and c). Typ-
25 ically the second electrocoagulation step is performed if more than one electrocoagulation steps are needed. According to an embodiment of the invention the method comprises a third balancing step after the second electrocoagulation step.

The method of the invention may also comprise a third or further
30 electrocoagulation step between the steps b) and c), steps b') and c) or steps b'') and c). The purpose of the second or further electrocoagulation step and the second or further balancing step is to add retention time to the process and enhance sulphate removal.

The present invention relates also to an apparatus of removing sul-
35 phate and soluble metals such as calcium from water, which apparatus comprises

a) a precipitating unit adapted for precipitating a first part of sulphate of the water by contacting the water with a first calcium compound and adjusting pH of the water to 10.5 or higher so as to form a first sludge containing gypsum and metal hydroxides,

5 b) an electrocoagulation unit adapted for subjecting the first sludge containing gypsum to electrocoagulation in the presence of at least one set of aluminium anodes or in the presence of at least one set of iron anode and aluminium anode for precipitating a second part of sulphate as ettringite,

10 c) a separation unit adapted for conducting the sludge formed in steps a) and b) to solid-liquid separation for separating precipitated solids from the water,

 d) a neutralization unit adapted for neutralizing the water received from step c) to provide water decreased in sulphate and soluble metal such as calcium content.

15 The apparatus may further comprise a balancing unit, which may be an integral part of the electrocoagulation unit. Typically the balancing unit is an integral part of the electrocoagulation cell. In another embodiment the balancing unit may be implemented as a separate balancing unit, such as a reactor, tank, pipe, vessel, hose or any suitable equipment for holding liquid. The balancing unit is used for providing the required retention time for precipitation of sulphate. In the balancing unit the first sludge is contacted with a second calcium compound.

20 Typically, when the electrocoagulation unit does not involve a balancing unit, then the first electrocoagulation unit is followed by a balancing unit as a separate unit.

 An embodiment of the invention is wherein the apparatus comprises an optional second separation unit a') between units a) and b), which is adapted for separating the gypsum contained in the first sludge by solid liquid separation before the first sludge is routed to electrocoagulation unit b).

30 According to an embodiment of the invention the apparatus comprises an optional balancing unit b') between units b) and c), adapted for balancing the pH to be 10.5 or higher and to provide retention time for the ettringite precipitation. In the balancing unit the sludge is contacted with a second calcium compound. According to an embodiment of the invention the electrocoagulation unit b) involves a balancing unit as integral part of the electrocoagulation unit. According to an embodiment of the invention the electrocoagulation unit b) is followed

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by a balancing unit as an additional, separate unit. The balancing unit is for providing the required retention time for precipitation of sulphate and in the balancing unit the sludge is contacted with a second calcium compound for ensuring the optimal conditions for completing sulphate precipitation.

5 According to an embodiment of the invention the apparatus comprises a second electrocoagulation unit b'') between units b) and c) or units b') and c).

 According to an embodiment of the invention the apparatus comprises a third or further electrocoagulation unit between the units b) and c),
10 units b') and c) or units b'') and c).

 According to an embodiment of the invention the electrocoagulation unit comprises at least one electrocoagulation cell. Typically the electrocoagulation unit comprises also at least one balancing tank.

 According to an embodiment of the invention the apparatus comprises two or more electrocoagulation units connected in series.
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 According to an embodiment of the invention the apparatus comprises two or more electrocoagulation units connected in parallel.

 According to an embodiment of the invention the apparatus is adjusted for performing the method of the invention described above.

20 Figure 1 is a flow diagram of one embodiment of the invention wherein the water to be treated, process water 1 is fed to a pH adjustment step 2, wherein the pH of the solution is adjusted to be at least 10.5 or higher using a first calcium compound 3 selected from the group consisting of calcium hydroxide, calcium oxide, calcium carbonate and a mixture thereof. In the pH adjustment step 2 gypsum precipitates due to the contact with the first calcium compound. Preferably the pH is adjusted to between 10.5 and 13. From the pH
25 adjustment step 2 the water and formed sludge is directed to an electrocoagulation step 4, wherein ettringite is precipitated to the sludge by using aluminium anodes or aluminium and iron anodes. The electrocoagulation step may involve also a balancing step 6, wherein the retention time is adjusted to an appropriate length. The balancing step 6 may be implemented as a separate balancing cell outside the actual electrocoagulation cell. In such a case the tank of the balancing step is in fluid communication with the electrocoagulation cell. Second calcium compound 5 may be added to balancing step 6 and the second calcium compound 5 is selected independently from the group consisting
30 of calcium hydroxide, calcium oxide, calcium carbonate and a mixture thereof.

When the method comprises the balancing step 6 the sludge containing gypsum, ettringite and other precipitated species is directed to a solid-liquid separation step 8, wherein a solid product 7 is separated from the sludge. The solid product comprises mainly ettringite and/or aluminium/iron sulphate hydroxides, gypsum and metal hydroxides. The liquid from the solid-liquid separation is directed to neutralisation 10, which may be performed in many different ways, as presented above. Typically the neutralisation is performed by diluting or by using a neutralising agent. Treated water is obtained from the method as stream 9.

Figure 2 is another embodiment of the present invention, which is performed otherwise in the same way as the embodiment disclosed in Figure 1, except that the balancing step 6 is an integral part of the configuration of the electrocoagulation step.

Figure 3 is a flow diagram of an embodiment of the present invention, which is performed otherwise in the same way as the embodiment disclosed in Figure 1, except that at least part of the water 11 is recycled from the solid-liquid separation step 8 back to the electrocoagulation step 2. Recycle of the treated water can sometimes be useful for diluting and thus changing the ionic strength of the feed to the electrocoagulation step.

Figure 4 is an embodiment of the present invention, wherein the flow from the pH adjustment step 2 is directed to electrocoagulation steps 4a, 4b and 4c connected in series, wherein ettringite is precipitated in the sludge by using aluminium anodes or aluminium and iron anodes. Otherwise the process is done in the same way as described in connection with Figure 1. Even though in the Figure 4 the balancing step 6 is disclosed as a separate step, it may alternatively be also involved as an integral part in each of the electrocoagulation steps 4a, 4b and 4c.

Figure 5 is an embodiment of the present invention, wherein the flow from the pH adjustment step 2 the formed sludge is directed to electrocoagulation steps 4a, 4b and 4c connected in parallel, wherein ettringite is precipitated in the sludge by using aluminium anodes or aluminium and iron anodes. Otherwise the process is done in the same way as described in connection with Figure 1. Even though in the Figure 5 the balancing step 6 is disclosed as a separate step, it may alternatively be also involved as an integral part in each of the electrocoagulation steps 4a, 4b and 4c.

As described above, a maintaining and thereby control of optimal precipitation conditions in the electrocoagulation step is desired.

Figure 7 is a block diagram of exemplary pH adjustment equipment located upstream of the electrocoagulation step or equipment. In the illustrated example, the pH adjustment equipment which may implement the pH adjustment step 2 described above, may comprise a stirred reactor tank 2", and necessary inlets and outlets for providing and recovering process streams, e.g. an incoming process water stream 1 and an outgoing sludge stream to a to the electrocoagulation step. Examples of commercial reactors applicable for precipitation reactor 2" include OKTOP® reactors manufactured by Outotec. The reactor tank 2" may further comprise inlets for feeding a calcium compound 3, as those described above. The feed of the calcium compound 3 to the reactor tank 2" may be controlled by a feeding valve 71 that may be any type of process control valve. Alternatively, a pump may be used instead of valve 71. Further, a pH measurement unit or sensor 72 may be provided to measure the pH of the solution in the tank. A pH measurement signal from the pH sensor 72 may be inputted to a controller unit 73 which is configured to control the feeding valve 71. The control signal from the controller 73 may be applied also to a control station 74 of the water processing system. The control station 74 may be, for example, a process control system or a control room computer. In an exemplary embodiment, the controller 73 may be part of the control station 74, in which case the pH measurement may be supplied to the control station 74 which is configured to control the feeding valve 71. The controller 73 may optionally receive calcium concentration data 76 determined based on sampling at the following electrocoagulation step or equipment, the subsequent piping or the balancing step. The sampling of the process material may be manual or automatic, and the calcium concentration data 76 may originate from an analyzer 75 analysing the sampled material.

An exemplary flow diagram of a pH adjustment and an optional adjustment of calcium concentration in the exemplary equipment of Figure 7 is illustrated in Figure 8. The control process may be an automatic or semi-automatic control. In a semiautomatic control some of the control phases, particularly the starting and ending of the process may be done manually e.g. from the control station 74 by an operator. First a process water stream 1 is fed to the reactor tank 2" (step 82). The pH of the solution in the reactor tank 2" may

be measured by the pH sensor 72, and the pH measurement may be inputted to the controller 73 (step 84). The controller 73 may compare the measured pH level with a desired pH level, such as 10.5 to 12.5 (step 85). The desired pH level may be a threshold level, such as 10.5 that shall be exceeded or a pH range within which the pH shall be. If the measured pH level is not at the desired pH level, the controller 73 may control the feeding valve 72 to feed an additional dose of the calcium compound 3 into the reactor tank 2" (step 86) and the pH measurement (step 85) may be repeated. If the measured pH level is at the desired pH level, i.e. the process has received a steady state, the control procedure may directly return to the pH measurement 84 without feeding any additional dose of the calcium compound 3 into the reactor tank 2", when only the pH adjustment is implemented.

In an embodiment of the invention, an optional adjustment of calcium concentration of the solution in the electrocoagulation process is also implemented in pH adjusting step, e.g. in the reactor tank 2" of Figure 7. An exemplary flow diagram of the optional adjustment of the calcium concentration is illustrated by dashed lines in Figure 8. In the optional adjustment, if the measured pH level is at the desired pH level, i.e. the process has received a steady state at step, the controller 73 may proceed to determine the calcium concentration in the subsequent electrocoagulation process (step 87) and to compare the determined Ca concentration with a desired Ca concentration for achieving the desired conditions for the ettringite precipitation (e.g. sufficient Ca ions and pH), step 88. Determination step 87 may comprise receiving the Ca concentration data 76 from the subsequent electrocoagulation step. If the Ca concentration is not the desired Ca concentration, the controller 73 may proceed to step 86 to control the feeding valve 72 to feed an additional dose of the calcium compound 3 into the reactor tank 2" (step 86) and the pH measurement (step 85) may be repeated. If the Ca concentration is the desired Ca concentration, the control procedure may directly return to the pH measurement 84 without feeding any additional dose of the calcium compound 3 into the reactor tank 2". This type of pH control, Ca control and measurement loop may continue maintaining the process in the steady state.

The additive dose of the calcium compound fed in step may be any small amount. The size of the additive dose may depend on the difference between the measured pH and the desired pH, or the determined Ca concentration and the desired Ca concentration and/or it may depend on a time constant

of the pH or Ca control loop. The size of the additive dose may be different for the pH control and the Ca control loop.

In an embodiment, only pH control may be implemented in the reactor tank.

5 As discussed above, the balancing step may be implemented as physically integrated into the electrocoagulation step (e.g. a compartment in the same equipment) or it may be implemented as a physically separate unit. Figure 9 is a block diagram of exemplary pH adjustment and an optional Ca concentration adjustment in a separate balancing equipment located down-
10 stream of the primary electrocoagulation step or equipment. In the illustrated example, the balancing equipment which may implement the balancing step 6 described above may comprise a stirred reactor tank 6", and necessary inlets and outlets for providing and recovering process streams, e.g. an incoming precipitation sludge and an outgoing sludge stream to a subsequent separator
15 8. Examples of commercial reactors applicable for reactor 6" include OKTOP® reactors manufactured by Outotec. The reactor tank 6" may further comprise inlet for feeding a calcium compound 5, as those described above. The feed of the calcium compound 5 to the reactor tank 6" may be controlled by a feeding valve 91 that may be any type of process control valve. Alternatively, a pump
20 may be used instead of valve 91. Further, a pH measurement unit or sensor 92 may be provided to measure the pH of the solution in the tank. A pH measurement signal from the pH sensor 92 may be inputted to a controller unit 93 which is configured to control the feeding valve 91. The control signal from the controller 93 may be applied also to a control station 94 of the water pro-
25 cessing system. The balancing equipment may further comprise an online sampling unit 95 taking samples from the solution in the tank for analysis in an online analyser 75. The analyser 75 may determine calcium concentration of the solution and provide respective concentration data 76 to the controller 93 of the balancing equipment, or to the controller 73 of the reactor in Figure 7, for
30 example, or to both of them, or to any other control device using the Ca concentration data. The control station 94 may be, for example, a process control system or a control room computer. In an exemplary embodiment, the controller 93 may be part of the control station 94, in which case the pH measurement may be supplied to the control station 94 which is configured to control the
35 feeding valve 91. In an embodiment, the controllers 73 and 93, and/or control stations 74 and 94 in the pH adjustment equipment and the balancing equip-

ment may be implemented in a common unit. The analyser 75 may also determine aluminium (Al) and/or sulphate (SO_4) concentration in the solution and provide respective concentration Ca, Al and/or SO_4 concentration data 115 to the controller 113 in Figure 11, for example. It should be appreciated that sampling 95 may alternatively made in the electrocoagulation equipment, in the piping, etc. The sampling may also be manual. An exemplary flow diagram of a pH adjustment and an optional Ca concentration adjustment in the exemplary equipment of Figure 9 is illustrated in Figure 10. The control process may be an automatic or semi-automatic control. In a semiautomatic control some of the control phases, particularly the starting and ending of the process may be done manually e.g. from the control station 94 by an operator. First a precipitation sludge stream is fed to the reactor tank" (step 102). The pH of the solution in the reactor tank 6" may be measured by the pH sensor 92, and the pH measurement may be inputted to the controller 93 (step 104). The controller 93 may compare the measured pH level with a desired pH level, such as 10.5 to 12.5 (step 105). The desired pH level may be a threshold level, such as 10.5 that shall be exceeded or a pH range within which the pH shall be. If the measured pH level is not at the desired pH level, the controller 93 may control the feeding valve 91 to feed an additional dose of the calcium compound 5 into the reactor tank 6" (step 106) and the pH measurement (step 105) may be repeated. If the measured pH level is at the desired pH level, i.e. the process has received a steady state, the control procedure may directly return to the pH measurement 104 without feeding any additional dose of the calcium compound 5 into the reactor tank 3. This type of pH control and measurement loop may continue maintaining the process in the steady state.

In an embodiment of the invention, an optional adjustment of calcium concentration of the solution in the electrocoagulation process is also implemented in balancing equipment, in place of or in addition to the adjustment of calcium concentration in the reactor tank of Figure 7. An exemplary flow diagram of the optional adjustment of the calcium concentration is illustrated by dashed lines in Figure 10. in the optional adjustment, if the measured pH level is at the desired pH level, i.e. the process has received a steady state at step, the controller 93 may proceed to determine the calcium concentration in the electrocoagulation process (step 107) and to compare the determined Ca concentration with a desired Ca concentration for achieving the desired conditions for the ettringite precipitation (e.g. sufficient Ca ions and pH), step 108. Deter-

mination step 107 may comprise receiving the Ca concentration data 76 from the preceding electrocoagulation process, from the balancing tank, or any other source. In the illustrated example, the Ca concentration data 76 may be received from the analyser 75. If the Ca concentration is not the desired Ca concentration, the controller 93 may control the feeding valve 91 to feed an additional dose of the calcium compound 5 into the reactor tank 6" (step 106) and the pH measurement (step 104) may be repeated. If the Ca concentration is the desired Ca concentration, the control procedure may directly return to the pH measurement 104 without feeding any additional dose of the calcium compound 5 into the reactor tank 6". This type of pH control, Ca control and measurement loop may continue maintaining the process in the steady state.

The additive dose of the calcium compound fed in step may be any small amount. The size of the additive dose may depend on the difference between the measured pH and the desired pH, or the determined Ca concentration and the desired Ca concentration and/or it may depend on a time constant of the pH or Ca control loop. The size of the additive dose may be different for the pH control and the Ca control loop.

The additive dose of the calcium compound fed in step may be any small amount. The size of the additive dose may depend on the difference between the measured pH and the desired pH, and/or it may depend on a time constant of the pH control loop.

Figure 11 is a block diagram of exemplary arrangement for adjusting the feed of electric power in the electrocoagulation step. As noted above, the electrocoagulation (EC) systems are typically constructed of a set of electrodes 112 (usually in form of plates), through which water flows between the spaces of the electrodes in the electrocoagulation cell(s). An electric power source 111 is connected to feed an electric power to the electrodes 112. Typically, direct current (DC) has been used in EC systems. The electrodes may provide a monopolar or bipolar configuration. In the monopolar systems all anodes are connected to each other and similarly all cathodes are also connected to each other. In bipolar systems the outermost electrodes are connected to a power source and current passes through the other electrodes, thus polarising them. In the bipolar systems the side of the electrode facing the anode is negatively polarised and the other side is positively polarised. In an embodiment, the feed of electric power in the electrocoagulation cell(s) may be adjusted within the selected range according to a control loop based on analysis of the concentra-

tion of one or a combination of the elements Ca, Al and SO_4 in or after electrocoagulation. The Ca, Al and/or sulphate SO_4 concentration data 115 may be received to a controller 113 from the analyser 75 shown in Figure 8, for example. The controller unit 113 which is configured to control the power source
5 111. The control signal from the controller 113 may be applied also to a control station 114 of the water processing system. The control station 114 may be, for example, a process control system or a control room computer. In an exemplary embodiment, the controller 113 may be part of the control station 114. In an embodiment, the controllers 73, 93 and 113, and/or control stations 74, 94 and
10 114 in the pH adjustment equipment, the balancing equipment, and the electrocoagulation equipment may be implemented in a common unit.

The controller 113 may control the power source 111 to increase the feed of the electric power to the electrodes, if the Ca/Al/ SO_4 concentration increases/decreases. For example, an increase in the Al concentration may
15 cause the controller 113 to decrease the the electric power feed to the electrocoagulation cell and/or current density at the anode(s), because such increase of Al concentration indicates that more aluminium (Al) is dissolved than can be used for the ettringite precipitation reaction in the prevailing process conditions. As another example, if the Ca concentration is too low, the electric power
20 feed to the electrocoagulation cell and/or current density at the anode(s) may be decreased to avoid unnecessary dissolution of the anodes. As still another example, if the SO_4 concentration is too high, the electric power feed to the electrocoagulation cell and/or current density at the anode(s) may be increased to increase the amount of dissolved aluminium required for the ettringite pre-
25 cipitation reactions to take place.

The control of feed of the electric power may be implemented by controlling the DC voltage level applied to the electrodes 112. As another example, the control of feed of the electric power may be implemented by selectively connecting and disconnecting the feed of the electric power to some of
30 the electrodes 112. For example, number of energized electrodes may vary according to the Ca/Al/ SO_4 concentration. The connection and disconnection may be implemented by an internal power switches in the power source, for example.

The control techniques described herein may be implemented by
35 various means. For example, these techniques may be implemented in hardware (one or more devices), firmware (one or more devices), software (one or

more modules), or combinations thereof. For a firmware or software, implementation can be through modules (e.g., procedures, functions, and so on) that perform the functions described herein. The software codes may be stored in any suitable, processor/computer-readable data storage medium(s) or memory unit(s) and executed by one or more processors. The data storage medium or the memory unit may be implemented within the processor or external to the processor, in which case it can be communicatively coupled to the processor via various means as is known in the art. Additionally, components of systems described herein may be rearranged and/or complimented by additional components in order to facilitate achieving the various aspects, goals, advantages, etc., described with regard thereto, and are not limited to the precise configurations set forth in a given figure, as will be appreciated by one skilled in the art.

An aspect of the invention is a method of controlling a process of removing sulphate, calcium and/or other soluble metals from waste water, said method comprising

- feeding a waste water into a reactor tank;
- measuring the pH of a solution in the reactor tank;
- determining a calcium concentration in a subsequent electrocoagulation process,
- feeding one or more additive doses of a calcium compound into the reactor tank if the measured pH is not at a predetermined pH level, in order to adjust the pH of the solution towards the predetermined pH level, and
- feeding one or more additive doses of a calcium compound into the reactor tank and/or in the subsequent electrocoagulation process, if the determined calcium concentration is not a desired calcium concentration, in order to adjust the calcium concentration in the subsequent electrocoagulation process towards the desired calcium concentration.

In an embodiment, the control method comprises measuring the pH of a solution in a balancing tank at the end of electrocoagulation process,

feeding one or more additive doses of a calcium compound into the balancing tank if the measured pH is not at a predetermined pH level, in order to adjust the pH of the solution towards the desired pH level.

In an embodiment, the control method comprises feeding one or more additive doses of a calcium compound into the balancing tank, if the de-

terminated calcium concentration is not a desired calcium concentration, in order to adjust the calcium concentration in the electrocoagulation process towards the desired calcium concentration.

5 In an embodiment, the desired pH level is in a range from about 10.5 upwards.

In an embodiment, the control method comprises determining the concentration of one or a combination of the elements Ca, Al and SO₄ in or after the electrocoagulation process, adjusting a feed of electric power in at least one electrocoagulation
10 cell within a selected range according the determined concentration of one or a combination of the elements Ca, Al and SO₄ in or after electrocoagulation.

An aspect of the invention is a control system for implementing the control method.

15 An aspect of the invention is a computer program comprising program code for performing the control method, when the program is run on one or more computer or processor.

EXAMPLES

Sulphate removal with electrocoagulation was tested using gypsum saturated mine water with pH >12. Before the electrocoagulation, the mine wa-
20 ter pH adjustment was made with 300 g/l lime milk (Ca(OH)₂), and solid gypsum was separated. Four electrocoagulation tests were made, and each test included 1-3 electrocoagulation (EC) treatment cycles. During one cycle the water (2-4 l) was passed through the electrocoagulation cell using constant flow rate (1 l/min) and either aluminium anodes or combination of aluminium
25 and iron anodes. The test variables were the following:

- Test 1: three sequential EC treatment cycles using aluminium anodes with no pH adjustment between EC treatment cycles
- Test 2: three sequential treatment cycles using aluminium anodes with pH adjusted to 12 with lime milk (Ca(OH)₂) after each EC treatment cycle
- 30 - Test 3: two sequential EC treatment cycles using aluminium anodes, pH ad-justed to 12 with lime milk (Ca(OH)₂) after each EC treatment cycle and using doubled power supply (i.e. doubled power supply compared to power supply used in tests 1-2)

- Test 4: two sequential EC treatment cycles using combination of aluminium and iron anodes, and with pH adjustment to 12 using lime milk ($\text{Ca}(\text{OH})_2$) between EC treatment cycles.

5 The water samples were collected directly after each EC treatment cycle and analyzed for pH, soluble calcium, aluminium, iron, sulphate and sulphur. The pH adjustment to 12 with lime milk for tests 2-4 was made only after the water sample was collected for chemical analysis. For second and following EC treatment cycles the water was fed to the EC cell as such with no other treatment but pH adjustment to 12 with lime milk.

10 The test results of sulphate removal in electrocoagulation using aluminium or combination of aluminium and iron anodes are shown in Figure 6. The Figure 6 shows that when EC treatment conditions are not controlled with pH adjustment to 12 with lime milk, the sulphate removal will be limited (Test 1). The reason for this is the water pH decreases due to protons released during ettringite precipitation, and the addition of lime milk provides sufficient amount
15 of calcium for ettringite precipitation. Two EC treatment cycles in Test 2 with pH adjustment to 12 in between is already sufficient to reduce sulphate concentration from 1730 mg/l to 534 mg/l, and third treatment cycle resulted in final sulphate concentration of 15 mg/l. The used volumes of lime milk for pH
20 adjustment were small (maximum 55 ml per 3 l of water), thus the sulphate removal is result of precipitation as ettringite or corresponding calcium aluminium sulfates and dilution caused by lime milk addition has only minimal effect on the decrease of sulphate concentration. The doubling of power supply (Test 3) increased the sulphate removal kinetics remarkably: two treatment cycles re-
25 sulted in residual sulphate concentration of 24 mg/l, while in Test 2 similar sulphate level was achieved only after three subsequent EC treatment cycles. The use of both aluminium and iron anodes in Test 4 resulted in similar sulphate removal rate as observed in Test 2, as sulphate concentration decreased from 1730 to 680 mg/l with two EC treatment cycles. However, the
30 iron as coagulant may improve the solid/liquid separation properties of the EC treated slurry.

It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above
35 but may vary within the scope of the claims.

CLAIMS

1. A method of removing sulphate and soluble metals such as calcium from water, which method comprises steps of

5 a) precipitating a first part of sulphate of the water by contacting the water with a first calcium compound and adjusting pH of the water to 10.5 or higher so as to form a first sludge containing gypsum and metal hydroxides,

b) subjecting the first sludge containing gypsum to electrocoagulation in the presence of at least one set of aluminium anodes or in the presence
10 of at least one set of iron anode and aluminium anode for precipitating a second part of sulphate as ettringite,

c) conducting the sludge formed in steps a) and b) to solid-liquid separation for separating precipitated solids from the water,

d) neutralizing the water received from step c) to provide water decreased in sulphate and soluble metal such as calcium content.
15

2. A method according to claim 1, wherein in the electrocoagulation step after precipitation step a) calcium-aluminium/iron-sulphate hydroxides are precipitated.

3. A method according to any one of the preceding claims, wherein
20 the electrocoagulation step b), involves a balancing step which is for providing the required retention time for precipitation of sulphate and in which balancing step the sludge is contacted with a second calcium compound for ensuring the optimal conditions for completing sulphate precipitation.

4. A method according to any one of the preceding claims, wherein
25 the electrocoagulation step b) is followed by a balancing step as a separate step, which balancing step is for providing the required retention time for precipitation of sulphate and in which balancing step the sludge is contacted with a second calcium compound for ensuring the optimal conditions for completing sulphate precipitation.

30 5. The method according to any one of the preceding claims, wherein the water is process water, effluent or sulphate-containing water, such as mine water, recycle water from concentrator or discharge water from concentrator.

6. The method according to any one of the preceding claims wherein
35 in the first calcium compound and the second calcium compound are selected

independently from the group consisting of calcium hydroxide, calcium oxide, calcium carbonate and a mixture thereof.

7. The method according to any one of the preceding claims wherein the pH of the precipitation step a) is adjusted to be in the range from 10.5 to
5 13.

8. The method according to any one of the preceding claims wherein the method comprises two or more electrocoagulation steps connected in series.

9. The method according to any one of claims 1 to 8 wherein the
10 method comprises two or more electrocoagulation steps connected in parallel.

10. The method according to any one of the preceding claims, wherein the retention time in the electrocoagulation step including the balancing step(s) is from 5 to 60 minutes.

11. The method according to any one of the preceding claims,
15 wherein in the balancing step(s) the pH of the process liquid is adjusted to the range of 10.5 to 13 by using a second calcium compound selected from the group consisting of calcium hydroxide, calcium oxide, calcium carbonate and a mixture thereof.

12. The method according to any one of the preceding claims,
20 wherein the neutralisation step is performed by diluting the liquid obtained from the first separation step with another water source or by contacting the liquid obtained from the first separation step with a neutralising agent for neutralising the liquid and precipitating calcium contained in the liquid as calcium compound.

25 13. The method according to any one of the preceding claims wherein the method comprises an optional second separation step a') between steps a) and b) wherein the gypsum contained in the first sludge is separated from the first sludge by solid liquid separation before the first sludge is routed to electrocoagulation step b).

30 14. The method according to any one of the preceding claims wherein the method comprises an optional balancing step b') between steps b) and c), wherein the second sludge is contacted with a second calcium compound for providing calcium ions and further retention time.

15. The method according to any one of the preceding claims
35 wherein the method comprises a second electrocoagulation step b'') between steps b) and c) or steps b') and c).

16. The method according to any one of the preceding claims wherein the method comprises a third or further electrocoagulation step between the steps b) and c), steps b') and c) or steps b'') and c).

17. An apparatus of removing sulphate and soluble metals such as calcium from water, which apparatus comprises

a) a precipitating unit adapted for precipitating a first part of sulphate of the water by contacting the water with a first calcium compound and adjusting pH of the water to 10.5 or higher so as to form a first sludge containing gypsum and metal hydroxides,

b) an electrocoagulation unit adapted for subjecting the first sludge containing gypsum to electrocoagulation in the presence of at least one set of aluminium anodes or in the presence of at least one set of iron anode and aluminium anode for precipitating a second part of sulphate as ettringite,

c) a separation unit adapted for conducting the sludge formed in steps a) and b) to solid-liquid separation for separating precipitated solids from the water,

d) a neutralization unit adapted for neutralizing the water received from step c) to provide water decreased in sulphate and soluble metal such as calcium content.

18. The apparatus according to claim 17, wherein the electrocoagulation unit b), involves a balancing unit as integral part of the electrocoagulation unit and/or the electrocoagulation unit b) is followed by a balancing unit as an additional, separate unit, which balancing unit is for providing the required retention time for precipitation of sulphate and in which balancing unit the sludge is contacted with a second calcium compound for ensuring the optimal conditions for completing sulphate precipitation.

19. The apparatus according to claim 17 or 18 wherein the apparatus comprises an optional second separation unit a') between units a) and b), which is adapted for separating the gypsum contained in the first sludge by solid liquid separation before the first sludge is routed to electrocoagulation unit b).

20. The apparatus according to any one of claims 17 to 19, wherein the apparatus comprises two or more electrocoagulation units connected in series and/or the apparatus comprises two or more electrocoagulation units connected in parallel.

21. The apparatus according to any one of claims 17 to 20, wherein the apparatus comprises a second electrocoagulation unit b'') between units b) and c) or units b') and c).

22. The apparatus according to any one of claims 17 to 21 wherein
5 the apparatus comprises a third or further electrocoagulation unit between the units b) and c), units b') and c) or units b'') and c).

23. The apparatus according to any one of claims 17 to 22 wherein the apparatus is adapted for performing the method of any one of claims 1 to 17.

10 24. A method of controlling a process of removing sulphate, calcium and/or other soluble metals from waste water, said method comprising
feeding a waste water into a reactor tank;
measuring the pH of a solution in the reactor tank;
determining a calcium concentration in a subsequent electrocoagu-
15 lation process,

feeding one or more additive doses of a calcium compound into the reactor tank if the measured pH is not at a predetermined pH level, in order to adjust the pH of the solution towards the predetermined pH level , and

20 feeding one or more additive doses of a calcium compound into the reactor tank and/or in the subsequent electrocoagulation process, if the determined calcium concentration is not a desired calcium concentration, in order to adjust the calcium concentration in the subsequent electrocoagulation process towards the desired calcium concentration.

25 25. A method according to claim 24, comprising
measuring the pH of a solution in a balancing tank at the end of electrocoagulation process,

feeding one or more additive doses of a calcium compound into the balancing tank if the measured pH is not at a predetermined pH level, in order to adjust the pH of the solution towards the desired pH level.

30 26. A method according to claim 25, comprising feeding one or more additive doses of a calcium compound into the balancing tank, if the determined calcium concentration is not a desired calcium concentration, in order to adjust the calcium concentration in the electrocoagulation process towards the desired calcium concentration.

35 27. A method according to any one of claim 24-26, wherein the desired pH level is in a range from about 10.5 upwards.

28. A method according to any one of claim 24-27, comprising
determining the concentration of one or a combination of the elements Ca, Al and SO₄ in or after the electrocoagulation process,
adjusting a feed of electric power to electrocoagulation cell and/or
5 current density at the anode(s) in at least one electrocoagulation cell within a
selected range according the determined concentration of one or a combination of the elements Ca, Al and SO₄ in or after electrocoagulation.

29. A control system for implementing the control method according to any one of claims 24-28.

10 30. A computer program comprising program code for performing
any of methods according to claims 24-29, when the program is run on one or more computer or processor.

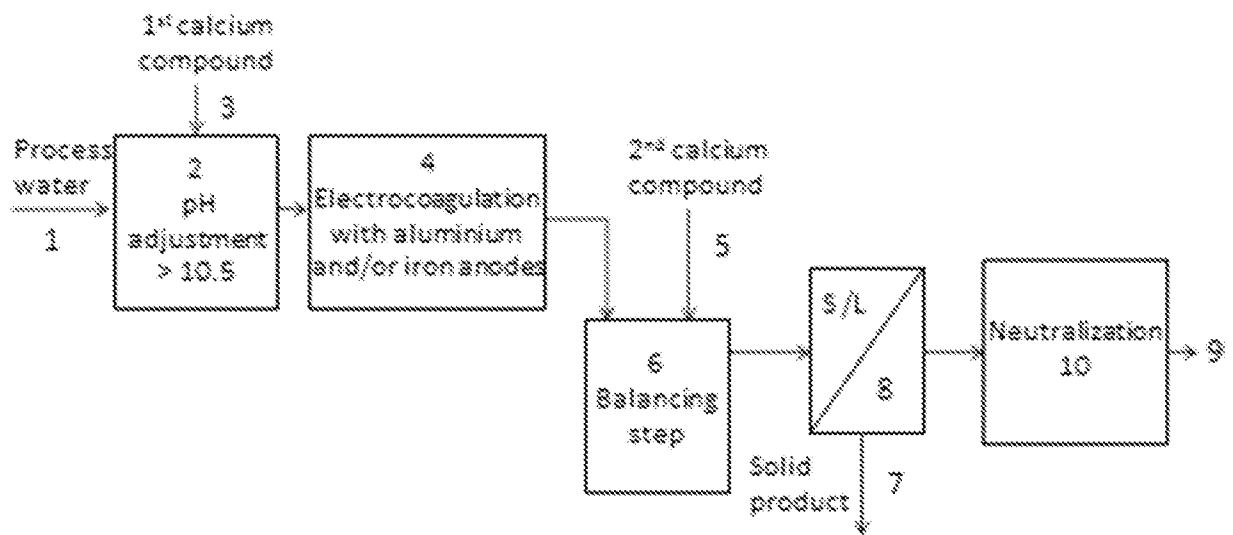
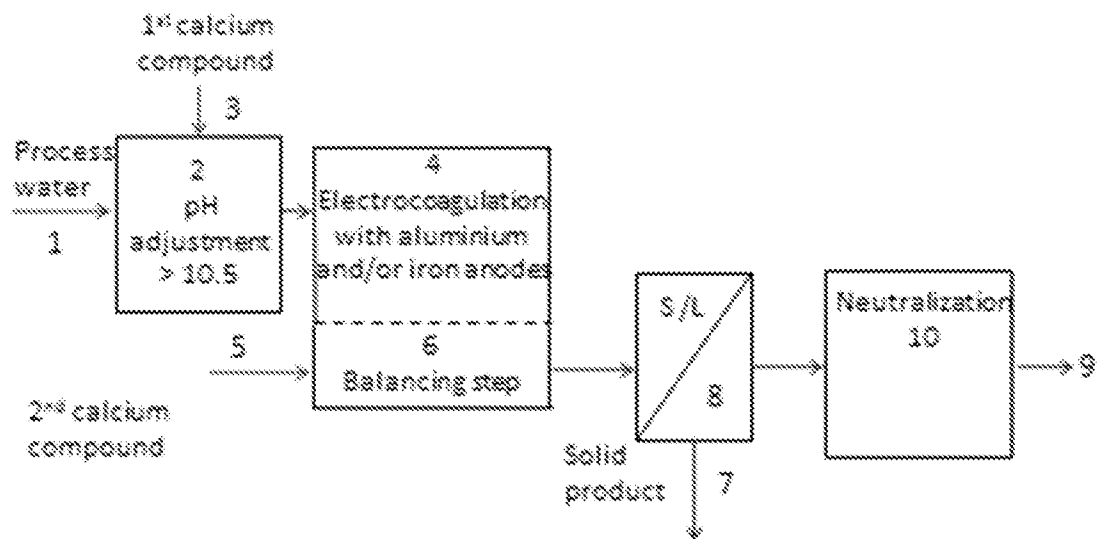


Fig. 1

**Fig. 2**

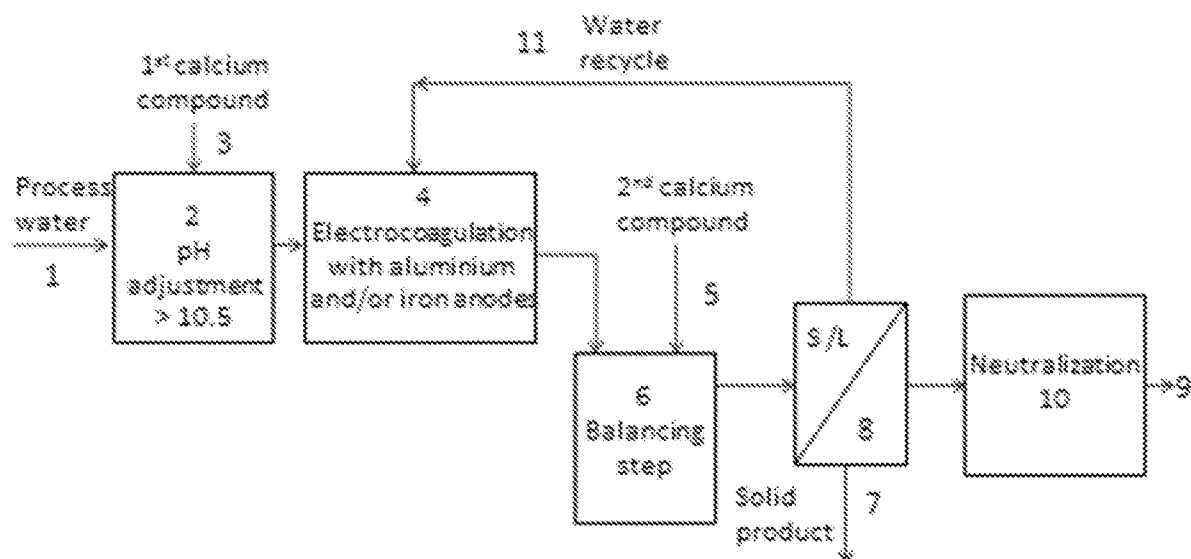


Fig. 3

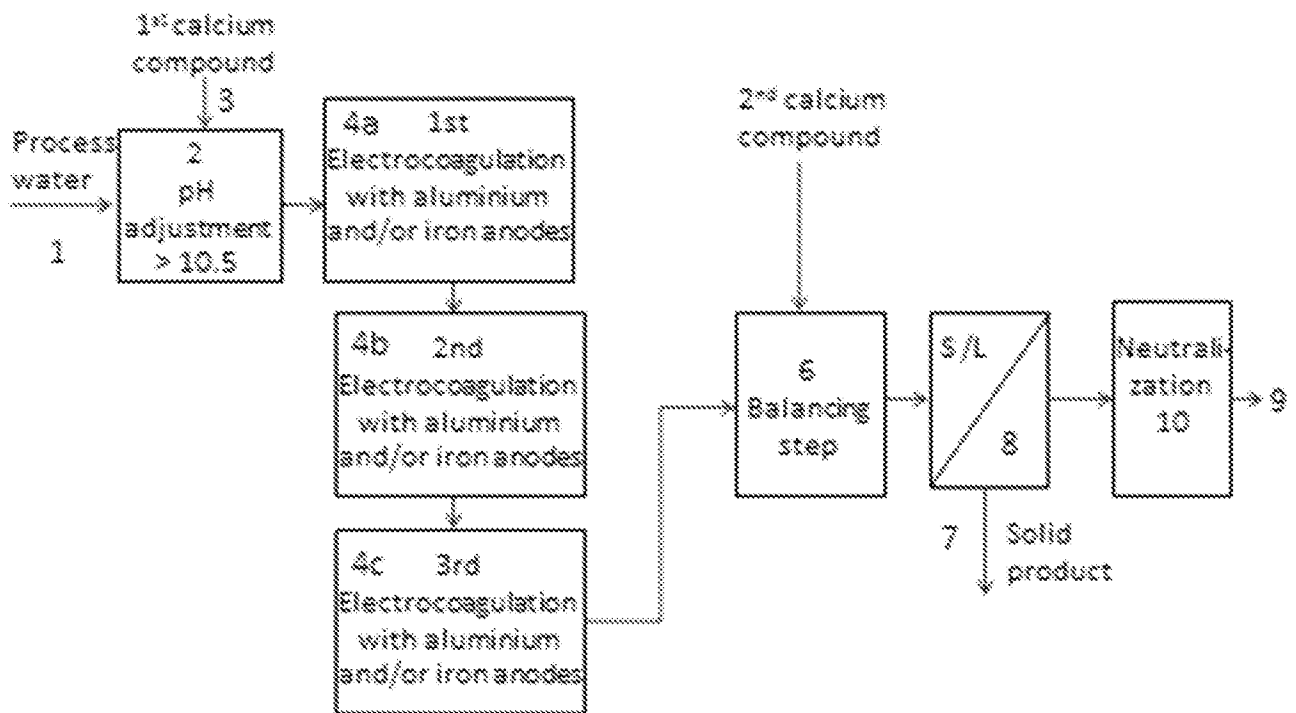


Fig. 4

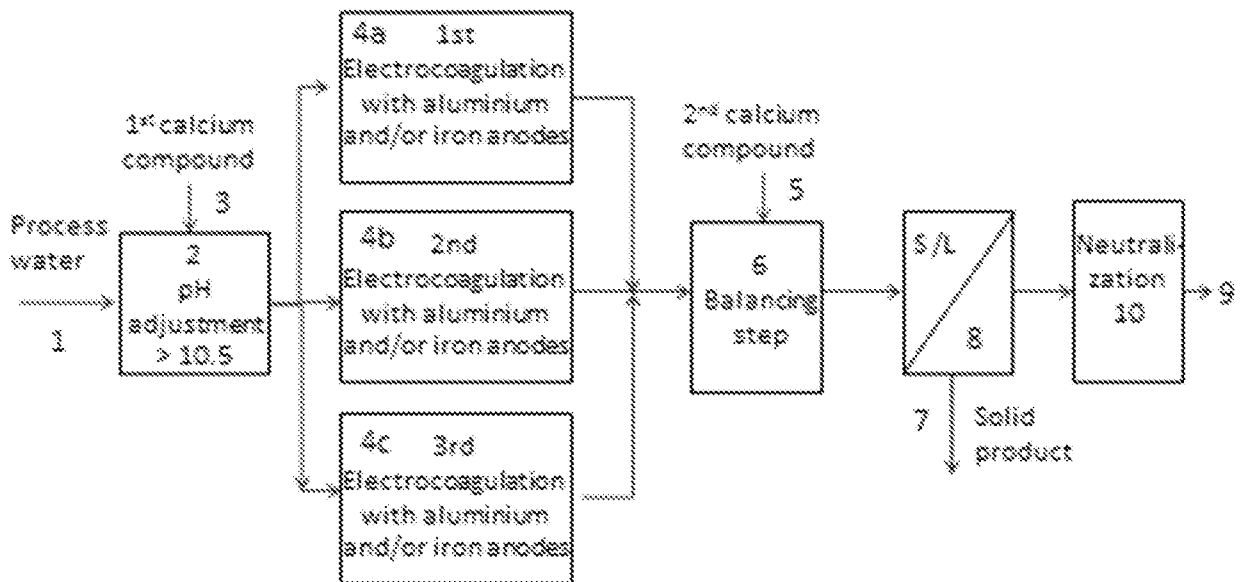
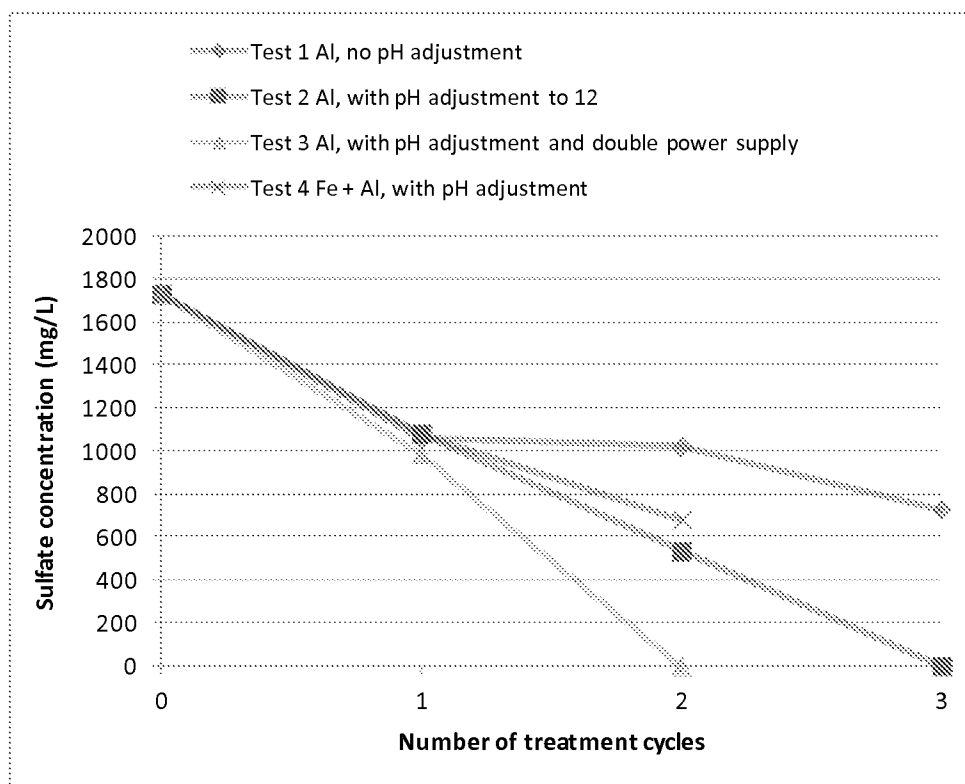


Fig. 5

**Fig. 6**

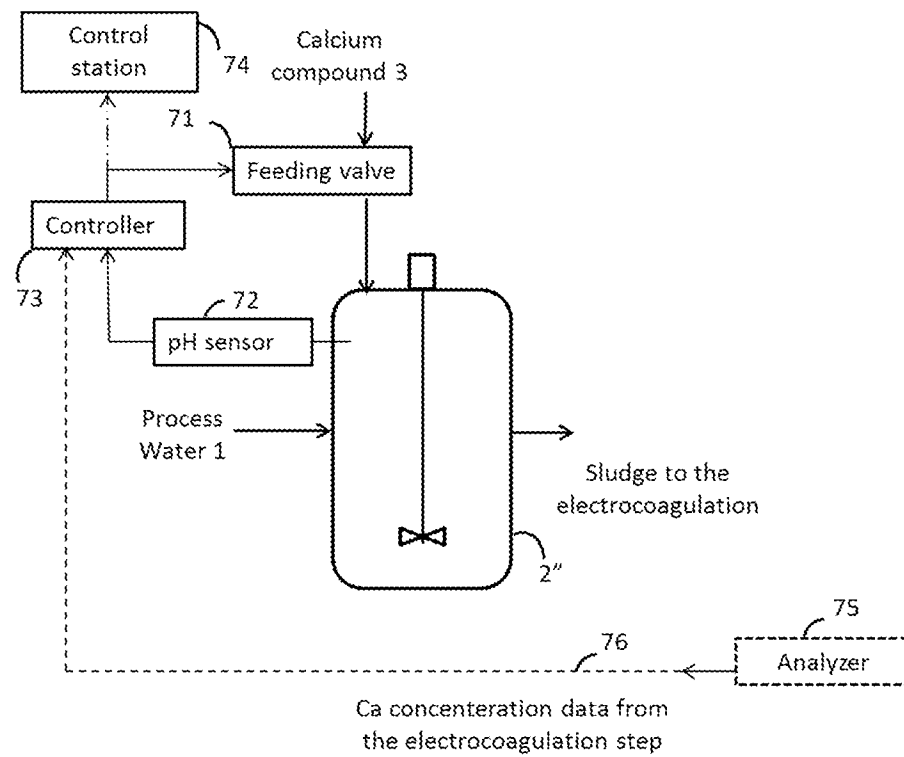


Fig. 7

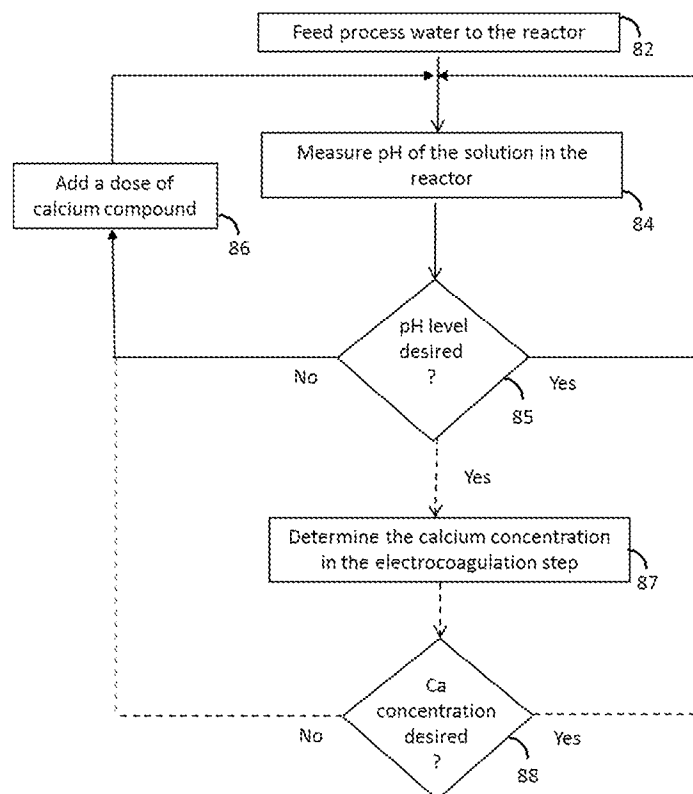


Fig. 8

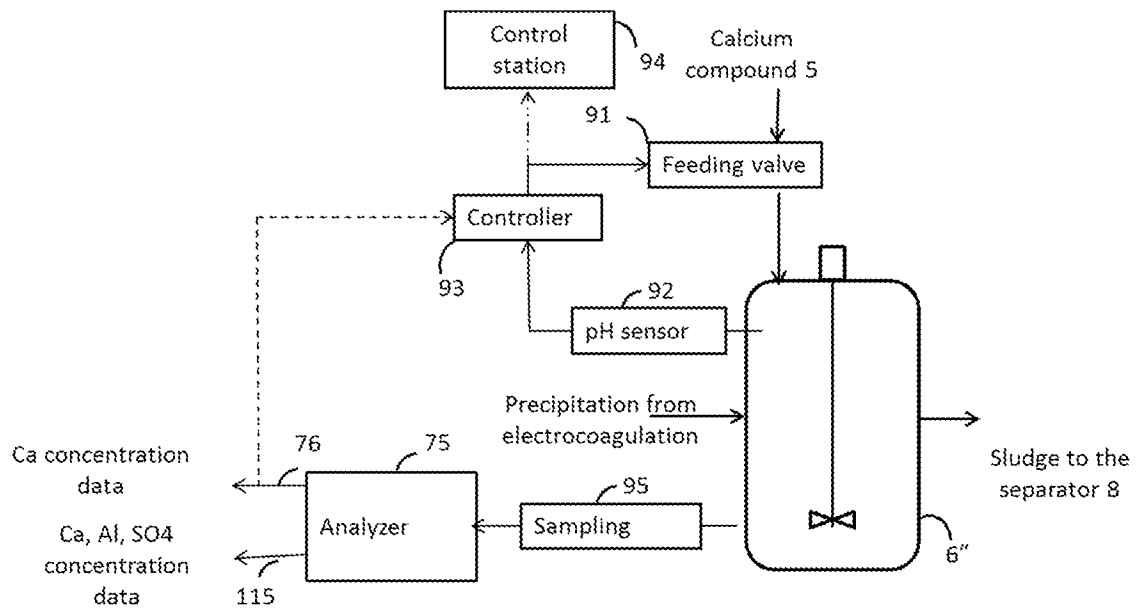


Fig. 9

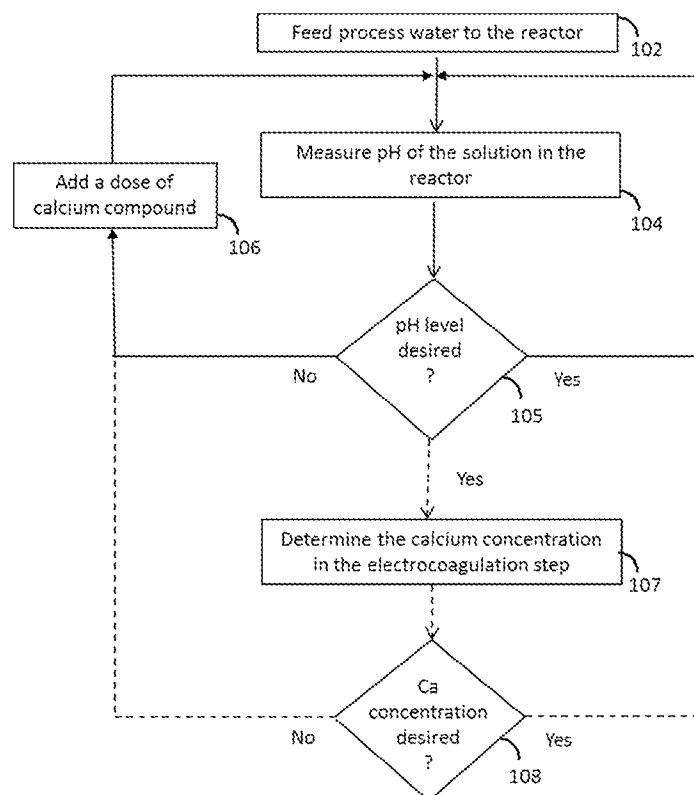


Fig. 10

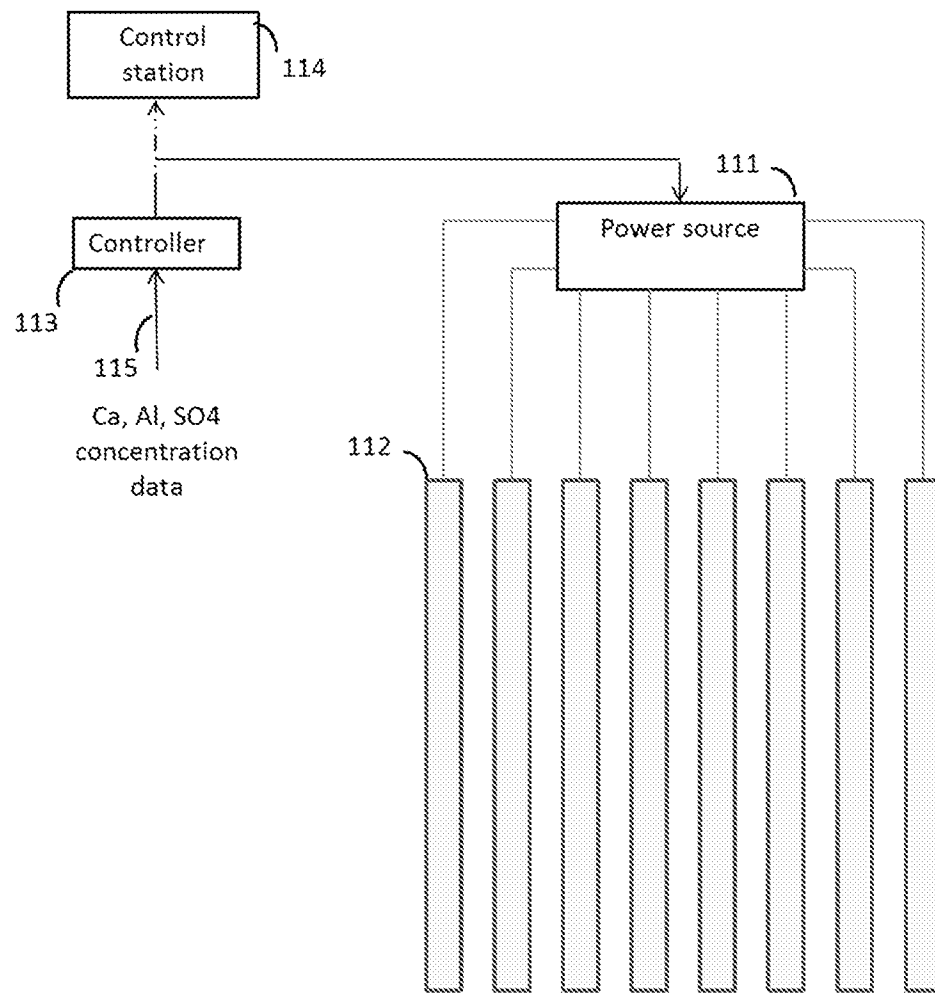


Fig. 11

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2013/051190

A. CLASSIFICATION OF SUBJECT MATTER

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: C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
FI, SE, NO, DK

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

EPO-Internal, WPI, INSPEC, COMPDX, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ORESCANIN V. & KOLLAR R. A combined CaO/electrochemical treatment of the acid mine drainage from the "Robule" Lake. Journal of Environmental Science and Health, Part A (Toxic/Hazardous Substances and Environmental Engineering) 01.07.2012, Vol. 47, Nr. 8, p. 1186 - 1191. ISSN 1093-4529 (print) the whole document, especially chapters Results and discussion and Conclusion cited in the application	17-30
A	MURUGANANTHAN M. et al. Separation of pollutants from tannery effluents by electro flotation. SEPARATION AND PURIFICATION TECHNOLOGY. 15.11.2004, Vol. 40, Nr. 1, p. 69-75. ISSN 1383-5866 the whole document cited in the application	1-30

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

* Special categories of cited documents:

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Date of the actual completion of the international search
31 March 2014 (31.03.2014)

Date of mailing of the international search report
07 April 2014 (07.04.2014)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2013/051190

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010187130 A1 (SMITH KEVIN W [US] et al.) 29 July 2010 (29.07.2010) the whole document	1-30
A	US 6280630 B1 (RAMSAY JAMES IAN [GB]) 28 August 2001 (28.08.2001) the whole document	1-30
L	WO 2014033361 A1 (OUTOTEC OYJ [FI]) 06 March 2014 (06.03.2014) the whole document for information	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2013/051190

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
US 2010187130 A1	29/07/2010	None	
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US 6280630 B1	28/08/2001	AU 740773 B2	15/11/2001
		AU 7779098 A	21/12/1998
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		ZA 9804724 A	02/12/1999
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WO 2014033361 A1	06/03/2014	None	
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CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C02F 1/463 (2006.01)**C02F 1/58** (2006.01)**C02F 9/04** (2006.01)**C02F 9/06** (2006.01)*C02F 101/10* (2006.01)*C02F 103/10* (2006.01)