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Declarations under Rule 4.17:

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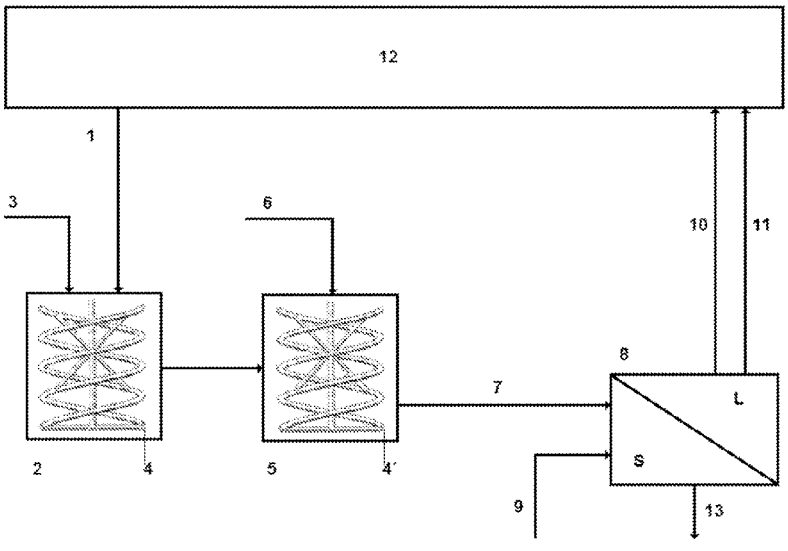
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(54) Title: METHOD AND ARRANGEMENT FOR REMOVING FLUORIDE FROM SULFATE SOLUTIONS

Figure 1



(57) Abstract: The invention relates to a method and an arrangement for removing fluoride and fluorine components from zinc containing process liquors and slurries. The method comprises the steps of i) withdrawing a flow of zinc sulfate containing process liquor or slurry from a zinc recovery process (12); ii) contacting the flow of zinc sulfate containing process liquor or slurry with a clay sorbent (3, 6) capable of sorbing fluoride or fluorine containing components present in the zinc sulfate containing process liquor or slurry to obtain a mixture of a clay sorbent comprising immobilized fluoride and a zinc sulfate containing process liquor or slurry at least partly depleted of fluoride; ii) separating the clay sorbent comprising immobilized fluoride from the mixture to obtain a treated zinc solution (10); and iv) returning the zinc solution back to the zinc recovery process (12).

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METHOD AND ARRANGEMENT FOR REMOVING FLUORIDE FROM SULFATE SOLUTIONS

FIELD OF THE INVENTION

The invention relates to a method and an apparatus for removing fluoride from sulfate solutions in a hydrometallurgical metal recovery process. More specifically the invention relates to removal of fluoride and fluorine compounds from acidic zinc sulfate solution. The method is continuous and two-stage, in which a zinc sulfate solution is first contacted with a solid sorbent in mixing tanks after which the sorbent is physically separated from the slurry. The process solution is treated in a continuous flow mode in the sorption stage.

BACKGROUND OF THE INVENTION

A hydrometallurgical zinc process consists of a sulfuric acid leach stage followed by solution purification and zinc electrowinning, from which the electrolyte, acidic sulfate solution, is recycled back to the leaching. Today, a zinc sulfide concentrate can be either leached directly or the concentrate is first roasted and then the zinc containing calcine is leached. Fluoride originating from the concentrate or from neutralizing chemicals ends up in the zinc electrolyte. Since the electrolyte is recycled in the process, fluoride accumulates in the process with time. The problem is pronounced in the direct leach process since fluorine content of the concentrate is largely removed to the gas phase in the roasting.

Fluoride is a problematic impurity in hydrometallurgical production of zinc even in low concentrations. It is understood that fluorine in the form of fluoride can be present in the zinc containing solutions and/or slurries, for example in zinc electrolyte, either as fluoride ions or fluorine compounds comprising fluorides or both. Aluminum cathodes are commonly used in zinc electrowinning and fluoride corrodes the aluminum cathodes. Corrosion causes zinc to stick on the cathode making stripping of zinc from cathodes difficult. Therefore the preferred fluoride concentration in zinc electrowinning is than 10 mg/l. In addition, fluoride increases significantly corrosion in other parts of the process equipment.

In state of the art processes the fluoride concentration of the zinc electrolyte is kept on a certain stationary level since part of the fluoride is co-precipitated in iron residues during the hydrometallurgical leaching process,

and part of the zinc electrolyte is drained as an overflow. However, these methods are ineffective or uneconomical in order to reach very low fluoride concentrations. Usually the fluoride concentration in industrial zinc process solutions is between 10 to 200 mg/l.

A known method to solve the problem in a zinc process is disclosed in US patent publication 4,567,027. According to the method, the acid is neutralized to a pH between 4 to 5 and aluminum and phosphate ions are added to the solution. Fluoride is precipitated, and at the same time also zinc precipitates as phosphates because of low solubility. The precipitate is separated from the solution. A drawback of the method is that a portion of zinc is lost to the precipitate.

Fluoride may be removed also by adding neutral or caustic aluminum anodizing waste treatment sludge into the zinc sulfate solution. Fluoride is complexed to aluminum and thus removed by separating the solids as disclosed in US patent 5,531,903. About 2 to 10 g/l of aluminum is necessary for fluoride removal and the pH has to be 4 to 5 in order to avoid the dissolution of the aluminum compounds.

US patent 5,324,499 discloses a method for fluoride removal from zinc sulfate containing sulfuric acid solution where sulfuric acid concentration is more than 45 wt-%. Silicon dioxide is added to the solution and it is fed to a spray drier. Hydrogen fluoride and silicon tetrafluoride are removed from the solution as gaseous species. This method requires high acid concentration which is much higher than in zinc electrolyte.

Previously described and known methods to decrease fluoride concentration level in electrowinning require the neutralization of zinc sulfate solution to above pH 4 before co-precipitating or removing fluoride by sorption onto different solids. These methods can also cause the co-precipitation of zinc and thus loss of the zinc product. Moreover, the literature describes the use of anion exchange resins, but such methods cannot be applied in the present case due to the high sulfate concentration as sulfate is sorbed on these materials.

BRIEF DESCRIPTION OF THE INVENTION

The object of the present invention is to provide a new method and a process arrangement for removing fluoride and/or fluorine components from zinc sulfate containing process liquors and slurries. The objects of the invention are achieved by a method and an arrangement, which are characterized by what is stated in the independent claims. Preferred embodiments of the invention are disclosed in the dependent claims.

LIST OF DRAWINGS

Figure 1 presents a flow diagram of preferred embodiment of the process apparatus to remove fluoride according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention covers a method for removing fluoride and fluorine components from zinc sulfate containing process liquors and slurries. The method comprises steps of i) withdrawing a flow of zinc sulfate containing process liquor or slurry from a zinc recovery process; ii) contacting the flow of zinc sulfate containing process liquor or slurry with sorbent material capable of sorbing fluorine or fluorine containing components present in the zinc sulfate containing process liquor or slurry to obtain a mixture of a clay sorbent comprising immobilized fluoride and a zinc sulfate containing process liquor or slurry at least partly depleted of fluoride; iii) separating the clay sorbent comprising immobilized fluoride from the mixture to obtain a treated zinc solution; and iv) returning the treated zinc solution back to the zinc recovery process.

It has been surprisingly found by the inventors that when the acid concentration is on a certain level clay, in particular solid bentonite, can effectively be used to remove fluoride from concentrated zinc sulfate solutions. Thus clay, in particular bentonite, can be directly used to treat zinc sulfate containing process liquors or slurries, e.g. a zinc electrolyte, in connection with a zinc recovery process. On the other hand the invention is applicable for removing fluoride in connection with a zinc leaching step when a process solution to be treated in accordance with the present invention is leaching slurry.

Bentonite is naturally occurring impure clay. Its main components are typically montmorilonite and kaolinite. Such clay adsorbents or absorbents, i.e. sorbents, are environmentally friendly and economical sorbents. It is thus

reasonable to use them only once and immobilize fluoride on the clay as waste.

The method now developed takes place in two stages, i.e. in the first stage, which is a reaction stage, the zinc sulfate containing process liquor or slurry, e.g. an acidic zinc sulfate solution, is treated with solid clay sorbent in order to bind fluoride and fluorine compounds to the clay. In the second stage the clay sorbent is physically separated from the solution.

Examples of zinc sulfate containing process liquors and slurries suitable to be treated in this process are return acid solution from zinc electrowinning, i.e. zinc electrolyte, containing 40 to 60 g/l zinc and 160 to 200 g/l sulfuric acid and process solution or slurry from leaching, e.g. leaching slurry, with 40 to 170 g/l Zn and 20 to 180 g/l H_2SO_4. These zinc sulfate containing process liquors and slurries contain typically 5 to 200 mg/L, preferably from 10 to 100 mg/L, fluorine, typically in the form of fluoride.

At low fluoride concentrations fluoride ions are in equilibrium with hydrofluoric acid (HF). The acid dissociation constant pK_a for HF is about 3.2, which means that approximately half of the total fluoride exists as hydrofluoric acid and the rest as fluoride ions at pH 3.2 assuming that the solution does not contain any metal ions which form complexes with fluoride. This means that the fraction of hydrofluoric acid increases with increasing sulfuric acid concentration.

Hydrofluoric acid concentrations are so low in the zinc process that HF cannot be removed in gaseous form in an economically viable method. The inventors of this invention discovered that hydrofluoric acid is sorbed on solid clay particles when clay sorbent is used. Moreover, it was found that the sorption increases at a higher acid concentration since a larger fraction of the fluoride exists as hydrofluoric acid. Example 2 illustrates how fluoride removal increases with increasing sulfuric acid concentration. Even though bentonite clay was used in the following examples as the sorbent, it is clear that alternatively other small sized clays or clay minerals (like e.g. montmorilonite, kaolinite or diatomaceous earth), can be used for this purpose. Since the clays tend to swell in aqueous solution one can assume that both adsorption on the solid surface and absorption into the clay lattice takes place.

Unlike in previously known methods, the present method does not require addition of any other chemicals, for example for pH control, or use of any water soluble complexing agents for fluoride. Thus the zinc electrolyte or

the process slurry in the leaching step will not be affected in any harmful manner. In order to improve mass transfer of fluoride and/or fluorine compounds comprising fluoride it is preferred that the fluoride removal is done in stirred tank reactors using fine clay powder allowing fast sorption in a suspension. That enables treatment of a continuous stream from the zinc process and the return of the treated solution back into the process.

In an example of the present invention the invention provides a continuous method for decreasing fluorine content in zinc electrolyte during the zinc recovery process. According to the example fluoride is removed from a continuous stream of zinc sulfate containing process liquors and slurries, e.g. acidic zinc sulfate solutions or slurries, without need for neutralization step or addition of other water soluble chemicals. This allows the removal of fluoride to a very low concentration so that corrosion problems caused by fluoride in electrolytic zinc recovery process are eliminated.

In accordance with another example, the invention further relates to a method for removal of fluoride from zinc sulfate containing process liquors and slurries, e.g. acidic zinc sulfate solutions, from a hydrometallurgical zinc process using solid, fine-grained clay sorbent. The particle size of the fine-grained clay sorbent is typically < 300 µm. The zinc sulfate containing process liquor or slurry, e.g. the acidic zinc sulfate solution, is withdrawn from a hydrometallurgical zinc process. It is then contacted with the clay sorbent, such as a clay aluminum silicate sorbent, in one or more mixed reactors where fluoride is removed from the solution by adsorption on the particle surface or absorption into the particle material of the clay sorbent. The zinc sulfate containing process liquor or slurry is fed continuously to the reactors and the treated solution is returned back to the zinc recovery process. Preferably the treated solution is returned continuously back to the zinc recovery process.

The zinc sulfate containing process liquor or slurry, e.g. an acidic zinc sulfate solution, typically contains at least 20 g/L sulfuric acid and zinc between 30 and 170 g/L. The amount of sorbent added to the liquor or slurry is typically between 0.01 to 10 wt-% of the weight of the liquor or slurry. The fluoride removal is not affected by solids present in the feed withdrawn from the zinc recovery process.

After fluoride and/or fluorine components comprising fluoride are bound to the clay sorbent, the zinc containing liquid, i.e. the zinc sulfate containing process liquor or slurry at least partly depleted of fluoride, is separated

from the clay sorbent by means of known solid-liquid separation methods. The solid-liquid separation takes place by thickening, settling, filtration, centrifugation or any combination of these methods.

For separating and recovering a trapped zinc content in the separated clay sorbent the solid material may be washed with sulfuric acid (pH < 1) and the washing liquor may be further processed for recovering the zinc. The washed clay sorbent is discarded and the washing liquor is returned back to the zinc recovery process. The thus treated acidic zinc sulfate solution from the solid-liquid separation step is returned back to the zinc recovery process. The acid used in the washing step may be returned back to the hydrometallurgical zinc process.

The invention also provides an arrangement for treating a zinc sulfate containing process liquor or slurry, e.g. a process liquor comprising acidic zinc sulfate solution. The arrangement comprises at least one fluoride removal reactor for mixing the zinc sulfate containing process liquor or slurry with a clay sorbent, the fluoride removal reactor is in fluid communication with a hydrometallurgical process from which the acidic zinc sulfate withdrawn, i.e. zinc recovery process, and a separation unit for separating the zinc sulfate containing process liquor or slurry at least partly depleted of fluoride, e.g. treated zinc sulfate electrolyte, from the clay sorbent to obtain a treated zinc solution, said separation unit being in fluid communication with a fluoride removal reactor and the hydrometallurgical process to which the treated zinc solution is returned.

Figure 1 depicts an example of the process arrangement of the invention. A zinc process vessel (12) containing acidic zinc sulfate solution or slurry is arranged in continuous fluid communication with a fluoride removal reactor (2). The clay sorbent (3) is fed to the reactor (2) continuously or in intervals. The reactor (2) is equipped with a mixer (4), which is preferably spiral in shape for ensuring uniform and soft mixing of the clay with the process feed avoiding strong shearing effects. Slurry from the reactor (2) is fed into a second fluoride removal reactor (5) equipped with a mixer (4'). The mixer (4') is again preferably spiral in shape. Fresh clay sorbent (6) can be fed to the second reactor (5) or alternatively the total sorbent amount is already fed to the first reactor (2). In Figure 1 there are two reactors in series but the system could also consist of more than two reactors like in Example 4. The invention

may be performed in a process arrangement comprising only one fluoride removal reactor.

The last fluoride removal reactor is arranged in fluid communication with subsequent solid/liquid separation unit (8). The slurry (7) processed in the last fluoride removal reactor is fed to the solid-liquid separation unit (8). The solids are separated from the solution and the thus obtained cake may be washed with sulfuric acid (9), preferably containing sulfuric acid more than 10 g/l, but the pH should be below 3, in order to recover any zinc solution trapped in the cake. If neutral water is used for washing some fluoride is lost from the sorbent.

The solid-liquid separation unit (8) and the zinc process vessel (12) are arranged in fluid communication so as to withdraw the liquid separated in the solid-liquid separation unit (8) back to the zinc process (12). In Fig. 1 the treated process solution (10) and the washing acid (11) are returned back to the zinc recovery process (12). Fluoride is immobilized in the clay sorbent (13) which can be transferred to a landfill, storage or for possible further use.

By this method it is possible to reduce fluoride concentration to less than 10 mg/l as shown in Example 1. Preferably more than one stirred reactors are used because it allows narrower residence time distribution in the reactors. Spiral shaped mixers with low shear mixing are preferred in the reactors because they were found to give uniform mixing of the slurry and avoid the abrasion of the clay sorbent. The clay sorbent is added continuously or semi-continuously into the reactors. The clay sorbent can be either in powder, spherical or fiber form. Fine particle size is desirable from process point of view as it allows rapid sorption kinetics.

The clay sorbent is separated from the slurry in the second stage. Separation can be by thickening, settling, filtration, centrifugation or any combination of these methods. Sorbent is washed during separation and then taken out of the process. Treated acidic zinc sulfate solution is returned to a suitable place in a zinc recovery process.

The following examples are to demonstrate the applicability of the method in acidic zinc sulfate solutions. Experiments were carried out by using fine Tonsil® Optimum 210FF bentonite powder by Clariant Süd-Chemie. According to the manufacturer's specifications the particle size is < 100 µm (for 83%) and the specific surface area is 200 m^2/g. Fluoride concentration was analyzed by using an ion-selective electrode, which is an accurate method.

However, due to the high sulfate matrix in the solutions the detection limit for fluoride was below 5 or 10 mg/l. Other metals were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Fluoride was detected from solid samples by pyrohydrolysis.

Example 1

Equilibrium tests were made in order to prove that the method fulfills fluoride removal requirements of the process. 10 g of bentonite and varying amounts of authentic zinc sulfate process solution were added to plastic bottles to get different bentonite/liquid ratios. The solution contained 61 g/L Zn, 4.5 g/L Mn, 14 g/L Mg and 170 g/L H_2SO_4. Bottles were shaken for 1h at 25 °C. Bentonite and the solution were analyzed before and after the experiment.

Table 1. The effect of solid/liquid ratios on fluoride removal

Sample	Bentonite/liquid ratio g/L	F in solution mg/L	F in bentonite wt%
Feed solution	-	23	0.062
Test 1	10	15	0.14
Test 2	25	<10	0.13
Test 3	50	<10	0.10

The results in Table 1 verify that fluoride concentrations below 10 mg/l are achieved with the method when the bentonite/liquid ratio is high enough.

Example 2

Four tests were conducted at different sulfuric acid concentrations to evaluate the effect of acidity on fluoride removal. Zinc was added as sulfate to four different water samples containing four different amounts of sulfuric acid. The zinc concentration in each solution was 52 g/L. Fluoride was added as sodium fluoride. Each solution was analyzed before and after the experiment 40 ml of each solution and 0.8 g of bentonite were measured into plastic bottles. Bottles were shaken for 2 h at 25 °C temperature. Table 2 shows that fluoride removal is increased at higher sulfuric acid concentration.

Table 2

Sulfuric acid, g/L	F (before test), mg/l	F (after test), mg/l	Fluoride removal, %
2	33	29	12.1
50	31	22	29.0
101	33	19	42.4
170	32	17	46.9

Example 3

Experiment was made in a batch reactor in order to study the sorption kinetics. A zinc sulfate solution was added to a stirred tank reactor and it was heated to the temperature of 39°C. The solution contained 170 g/L H_2SO_4 and 52 g/L Zn. Stirring was started and 10 g of bentonite was added to the reactor at the start of the experiment. Solution samples were taken at certain intervals and the results are shown in Table 3. The results show that fluoride removal is fast enough so that the method can be applied industrial scale for a continuous feed solution so that the equipment size remains reasonable.

Table 3

Time, min	Fluoride mg/L
0	32
2	27
5	19
10	15
30	14
120	11

Example 4

The following experiment was done to demonstrate the method in continuous flow mode which is preferred in industrial applications. It is advantageous to have more than one reactor in series in order to obtain a narrower residence time distribution. Three two-liter reactors were connected in series and operated at the temperature of 39 °C. The synthetic feed solution contained 51 g/L Zn, 170 g/L H_2SO_4 and 37 mg/L F. The solution was pumped to the first reactor at a flow rate of 200 mL/min corresponding to 30 minutes total residence time and the solutions in the reactors were heated to 39 °C tempera-

ture. Bentonite was fed to the first reactor by a vibrating feeder so that the bentonite/liquid ratio in reactors was 50 g/L. Solution samples were taken after 3 and 4 hours from the output of the last reactor. Fluoride concentrations in the treated solutions were 16 mg/L and 14 mg/L, respectively.

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CLAIMS

1. A method for removing fluoride and fluorine components from zinc sulfate containing process liquors and slurries, comprising the steps of

i) withdrawing a flow of zinc sulfate containing process liquor or slurry from a zinc recovery process;

ii) contacting the flow of zinc sulfate containing process liquor or slurry with a clay sorbent capable of sorbing fluorine or fluorine containing components present in the zinc sulfate containing process liquor or slurry to obtain a mixture of a clay sorbent comprising immobilized fluoride and a zinc sulfate containing process liquor or slurry at least partly depleted of fluoride;

iii) separating the clay sorbent comprising immobilized fluoride from the mixture to obtain a treated zinc solution ; and

iv) returning the zinc solution back to the zinc recovery process.

2. The method as claimed in claim 1, wherein the zinc sulfate containing process liquor or slurry is process solution or slurry from leaching or acid solution from zinc electrowinning.

3. The method as claimed in claim 1 or 2, wherein the withdrawing of the zinc sulfate containing process liquor or slurry takes place in continuous flow mode.

4. A method according to any one of claims 1 to 3, wherein returning the zinc solution back to the zinc recovery process takes place in continuous flow mode.

5. A method according to any one of claims 1 to 4, wherein the zinc sulfate containing process liquor or slurry withdrawn from the zinc recovery process contains at least 20 g/l sulfuric acid.

6. A method according to any one of claims 1 to 5, wherein the zinc sulfate containing process liquor or slurry withdrawn from the zinc recovery process contains 30-170 g/l zinc.

7. A method according to any one of claims 1 to 6, wherein the zinc sulfate containing process liquor or slurry withdrawn from the zinc recovery process contains 5 to 200 mg/L, preferably from 10 to 100 mg/L, fluorine, typically in the form of fluoride.

8. A method according to any one of claims 1 to 7, wherein the clay sorbent is fine-grained clay.

9. A method according to claim 8, wherein the particle size of the clay sorbent material is < 300 µm.

10. The method according to any one of claims 1 to 9, wherein the clay sorbent is selected from a group consisting of small sized clays and clay minerals, such as bentonite, montmorilonite, kaolinite or diatomaceous earth.

11. A method according to any one of claims 1 to 9, wherein the clay sorbent contains more than 90% bentonite.

12. The method according to any one of claims 1 to 9, wherein the clay sorbent is bentonite.

13. The method according to any one of claims 1 to 12, wherein the concentration of the clay sorbent in the slurry is between 0.01 to 10 wt-%.

14. A method according to any one of claims 1 to 13, wherein the zinc containing solution is separated from the clay sorbent material by solid liquid separation such as thickening, settling, filtration or centrifugation.

15. A method according to any one of claims 1 to 14, wherein the zinc content trapped in the clay cake after the solid-liquid separation step is washed with sulfuric acid solution and the washing liquor is returned back to the zinc recovery process.

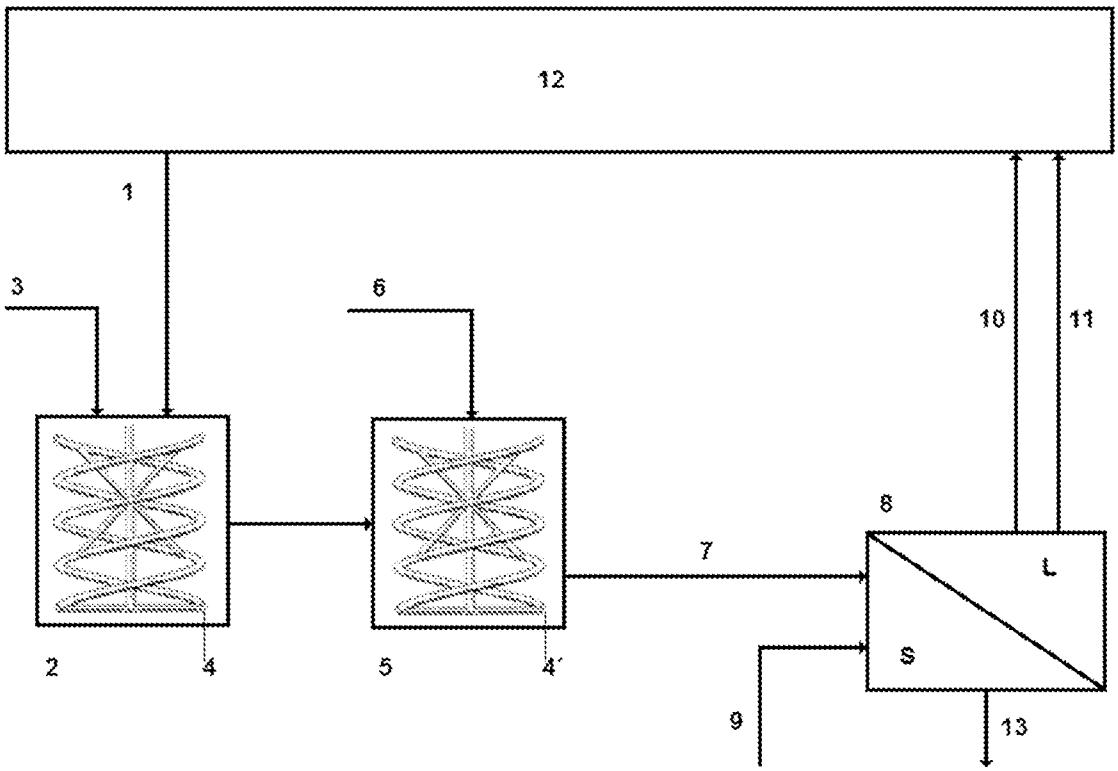
16. The method according to any one of claims 1 to 15, wherein the zinc sulfate containing process liquor at least partly depleted of fluoride contains less than 10 mg/l fluoride.

17. An arrangement for treating a zinc sulfate containing process liquor or slurry, wherein the arrangement comprises at least one fluoride removal reactor for mixing said zinc sulfate containing process liquor or slurry with a clay sorbent, the fluoride removal reactor is in fluid communication with a hydrometallurgical process from which the zinc sulfate containing process liquor or slurry is withdrawn, and a separation unit for separating the zinc sulfate containing process liquor or slurry at least partly depleted of fluoride from the clay sorbent to obtain a treated zinc solution, said separation unit being in fluid communication with the fluoride removal reactor and the hydrometallurgical process to which the treated zinc solution is returned.

18. An arrangement according to claim 17, wherein the fluoride removal reactor comprises a spiral shaped mixer.

19. An arrangement according to claim 17 or 18, wherein the separation of the zinc sulfate containing process liquor or slurry from the clay sorbent takes place in a solid liquid separation unit, such as thickener, settler, filter, centrifuge or in any combination of these units.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2013/051189

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: B01D, B01J, C01B, C01G, C02F, C25B, C25C

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, COMPDX, INSPEC, PUBCOMP, PUBSUBS, NPL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 102228746 A (DEYANG NANFANG REGENERATION RESOURCE CO LTD) 02 November 2011 (02.11.2011) abstract [online] EPOQUENET EPODOC & WPI	1-19
A	US 8158006 B2 (HATA HIROSHI [JP] et al.) 17 April 2012 (17.04.2012) column 3, line 32 – column 9, line 27	1-19
A	JP 2002105685 A (MITSUI MINING & SMELTING CO) 10 April 2002 (10.04.2002) abstract [online] EPOQUENET EPODOC & WPI	1-19
A	JP 2009285541 A (MITSUI MINING & SMELTING CO) 10 December 2009 (10.12.2009) abstract [online] EPOQUENET EPODOC & WPI	1-19
A	CN 101492772 A (ZHIHONG SONG [CN]) 29 July 2009 (29.07.2009) abstract [online] EPOQUENET EPODOC & WPI	1-19

☒ 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
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Date of the actual completion of the international search	Date of mailing of the international search report
17 March 2014 (17.03.2014)	20 March 2014 (20.03.2014)

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1736236 A1 (KURITA WATER IND LTD [JP]) 27 December 2006 (27.12.2006) abstract; paragraphs [0016]-[0017])	1-19
A	MURRAY H.H. Clay sorbents: The mineralogy, processing and applications. Acta Geodyn. Geomatr., 2005, Vol. 2, No. 2(138), p. 131-138 the whole document	1-19
A	WO 2010142841 A1 (OUTOTEC OYJ [FI]) 16 December 2010 (16.12.2010) page 10, line 9 - page 11, line 24	1-19

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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